Selected papers on water quality and pollution in New Mexico

compiled by WILLIAM J. STONE

HYDROLOGIC REPORT 7 **New Mexico Bureau of Mines and Mineral Resources** **1984**

A DIVISION OF
NEW MEXICO INSTITUTE OF MINING & TECHNOLOGY

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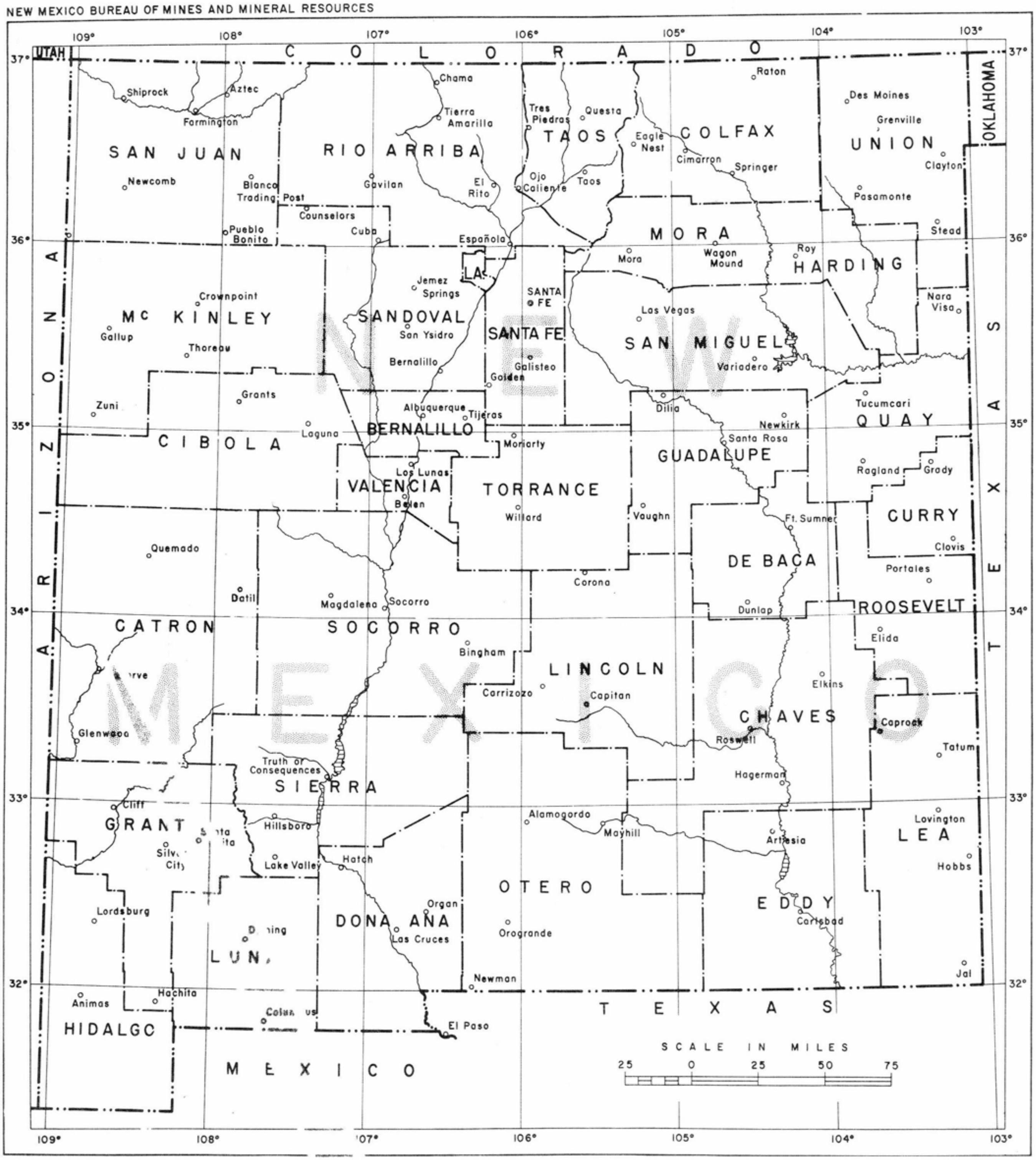

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Hydrologic Report 7

New Mexico Bureau of Mines & Mineral Resources

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NEW MEXICO INSTITUTE OF MINING & TECHNOLOGY

Selected papers on water quality and pollution in New Mexico

Proceedings of a Symposium on
Water Quality and Pollution in New Mexico
April 12, 1984, Socorro, NM

Compiled by William J. Stone

New Mexico Bureau of Mines and Mineral Resources

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New Mexico Bureau of Mines and Mineral Resources
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PREFACE

This report deviates from the normal theme of the hydrologic report series in that it contains the oral and poster papers presented at a one-day symposium on Water Quality and Pollution in New Mexico. The symposium was organized in order to provide an opportunity for exchanging information currently available on the chemistry and microbiology of precipitation, surface water, soil water, and ground water in the state, as well as water-treatment technology, resource-development impacts, and legal aspects of ground-water pollution. The purposes of this document are (1) to record the papers presented at the symposium and (2) to gather together under one cover a selection of overviews, case studies, and theoretical papers reflecting available information on water quality and pollution in New Mexico.

The symposium was initially conceived by Dennis McQuillan (New Mexico Environmental Improvement Division). Assisting him on the organizing committee were Daniel Stephens (Geoscience Department, New Mexico Tech), William Stone (New Mexico Bureau of Mines and Mineral Resources), Kelly Summers (W. K. Summers and Associates), Bruce Gallaher (New Mexico Environmental Improvement Division), and George O'Connor (Department of Crop and Soil Sciences, New Mexico State University).

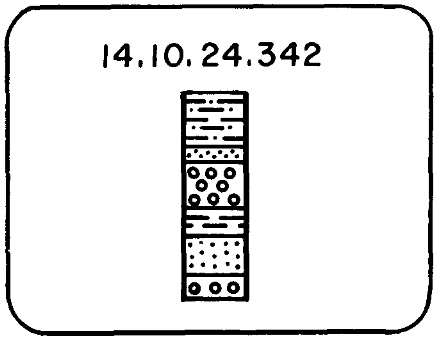
It was recognized that for symposium papers to be of value to water-resource professionals in the future, they should be published in an established, readily accessible outlet, such as the Bureau's Hydrologic Report series. Furthermore, it was decided that the proceedings should be distributed at the meeting. These decisions placed several restrictions on the authors. First of all, there was no time for the editing process through which Bureau publications normally go. Nonetheless, because the papers were being published in a formal Bureau series, they had to be standardized and prepared in conformance with Bureau style.

Time and editorial constraints were overcome by requiring colleague-reviewed, camera-ready manuscripts. Two reviewers were suggested; most papers identify reviewers in the acknowledgements. Standardization was attempted by providing authors with an abbreviated set of Bureau style guidelines. Nonetheless, minor inconsistencies crept in. It is hoped that these do not detract from the usefulness of this volume. Authors were also instructed to limit their papers to 10 pages, including illustrations, and to focus mainly on material actually presented at the meeting. Large data files were to be presented elsewhere and merely cited, whenever possible.

It was also requested that authors present measurements in both FPS and SI units, giving the measured value first, regardless of system, followed by the calculated equivalent in the other system in parentheses. Thus, where conversion errors went unnoticed, the reader could distinguish between the measured and calculated values. Conversions were not required in illustrative material. The new standard Bureau conversion table inside the back cover includes conversions provided to authors for use in preparing their manuscripts.

The conclusions presented herein are those of the individual authors and publication should not be construed as an endorsement by the sponsoring agencies.

William J. Stone
January 1984



Contents

SURFACE WATER

SUBSURFACE WATER

NATURE OF PRECIPITATION AND ATMOSPHERIC PARTICULATES IN CENTRAL AND NORTHERN NEW MEXICO

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ABSTRACT

Data are presented documenting the presence of regional acidic precipitation at five sample sites in central and northern New Mexico. The volume-weighted pH values are in the 4.0-4.9 range. The basic nature of atmospheric particulates in the region can cause neutralization of acids during small events but does not have much effect during large events. As a result, event-averaged pH's are always greater than volume-weighted pH's. The major ion and trace metal composition of precipitation are reported. Fly ash particles washed out in precipitation and trapped on air filters have been identified by scanning electron microscopy. Particle number densities in the 0.4-1.7% range are presented.

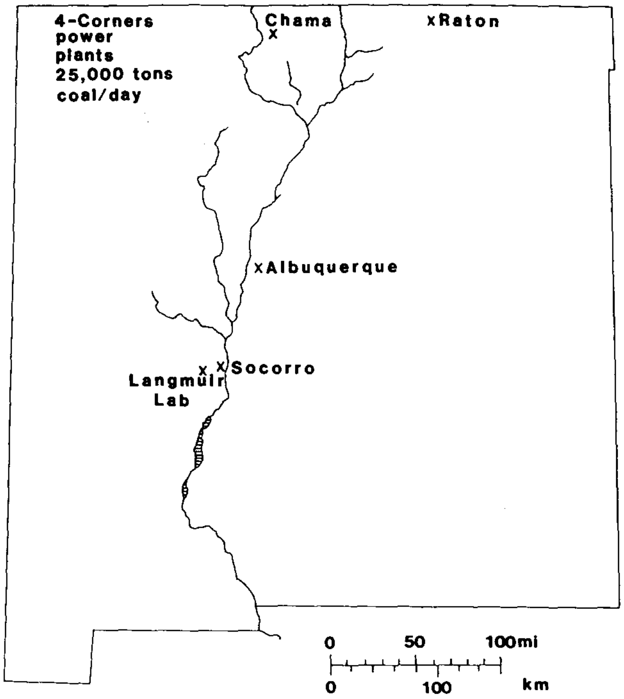
INTRODUCTION

The presence of acid rain in the arid, high desert region of central New Mexico has been established (Popp et al., 1982; 1983). The volume-weighted pH values averaged slightly less than 5 and, although not as low as the pH values found in more highly industrialized and populous areas of the United States and Europe (Galloway, 1976; Likens, 1979), values are indicative of the widespread nature of the acid rain phenomenon. The acidic nature of precipitation in this arid region can easily be masked by neutralization accompanying interaction with atmospheric particulates. Rapid reaction between washed out particles and precipitation in wet-only collectors can change the dissolved species in precipitation in this region drastically (Popp et al., 1982), requiring immediate stabilization of samples after collection. This is due both to the lack of rainfall to wash out particulates and to greater entrainment of particulates when ground cover is sparse. Because the area is located long distances from marine sources and urban environments, the contribution of sea salt and urban activities to atmospheric particulate composition is small.

In this study, both the chemistry of the precipitation and the nature and distribution of atmospheric particulates in central and northern New Mexico have been investigated over a 1-4 year period. In addition, the effect of these particulates on precipitation chemistry has been evaluated in an attempt to determine particulate sources. The pH values calculated on a volume-weighted basis for all sites are lower than those averaged on an event basis. Also of interest have been the observations of fly ash particles in particulate wash-out at all sample sites and the characterization of collected particles by scanning electron microscopy (SEM).

STUDY AREAS

The locations of the study areas are shown in Fig. 1.



The cities of Socorro and Raton have populations of about 7000, are located in farming and ranching areas in the transition between lower and upper Sonoran life zones, and are widely separated geographically (400 km). A coal-fired power plant with a 25,000 metric ton/year capacity is located in Raton while there is none in the Socorro area. The Chama area in northern New Mexico is located in a mountain valley at an altitude of 8000 feet (2430 m), has a low population density, and is in a transition life zone. Two of the largest coal-fired power plants in the Southwest are located about 160 km west of Chama, burn about 25,000 metric tons of coal per day, and are equipped with electrostatic precipitators. The Langmuir Atmospheric Research Laboratory is located on a high mountain ridge (3200 m) in a spruce-fir climate zone and is free of much of the entrained dust which is prevalent at lower altitudes. Aircraft samples were collected in thunderstorms above the Langmuir Laboratory. The city of Albuquerque has a metropolitan area population of about 400,000 and is by far the largest urban area in a state with a population of 1.2 million. Albuquerque experiences air pollution alerts in the winter due to carbon monoxide accumulation under temperature inversion conditions. Regional weather patterns move to the east and southeast except in the summer when thunderstorms are caused by warm air rising up mountain flanks.

METHODS

PRECIPITATION SAMPLING AND ANALYSIS

The large, one meter diameter plastic funnels used to maximize sample size from the usually small rainfall events have been previously described (Popp, 1982). Wet-only and bulk precipitation samples were collected and stored in acid-washed polyethylene bottles. Bulk sample collectors are open at all times and samples are collected periodically while wet sample collectors are closed except during a precipitation event. Precautions were taken during sample handling to minimize contamination. Filtration through pre-weighed 0.2 pm membrane filters for stabilization was performed as soon as possible after collection and the samples were split for analysis. Samples for metal analyses were stabilized by acidification with redistilled nitric acid after filtration, while a non-acidified portion was used for anion analysis. Standard solutions from the U.S. Environmental Protection Agency (USEPA) and duplicates were always determined for quality control.

The precipitation filters were dried at room temperature and reweighed to determine particulate washout. Bulk samples were filtered after collection and stored in polyethylene bottles.

Sodium, potassium, magnesium, and calcium were analyzed by flame atomic absorption (A.A.), while trace metals were analyzed using an A.A. graphite furnace. Selenium and arsenic were determined by A.A. using a hydride generator. Mercury was analyzed by reduction with SnC12 using a Coleman MAS-50 mercury analyzer.

Anions, Kjeldahl nitrogen, and ammonia were determined using procedures from USEPA manual EPA-60014-79-020 (USEPA 1979) or anion chromatography (anions only).

A powered sailplane was used to penetrate thunderclouds up to about 7 km altitude. This aircraft has been assigned by the Navy to the Langmuir Laboratory of New Mexico Tech. The airborne precipitation sampler is described in Popp et al., 1983. Collection was performed at altitudes of 6.1-7 km with temperatures about -15°C and all of the samples collected were ice.

PARTICLE SAMPLING AND ANALYSIS OF ENVIRONMENTAL SAMPLES

Air filter samples were collected on pre-weighed, 0.45-um pore-size glass fiber filters using a high volume air sampler operating 24 hours at flow rates of about 60 cfm (1680 lm^{-1}).

Counting data from the SEM on the glass fiber and membrane filters were obtained directly from photographs. Details of the procedure are found in Popp et al., 1983.

Fly ash analysis spectra obtained using the X-ray attachment were similar to those for NBS Standard Reference Material 1633a (Trace Elements in Coal Fly Ash).

RESULTS AND DISCUSSION

VOLUME-WEIGHTED AND EVENT-AVERAGED pH VALUES

The average pH values for precipitation on an event-averaged and volume-weighted basis at the various study sites are shown in Table 1.

Table 1. Volume-weighted and event-averaged pH values for sample sites.

Study Area	Average pH-Event Basis[a]	Volume Weighted pH	Study Period Months
Socorro	5.2 (127)	4.5	48
Langmuir[b]	4.8 (42)	4.6	July-Aug (1979,80,81,82)
Chama	4.5 (20)	4.2	42
Raton	5.5 (23)	4.9	21
Albuquerque	5.5 (26)	4.0	11
Aircraft[c]	4.8 (11)	-	July-Aug (1981,82)

a. Number of events shown in parentheses.
b. Samples collected primarily when thunderstorm activity is greatest in June-August months.
c. Samples were collected in a thundercloud where precipitation is not possible to calculate.

The volume-weighted pH values have been calculated as suggested by Liljestrand and Morgan (1978) to estimate the total acid contributed through precipitation. In all cases the volume-weighted pH values were lower than the event averages, and in the case of Albuquerque, lower by 1.5 pH units. These data suggest that the large volume events have lower pH values than small volume events. This phenomenon is attributable to the neutralizing effect of atmospheric particulates being more important in small than in large precipitation events. We have previously noted that the pH of precipitation at the beginning of events in this region is higher than the pH of succeeding samples (Popp et al., 1982; 1983). The lowest volume-weighted average pH value obtained was for Albuquerque which suffers severe temperature inversions in the winter months, as do many western cities. These inversions trap pollutants such as CO and NO($_x$) from automobiles. The average event pH value obtained at Langmuir Laboratory (4.6) compares closely with that obtained from the aircraft at 7 km in thunderstorms above the Laboratory (4.6). These local summer thunderstorms are created as warm updrafts draw moist air above the mountains suggesting that acid causing species may be contributed from the upper troposphere or lower stratosphere.

pH data have been collected at the Socorro and Langmuir sites for four years and are summarized in Table 2. The Socorro averages (both event and volume-weighted) have varied considerably as has the rainfall. At both sites the event averages show a downward trend with a leveling off in the last two years.

Table 2. Yearly pH changes at Socorro and Langmuir Laboratory.

Average Yearly pH for Socorro (1400 m)

	8/79-7/80	8/80-7/81	8/81-7/82	8/82-7/83
Event Average[a]	5.3(37)	5.5(28)	4.9(28)	5.1(34)
Vol.Wt. Ave.	4.6	4.7	4.2	4.5
Vol. Precip.	122 mm	222 mm	192 mm	147 mm

Average Yearly pH for Langmuir (3200 m)- Summer Thunderstorms Only

	1979	1980	1981	1982
Event Average[a]	5.4(7)	5.0(10)	4.5(16)	4.6(9)
Vol.Wt. Ave.	5.1	4.6	4.2	4.5
Vol. Precip.	71 mm	147 mm	77 mm	74 mm

a. Assume volume proportional to amount in mm.

The sites are separated by only 20 km but Langmuir is about 1800 m higher in altitude, is relatively dust-free, and may reflect upper atmosphere contributions to the chemistry of precipitation.

MAJOR IONS AND TRACE METALS IN REGIONAL PRECIPITATION

Event-averaged concentrations of major ions are shown in Table 3. In general, the high altitude samples from Chama, Langmuir, and the aircraft have lower total ion concentrations than the more urban, low altitude sites at Albuquerque, Socorro, and Raton, suggesting more entrained dust at sites with the most human activity and least ground cover.

Table 3. Event-averaged concentrations of major ions in precipitation. Values in ppm.

	Site					
Species	Chama	Aircraft	Albuq.	Socorro	Raton	Langmuir
Ca^{2+}	0.8	0.6	2.9	4.2	2.1	1.2
Mg^{2+}	0.20	0.05	0.18	0.42	0.19	0.10
Na^{+}	0.7	0.8	0.84	1.8	1.3	0.96
K^{+}	0.7	0.3	0.3	0.97	1.0	0.9
SO_4^{2-}	2.6	0.7	4.0	5.8	3.5	2.8
Cl^{-}	1.0	0.8	1.4	2.5	3.1	1.0
NO_3^{-}-as N	0.30	0.18	0.50	0.52	0.88	0.33
meq cations[a]	0.11	0.08	0.20	0.35	0.20	0.13
meq anions[a]	0.10	0.05	0.16	0.23	0.22	0.11

a. Only the major ions shown in the Table are included.

As shown in Table 4, there are no large differences in trace metal content as a function of altitude or location. It might be expected that lead values would be higher in Albuquerque than at other sites because of its relatively high population density, but there is no significant difference among the sites. This may be due to the use of unleaded fuel coupled with an overall low automobile density. The closest parallel for trace metal composition seems to be Socorro and Albuquerque. These sites are located in similar geographic settings suggesting a strong terrestrial influence. The Langmuir trace metal values are generally lower than Albuquerque and Socorro, especially for elements such as Ba and Fe which are quite prevalent in local soils. This indicates a smaller terrestrial influence at higher altitudes.

Table 4. Trace metal content in precipitation. Values in ppb are event averaged.

	Site					
Metal	Socorro	Raton	Albuq.	Chama	Langmuir	Aircraft
Ag	0.3	0.8	1.3	0.3	0.1	0.4
Ba	41	21	37	27	16	15
Cd	2.3	0.63	1.6	0.7	3.0	5.4
Co	2.0	1.0	0.8	6.2	1.1	0.3
Cr	8.5	1.3	2.0	1.4	2.1	3.2
Cu	16	8.7	14	8.4	8.3	12
Fe	82	140	73	37	41	74
Hg	0.6	0.4	0.5	0.2	0.3	-
Mn	58	29	20	35	20	4.6
Ni	2.0	7.8	2.2	1.3	1.7	2.2
Pb	3.8	1.7	3.4	1.6	5.4	2.5

EFFECTS OF ATMOSPHERIC PARTICULATES ON PRECIPIATION ANALYSES

Bulk vs. Wet-only Samples

Precipitation samples are commonly collected by one of two methods: as bulk samples or as wet-only (wet) samples. Both dry deposition and washout of atmospheric particulates can have a profound effect on dissolved species present in precipitation in this region. Average values for pH and major ions in precipitation in bulk vs. wet samples collected at the three urban sites are shown in Table 5.

Table 5. Average concentrations of major ions and pH in bulk vs. wet-only (wet) precipitation samples at three urban sites. Only samples collected on the same days are compared. Values in ppm except pH.

	Socorro		Raton		Albuquerque	
Species	Bulk	Wet	Bulk	Wet	Bulk	Wet
Ca^{2+}	8.0	1.5	7.2	2.0	2.1	0.44
Na^{+}	1.6	0.40	4.4	1.3	0.30	0.13
Cl^{-}	3.4	0.8	8.4	2.9	2.7	0.2
SO_4^{2-}	8.9	3.7	9.1	3.2	2.2	1.0
pH	5.5	4.9	6.1	5.5	5.5	5.1
SO_4/Ca	0.5	1.0	0.6	0.6	0.4	0.9
Cl/Na	1.4	1.3	1.2	1.4	5.8	1.0

Bulk deposition contributes from three to ten times the concentration of the major ions Ca^{2+}, Na^{+}, Cl^{-}, and SO_4^{2-} found in wet samples. Also, the pH values are approximately one-half pH unit higher for the bulk samples than for the wet samples indicating a considerable neutralization effect (about 30% less acidity). Comparison of ion mole ratios in bulk and wet precipitation indicates the relative contribution and composition of dry deposition. The SO_4/Ca ratios are about 0.5 for the three widely separated sites with only the Socorro and Albuquerque wet ratios equal to about 1.0. A ratio of 1:1 may indicate contribution from material such as gypsum which is a commonly occurring surface mineral in the region. Ratios less than 1:1 for SO_4/Ca may represent excess calcium produced from the reaction of calcareous entrained terrestrial material with precipitation such as the reaction of calcite with acid.

$$(CaCO_3(_s) + Hf \qquad Ca^{2+} + HCO_3\ )$$

The Cl/Na ratios are very similar in bulk and wet samples collected at Socorro and Raton and wet samples collected at Albuquerque. These Cl/Na ratios are generally higher than those observed in coastal regions which are about 1:1 due to the presence of sea salt aerosols (Liljestrand, 1981). There is no obvious reason why the bulk Albuquerque Cl/Na ratio is so much higher than the others.

Particle Scavenging

Relative differences of washout of particles by precipitation are shown in Table 6. The aircraft and Langmuir Laboratory samples are low in scavenged particulates while the highest value is found for the Albuquerque samples. Air filter particulate densities are also shown in Table 6. Again, Albuquerque has the highest particulate density. Similar relationships between air filter particulate density and particulate washout by precipitation are not consistent. For instance, Langmuir has a higher particulate density than Chama determined from air filters but a lower washout particulate concentration determined from precipitation filters. Because washout occurs starting with the formation of the raindrop in the atmosphere at a higher altitude while the air filter densities are measured at ground level, there may not necessarily be ground level-washout concentration correlation for particles.

Table 6. Weight of material collected on precipitation filters and air filters.

Site	# Samples	Average Weight on Rain Filters mg/l	Particle Density on Air Filters g/m^3 (a)
Raton	16	18	60
Socorro	24	25	40
Chama	9	20	5
Langmuir	7	3	20
Aircraft	3	2	-
Albuquerque	25	48	100

a. Chama and Langmuir data from our laboratories, remaining data from New Mexico E.T.D. (1980)

Fly Ash Counts on Precipitation Filters

Fly ash particle number densities at the sample sites determined using the SEM are summarized in Table 7. The % values for fly ash in total particulates washed out by precipitation and collected on 0.2 pm membrane filters range from 0.3 to 1.7. The 1.7% value was found in Chama and the 0.3% value was in Socorro. Chama is the closest site to the Four Corners power plants and Socorro is the most distant (see fig. 1). The 1.0% number density in the aircraft-collected samples may be due to the small total particle counts at high altitudes away from terrestrial influence. The uncertainties in elemental composition differences between particles from a single source are as large as those between different sources (e.g. Raton and San Juan, Four Corners) and, hence, identification of the source of a given fly ash particle using the SEM does not seem possible at this time (Popp et al., 1983).

Table 7. Fly ash particle number densities on material collected on precipitation filters.

Site	# Events (Filters)	F.A./Total	Percent	Size-μm[a]
Raton	4 (6)	16/1,289	1.2	2.9 ± 3.7
Socorro	3 (6)	4/1,180	0.3	4.2 ± 5.3
Chama	3 (3)	30/1,788	1.7	2.6 ± 1.8
Langmuir	3 (5)	12/1,053	1.1	2.3 ± 2.5
Aircraft	1 (3)	7/670	1.0	3.8 ± 1.7
Albuquerque	2 (4)	6/915	0.7	4.5 ± 1.8

a. Standard deviations are indicated.

Ion Mole Ratios

Ion mole ratios can be useful in comparing relative concentrations at various sites and selected mole ratios are shown in Table 8.

Table 8. Selected ion mole ratios in precipitation.

	Site							
Ion Mole Ratio	Socorro	Raton	Lang-muir	Air-craft	Albuq.	Chama	So. Cal.[a]	Eastern U.S.[b]
Cl/Na	1.1	1.5	0.68	0.65	1.1	0.9	1.1-1.2	2.0
SO_4/Ca	0.58	0.69	0.97	0.49	0.80	1.4	1.8-5.8	11
NO_3/SO_4	0.61	1.7	0.81	1.8 (summer=0.80) (winter=2.6)	0.86	0.80	0.7-5.2	0.9

a. Liljestrand and Morgan (1978)
b. Likens, et al. (1979)

The SO_4/Ca and Cl/Na ratios were used earlier in discussing neutralization effects. If $CaSO_4$ and NaCl were dissolving, the ion mole ratios would bc_1.0. Terrestrial sources for the four ions Na^+, Ca^{2+}, SO4 and Cl^- are generally far more enriched in Na+ and Ca^{2+} than in Cl^- and $SO4^-$ so the SO4/Ca and Cl/Na ratios should be small. Using terrestrial abundances from Krauskopf (1979) one calculates terrestrial SO4/Ca and Cl/Na ratios of <.01. Using Liljestrand and Morgan's data from southern California (1981) one calculates Cl/Na ratios of 1.1-1.2 for all sites, SO_4/Ca ratios of 1.8-5.8 from urban sites, and a ratio of 0.7 for a mountain site. The SO4/Ca ratios are generally <1 in the New Mexico study area, probably due to excess Ca^{4+} introduced upon reaction with rain. The SOL_E/Ca ratio at Chama was 1.4, which may reflect proximity to the Four Corners power plants. In the New Mexico study region, the Cl/Na ratios range from 0.65 to 1.5 with the lowest values at high altitude sites. It appears that excess chloride is washed out in this region far from coastal influence. The NO3/SO4 mole ratios range from 0.7 to 5.2 in the Los Angeles basin with an average of 2.0. The southern California study area is arid like New Mexico but there the similarity ends because of the high population density in the Los Angeles basin and its proximity to coastal influence. The NO3/SO4 ratios indicate relative contributions of the respective acids. Lewis and Grant (1981) concluded that nitric acid predominated in precipitation in a mountain region in northern Colorado. In the New Mexico study areas, the NO3/SO4 ratios varied considerably

(Table 8). The highest ratios were found at Raton (1.7), in the aircraft-collected thunderstorm samples (1.8), and in the Albuquerque winter samples (2.6). The 0.8 km proximity of a small coal-burning facility to the Raton sampling site may be the reason for the high NO3/SO4 ratio. The winter samples in Albuquerque were collected during air pollution alerts for CO (and, hence, also NO($_x$)) while temperature inversion conditions prevailed and had much higher NO_3/SO_4 ratios than samples collected during the rest of the year (2.6 vs. 0.8). The high NO_3/SO_4 values collected by aircraft at 7000 m in active thunderstorms may be due to increased N-fixation and/or lower amounts of terrestrial sulfate at altitude (Table 2.).

Air Filter Leachates

A comparison of the ratios of Cl/Na and SO_4/Ca in air filter leachates and in rain and surface waters in two of the study areas is shown in Table 9.

Table 9. Selected ion mole ratios for air filter leachates, surface water and rain for two study areas. Number of samples shown in parentheses.

Ion Mole Ratio	Air Filter Leach		Surface Water		Rain (by event)	
	Raton(3)	Soc(3)	Raton(3)	Soc(3)	Raton(19)	Soc(84)
SO_4/Ca	0.65	0.57	1.1	1.4	0.69	0.58
Cl/Na	0.67	0.19	0.15	0.41	1.5	1.1

(Soc = Socorro)

The SO_4/Ca ratios in the air filter leachates are about the same for the Raton (0.65) and Socorro (0.67) samples. The surface water ratios for these ions are also similar for the two areas but the ratios are higher than found in the air filter leachates. This may not be surprising because the highly alkaline surface waters in this region may be gypsum-dominated or are often saturated with respect to calcite and precipitation of calcite would lower the calcium concentration and increase the SO_4/Ca ratio.

Rain waters from Raton and Socorro exhibit SO_4/Ca ratios almost identical to the air filter leach data. This implies that the particulates in the air at ground level (terrestrial origin) strongly influence the dissolved species in precipitation in this region and high SO_4/Ca ratios (>1) indicate excess sulfate of atmospheric origin.

Examination of the Cl/Na ratios for the same samples shown in Table 9 shows low values for local surface water (0.15 Raton and 0.41 Socorro), compatible with terrestrial abundances of these elements. The ratios of 1.1 for Cl/Na in precipitation collected in the Socorro area and 1.5 in the Raton area when compared to air filter leach ratios of 0.19 and 0.67 indicate a source of excess chloride other than locally derived airborne particulates. It is possible that excess chlorine may be derived on a regional basis from chlorine liberated in coal burning. This aspect warrants further study in areas closer to the power plants.

SUMMARY

Average pH values for precipitation in the arid, high desert and mountain regions of central and northern New Mexico are lower than expected for CO2 equilibrium and range from 4.5 - 5.5 on an event basis. Volume-weighted averages are lower than event averages ranging from 4.0 - 4.9 and indicate greater acid contribution from larger events. Terrestrially derived atmospheric particulates play a major role in neutralizing acidity in low volume precipitation events. Reaction of calcareous material lowers SO4/Ca ratios in precipitation as a function of time of exposure of the precipitation with washout particulate matter. Fly ash particle number densities were calculated for precipitation washout.

Ratios of Cl/Na seem high if both ions are derived from exposure of precipitation to regional terrestrial material. The source of this apparently excess chloride is not known. The nitric acid contribution to the acidity as reflected in NO3/SO_4 ratios appears to be large considering the amount of sulfate probably contributed by entrainment processes. Wintertime NO_3/SO_4 ratios are high in Albuquerque during temperature inversions and high NO3/SO4 ratios are observed in precipitation collected in thunderstorms at high altitudes.

REFERENCES

Galloway, J.N., Likens, G.B., and Edgerton, E.S., 1976, Acid precipitation in the Northeastern United States: Science, v. 194, pp. 722-724.

Krauskopf, K.B., 1979, Introduction to Geochemistry: McGraw-Hill Book Company, 2nd edition.

Lewis, Jr., W.M., and Grant, M.C., 1981, Acid precipitation in the Western United States: Science, v. 207, pp. 176-177.

Likens, G.E., Wright, R.F., Galloway, J.N., and Butler, T.J., Acid rain: Scientific American, v. 241, pp. 43-51.

Liljestrand, H.M., and Morgan, J.J., 1981, Spatial variations of acid precipitation in Southern California: Environmental Science and Technology, v. 15, no. 3, pp. 333-339.

Liljestrand, H.M., and Morgan, J.J., 1978, Chemical composition of acid precipitation in Pasadena, California: Environmental Science and Technology, v. 12, pp. 1271-1273.

Methods for the Analyses of Water and Wastes, 1979, EPA-60014-79-020: U.S. Environmental Protection Agency, Cincinnati, Ohio.

Popp, C.J., Brandvold, D.K., Ohline, R.W., and Brandvold, L.A., 1983, Nature of precipitation and atmospheric particulates in Central and Northern New Mexico, in Deposition, Both Wet and Dry, Ann Arbor Science Press, Ann Arbor, Michigan.

Popp, C.J., Jensen, C.M., Brandvold., D.K., and Brandvold. L.A., 1982, Precipitation analysis in Central New Mexico, in Energy and the Environment, II, Ann Arbor Science Press, Ann Arbor, Michigan.

State of New Mexico Air Quality Bureau Annual Report - 1979-80, 1980: New Mexico Environmental Improvement Division, Santa Fe.

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HEAVY METALS AND PESTICIDES IN WATER, SEDIMENTS, AND BIOTA IN THE MIDDLE RIO GRANDE VALLEY

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INTRODUCTION

The Rio Grande is the most significant surface water source in New Mexico. Its waters are heavily used for irrigation and recreation. Through links with aquifers, it also affects groundwater quality. The present and future condition of the Rio Grande system is of paramount importance to New Mexico. A very important part is that concerning the concentrations, sources, transport mechanisms and ultimate fates of toxic or potentially toxic substances in the system.

The Rio Grande differs from many other rivers in that much of the material is transported by sediment containing a relatively small organic phase. Characterization and fate of the sediment is of prime importance.

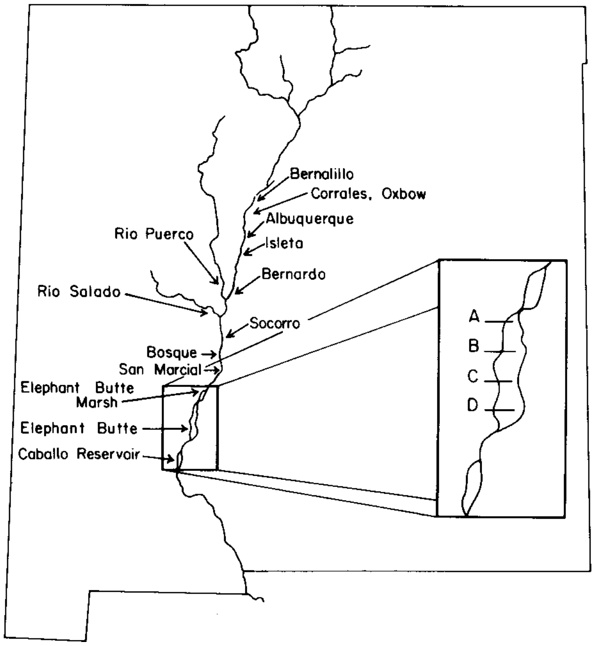
The study area and location of main sampling sites are shown in Figure 1. These sites were selected to detect changes in the main river caused by tributaries or other inputs and to investigate reservoir conditions. Data for sites north of Bernardo are primarily from a study completed in 1978 (Popp et al, 1980). Data for other sites was collected through 1983 (Popp et al, 1983).

Relatively sediment free water is released from Cochiti reservoir but by the time the water reaches Corrales, sediment loads are appreciable. Below Corrales, the major inputs are the Albuquerque metropolitan area, the Rio Puerco and the Rio Salado. Surface run off and irrigation returns are also important.

The Rio Puerco, an intermittent stream, enters the Rio Grande at Bernardo and when running carries very heavy sediment loads. This sediment tends to be high in clay-sized particles which are transported long distances. The Rio Puerco drains the eastern part of the Grants uranium area. The Rio Salado, another intermittent sediment-laden stream joins the Rio Grande south of the La Joya waterfowl refuge. At least 60% of the sediment in the Rio Grande below this point originates in these two tributaries, (Waite et al, 1972; Popp and Laquer, 1980; U.S. Army Corps of Engineers, 1972; United State Geological Survey, 1978).

South of here, the river flows past Socorro and San Marcial and enters Elephant Butte Reservoir where most of the sediment load is deposited. Since the closing of the dam in 1916, it is estimated that 0.42 Km (430,000 acre feet) of sediment have been deposited. The yearly average sediment load delivered to the reservoir is 10,600,000 tonnes (Bureau of Reclamation, 1976).

Figure 1. Study area and location of main sampling sites.



The ultimate fate of substances associated with this sediment is important. It is not known whether they are effectively trapped or released to the water or the food chain.

METHODS

Water samples were collected by messenger-activated Kemmerer bottles. Those destined for trace metal analysis were placed in acid-washed plastic bottles containing a small quantity of redistilled nitric acid. Samples to be used for pesticide analysis were stored in solvent-rinsed amber glass bottles.

Bottom sediment was collected by a Ponar bottom-grab sampler. These samples were stored on crushed ice and frozen upon return from the field. Suspended sediment was obtained by filtering water samples through a 0.45 p filter.

Fish from the reservoirs were collected by gillnetting and electroshocking in cooperation with personnel from the New Mexico Department of Game and Fish and the Department of Fish and Wildlife, New Mexico State University. Other biological samples were collected by personnel from the Museum of Southwestern Biology, University of New Mexico. In addition to fish: amphibians, reptiles, plankton, and aquatic insects were collected. A summary of all organisms collected and detailed sample preparations has been reported elsewhere (Popp et al, 1980).

Metals in sediments were fractionated into categories labeled: exchangeable, organic, hydrous metal oxide, and crystalline (Popp and Laquer, 1980). Whole sediment or sediment fractions were digested by standard methods.

All metals except mercury and uranium were analyzed using atomic absorption spectrometry in the flame (Cu, Pb, Mn, Fe, Cr), carbon furnace (Mo, V, Cd) or hydride generator mode (Se, As). Mercury was analyzed using a Coleman MAS-50 Mercury Analyzer. Uranium was determined by the colorimetric dibenzoyl-methane method.

Samples for radionuclide analysis were counted for 12 hours using a (GeLi) detector. Wet weights were used for tissue digestion. For metals except mercury, 10 mL of concentrated HNO_1 was added to one gram of tissue. The sample was heated gently until the tissue dissolved. After cooling, 5 mL of 30% H_2O_2 was added and the sample slowly brought to boiling. The sample was cooled and diluted. For mercury analysis, 50 mL H20, 10 mL H2SO4 and 5 mL HNO_3 were added to one gram of tissue. After cooling 1:5 g $KMNO_4$ and 0.5 g $K_2S_2O_8$ were added and the sample digested at 60°C and cooled. Then 1.5 gram of hydroxylamine hydrochloride was added and the sample diluted to 100 mL.

Fish and other tissue were extracted and cleaned up for analysis of organic compounds using standard procedures (Popp et al, 1983). Compound identification and quantitation was by gas chromatography. Aldrin was used as an internal standard.

RESULTS AND DISCUSSION

HEAVY METALS

Water

Average concentrations of heavy metals in filtered water are listed in Table 1. The 1978 values are for surface water while those for 1982 are for both surface and bottom water. The highest values are in samples from the Rio Puerco and Rio Salado which probably account for elevated concentrations found at Socorro. None of these concentrations of dissolved species appear to be a problem with the possible exception of mercury.

Sediments

Average values for trace metals in sediments are shown in Table 2. For the bottom sediments, mercury is higher at the reservoir sites. Uranium, iron and manganese increase from San Marcial down through Elephant Butte Reservoir.   This may be due to association with finer grained sediments which are transported further down the reservoir, and the association of uranium with the hydrous metal-oxide phase.

The elements Cd (X10), Hg (X100), Pb (X5) and U (X100) are present in considerably higher concentrations than in average crustal material. Uranium, cadmium, mercury, and lead have been found in high concentrations associated with sediment in the Rio Puerco (Brandvold et al., 1981). Efficient regional transport of suspended sediments is

TABLE 1. Average concentrations in ppb of metals in filtered water at river and reservoir sites. For 1982, S = Surface and B = Bottomwater

		As	Cd	Cr	Pb	Mn	Hg	Mo	Se	U	V	Zn
1978												
Corrales		NA	0.57	6.8	13	430	1.8	12	NA	14	92	230
Oxbow			0.31	2.3	6.9	280	1.2	9.3		22	18	78
Isleta			0.39	2.5	13	400	1.4	19		15	150	28
Bernardo			0.24	2.9	17	570	1.5	13		33	250	30
Socorro			0.75	2.7	6.5	270	4.9	12		21	51	30
Bosque			0.91	4.5	14	770	0.45	18		NA	150	43
San Marcial			0.85	5.9	6.7	480	0.66	15		12	90	43
Monticello Point			1.10	8.4	15	610	1.7	9.5		19	98	42
Elephant Butte Marsh			2.3	2.1	18	430	0.42	13		21	42	48
Elephant Butte Dam			0.65	1.2	5.8	14	1.4	9.8		37	26	25
La Joya			7.5	4.1	39	1100	2.5	27		24	80	21
Rio Salado			2.1	6.1	28	5500	3.3	31		22	200	47
Rio Puerco			0.86	7.7	26	3300	3.9	21		47	320	20
1982												
Socorro			0.01		4.9	NA						
San Marcial		25	0.73	1.4	4.8		1.5	13	1.0	NA	27	NA
Elephant Butte	A-S	11	0.39	1.8	5.9		0.51	6.7	1.4		7.8	
	A-B	11	0.20	11	2.8		0.88	3.9	1.0		16	
	D-S	9	0.80	6.9	5.5		0.44	5.8	2.2		12	
	D-B	8	0.15	2.9	3.7		1.1	4.1	0.11		12	
Caballo	S	12	0.32	7.1	7.2		0.62	3.7	2.1		14	
	B	11	0.35	12	6.3		0.57	5.2	0.07		16	

NA = not analyzed

TABLE 2. Average concentrations of heavy metals in sediments at river and reservoir sites. Values in ppm dry weight except Fe(%)

Suspended Sediments	As	Cd	Cr	Pb	Mn	Hg	Mo	Se	U	V	Zn	Fe
Corrales		0.51	27	23.9	1035	1.3				51.0	128	2.43
Oxbow		0.83	28	114	713					37.3	166	2.82
Isleta		0.78	27	24.6	1096	.93				47.1	112	2.86
Bernardo		1.25	24	27.0	436	.68	8.57			37.1	72.9	4.40
Socorro		10.5	212	15.4	1885	.0	10.0	NA	NA	285	880	8.03
San Marcial	NA	16.2	43	170	3550		2.68			107	600	243
Monticello Point		0.62	11	10.8	438		4.3			19	49	1.25
Elephant Butte Marsh		1.0	10	10	7960		2.9			374	183	1.07
Rio Puerco		1.11	62	15.4	223	.06	2.98			85.4	1390	2.79
Rio Salado		0.6	9.5	6.1	235	.034	4.0			21	39.4	1.25
Bottom Sediments												
Socorro	5.6	2.3	44	49	400	0.68	2.7	0.04	200	87		2.37
San Marcial	6.6	0.66	28	33	230	0.98	1.4	0.18	180	83		1.96
Elephant Butte A	9.1	2.5	40	48	280	3.3	0.76	0.09	180	80		2.67
B	5.4	4.0	28	41	300	8.1	0.98	0.12	200	40	NA	2.96
C	4.5	2.7	53	55	410	3.0	1.5	0.34	230	110		3.84
D	3.1	2.0	42	57	450	2.9	1.5	0.16	250	67		3.16
Caballo	8.3	3.6	42	55	1070	2.5	1.7	0.16	280	83		3.18
Crustal Abundance												
(Krauskopf 1979)	1.8	0.15	100	12.5	1000	0.02	1.5	0.05		110	70	

NA = not analyzed

probably responsible for the high reservoir values.

Results of the analyses of the partitioning of metals within sediment phases were variable, but some general trends were observed: As, Cr, Cu, Pb, U and Fe were present primarily in the crystalline phase. Cd, Mo, Fe, V and Mn were usually less than 60% in the crystalline phase. Cd and V were primarily in the hydrous metal-oxide and crystalline phases.

Fish

Values found for trace metals in fish muscle are listed in Table 3. Carp (Cyprinus carpio) data is given for both the 1978 and 1982 studies. Data for white bass (1982) and largemouth bass (1978) are included, as these fish represent ends of food chains and are consumed by humans. Several metals were elevated. The only one that is of concern is mercury which is close to 1 ppm.

PESTICIDES

Water

Gas chromatographic analysis of Elephant Butte Reservoir surface water samples indicated the occasional presence of 18 different chlorinated organic pesticides. The frequency of occurrence of the various pesticides in whole water surface samples varied from a low of 8.4% for alpha chlordane to 90.4% for heptachlor. The most commonly detected pesticides in declining order of occurrence were heptachlor, kepone, p,p'-DDD, heptachlor epoxide, alpha BHC, lindane, endrin, and methoxychlor. These pesticides were detected in at least 30% of all whole water surface samples. Pesticide concentrations were highly variable ranging from non-detectable to values in excess of 500p g/L, a span which exceeded three orders of magnitude. Mean concentrations however were usually less than 0.5p g/L. Intersample variability was high but can be explained in part by seasonal and annual differences in hydrological, chemical, and biological conditions within and between the sampling stations.

Sediments

Analysis of bottom sediment samples from the Rio Grande, Elephant Butte, and Caballo Reservoirs revealed the presence of all 18 chlorinated organic pesticides for which the samples were examined. Most however were detected in less than 30% of the sediment samples. The most commonly detected pesticides in declining frequency of occurrence were heptachlor, heptachlor epoxide, kepone, alpha BHC, beta BHC, lindane and one designated as an analytically unseparated mixture of dieldrin and o, p'-DDE. The mean concentrations of these seven pesticides were usually less than 25 pg/g. These mean values are overestimates of the true mean because only those samples in which a pesticide was detected were used in the computations. Thus the means do not reflect the large number of samples in which the pesticide of

TABLE 3. Average concentrations of selected heavy metals in fish muscle.
values in ppm

Species and Site	As	Cd	Cu	Cr	Hg	Mo	Pb	Se	V
Cyprinus Carpio (Carp)									
Elephant Butte (1982)	.54	.04	.46	.56	0.61	.86	.17	.5	0.1
Caballo (1982)	.11	.11	.05	.50	0.47	.20	.02	.05	0.1
Bernalillo (1978)		.11		.54	.50		.46		
Oxbow (1978)		.26	.54	.76	1.2		.26		
Isleta (1978)	NA	.6	1.2	.24	1.2	NA	.44	NA	NA
Bosque (1978)		.13	2.4	.58	.46		.54		
<u>Morone Chrysops</u> (White Bass)									
Elephant Butte (1982)	0.27	0.30	0.08	0.53	0.63	1.1	7.5	0.91	1.32
Caballo (1982)	0.12	0.01	0.57	1.6	0.01	0.02	0.12	0.52	0.1
<u>Micropterus Salmoids</u> (Large Mouth Bass)									
Oxbow (1978)	NA	0.23	4.9	0.20	2.8	NA	1.3	NA	NA
Bioaccumulation determined at Oxbow and Isleta (1978) (X water concentration)		388	307	413	1936		108		

NA = not analyzed

interest was not detected. The river sediments are more contaminated with alpha BHC, beta BHC, and lindane than the reservoir sediments while the reverse is true for heptachlor, heptachlor epoxide, and kepone. This dichotomy between the river and reservoirs may be due to differences in particle size distributions of the sediments. The reservoir sediments contain higher percentages of silt and clay-sized particles. When pesticide concentrations in the silt-clay fraction only are examined, the river and reservoir sediment pesticide concentrations are more equitably distributed.

Fish

Pesticide analysis of a pool of 55 edible muscle fillets taken from white bass (Morone chrysops), carp (Cyprinus carpio), and gizzard shad (Dorosoma cepedianum) indicated that beta BHC, heptachlor, and p,p'-DDT occurred in 22%, 36%, and 51% of the samples respectively. All other pesticides were detected much less frequently. Beta BHC and heptachlor were detected more often in muscle from white bass than from the other two species, whereas DDT was detected more frequently in gizzard shad. When detected, concentrations of these pesticides were usually less than 0.4 pg/g.

RADIONUCLIDES

Data for radionuclide analysis is shown in Table 4. The elements Pb-210, Ra-226 and Th-234 are part of the U-238 decay series. These correlate with stream sediments from the Grants Mineral Belt (Popp et al., 1983; Brandvold et al, 1980). Cs-137 results from fallout. The low values in Elephant Butte sediments indicate dilution with older Cs-137 free material. The higher values in Caballo Reservoir indicate less dilution.

CONCLUSIONS

Rather large quantities of some heavy metals are being transported by the Rio Grande and deposited in Elephant Butte Reservoir. These are primarily bound to sediments. Appreciable amounts of pesticides are also deposited. Some cycling of metals and pesticides to reservoir water from sediments is apparently taking place. The extent is unknown. The ultimate fate of the material stored in the reservoir is cause for concern.

TABLE 4. Radionuclide activities in sediments. Values in pCi/g dry weight.

	Rio Grande		Elephant Butte			Caballo
Radionuclide	Soc	SM	B	C	D	CAB
Cs-137	0.26	0.067	0.19	0.39	0.20	0.71
Pb-210	1.61	0.99	1.55	2.08	1.68	2.70
Ra-226	2.71	1.62	2.05	2.70	2.82	2.67
Th-234	1.20	0.82	1.06	1.22	1.09	1.00
Ac-228	1.40	0.88	0.39	1.82	1.53	0.70

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REFERENCES

Brandvold, D. K., Brandvold, L. A., and Popp, C. J., 1 98 1, Effects of Uranium Mining and Milling on Surface Water in New Mexico, in Reynolds, J. P., McCarthy, W. N., and Theodore, L. (Eds.). Environmental and Economic Considerations in Energy Utilization: Ann Arbor Science Press, Ann Arbor, MI, pp. 467-476.

Bureau of Reclamation, 1976, New Mexico Water Resources. Assessment for Planning Purposes: United States Department of the Interior. 218 p.

Krauskopf, K. B, 1979, Introduction to Geochemistry 2nd. Ed.: McGraw-Hill Book Company, New York, New York.

Popp, C. J., Brandvold, D. K., Scott, N. and Gloss, S., 1980, Heavy Metals and Pesticides in Selected Tissue Samples of Aquatic Life in the Middle Rio Grande Valley in New Mexico: Report to the New Mexico Environmental Improvement Division, Santa Fe, N.M.

Popp, C. J. and Laquer, F., 1980, Trace Metal Transport and Partitioning in the Suspended Sediments of the Rio Grande and Tributaries in Central New Mexico: Chemosphere 9, p 41-46.

Popp, C. J., Brandvold, D. K., Lynch, T. R. and Brandvold, L. A., 1983, An Evaluation of Sediments in the Middle Rio Grande, Elephant Butte Reservoir, and Caballo Reservoir as Potential Sources for Toxic Materials: Technical Completion Report, Project 1423626, New Mexico Water Resources Research Institute, Las Cruces, NM.

United States Army Corps of Engineers, 1972, Rio Grande and Tributaries, Rio Puerco and Rio Salado, New Mexico. Report on Review Survey for Flood Control and Allied Purposes: Albuquerque, NM serial 170 61.

United States Geological Survey, 1978, Water Year Data, New Mexico. United States Department of the Interior.

Waite, D. A., Davis, J., Rice, L., Wilson, L., Kinsinger, F., Leifeste, W. and Rathburn, D, 1972, Rio Puerco Special Project Evaluation Report, 1242,3: United States Department of the Interior, Bureau of Land Management, Santa Fe, NM.

NATURAL SURFACE-WATER QUALITY IN THE GRANTS MINERAL BELT

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ABSTRACT

A water sampling program was carried out in the Grants area in order to quantify natural surface-water chemistry in this region of uranium mineralization.Most stream flow in the region results from summer thunderstorms that generate flash floods in otherwise dry arroyos. These floods carry some of the largest known suspended sediment concentrations in the world. Chemically, regional surface waters are neutral to slightly alkaline (pH 7 to 8.5). Principal dissolved constituents, e.g. sodium and calcium, are derived from sulfate and carbonate rich salts.

Presence of trace elements and radionuclides in runoff is extremely variable depending chiefly upon the amount of suspended sediment. Samples filtered to remove suspended sediment usually exhibit undetectable amounts of most trace elements and radionuclides. In contrast, unfiltered water samples contain high levels of several elements associated with uranium ore, including arsenic, lead, selenium, vanadium, uranium, radium-226 and lead-210. For the most part, these elements are relatively insoluble in regional surface waters, remaining tightly bound to silt and clay particles.

INTRODUCTION

Since 1978, the New Mexico Environmental Improvement Division (EID) has systematically sampled perennial water in the Grants Mineral Belt (Figure 1). These data were augmented in 1982, when samples of snowmelt and thunderstorm runoff from ephemeral watercourses were collected. These sampling programs allow the quantification of the quality of natural-surface waters in the region, thereby establishing a baseline against which the quality of uranium industry effluents can be evaluated.

Three aspects of natural-water quality are specifically addressed in this paper. The first and most obvious characteristic is the great turbidity that is typical of streams in semi-arid regions. Second is the chemical quality of sediment-free water; that is, dissolved salts, trace elements, and radioactivity. Finally, the chemical and radiological quality of raw, unfiltered runoff is discussed. Sediment-laden runoff characteristically has large

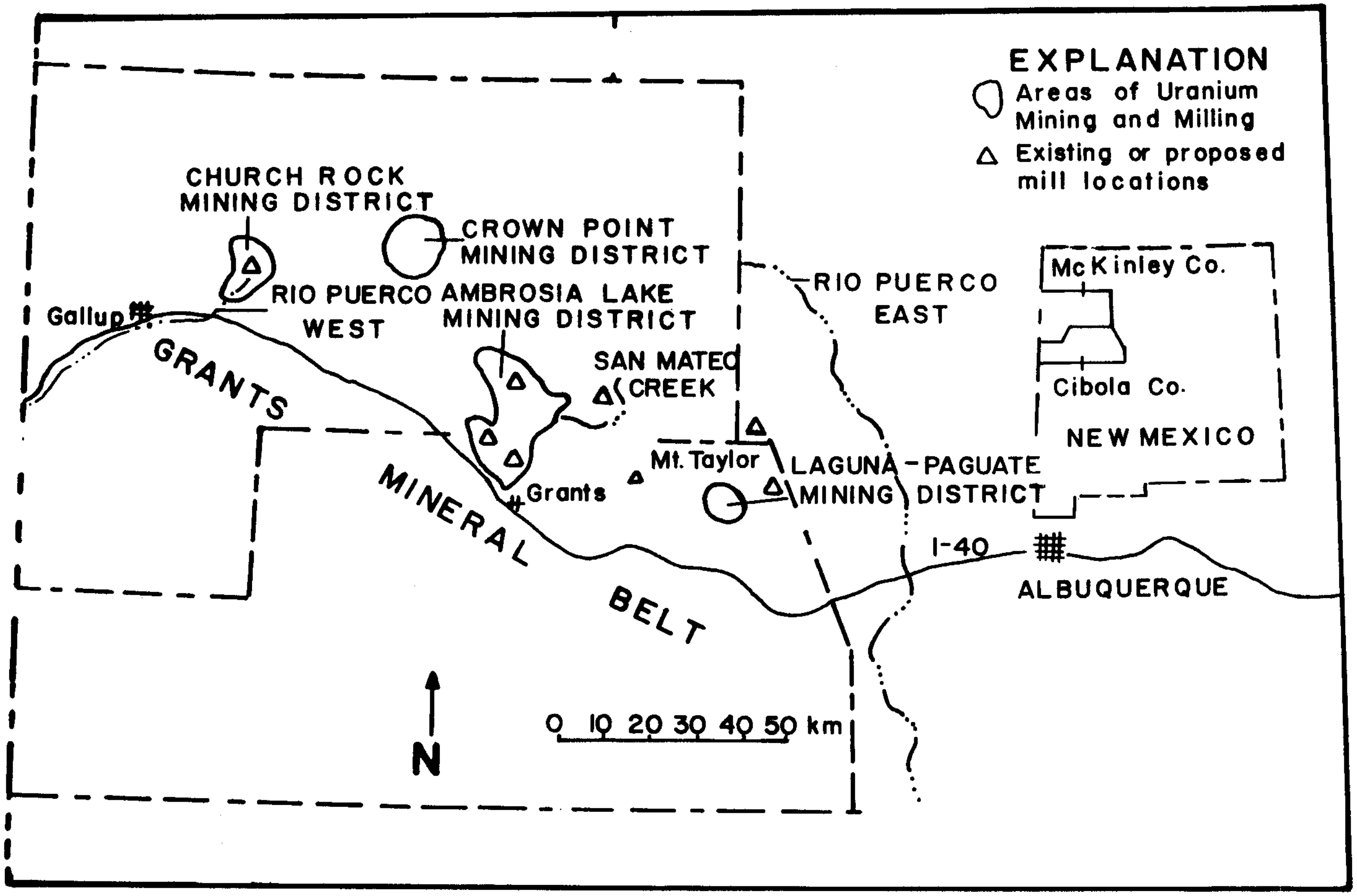

Figure 1. Location map of the Grants Mineral Belt.

concentrations of metals and radionuclides.These substances are present in quantities that are of concern to regional inhabitants and their agricultural activities.

SUSPENDED SEDIMENT

Suspended sediment levels in surface waters of the Grants mineral belt span a wide range of concentrations (Table 1). The few naturally perennial streams are virtually sediment-free, but most of the region is drained by dry arroyos that carry turbid flash floods after summer thunderstorm activity. The tremendous sediment concentrations of regional arroyos are among the world's highest (Gregory and Walling, 1973).

PERENNIAL STREAMS

Rio Paguate and Rio Moquino originate on the well-vegetated north-east slope of Mount Taylor and traverse the Laguna-Paguate uranium mining district (Figure 1). Since construction of San Mateo Reservoir, San Mateo Creek has flowed continuously near the community of San Mateo, located on the northwest side of Mount Taylor. Rio Paguate, Moquino and, locally, San Mateo Creek are perennial and virtually sediment free except during storm water runoff.

EPHEMERAL STREAMS

The majority of stream flows in watercourses in the Grants mineral belt and the Colorado Plateau of northwestern New Mexico are intense, short-lived and turbid . Suspended sediment concentrations in these arroyos vary up to hundreds of thousands of milligrams per liter (mg/1) (Busby, 1979). The Puerco River exemplifies this type of stream; one composite sample collected by EID in 1982 contained over 500,000 mg/1 of sediment (Table 1). The name "Puerco", which means "muddy", has been applied to several regional streams that are "to thick to drink, too thin to plow."

The large suspended sediment loads are due to three major environmental factors. First, several geologic strata in the region are erodible, weathering to silt and clay-sized particles that are easily carried in suspension by flowing water. Important sediment-producing rock units are chiefly shales, including the Mancos Shale of the Puerco River valley (Dane and Bachman, 1965; Jackson and Julander, 1982). Second, the semi-arid climate prevents establishment of protective vegetative cover on the soil. In lowland areas, the soil is sparsely vegetated with drought-resistant plants,
including shrubs and bunch grasses. Overgrazing by livestock has rendered the ground surface even more vulnerable to erosion. Third, the late summer (July-September) rainy season brings intense thunderstorms that rapidly generate large volumes of runoff. Whether overland or in a channel, these flows readily entrain exposed sediment grains.

Table 1. Natural suspended sediment concentration in surface waters of the Grants Mineral Belt.

	Suspended Sediment Concentration (mg/1)			
	Log mean	**low**	**high**	**no. of samples**
perennial streams[1]	8	0	82.8	32
emphemeral washes[2]	42,000	3,680	561,000	9

[1] Grab samples from San Mateo Creek near San Mateo, Rio Paguate near Paguate, and Rio Moquino near Paguate.

[2] Grab samples and single-stage runoff samples from South Fork Puerco River near Church Rock, Puerco River near Pinedale, and two unnamed arroyos near Ambrosia Lake and San Mateo, respectively.

Table 2. Background median concentrations of dissolved trace elements and radionuclides in perennial and ephemeral streams of the Grants Mineral Belt. Number of samples given in parentheses.

	Dissolved Concentrations (ug/l)			
Constituent	Perennial Streams		Ephemeral Washes	
Arsenic	<5	(39)	<5	(3)
Barium	<100	(30)	<100	(3)
Cadmium	<1	(26)	<1	(3)
Lead	<5	(26)	<5	(3)
Molybdenum	<10	(39)	<10	(8)
Selenium	<5	(39)	<5	(7)
Uranium-natural	<5	(37)	<10	(5)
Vanadium	<10	(29)	25	(3)
Zinc	<50	(27)	<50	(3)
Gross alpha (pCi/l)	2	(29)	17	(3)
Radium-226 (pCi/l)	0.1	(36)	1.2	(3)
Lead-210 (pCi/l)	1	(2)	4.5	(10)
Polonium-210 (pCi/l)	--	--	2.3	(7)
Thorium-238 (pCi/l)	--	--	0.3	(7)
Thorium-230 (pCi/l)	--	--	0.3	(7)
Thorium-232 (pCi/l)	--	--	0.2	(7)

RELATION BETWEEN SUSPENDED SEDIMENT AND CHEMICAL QUALITY OF SURFACE WATER

Suspended sediment can be a significant transport agent for chemical substances in water. In the emphemeral watercourses of the Grants Mineral Belt, high suspended sediment concentrations account for the major portion of the contaminant transport.

Metals and Trace Elements

The behavior of various trace elements in surface-water environments depends on factors such as pH and redox potential. Those elements that form cations (barium, cadmium, lead, zinc) usually are adsorbed onto sediment grains, with only small amounts dissolved in the water. In the solid phase, these metals can occur as constituents in minerals such as carbonate, hydroxide, oxyhydroxide and sulfate precipitates. Additionally, they may occur as cations adsorbed onto clays and organic matter, or may form complexes sorbed onto metal-oxide coatings present on mineral surfaces (Runnells, 1976; Korte and others, 1976; Fuller, 1977; Popp and Lacquer, 1980; Zimdahl and Skogerboe, 1977). In regional surface waters, geochemical conditions are oxidizing and the pH is slightly alkaline. For barium, cadmium, lead, and zinc, conditions strongly favor immobilization and dissolution is minimal. These trace elements are concentrated on sediments suspended in runoff, rather than existing as dissolved constituents.

For other elements, the slightly alkaline, oxidizing environment causes formation of oxyanions, which have a greater tendency to dissolve. Arsenic, molybdenum, selenium, and vanadium are four such elements.

Radionuclides

The same principles that govern the chemical behavior of trace metals also govern the chemical behavior of radioactive elements. Uranium can *be* present as an anion [$UO2(CO3)2^{2-}$] and is soluble and mobile under the oxidizing, alkaline conditions of the region (Ames and Rai, 1978). To the contrary, most thorium-230, radium-226, polonium-210, and lead-210 found in Grants mineral belt surface waters are expected to be attached to the clay fraction of stream sediment; only a small portion should be in solution.

DISSOLVED SUBSTANCES

Dissolved salts in surface waters of the study area originate chiefly from weathered rocks and residues from evapotranspiration. Shale and limestone strata are the primary geologic sources of dissolved solids in the region. Perennial waters originating at high elevations have few dissolved solids (TDS). The dissolved load increases as these streams traverse more saline lowland areas. Flows in ephemeral lowland streams tend to be moderately high in TDS.

GENERAL CHEMISTRY

Evaluation of sampling data shows that concentrations of total dissolved solids vary from less than 200 mg/1 to over 1500 mg/l. The least saline waters, San Mateo Creek and Puerco River-South Fork, drain wooded upland slopes. The most saline water is the Rio Moquino.The Mancos Shale, from which the Rio Moquino valley is excavated, has been shown to be one of the largest sources of salinity in the entire Colorado River basin (Jackson and Julander, 1982).

A Piper (1953) graphical analysis of the data indicates that natural waters from Rio Moquino and Puerco River-North Fork are dominated by dissolved calcium and sulfate, which are abundant in the Mancos Shale. Puerco River-South Fork and San Mateo Creek flow chiefly in limestone terrain. Accordingly, these waters are enriched with bicarbonate ions. Rio Paguate waters have a chemical composition intermediate between these two types. All of the surface waters tested are neutral to slightly alkaline (pH 7 to 8.5).

TRACE ELEMENTS AND RADIONUCLIDES

Table 2 shows that in perennial streams dissolved trace elements are rarely detected. High sediment loads in ephemeral flow may result in slightly higher dissolved concentrations of trace elements, but overall the load of dissolved trace elements is also very small in ephemeral washes (Table 2). Dissolved gross alpha radioactivity, representing the sum of alpha particle-emitting radionuclides, is also quite low in regional surface waters.

CHEMICAL QUALITY OF TURBID WATERS

RELATION OF CHEMICAL QUALITY TO SUSPENDED SEDIMENTS

Concentrations of most trace elements and radionuclides in turbid runoff demonstrate a strong, statistically significant dependence on the amount of sediment present in the sample. Regression analyses show that, in most cases, the amount of a particular constituent detected in an unfiltered water sample is a positive, linear, first-order function of total suspended sediment; correlation coefficients (R) are ofter greater than 0.90. In other words, each additional quantity of sediment added to a surface water volume adds constant proportions of attached metals and radionuclides. The concentration of each element associated with sediment (i.e. the slope of a regression line) varies between drainages and depends chiefly on the elemental composition of rocks and sediments in the basins.

TRACE ELEMENTS AND RADIONUCLIDES

Metal and radionuclide data presented in Tables 3 and 4 illustrate the extreme variability in metals and radionuclides levels in unfiltered waters. Concentrations of those constituents may range from below analytically detectable levels up to 1000 times greater. Because of the strong relationship between sediment load and contaminant concentration, this range can be mathematically described, but "typical" or "average" concentrations realistically can not be.

Trace Elements

For several elements studied, recommended safe limits for livestock (National Academy of Sciences/National Academy of Engineering, 1972) are exceeded if the suspended-sediment concentration is great enough. Total suspended solids concentrations of 10,000 mg/1 are often sufficient to exceed those recommended limits.People are not likely to drink turbid-surface waters, but livestock are.By ingesting turbid water, the suspended sediments and any attached contaminants are also ingested.The most serious concerns are associated with vanadium and lead.Among 16 samples, the vanadium criterion was exceeded by 88 percent of the samples, and the lead criterion by 82 percent.

Radionuclides

Radioactive substances are present in detectable concentrations in all of the runoff samples analyzed during this study. Gross alpha radioactivity measurements ranged from 9 pCi/1 to 2100 pCi/1 with a median concentration of 685 pCi/l. Gross beta radioactivity ranged from 135 pCi/1 to 2000 pCi/1 with a median concentration of 860 pCi/l. Complete isotopic analyses of unfiltered-runoff samples from background sites indicate that radium-226 and lead-210 are of concern in areas unaffected by the uranium industry. Seven samples from three sites were tested for natural uranium; thorium-228, -230 and -232; radium-226; lead-210; and polonium-210. These isotopes constitute all the major non-gaseous radionuclides in the uranium-238 decay series.

In Table 4, observed radionuclide concentrations are compared to limits allowed for State-licensed uranium industry dischargers New Mexico Environmental Improvement Board 1980). These limits are known as maximum permissible concentrations (MPCs), and pertain only to effluents discharged under a state license. Thus, MPCs do not pertain to natural waters, but they do provide a means of evaluating the relative importance of radionuclide concentrations.

The results, indicate that uranium and thorium are present in small amounts in comparison to the MPCs. Polonium-210, on the other hand, occasionally reaches concentrations of more than half of the

Table 3. Comparison of whole water trace elements concentrations in the Grants Mineral Belt with recommended agricultural limits (National Academy of Sciences/National Academy of Engineering, 1972). All data given in ug/l.

Constituent	Range in Natural Waters	Ephemeral Waters Median Concentration	Recommended Limit
Arsenic	5 - 302	70	200*
Barium	100 - 43,500	4,700	---
Cadmium	1 - 55	3	50*
Lead	5 - 2,040	250	100#
Molybdenum	5 - 10	10	100#
Selenium	5 - 147	5	50*
Uranium - natural	5 - 560	30	---
Vanadium	10 - 3,180	410	100*
Zinc	250 - 8,500	365	25,000*

*Livestock criterion;

#irrigation criterion

Table 4. Comparison of natural whole-water radionuclide concentrations in the Grants Mineral Belt with Maximum Permissible Concentrations (MPCs).

Radionuclide	Concentration Range In Natural Waters (pCi/l)	Turbid Waters Median Conc. (pCi/l)	Unrestricted* MPCs (pCi/l)
Radium-226	0 - 321	19	30
Lead-210	0 - 720	39	100
Polonium-210	0 - 450	56	700
Thorium-230	0 - 42	22	2,000
Thorium-232	0 - 43	24	2,000
Thorium-228	0 - 43	22	7,000
Uranium-natural	0 - 400	20	30,000

*Although natural levels may exceed MPCs, such exceedances do not constitute violations of regulations (NMEIB, 1980); MPCs are presented for comparison purposes only.

maximum permissible concentration. Of greatest concern, though, are radium-226 and lead-210. EID data indicate that between 85 to 95 percent of the radium-226 and lead-210 detected in a turbid water sample is bound to the sediment. These radionuclides frequently approach or exceed their respective MPCs in uncontaminated, natural runoff in the Ambrosia Lake and Church Rock areas.

Although the radionuclide concentrations in Table 4 are heavily weighted toward the Church Rock area, they are thought to be representative of the entire Grants mineral belt. Of the seven samples, four were collected from the Puerco River-South Fork and two were collected from the North Fork; one was collected from the San Mateo Creek in the Ambrosia Lake area. All samples had the same general radiological quality, with the usual amount of variation. The Church Rock, Ambrosia Lake, and Laguna-Paguate mining districts are very similar in terms of sedimentary geology and landform development. Therefore, turbid runoff in the region of uranium mineralization probably has a similar radiological character that is relatively high in radium-226 and lead-210, under natural conditions (see paper by Popp and others, this volume).

U. S. Geological Survey data from nearby watersheds support this contention. Ephemeral washes draining northward from the Grants mineral belt into the San Juan Basin are similar to those within the study area. During turbid flow conditions, gross alpha and gross beta activities as high as several thousand pCi/1 have been measured in the Chaco Wash drainage basin (USGS, 1979).Analyses were not performed for specific radionuclides.It is evident, nevertheless, that high radionculide content is typical of turbid flows throughout northwestern New Mexico, including the Grants mineral belt.

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REFERENCES

Ames, L. L. and Rai, D., 1978, Radionuclide interactions with soil and rock media: Office of Radiation Programs, U. S. Environmental Protection Agency, EPA 520/6-78-007, 307 p.

Busby, M. W., 1979, Surface water environment in the area of the San Juan Basin Regional Uranium Study; New Mexico, Colorado, Arizona, and Utah: U. S. Geological Survey Open-File Report 79-1499, 58 p.

Dane, C. H. and Bachman, G.O., 1965, Geologic map of New Mexico, 1:500,000: U. S. Department of the Interior, Geological Survey.

Fuller, W. H., 1977, Movement of selected metals, asbestos, and cyanide in soils: Application to waste disposal problems: U. S. Environmental Protection Agency, EPA 600/2-77-020, 242 p.

Gregory, K. J. and Walling, D. E., 1973, Drainage basin forms and processes, a geomorphological approach: John Wiley and Sons, New York, 456 p.

Jackson, W. L. and Julander, R. P., 1982, Runoff and water quality from three soil landform units on Mancos shale: Water Resources Bulletin v. 18, no. 6, pp. 995-1001.

Korte, N. E.,Skoop, J., Fuller, W. H., Niebla, E. E., and Alesii, B. A., 1976, Trace element movement in soils:Influences of soil physical and chemical properties:Soil Science, v. 22, no. 6, pp. 350-359.

National Academy of Sciences and National Academy of Engineering, 1972, Water quality criteria 1972: Prepared for the U. S. Environmental Protection Agency, EPA/R3/73/033, U. S. Government Printing Office, Washington, D.C., 594 p.

New Mexico Environmental Improvement Board, 1980, Radiation Protection Regulations, as amended October 9, 1981.

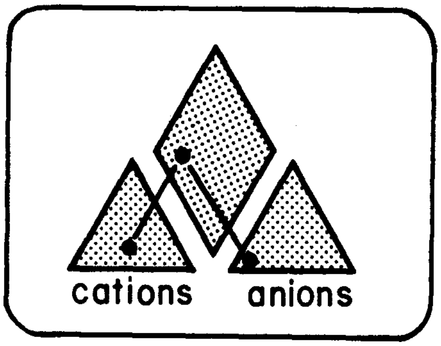
Piper, A. M., 1953, A graphical procedure in the geochemical interpretation of water analyses: Ground Water Note 12, U. S. Geological Survey,

Popp, C. J. and Laquer, F., 1980, Trace metal transport and partitioning in the suspended sediments of the Rio Grande and tributaries in central New Mexico: Chemosphere, v. 9, pp. 89-98.

Runnells, D. D., 1976, Wastewaters in the vadose zone of arid regions, geochemical interactions: Ground Water, v. 14, no. 6, pp. 374-385.

U. S. Geological Survey, 1979, Water resources data for New Mexico, water year 1979: U. S. Geological Survey Water-Data Report NM-79-1, 749 p.

Zimdahl, R. L. and Skogerboe, R. K., 1977, Behavior of lead in soil: Environmental Science and Technology, v. 11, no. 13, pp. 1202-1207.



RADIONUCLIDE AND HEAVY METAL DISTRIBUTION IN 20TH CENTURY SEDIMENTS OF MAJOR STREAMS IN THE EASTERN PART OF THE GRANTS URANIUM REGION, NEW MEXICO

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ABSTRACT

Geomorphic and geochemical techniques were combined to study radionuclides and heavy metals in historic deposits of the Rio Puerco drainage in order to establish baseline geochemistry of sediments derived from the eastern part of the Grants uranium region and to evaluate possible impacts of uranium mining and milling. Because these elements adsorb to clays, we chose sample sites where relatively thick sequences of fine-grained sediments accumulated along drainages, including deposits behind a dam on the Rio Paguate and in abandoned channels (oxbows) along the Rio San Jose and Rio Puerco. Comparison of old and more recent sets of aerial photographs and maps established the age of formation of the sampled channels; stream-flow records and modern channel geometry provided estimates of possible numbers of flood events at each site; and the presence or absence of Cs-137 in sediments established whether they had been deposited prior to or after 1950 (pre- or post-mining). Concentrations of radionuclides and heavy metals in sediments show regionally high values of U, As, Se, Cd, Hg, and U-decay products related to regional mineralization but unrelated to mining. Surface samples show higher levels of U-decay products than subsurface samples. Locally increased amounts of decay products of U-238 and Se which clearly postdate the onset of mining are trapped in Paguate Reservoir downstream from an extensive mine complex. Further refinement of the age of sediments may be possible using flood data combined with oxbow stratigraphy and dendrochronology, or using stratigraphic changes in relative abundance of Cs-137 or Pb-210.

INTRODUCTION

The lack of pre-1979 baseline studies complicated evaluation of a spill from a uranium tailings pond of 95 million gallons of pH 1.5 waste water containing high concentrations of radionuclides, trace metals and suspended sediments that contaminated the Puerco River in western New Mexico (Millard and others, 1983; Gallaher and Cary, in press). We initiated a study of the Rio Puerco drainage along the eastern margin of the Grants uranium region to (1) obtain baseline data on chemical and physical properties of sediments in the drainage and (2) determine whether uranium mining and milling which began there in 1950 are contributing elevated amounts of trace metals and radionuclides to the drainage. We used both geomorphological and chemical techniques to determine (A) the sources, mechanisms of transport and deposition, and physical characteristics of the fluvial sediments, (B) the most favorable places to sample historical fine-grained sediments, (C) the ages of deposits, and (D) the radionuclide and trace metal content of the samples. This report summarizes the techniques and results of the study; Popp and others (1983) give details of the procedures used and the results at each sample site.

The strategy for determining the age of the samples depends on using both geomorphological and chemical techniques. Abandoned channel loops (oxbows) were chosen for study because they are easy to locate on aerial photographs taken since 1935, can be assigned an age for development using subsequent photographs and maps, and commonly have thick, clay-rich fill. Adjacent reaches of the present stream channel were studied for comparison and to determine frequency of floods.

The use of radionuclides with relatively short half-lives, such as Pb-210 and Cs-137, to date recent sediments is well established (Krishnaswami and Lal, 1978). Cesium 137 is an artificial radioisotope formed by nuclear fission and has a half-life of about 30 years (Lederer and others, 1967). This isotope has been introduced into the atmosphere in irregularly varying amounts since above-ground nuclear testing began in 1945 (Durham and Joshi, 1980). Dating methods based on Cs-137 depend on the imprint of an irregular influx of wet and dry atmospheric deposition in sediment layers and/or on its absence before 1945. Lead 210 is a naturally occurring radioisotope in the uranium-238 decay series with a half-life of approximately 22.3 years (Lederer and others, 1967). The presence of Pb-210 in atmospheric deposition is due to the escape of a fraction of its precursor, Rn-222, from the earth's crust into the atmosphere and subsequent rapid decay to Pb-210 which undergoes deposition like Cs-137. The exponential decay of the atmospherically derived Pb-210 can then be used to estimate the age of a sediment layer as long as the sediment is significantly higher in activity than the Pb-210 already present.

Both Pb-210 and Cs-137 are strongly bound by sediments and tend to remain trapped in a sediment layer which may become buried. Generally, radionuclides and associated trace metals are significantly enriched in the finest size fractions (Robbins and Edgington, 1975; Smith and Walton, (1980), due to the greater surface area, cation exchange capacity, hydrous metal oxide, and organic contents of these fractions. As a result, activities of radionuclides may be significantly affected by the silt and clay content of the samples.

In previous studies, deposition occurred in environments under regular and continuous sedimentation where individual samples typically represented a year or more of accumulation. Sediment deposition is complicated in the ephemeral, flashy-discharge streams in this study, however, and occurs over a matter of a few hours or a few days in highly irregular episodes. Moreover, significant mixing, dilution, and redisposition of sediments may occur.

METHODS

SELECTION AND CHARACTERIZATION OF SAMPLE SITES

Because metals and radionuclides are adsorbed on clays, we looked for thick deposits of fine-grained sediments, particularly in oxbows formed after 1935, and in some cases, after 1954. The oxbows were chosen upstream, near, and downstream from uranium mine-mill activity (fig. 1). We also selected a sample site in the delta of Paguate Reservoir, a small impoundment 7 km downstream from the Jackpile uranium mine. Oxbows along the Rio Puerco and Rio San Jose were located by comparing maps and aerial photographs from the 1930's, 1940's, 1950's and 1970's.

After site selection, we dug pits in both the oxbows and in adjacent modern channels to sample and describe sedimentary structures, colors and textures. We augered from 1.5 to 5 m to sample deeper sediments. We constructed topographic profiles across channels and oxbows to interpret flow characteristics of the channels and to estimate the possible number of floods reaching the oxbows. Possible sources of radionuclides were determined by examination of geologic reports (e.g. McLemore, 1983; Anderson, 1981), geologic maps (Dane and Bachman, 1965), and local reconnaissance studies (Young, 1982; Love and Young, 1983).

LABORATORY PROCEDURES

In the laboratory, 450 ml of material were removed from each sample using a riffle splitter with 1 cm openings. Any objects larger than 1 cm were removed from the sample. A series of smaller samples were processed to determine grain size, grain mineralogy, percent clay, clay mineralogy, and trace-metal chemistry. About half the sample was saved in case a duplicate sample was needed.

Determination of Radionuclides

Each 450 ml split was mixed to ensure homogeneity and put in plastic Marinelli beakers for gamma ray counting. The beakers were sealed with tape and, for Pb-210 analyses, allowed to stand for a minimum of two weeks to allow for Rn-222, and hence Pb-214 ingrowth (see Schery, 1980).

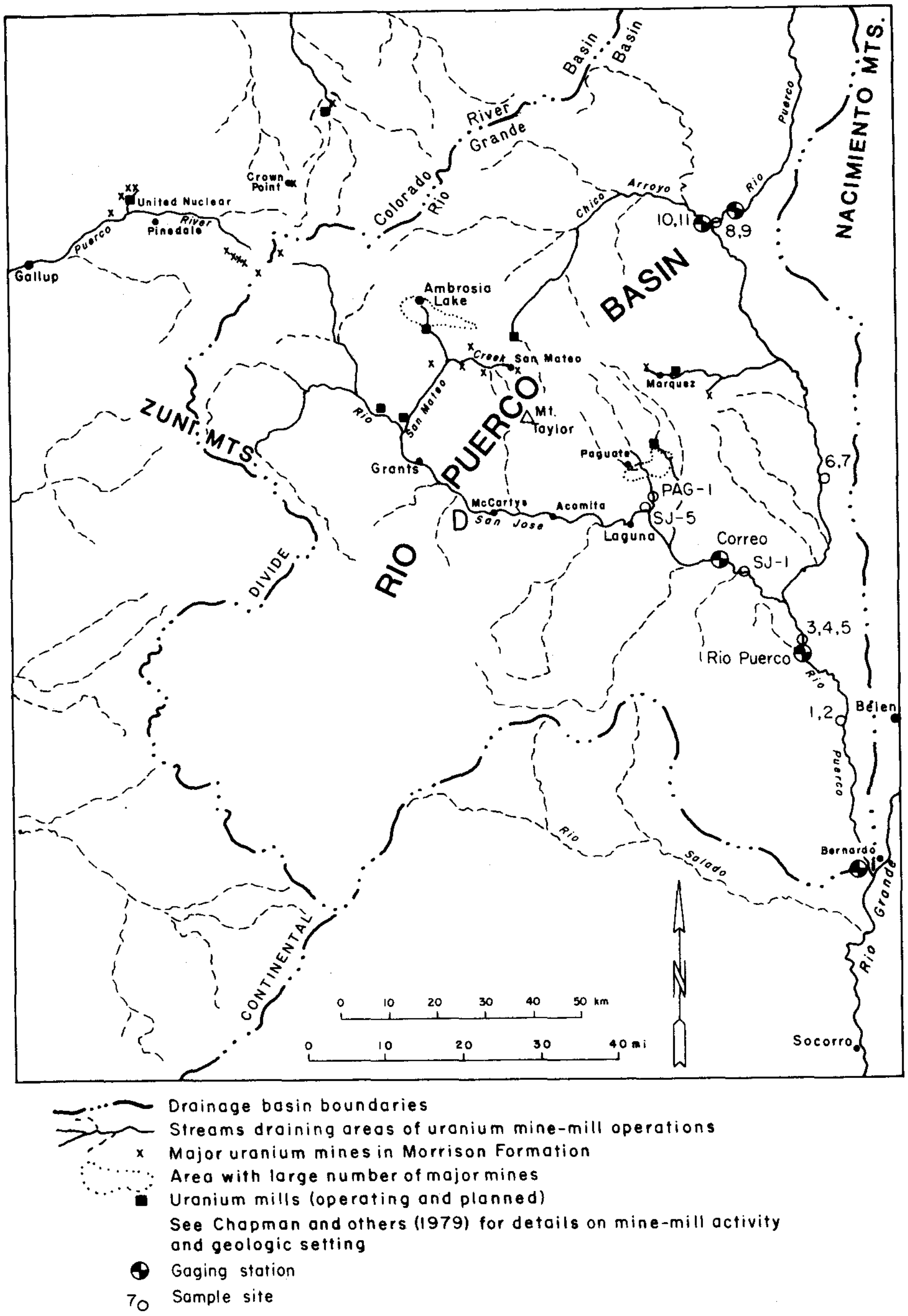

Figure 1. Location of mines and mills of the Grants uranium region, gaging stations, and sample sites in the Rio Puerco drainage basin.

Activities of the radioisotopes were obtained by gamma spectrometry using an N-type, high purity, low background, lithium-doped germanium detector. The gamma spectra were obtained using one of three lead-shielded Ortec Gamma-X spectrometers linked to a 4096-channel pulse-height analyzer. Minimum counting times for Cs-137 and Pb-210 were 4,000 and *16,000* seconds respectively. The energy range of the spectra in both cases was approximately *0.1500* KeV. For low levels, counting times of about *40,000* seconds were sufficient. Activities of each isotope (in pCi/g) were calculated from the peak areas, sample weights, and branching ratios using previously determined efficiencies at these energies (see Popp and others, 1983, for details).

Determination of Trace Metals

Trace metals were measured by atomic absorption (A.A.). Samples were prepared for A.A. by digesting selected silt (<63 MM) and clay (<2) fractions in hydrofluoric acid-aqua regia-perchloric acid (Johnson and Maxwell, 1981). In general, 2.00 g of silt fraction and 0.25 g of clay samples were digested and brought up to *100* ml using 10% nitric acid. Standard materials SY-2, SY-3 (Canadian Certified Reference Material), SL-1 (Canadian Atomic Energy Commission), and NBS 1645 river sediment were used to test analytic procedures.

Mercury was determined by cold vapor A.A. according to USEPA (1979) procedure No.'s 218.1 and 220.1. Mo, Ni, Cd, Pb, and V were determined by furnace techniques as described by USEPA (1979) method No.'s 246.2, 249.2, 239.2, and 286.2, respectively. Uranium was analyzed spectrophotometrically with dibenzoylmethane after separation by solvent extraction with tri-n-octylphosphine (adapted from Horton and White, 1958).

RESULTS

FIELD RELATIONS

Oxbows were found where predicted from interpretation of aerial photographs and maps. Changes in the configuration of the channel of the Rio Puerco between 1954 and 1983 (29 years) are much larger than between 1935 and 1954 (19 years). These changes may be related to hydrologic changes in the drainage basin and to changes in vegetation along the floodplain. Spot sampling within each oxbow and within each pit showed that the oxbows have extremely variable amounts of clay. Unexpectedly, some oxbows (particularly those formed between 1935 and 1954) have more sand than clay. Moreover, sediment eroded from adjacent arroyo walls contributed major proportions of surficial and shallow deposits in some of the oxbows. Along the Rio San Jose and the lower Rio Puerco, sediments from different source areas may be distinguished in a general way by color.

None of the deposits contained artifacts to help date sediments more closely, but dendrochronology of tamarisks colonizing abandoned parts of the floodplain was used successfully to date one site. Based on present channel configuration, all the sites probably have been flooded between 8 and 22 times since mining began in 1950.

MINERALOGY OF SEDIMENTS

Eighteen samples from four sample sites were analyzed for mineralogy of clay and non-clay-size fractions. The most abundant non-clay mineral in all size fractions is quartz. Feldspar (largely albite and microcline) and calcite are also present in clay-sized fractions. Although evaporites and magnetite were noted in the field, these minerals were not detected using X-ray diffraction.

The most abundant clay mineral group in all eighteen samples is kaolinite. Significant quantities of smectite, illite, and chlorite are common, but show a wide range among samples. Randomly oriented mixed-layer illite-smectite is also common.

No systematic variations in mineralogy of individual size fractions occurred between sites or with depth at each site, except for a possible increase in the proportion of chlorite in the clay-size fraction with depth. No systematic variations were noted in the proportion of fine-grained sediment (silt and clay) in samples of a given mean grain size, nor in the silt/clay ratio.

RADIONUCLIDE ACTIVITIES

Naturally occurring radionuclides which commonly are present in uranium deposits as daughters of U-238 decay and which may be transported with sediments away from mine and mill sites are Pb-210, Pb-214, Ra-226, and Th-234. Actinium-228, a long-lived daughter of Th-232 (Th is not regionally enriched) provides an independent measure of radionuclide behavior. Average radionuclide activities in surface samples compared to valley fill for various sections of the study region are shown in Table 1. In all cases, the recently deposited surface samples exhibit higher activities than the much older valley fill. The highest radionuclide activities were found in the Paguate Reservoir sediments which are trapped immediately downstream from the Jackpile mine. The surface samples from the lower Rio Puerco (downstream from the confluence with the Rio San Jose) exhibit higher activities than the upper Rio Puerco samples.

Variations in Pb-210 activity with sample depth at two contrasting sites are shown in figs. 2a and b. The Paguate Reservoir auger sample (fig. 2a) clearly shows enrichment at the upper end of the hole while activities in the hole from site 9 (fig. 2b), upstream of all mining and milling activity, are quite constant throughout (Popp and others,

Table 1. Activities in pCi/g of nuclides in surface (S), lower auger samples (before 1950) (L), and valley fill samples (V) for the upper Rio Puerco (URP), lower Rio Puerco (LRP), Rio San Jose (RSJ), and Paguate Reservoir (PR). Detailed tabulation of radionuclide activities may be found in Dehn (1983), Novo-Gradac (1983) and Popp and others (1983).

Radionuclide		URP	LRP	RSJ	PR*
Pb-210	S	1.26	2.00	2.15	5.39 (15.6)
	L	0.96	1.08	1.04	1.36
	V	0.88	1.03	---	1.44
Ra-226	S	1.19	2.84	3.29	11.5 (26.9)
	L	1.77	1.92	1.89	2.55
	V	1.63	1.89	---	2.74
Th-234	S	1.01	1.25	1.49	4.45 (9.35)
	L	0.85	0.94	0.96	1.30
	V	0.70	0.75	---	1.26
Pb-214	S	0.92	1.25	1.60	5.38 (13.6)
	L	0.89	0.94	1.01	1.29
	V	0.78	0.85	---	1.40
Ac-228	S	1.21	1.57	1.51 (2.31)	2.02
	L	1.04	1.13	1.03	1.41
	V	0.87	1.02	---	1.81

*Values in parentheses are highs for all samples and were found in Paguate Reservoir samples with the exception of Ac-228 (a Th-232 daughter). Th is not regionally enriched.

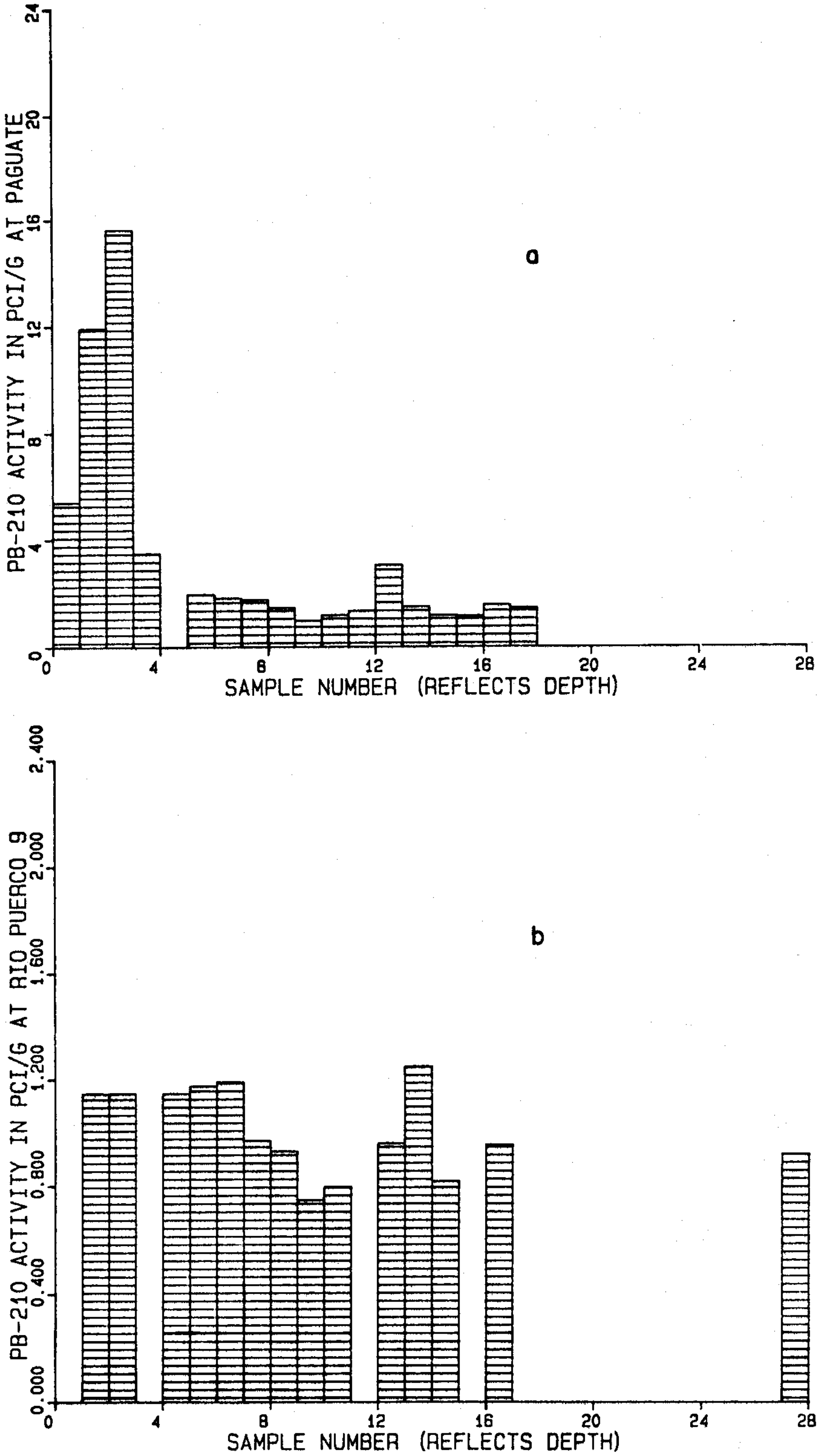

Figure 2. Pb-210 activity as a function of depth: a) Paguate Reservoir; b) Site 9, Rio Puerco (Popp and others, 1983).

1983). This behavior was mimicked by all the U-238 daughters measured.

A more typical auger sample in an oxbow is shown in fig. 3. The steady decline of Pb-210 activity is a function of larger grain size with depth. It should be noted that the deepest samples in fig. 3 have the same activities as all the samples from site 9.

DATING SEDIMENTS WITH Cs-137 AND Pb-210

Measured Cs-137 activities of the samples ranged from <*0.0002* pCi/g to 0.73 pCi/g, with most samples ranging from 0.1 to 0.3 pCi/g. Uncertainties were typically *0.01-0.03* pCi/g. Profiles of normalized Cs-137 activity show a consistent pattern of a broad subsurface maximum. This is followed by a transition at a depth of a few meters to little or no detectable activity (see fig. 4). Dating the sediments using peaks in the Cs-137 profiles, the common procedure in previous studies, was not possible because relatively narrow and well defined maxima were not seen in any of the oxbow sites. The lack of sharp maxima maybe due to dilution by sediments, reworked from arroyo walls during times of peak Cs-137 fallout and/or later redistribution of the sediments. Several peaks were noted in the auger samples from Paguate Reservoir, but a more detailed analysis of a new core is needed to corroborate the data. In the absence of datable maxima in the profiles, the scope of Cs-137 dating is limited to determining whether or not significant levels of Cs-137 are present, and, therefore, whether or not the samples in question postdate 1950.

Pb-210 dating of the samples was not possible for several reasons, the most important of which is the variable amount of radon emanation. Additional factors include the variability of the initial unsupported Pb-210 activity among relatively similar surface samples, and the high amounts of supported (background) Pb-210. The non-atmospherically-derived Pb-214 typically reaches a maximum at some point below the surface, but, the Pb-210/Pb-214 ratio does not gradually decrease to unity with depth. Rather, it immediately drops from a value of about 2 to a value of approximately *0.8-0.9* and commonly remains between 0.8 and 1.0 throughout the rest of the core. This clearly indicates that the majority of the samples have not remained closed with respect to the immediate precursors of Pb-210 (presumably Rn-222) after deposition.

Both the ratio of Pb-210/Pb-214 and the Cs-137 activities showed large variations among samples with similar grain size, but, in general, the activities are highest in samples with large amounts of silt and clay. The variations among similar samples may be partially explained by fluctuations in the rates of Pb-210 and Cs-137 deposition over the course of years.

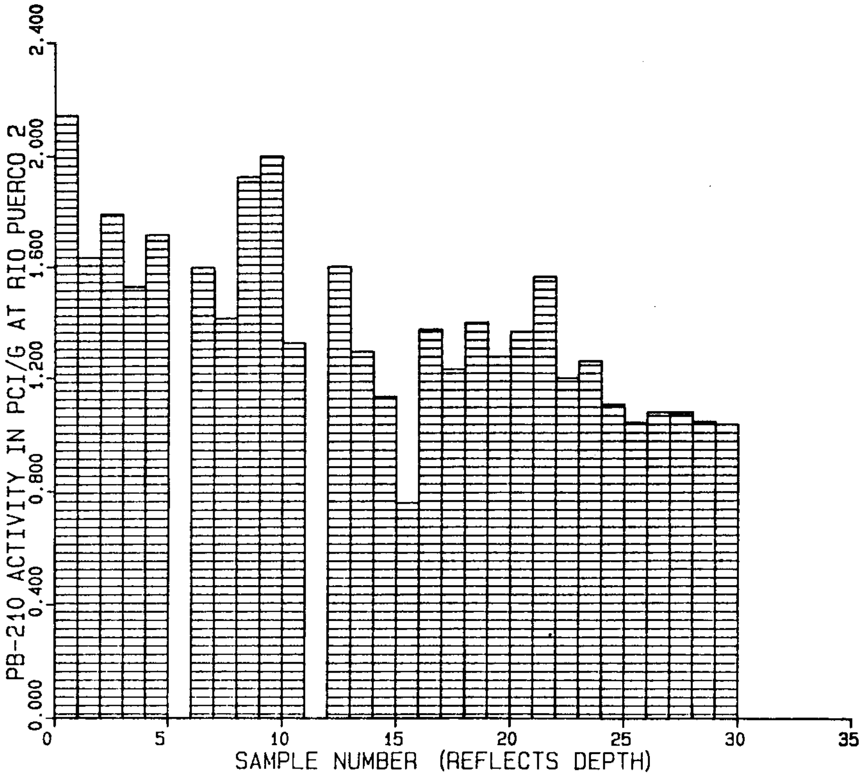

Figure 3. Pb-210 activity as a function of depth at site 2, Rio Puerco (Popp and others, 1983).

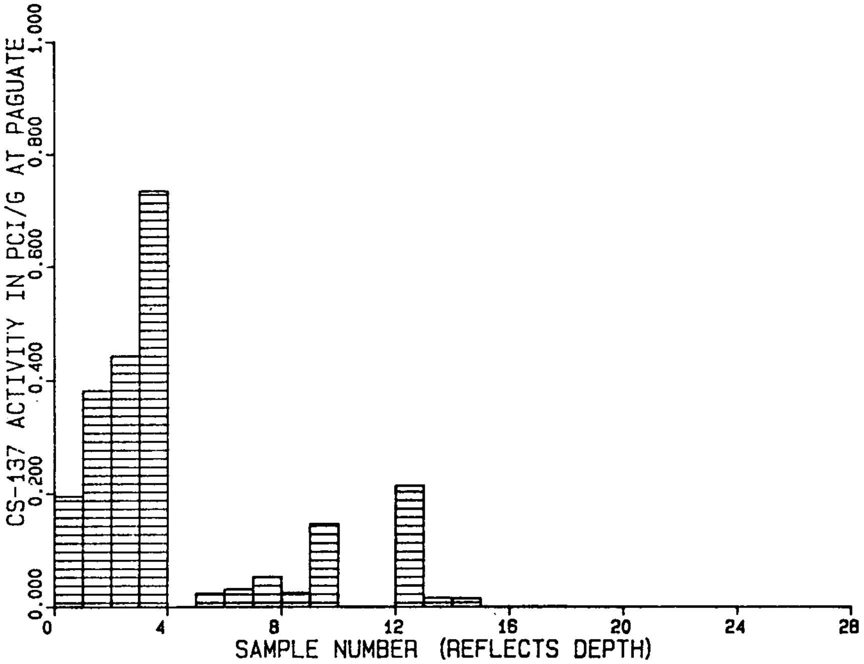

Figure 4. Cs-137 activity as a function of depth at Paguate Reservoir (Popp and others, 1983), measured to depth = 18. Zeros indicate no detectable activity. Sample 15 marks approximately 1950.

TRACE METAL DISTRIBUTION

The silt and clay fractions (<63 Pm) of sediments were analyzed for As, Cd, Cr, Cu, Hg, Mo, Pb, Se, V, and U. Previous studies (Brandvold and others, 1981; Popp and Laquer, 1981; Dreesen and others, 1982) indicate that concentrations of these trace metals are elevated in uranium mill tailings and in stream sediments in the Grants Mineral Region. Comparison of data from this study of fine-grained sediments to previous studies of suspended sediment from the Rio Puerco and Rio Grande and to average crustal abundances of the elements is shown in Table 2.

Both surface samples and subsurface samples show concentrations of As, Se, Cd, Hg, and U considerably elevated above average crustal abundances. Uranium concentrations are two orders of magnitude higher and Hg concentrations are an order of magnitude higher than crustal abundances. Along the Rio San Jose, Hg concentrations are even higher. The surface samples show trends similar to the older valley fill samples, suggesting long term regional elevation of these elements. The surface samples show concentrations consistent with previous work by Brandvold and others (1981) on suspended sediments in the Rio Puerco and Rio San Jose. Resuspension of surface sediments simply tranports the sediments and associated trace metals to an eventual sink in Elephant Butte Reservoir.

Paguate Reservoir has maximum U and V values at the surface, but only Se shows a significant trend with depth similar to the radionuclide concentrations. Apparently the solubilities of As, Cd, Hg, V, and U under oxidizing conditions are sufficiently high that they are eventually transported downstream while the radioactive species are less likely to be transported. Because most of the Pb is not radioactive, the overall Pb values may not be elevated even when radioactive Pb is high.

CONCLUSIONS

In the absence of historic geochemical baseline data for the Grants uranium region, environmental changes resulting from uranium mine-mill activities can only be determined by indirect methods. As summarized above, we developed a methodology for determining the age of recent sediments in streams draining the region, based on combined geomorphic, stratigraphic, and radiometric dating techniques. Because clay-sized and clay-mineral-rich sediments retain radionuclides and heavy metals derived from mineralization and mined sources, sample sites that contain fine-grained deposits that both predate and postdate mine-mill activity were located in abandoned-channel segments (oxbows) of major streams draining the eastern Grants uranium region. Aerial

Table 2. Surface (S), lower auger samples (L), and valley fill (V) averages for each stream reach. Upper Rio Puerco (URP), lower Rio Puerco (LRP), Rio San Jose (RSJ), Paguate Reservoir (PR), Rio Puerco Suspended Sediments (RP, Brandvold and others, 1981), Rio Grande Suspended Sediments (RG, Popp and Laquer, 1981) and average crustal abundance (CA). Values in ppm.

		Sample Site						
Trace Metal	Depth	URP	LRP	SJ	PR*	RP	RG	CA
As	S	8.0	14.7	17.2	4.6	16	-	1.8
	L	11.0	7.9	6.9	7.2			
	V	5.7	12.9	6.5	—			
Cd	S	0.29	0.31	1.10	0.31	0.15	4.8	0.15
	L	0.33	0.50	0.35	0.82			
	V	0.30	0.25	0.34	—			
Cr	S	56	46	33	26	26	73	100
	L	39	45	36	33			
	V	46	40	33	—			
Cu	S	62	69	21	20	87	41	50
	L	34	51	20	19			
	V	27	27	24	—			
Hg	S	0.31	0.22	1.02	0.06	0.05	0.72	0.02
	L	1.11	7.6	5.65	0.56			
	V	0.21	2.3	0.10	—			
Mo	S	2.9	11.1	1.2	2.4	0.58	19	1.5
	L	2.7	20.0	1.5	2.2			
	V	8.5	2.6	1.1	—			
Pb	S	17	36	32	16	37	20	13
	L	33	56	35	30			
	V	32	24	43	—			
Se	S	0.20	0.28	0.15	2.0	—	—	0.05
	L	0.20	0.32	0.26	0.48			
	V	0.48	0.26	0.37	—			
V	S	87	116	93	175	24	75	123
	L	103	87	98	91			
	V	103	107	111	—			
U	S	405	372	301	550	55	—	2.7
	L	139	265	176	412			
	V	500	275	125	—			

photographs and derivative maps made between 1935 and 1978 provided the historical and geomorphic documentation of approximate dates of oxbow formation and ages of alluvial fills in the abandoned-channel segments. Pits dug at these oxbow sites revealed the stratigraphy and composition of the deposits. Refinements in dating the sediments may be possible using dendrochronology and flood data to determine oxbow stratigraphy.

Samples collected from pit walls and auger holes below the pits were subjected to radiometric analysis by gamma ray spectrometry for the artificial radionuclide Cs-137 and the natural radionuclide Pb-210 as well as other U-238 and Th-232 daughters. Because of the dynamic nature of the system, absolute dating with Cs-137 was not possible but samples could be dated as either pre- or post-1950. The 1950 date is important because it marks the beginning of uranium mining activity in the region. Lead-210 dating was not possible because background Pb-210 was high relative to fallout Pb-210. It may be possible to separate effects of uranium mining and milling activity by comparing U-238 daughter accumulation to daughters in the Th-232 series.

Sediments dated by Cs-137, stratigraphic, and historic techniques were analyzed for radionuclides and trace metals which may be derived from uranium ores. The U-238 daughters are generally high in the region and little difference was found between present channels and past oxbow fills, except for the Paguate Reservoir site and surface samples. Recent sediments at Paguate Reservoir clearly show elevated levels of U-238 daughters in sediments dated after the mid-1950's. Sediments from the Jackpile uranium mine have been trapped in the reservoir fill.

Trace metals As, Se, Cd, Hg, and U show elevated values on a regional basis but no correlation with age (i.e. pre- or post-1950). These elevated trace metal values may simply be due to their association with the regionally mineralized rocks. Reworking of older sediments eroded from the arroyo walls apparently partially masks contributions of mine and mill-related trace metals and radionuclides in sediments.

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REFERENCES CITED

Anderson, 0. J., 1981, Abandoned or inactive uranium mines in New Mexico: New Mexico Bureau of Mines and Mineral Resources Open-file Report 148, 778 p.
Brandvold, L. A., Brandvold, D. K., and Popp, C. J., 1981, Effect of uranium mining and milling on surface water in New Mexico, in Environmental and Economic Considerations in Energy Utilization: Ann Arbor, Ann Arbor Science, p. 467-476.
Dane, C. H., and Bachman, G. O., 1965, Geologic map of New Mexico: U.S. Geological Survey, scale *1:500,000.*
Dehn, M., 1983, Lead-210 and Cesium-137 dating of sediments from the Rio Puerco, New Mexico: M.S. thesis, New Mexico Institute of Mining and Technology, 85 p.
Dreesen, D. R., and Williams, J. M., 1982, Mobility and bioavailability of uranium in mill tailings contaminants: Environmental Science and Technology, v. 16, p. 702-708.
Durham, R. W., and Joshi, S. R., 1980, The Pb-210 and Cs-137 profiles in sediment cores from Lakes Matagami and Quevillon, Northwest Quebec, Canada: Canadian Journal of Earth Science, v. 147, p. 1746-1750.
Gallaher, B., and Cary, S., in press, Church Rock uranium mill tailings spill: A health and environmental assessment: Technical report 2, Water quality impacts: New Mexico Environmental Improvement Division.
Horton, C. A., and White, J. C., 1958, Separation of uranium by solvent extraction with tri-n-octylphosphine oxide: Analytical Chemistry, v. 11, p. 1779-1984.
Johnson, W. M., and Maxwell, J. A., 1981, Rock and mineral analysis, 2nd edition: John Wiley and Sons, New York, -489 p.
Krishnaswami, S., and Lal, D., 1978, Radionuclide limnochronology, in Lerman, A., ed., Lakes--Chemistry, Geology, Physics: Springer-Verlag, New York, p. 153-177. Lederer, C. M., Hollander, J. M., and Perlman, I., 1967, Table of isotopes, 6th edition: John Wiley and Sons, New York.
Love, D. W., and Young, J. D., 1983, Progress report on the late Cenozoic geologic evolution of the lower Rio Puerco: New Mexico Geological Society Guidebook, 34th field conference, p. 277-284.
McLemore, V. T., 1983, The uranium industry in New Mexico--history, production, and present status: New Mexico Geology, v. 5, p. 45-51.
Millard, J., Gallaher, B., Baggett, D., and Cary, S., 1983, Church Rock uranium tailings spill: A health and environmental assessment: summary report: Environmental Improvement Division, 37 p.
Novo-Gradac, K. 1983, Trace metal and radionuclide

distributions in recent sediments of the Rio Puerio, Rio San Jose and Paguate Reservoir in the Grants Mineral Belt, M.S. thesis, New Mexico Institute of Mining and Technology, 133 p.

Popp, C. J., and Laquer, F., 1980, Trace metal transport and partitioning in suspended sediments of the Rio Grande and tributaries in central New Mexico: Chemosphere, v. 9, p. 89-98.

Popp, C. J., Brandvold, L. A., and Brandvold, D. K., 1981, Transport mechanisms in sediment-rich streams: Heavy metal and nutrient load of the Rio San Jose-Rio Puerco systems: New Mexico Water Resources Research Institute Report No. WRRI 1423642, Las Cruces, New Mexico, 30 p.

Popp, C. J., Hawley, J. W., and Love, D. W., 1983, Radionuclide and heavy metal distribution in recent sediments of major streams in the Grants mineral belt: U.S. Department of Interior, Final Report to Office of Surface Mining, Washington, D. C., 130 p.

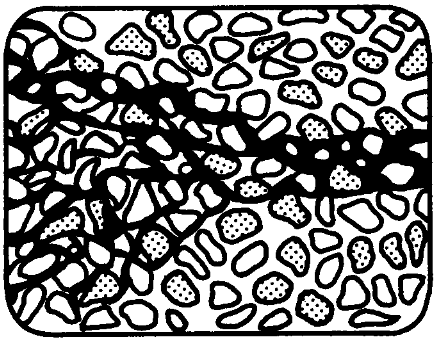
Robbins, J. A., and Edgington, D. N., 1975, Determination of recent sedimentation rates in Lake Michigan using Pb-210 and Cs-137: Geochimica et Cosmochimica Acta, v. 39, p.285-304.

Schery, S. D., 1980, Determination of Lead-210 in environmental samples by gamma spectrometry with high purity Germanium detectors: Analytical Chemistry, v. 52, p. 1957-1958.

Smith, J. N., and Walton, A., 1980, Sediment accumulation rates and geochronologies measured in the Sanjuenay Fjord using the Pb-210 dating method: Geochimica et Cosmochimica Acta, v. 44, p. 225-240.

U.S. Environmental Protection Agency, 1979, Methods for chemical analyses of water and wastes: U.S. Environmental Protection Agency, Cincinnati, Ohio, 430 p.

Young, J. D., 1982, Late Cenozoic geology of the lower Rio Puerco, Valencia and Socorro Counties, New Mexico (M.S. thesis): Socorro, New Mexico Institute of Mining and Technology, 126 p.



SPATIAL AND TEMPORAL VARIATIONS IN WATER QUALITY OF THE RIO GRANDE - RED RIVER. WILD AND SCENIC RIVER, TAOS COUNTY, NEWNEXICO

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ABSTRACT

The upper Rio Grande in New Mexico and the lower 4 miles (6.4 lam) of the Red River, both in Taos County, were designated as "instant" components of the National Wild and Scenic Rivers System. Almost no water quality data existed at the time these rivers were designated wild and scenic. The BIN initiated a water quality study of these rivers in 1978 to evaluate the current water quality conditions and to identify and evaluate the nature, importance, sources, and effects of existing or potential pollutants. Since the major impact to the wild and scenic river is due to mining and related activities in the Red River drainage, emphasis was placed on monitoring water quality of this river.

Variations in water quality of the upper Rio Grande and Red River are presented. A downstream increase in concentrations of various constituents, at this approaching or exceeding water quality standards, occurs due to leaching of natural ore bodies, permitted discharges from molybdenum mill tailings ponds, and discharges from wastewater treatment plants and individual sewage treatment systems. Nonpoint sources are a major cause of elevated trace element concentrations. Relationships among water quality variables and flow conditions are also investigated.

INTRODUCTION

The lower 4 miles (6.4 Ian) of the Red River in New Mexico as well as 48 miles (77.3 km) of the Rio Grande downstream from the Colorado State line were designated as one of the "instant" components of the National Wild and Scenic Rivers System by the Wild and Scenic Rivers Act of 1968. The Bureau of Land Management (BIM) is the managing agency of the wild and scenic river. Almost no water quality data existed at the time these rivers were designated to define base-line water quality conditions. Such data are necessary for the administration of the rivers and for the protection of their outstanding scenic, recreational, and fisheries values (which are closely related to water quality). A water quality monitoring program of these rivers was initiated by the BUM in October 1978. Under the provisions of the Wild and Scenic Rivers Act, the BUM is directed to administer a component of the national wild and scenic rivers system under its control in such a manner as to protect and enhance the values which caused it to be included in the system.

One of the major impacts to the Rio Grande - Red River is due to the mining and milling of molybdenum in the Red River drainage. The Red River drainage, containing prospects for gold, copper, lead, silver, zinc, and molybdenum has been a center of mining activity since 1895 (Schilling, 1960). Molybdenum ore was discovered in 1916 and is the only prospect to achieve much importance. Production by the Molybdenum Corporation of America (now Molycorp, Inc.) mill near the village of Red River was minimal until the early 1960's. Facilities for expanded mining and milling operations were constructed during 1964-65, including a change to open pit mining methods and tailings disposal facilities. An 8.5 mile (13.7 km) pipeline transports tailings along the Red River from the mill to tailings ponds about 1 mile (1.6 km) west of Questa. In 1968 the mill was expanded to about the present capacity. Mining and milling operations were shut *down* August 1981 to September 1983 to develop a new underground mine and modify the mill, tailings lines, and tailings disposal facilities.

The objectives of this water quality study are to: (1) characterize existing water quality under natural conditions and at the present level of basin development; (2) monitor changes in water quality due to natural and artificial causes; (3) identify and evaluate the nature, importance, source, and effect of existing and potential pollutants; and (4) evaluate water quality in relationship to State and Federal water quality standards and criteria.

STUDY AREA DESCRIPTION

The study area is located in Taos County in north central New Mexico (Figure 1). The Red River is the major perennial tributary to the wild river portion of the Rio Grande and contains both municipal and industrial (mining and milling) discharges to the river. Since the major impact is from the Red River drainage, emphasis was placed on monitoring water quality of this river.

The Red River has its headwaters in the Sangre de Cristo Mountains, containing the highest point in New Mexico at 13,161 feet (4,012 m). A lava-capped plateau along the Rio Grande and piedmont alluvial plains between the Rio Grande and the mountain range make up the Rio Grande Valley in Taos County. The Rio Grande is entrenched in a gorge that begins about 6 miles (9.7 km) north of the Colorado state line and gradually deepens to a maximum depth of 860 feet (262 n). The lower portion of the Red River immediately below Questa is also entrenched in a similar gorge.

The Red River drainage contains a belt of high-angle faults within which rocks were irregularly faulted and brecciated. The more highly brecciated areas served as conduits for hydrothermal solutions which further altered the rocks. The igneous activity and hydrothermal alteration formed the molybdenum ore deposits associated with the stocks and dikes in this area (Schilling, 1956; 1965). These altered, highly weathered, and erodable areas are a natural source of sediment load and mineralization in the Red River.

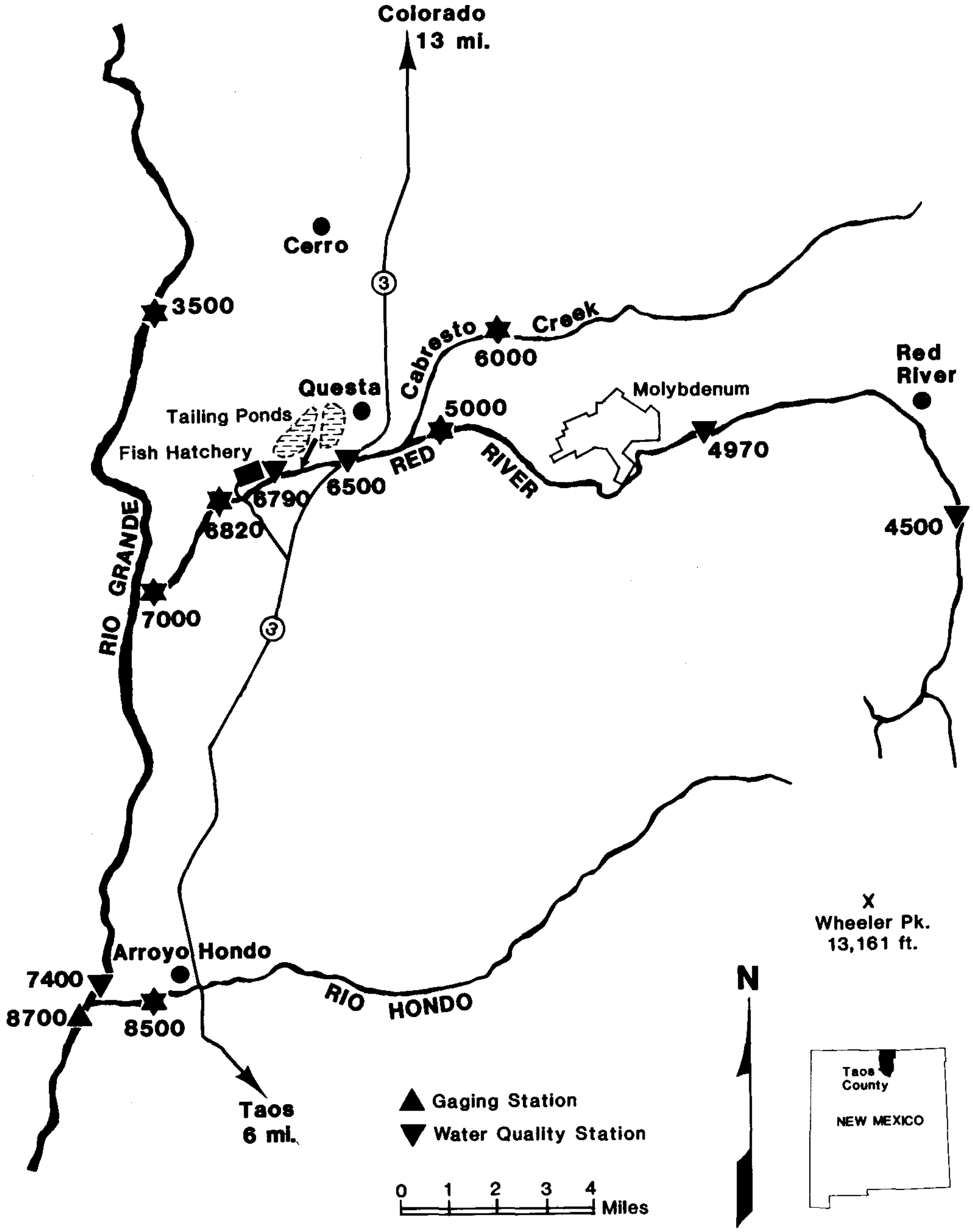

Figure 1. Vicinity Map of Study Area and Identification of Sampling Stations.

The pattern of runoff in these streams is typical of mountainous areas, where snowmelt is the major source of runoff. Streamflows of both the Rio Grande and the lower Red River are maintained by ground water discharged from springs, which represents a significant contribution, especially during low flows. Between the Colorado-New Mexico state line and the Red River, the Rio Grande gains about 96 cfs (2.72 ems) annually from groundwater accretion (Winograd, 1959). The total gain in flow from groundwater discharge between the mouth of the Red River and the head of its canyon near Questa averages 35 cfs (0.99 ems).

The Red River component of the wild river is unique in that it is downstream from all developments and effects of man within its drainage basin. Developments along the Red River, in downstream order, include scattered rural hones and recreation facilities, the town of Red River and a ski area, a molybdenum mine and mill, the town of Questa, pasture and irrigated lands surrounding Questa, molyboderm mill tailings ponds, and a state fish hatchery at the upper end of the wild river segment (Figure 1). The remainder of the basin is undeveloped forest land within the Carson National Forest. Other than inflows from Colorado and tributaries, the Rio Grande below the state line is essentially undeveloped and receives no direct wastewater discharges. The lower Red River and the Rio Grande are renowned for their high-quality rainbow and brown trout fisheries and represent one of the top two trout fishing areas in the State.

METHODS

The location of sampling stations and water quality constituents to be measured were tailored to the objectives of the study, environmental conditions, and pollution problems of the area. Sampling stations (see Figure 1) were located upstream and downstream of population and industrial centers, major wastewater outfalls and return flaws and natural features that may affect water quality. The frequency of sample collection was about 10 times per year, with emphasis on characterizing seasonal and discharge related water quality variations. Samples were collected roughly on a monthly basis except during spring snowmelt runoff, when samples were collected near peak flow and during rising and falling stages.

Samples were analyzed for physical, chemical (including common ions, nutrients, and trace elements) and bacteriological characteristics. Water samples were collected, preserved, and shipped to the U.S. Geological Survey (USGS) Central Laboratory in Denver, Colorado for analysis; standard methods employed by the USGS were used. Time-sensitive constituents such as pH, alkalinity, and bacteria were measured in the field. Each sample was accompanied by a discharge measurement. All data were stored in the USGS WATSTORE computer storage and retrieval system.

Statistical hypothesis testing employed nonparametric tests to determine if significant differences in a measured water quality characteristic existed over time or space. The Kruskal-Wallis test was used to test for differences of seasonal, data among the sites on the Rio Grande and the sites on the Red River. Differences among pairs of sites (paired in downstream order) were determined by using the Mann-Whitney test and a test for equality of variance (Conover, 1971). Only base flow conditions (late suns r to early spring) had enough data points to perform spatial tests with any validity.

Several methods were used to test for temporal differences in water quality. The first test determined if there was a monotonic relationship between discharge and selected characteristics measured at each station. The test, based on an analysis of covariance, tested the null hypothesis that the expected level of the characteristic *was* centered about a mean value for all discharge versus the alternative that the level was a function of discharge (Conover and Iman, 1982). The discharge relationship was estimated by a linear model after a log-log transformation of the data for all tests that were significant.

The relationship of specific conductance and discharge was further explored for stations on the Red River by grouping the data into periods when tailings pond discharge was occurring and when it was not occurring. An analysis of covariance was performed to find the best fit of one of four models for the two data groups: (I) two slopes and two intercepts; (2) one slope and two intercepts; (3) one slope and one intercept; or (4) a constant value for all discharge. Other water quality characteristics were similarly grouped into these two time periods to determine whether differences in quality occurred between the two groups. Testing for differences between the groups was done with the Mann-Whitney test; data were adjusted for flow if a significant relationship with discharge existed (Conover, 1971).

Finally, a simple trend analysis, using the analysis of covariance test with time as the covariate, was performed on the data from each site. Again, the data were adjusted for flow, where necessary.

RESULTS

Preliminary analysis results from 5 years of data are presented for the following water quality characteristics; specific conductance (SPC), pH, sulfate (SO4), nitrite plus nitrate (402+), total phosphorus (P), dissolved manganese (Nn), total molybdenun (Mo), total zinc (Zn), dissolved iron (Fe), and total copper (Cu). pH was converted to hydrogen ion concentration for all testing.

SPATIAL VARIABILITY

A useful technique for summarizing data and displaying the spatial variability of water quality is to plot "box-and-whisker" diagrams for each sampling site (McLeod, Hipel, and Comancho, 1983). Box-and-whisker plots for various water quality characteristics are presented in Figure 2. The lower and upper ends of the box represent the 25 and 75 percentile values, the line in the box is the median value, and the end points of the lines (whiskers) are the minimum and maximum values of the data set.

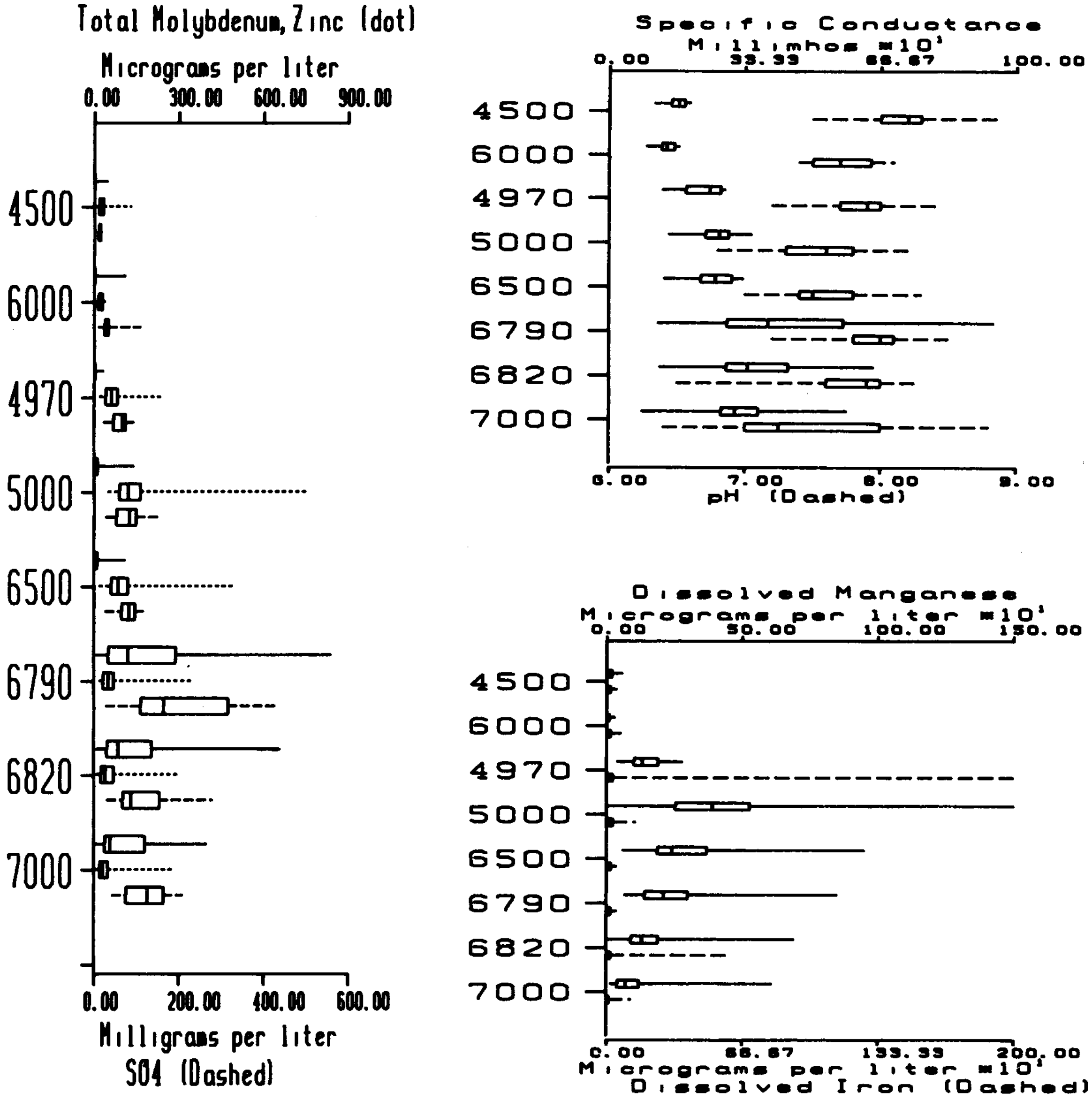

Figure 2. Box-and-Whisker Plots for Various Water Quality Characteristics at Sampling Sites in the Red River Basin.

Results from the testing of spatial differences are given in Table 1. For the two rivers as a whole, the Kruskal-Wallis test indicates there are highly significant differences in seasonal water quality among the various sites. Generally, all levels of constituents (except pH) in the Red River increase downstream, until they are diluted by higher quality inflows. The greatest concentrations of trace elements usually occur immediately above Questa, except for molybdenum. Highly significant increases in Mo, SPC and SO4 occur below the tailings pond discharge, while Mn and Zn decrease. Nutrients increase below the town of Red

TABLE 1. Summary of Test Results for Spatial Differences
Abbreviations: * = not significant; 01 or 05 = significant at the stated percent; + or - = indicate a rising or falling level; ND = no data; K-W = Kruskal-Wallis test; M-W = Mann-Whitney test; NVAR = test for equality of variance.

Station/Test	SPC	pH	SO4	NO2+	P	Mn	Mo	Zn	Fe	Cu
RED RIVER										
K-W	01	01	01	01	01	01	01	01	01	05
RIO GRANDE										
K-W	*	*	*	01	01	01	01	*	01	ND
08264500 TO 08264970										
M-W	01+	01-	01-	01+	01+	01+	*	01+	*	ND
NVAR	*	*	01+	*	*	01+	05+	*	05-	ND
08264970 TO 08265000										
M-W	01+	01-	01+	*	*	01+	01+	01+	01+	ND
NVAR	*	*	*	*	*	01+	01+	*	01+	ND
08265000 TO 08266000										
M-W	01-	05+	01-	01-	01-	01-	01-	01-	05-	ND
NVAR	05-	*	*	05-	01-	01-	01-	01-	01-	ND
08266000 TO 08266500										
M-W	01+	*	01+	05+	*	01+	01+	01+	*	ND
NVAR	*	*	*	05+	*	01+	05+	01+	*	ND
08265000 TO 08266500										
M-W	*	*	*	*	*	01-	*	01-	01-	*
NVAR	*	*	*	*	05-	*	01-	01-	01-	01-
08266500 TO 08266790										
M-W	01+	01+	01+	*	*	01-	01+	05-	*	*
NVAR	*	*	01+	*	*	*	01+	*	*	*
08266790 TO 08266820										
M-W	01-	01-	01-	01+	01+	01-	05-	*	*	05-
NVAR	*	*	05-	*	*	*	05-	*	*	*
08266820 TO 08267000										
M-W	*	05+	*	*	*	01-	05-	*	*	*
NVAR	*	*	*	*	*	*	05-	*	*	*
08263500 TO 08267400										
M-W	*	*	*	*	*	*	01+	*	*	ND
NVAR	*	*	*	*	*	01+	01+	*	*	ND

TABLE 2. Summary of Test Results at Individual Stations.
Abbreviations: * = not significant; 05, 01 = significant at the stated percent; Q-REL = test for relationship with discharge; TP/NTP = test for periods of tailings pond discharge versus no discharge; TREND = test for time trend.

Station/Test	SPC	pH	SO4	NO2+	P	Mn	Mo	Zn	Fe
08264500									
Q-REL	01-	*	01-	*	*	*	*	*	*
TP/NTP	*	*	*	*	*	*	*	05+	*
TREND	01-	*	*	*	*	01+	05+	*	01+
08264970									
Q-REL	01-	*	01-	*	*	01-	*	*	01+
TP/NTP	*	*	*	*	*	*	*	*	*
TREND	*	*	*	*	*	*	01+	*	*
08265000									
Q-REL	01-	*	01-	*	*	01-	*	01-	*
TP/NTP	*	*	*	*	*	*	05-	*	*
TREND	*	01-	*	*	*	*	*	*	*
08266000									
Q-REL	01-	*	01-	*	*	*	*	*	*
TP/NTP	*	*	*	05+	*	*	*	*	*
TREND	*	05-	*	*	*	*	*	*	05-
08266500									
Q-REL	01-	*	01-	*	*	01-	*	*	*
TP/NTP	*	05-	*	*	*	*	*	05+	*
TREND	01+	01-	*	*	*	*	01-	*	*
08266790									
Q-REL	01-	01-	01-	*	*	*	01-	05+	01+
TP/NTP	01-	01-	*	*	*	*	01-	01+	*
TREND	*	*	*	05+	*	*	01-	05+	*
08266820									
Q-REL	01-	*	01-	01+	*	*	01-	01+	*
TP/NTP	01-	05-	01-	05+	05+	*	01-	01+	*
TREND	01+	*	01+	*	*	*	01-	05+	*
08267000									
Q-REL	01-	01-	*	*	*	05+	01-	*	*
TP/NTP	01-	01-	*	05+	*	*	01-	*	*
TREND	*	*	*	*	*	*	01-	*	*
08263500									
Q-REL	01-	01-	01-	*	01+	*	01-	*	01+
TREND	*	01-	*	*	*	*	*	*	*
08274000									
Q-REL	01-	01-	01-	*	01+	*	01-	01+	01+
TREND	*	01-	*	*	*	01+	*	*	05+

River and the state fish hatchery. Trace element concentrations decrease by dilution due to inflows from Cabresto Creek (08266000), an undeveloped drainage, and from springs below the tailings pond discharge (stations 08266790 to 6820, and 6820 to 7000). In the Rio Grande, only No increases significantly between Cerro and the Rio Lando, due to inflow from the Red River. Since only seasonal data during base flow conditions were used in this analysis, these differences may not be representative of higher flow periods, but do represent differences for flows that occur about 70 percent of the time.

Although a limited data base exists to conduct similar testing for the toxic trace elements cadmium (Cd), copper (Cu), and cyanide ow, concentrations of these elements also appear to increase downstream in the Red River. The greatest frequency of occurrence and concentration of Cd and Cu occur near Questa. Cyanide is used in the molybdenum milling process and occurs in the Red River as a result of accidental tailings pipeline leaks and spills and as a result of the permitted discharge from the tailings ponds. Approximately 20 percent of the samples downstream from the tailings ponds had total CN concentrations equal to or greater than 10 ug/1.

TEMPORAL VARIABILITY

At all sites on the Red River and the Rio Grande there exists a highly significant relationship between discharge and SPC and discharge and SO4. The relationships between discharge and SPC in the lower Red River changed between periods of tailings pond discharge and no discharge. The slopes of the regression for the two periods are the same but the intercept increases during periods of tailings pond discharge. Molybdenum concentrations are also related to discharge in the lower Red River and in the Rio Grande. These results of testing for temporal and other relationships are shown in Table 2. Other constituents show a strong relationship with discharge at various sites, but not on a consistent basis.

The impact of tailings pond discharge is apparent at the three most downstream sites on the Red River. SPC, pH, SO4 and Mo have lower average levels during periods of no discharge, while Zn, NO2+ and P have higher average concentrations. Stations along the upper Red River also have test results that indicate changes in concentration levels. Changes in NO2+ and P are probably a result of changes in effluent discharge from wastewater disposal systems at the fish hatchery and disposal systems in and around Questa. Dropping pH levels may in part be due to lower than normal levels of pH in precipitation and runoff. Lower levels of SPC, SO4 and No in the lower Red River are due to a lack of tailings pond discharge.

Results of the trend analysis (Table 2) indicate that trends are detectable in many cases. Mo appears to be decreasing in the lower four stations of the Red River while increasing in, the two most upstream stations. Using data from periods of no tailings pond discharge to remove bias caused by the elevated levels, the lower three stations on Red River indicated no trend in Mo. Zn and SO4 appear to be increasing below the fish hatchery. Test results of all Rio Grande stations and three Red River stations, upstream of the tailings pond discharge, indicate dropping pH levels. Although significant trends were detected, these are based on a limited number of years of data and should be used with caution.

DISCUSSION

Maximum concentrations of the trace elements Mn, Zn, Cd, and Cu in the Red River occur above its confluence with Cabresto Creek. Elevated levels of these elements are most likely due to the natural leaching of mineralized areas and dispersed inflows from nonpoint sources in the vicinity of the molybdenum mine. Tailings pond effluent discharged into the Red River above the fish hatchery has significantly increased SPC (dissolved solids), SO4, CN, and No concentrations; Mn and Zn concentrations decrease above the fish hatchery. Concentrations of toxic trace elements are of concern because of their effect on the fisheries and recreation values of the wild and scenic river.

A study conducted for BIM by the Columbia National Fisheries Laboratory of the U.S. Fish and Wildlife Service (J.K. Andreasen, 1981, unpublished report) found that fish in the Red River are bio accumulating trace metals, although ambient concentrations of the metals in the Red River are below acutely toxic levels. Whole fish tissue residues for Cd and Cu exceeded the 85th percentile values of fish collected throughout the United States under the National Pesticide Monitoring Program.

Water quality criteria for the protection of freshwater aquatic life (Environmental Protection Agency, 1980) and New Mexico water quality standards (Water Quality Control Commission, 1981) for the Red River are given in Table 3. The New Mexico general standard for hazardous substances reads in part that "toxicities of substances in receiving waters will be determined by appropriate bioassay techniques, or other acceptable means, for the particular form of aquatic life which is to be preserved with the concentrations of toxic materials not to exceed 57, of the 96-hour LC50 provided that: toxic substances which, through uptake in the aquatic food chain and/or storage in plant and animal tissues, can be magnified to levels which are toxic to man or other organisms, shall not be present in concentrations which result in this biological magnification." In the absence of bioassay data for the Red River, toxicity data for fish species found in the Red River were taken from the available literature. The 96bour LC50's for the most sensitive life stage of trout species in the Red River are estimated to be 6 ug/1 Cd (EPA, 1980; Hale, 1977) 100 ug/1 Cu (EPA, 1980; Page's and Sprague, 1977), 60 ug/1 free CN (EPA, 1980; Smith, et al, 1979), and 1500 ug/1 Zn (EPA, 1980; Holcombe and Andrew, 1978).

The State standard in Table 3 is estimated based on these acute toxicity values The toxicity of cyanides is due mostly to the presence of "free' cyanide, which is defined as the sum of the cyanide present as ECN and the CN ion. Free cyanide is a more reliable indicator of toxicity

Table 3. Water Quality Criteria and Projected State Water Quality Standards for the Red River (see text for explanation).

Characteristic	EPA Criterion	Estimated 96-Hour LC-50	Projected State Standard (.05x LC-50)
Ph	6.5 - 9.0	-	6.6 - 8.8
Cadmium (ug/1)	0.03	6	0.3
Copper (ug/1)	5.6	100	5
Free Cyanide (ug/1)	3.5	60	3
Zinc (ug/1)	47.	1500	75

than total cyanide since total cyanide could also include stable organic cyanides and metallocyanide complexes. A cyanide speciation model developed for BLM for the Red River (Bil. Thomson, 1980, 1983, unpublished report, Department of Civil Engineering, University of New Mexico) predicts that at a pH of 7.0 and below, up to 50 percent of the total CN may be in the free form.

A cadmium concentration of 1 ug/1 was equaled or exceeded by 54 percent of the samples from above Questa and by 39 percent of the samples from below Questa. The criterion and standard for Cu was exceeded by all samples taken above and below Questa. A total CN concentration of 10 ug/1 was equaled or exceeded by 1 percent of the samples from above Questa, by 16 percent of the samples from below Questa, and by 20 percent of the samples from below the tailings pond discharge. Seventy-five percent of the samples above Questa and 55 percent of the samples below Questa exceeded 75 ug/1 of Zn.

Although ambient concentrations of toxic elements are below acutely toxic levels in the Red River, chronically toxic levels maybe present, affecting the survival, reproduction and physiology of aquatic organisms. The ERA criteria and State standards in Table 3 are based upon the effects of individual toxic elements. The actual effects on aquatic organisms are not known due to the complex chemical interactions which affect the fate and impact of these toxic elements.

CONCLUSIONS

Significant spatial and temporal differences in water quality occur in the Red River. Maxim= trace element concentrations (Cd, Cu, Mn and Zn) from nonpoint sources occur upstream from Questa. Molybdenum tailings pond effluent has significantly increased SPC, $04, CN and Mo concentrations iR the lower Red River. Toxic elements exceed recommended EPA criteria for the protection of aquatic life and projected State water quality standards, although more research is needed on the interactions of these elements and their overall chronic toxicity.

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REFERENCES

Conover, W.J., 1971. Practical Nunparametric Statistics. John Miley and Sons, N.Y., N.Y., pp. 239-250.

Conover, W.J. and R.L. Iman, 1982. Analysis of covariance using the rank transformation. Biometrics 38:715-724.

Environmental Protection Agency, 1980. Ambient water quality criteria for cadmium; copper; cyanides; and zinc (separate documents). Office of Water Regulations and Standards. Washington, DC.

Fogels, A. and J.B. Sprague, 1977. Comparative short-term tolerance of zebrafish, flagfish and rainbow trout to five poisons including potential reference toxicants. Water Research 11: 811-817.

Hale, J.G., 1977. Toxicity of metal mining wastes. Bulletin of Environmental Contamination and Toxicology, 17 (1): 66-73.

Holcombe, G.W. and R.W. Andrew, 1978. The acute toxicity of zinc to rainbow trout, comparisons in hard and soft water. Environmental Protection Agency, ETA-600/3-78-094.

McLeod, A. Ian, K.W. Hipel, and F. Comancho, 1983. Trend assessment of water quality time series. Water Resources Bulletin 19 (4): 537-547.

Schilling, J.H., 1956. Geology of the Questa molybdenum mine area, Taos County, New Mexico. New Mexico Bureau of Mines and Mineral Resources, Bulletin 51.

Schilling, J.H., 1960. Mineral Resources of Taos County, New Mexico. New Mexico Bureau of Mines and Mineral Resources, Bulletin 71.

Schilling, J.H., 1965. MAybdenum resources of New Mexico. New Mexico Bureau of Mines and Mineral Resources, Bulletin 76, pp. 26-34.

Smith, L.L., et al., 1979. Acute and chronic toxicity of HCN to fish and invertebrates. Environmental Protection Agency, EPA-600/3-79-009.

Water Quality Control Commission, 1981. Water quality standards for interstate and intrastate streams in New Mexico. Santa Fe, NM.

Winograd, 1.J., 1959. Groundwater conditions and geology of Sunshine Valley and western Taos county, New Mexico. Technical Report No. 12, New Mexico State Engineer Office, Santa Fe, NK.

SMALL MOUNTAIN LAKES AND THE CLEAN LAKES PROGRAM

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ABSTRACT

During Classification Phase I of the NM Clean Lakes Program (1981-1982) ten small fishing lakes were classified according to trophic state. The study lakes were Alto Reservoir, Bonito Lake, Bear Canyon Reservoir, Fenton Reservoir, Hopewell Lake, Morphy Lake, Quemado Lake, Lake Roberts, Snow Lake and Wall Lake. Four indices (TSIs) were used to compare the trophic states: the EPA multi-variable TSI, the Carlson univariable TSIs, plankton diversity, and the Krieger TSI based on relative abundance of calanoid copepods. Alto Reservoir and Morphy Lake were least eutrophic, presumably due to artificial aeration and copper sulfate treatment of Alto Reservoir and the small drainage basin of Morphy Lake. Lake Roberts, Quemado Lake and Fenton Reservoir were selected for further study to recommend restoration and watershed management strategies.

During Classification Phase II (1982-1983) calculated N and P loadings were used to establish water quality goals to inhibit nuisance algal blooms and improve the quality of the coldwater fisheries. Phosphorus precipitation - inactivation and sediment screens for macrophyte control were the suggested restoration alternatives for Lake Roberts and Quemado Lake. Watershed management recommendations addressed effluent from a trout hatchery above Fenton Reservoir, fence construction and repair to enforce cattle grazing restrictions, on-site wastewater disposal, and erosion control.

INTRODUCTION

The New Mexico Clean Lakes Classification Program was conducted in two phases. During Classification Phase I (June 1981 to June 1982), ten small mountain lakes were sampled during three seasons and the physical, chemical and biological data were translated into trophic state indices. The lakes were then ranked from most eutrophic to least eutrophic relative to one another. During Classification Phase II (July 1982 to July 1983), N and P loading rates were calculated, target water quality goals were specified, and restoration and watershed management recommendations were proposed for selected priority lakes.

The trophic state is a measure of the production of biota and the amount of nutrients (especially N and P) within the lake. The nutrient supply from precipitation, runoff, and point and nonpoint sources largely determines the trophic state. However, internal processes such as N fixation or sediment exchange equilibria can contribute significantly to the total nutrient supply.

Nutrient budgets are used to quantify current loading rates, to predict the effects of altering loading rates from a given source, and to predict the response time required for a specific change in trophic state to occur. Similarly, a water quality management plan can be evaluated by comparing total nutrient loading and lake nutrient concentrations before and after implementation.

In general, high chlorophyll a and nutrient concentrations (e.g., greater than 10 pg TP/1, 500 pg N/T, and 15 pg chi a/1), dissolved oxygen depletion in the hypolimnion (lake bottom waters during stagnation), and low biotic diversity indicate eutrophic conditions (high trophic state). Other water quality concerns might include density of macrophytes (rooted aquatic plants) and blue-green algae.

STUDY SITES

Table 1 contains descriptive information for each watershed. All lakes are artificial impoundments, although Morphy Lake occupies a natural sump. Surface areas range from 8 to 55 ha, and drainage areas from 10^2 to 10^4 ha. The ratios of drainage basin to lake surface area range from 10^2 to 10^3:1, (except Morphy Lake) and therefore, are much larger than ratios for natural lakes, which are closer to 10:1.

The ten lakes are used for fishing and other recreational activities. In addition, Alto Reservoir and Bonito Lake supply water to the cities of Ruidoso and Alamogordo, respectively. The watersheds are located on national forest land and the main land uses are cattle grazing and silviculture. Nutrient sources for Fenton Reservoir include a trout hatchery and approximately 70 vacation homes with pit toilets or septic systems located along Rio Cebolla at Seven Springs. Although all ten lakes have had excessive algal or macrophyte growth, only Alto Reservoir had been treated to improve water quality: aeration and copper sulfate addition were implemented by the City of Ruidoso.

METHODS

During Classification Phase I each lake was sampled at two sites in the summer, fall and spring for physical and chemical variables. Plankton and benthic macroinvertebrate communities were sampled in the summer and fall of 1981. During Classification Phase II, Fenton Reservoir and Rio Cebolla (lake inlet and outlet) were sampled monthly from August 1982 to July 1983. In addition, seven stream stations in the Fenton Reservoir watershed were sampled for N and P concentrations on six dates during the second study year. These included stations located above and below the fish hatchery and Seven Springs. Only flow, residue and nutrient concentrations were monitored at the stream stations.

Dissolved oxygen concentrations, specific conductance and temperature were measured at one-meter intervals throughout the water column using a field DO meter and conductivity meter (Yellow Springs

Table 1. Descriptive information for ten lakes monitored during Classification Phase I. Quantitative data were provided by the office of the state engineer, except for drainage basin (determined by planimetry) and: * indicates observed maxima, ** indicates data from Solomon and Kingston 1975, *** indicates Warren McNall, written comm.

	Alto	**Bear Can.**	**Bonito**	**Fenton**	**Hopewell**	**Morphy**	**Quemado**	**Roberts**	**Snow**	**Wall**
elevation, m above sea level	2214	1890	2248	2286	2976	2390	2326	1845	2263	1948
year dam was built	1964	1934	1931	1942	1930	1940	1971	1963	1966	1959
drainage area, ha	3162	6038	8700	12382	1419	58 natural 625 total	20604	22599	23540	25842
maximum surface area, ha acres	8.1	14.2	40.5	12.1 26.1***	5.7	12.9	55	28.7	40.5**	8.1
maximum volume, $10^3 \times 10^6$ ac ft	0.30	0.4	2.2	0.41 172***	0.10	0.50	2.53	< 1.23**	1.97	0.23
maximum depth, m	11.6	18.3	23	7.0	4.57	4.2	14.6	10.7	12.2	2.6* (< 4.9)
mean depth as max vol/ max surface area	3.7	4.2	5.6	3.4	1.7	3.9	4.6	< 4.3	4.9	< 2.9
watershed, National Forest (% wilderness)	**Lincoln**	**Gila**	**Lincoln (46)**	**Santa Fe**	**Carson**	**Santa Fe**	**Apache**	**Gila (42)**	**Gila (8)**	**Gila (11)**

Lake	**Major inflows; minor inflows**	**Major outflows**
Alto	south fork of Eagle Creek; water is piped from a holding pond west of the lake	Eagle Creek (intermittent) tributary of the Rio Hondo
Bear Canyon	Bear Canyon Creek tributary to the Mimbres River	Mimbres River
Bonito	Rio Bonito	Rio Bonito
Fenton	Rio Cebolla tributary to Jemez River; unnamed intermittent creek, spring-fed	Rio Cebolla
Hopewell	Placer Creek; spring-fed	Placer Creek
Morphy	diversion intake canal from Rito Morphy	small arroyo into Rio San Jose
Quemado	Largo Creek (intermittent); 3 unnamed tributaries; El Caso Spring Canyon tributary	Largo Creek -- intermittent discharge
Roberts	Sapillo Creek; spring fed	Sapillo Creek
Snow	Snow Canyon Creek; spring-fed	Snow Canyon Creek (middle fork of Gila River)
Wall	Taylor Creek, Hoyt Creek	Taylor Creek (east fork of Gila River)

Instrument Company). Hydrogen ion concentration was measured on site with a pH color comparator kit (Hellige). Light attenuation was read at one-meter intervals using an underwater photometer (MontedoroWhitney Corporation), and secchi disc visibility depth was recorded.

Lake water samples were collected from the top, middle and bottom of the euphotic zone using a Kemmerer bottle and composited in an acid-washed carboy. New one-liter cubitainers were filled with composited samples for total phosphorus, total dissolved phosphorus, dissolved orthophosphate-P, total Kjeldahl nitrogen, nitrate plus nitrite and ammonia concentrations, and preserved with two ml concentrated H2SO4. Nutrient and total nonfilterable residue analyses were performed by the Scientific Laboratory of the New Mexico Health and Environment Department in Albuquerque in accordance with APHA (1975) or USEPA (1979).

Total organic nitrogen was calculated as Kjeldahl nitrogen minus ammonia-N, total inorganic nitrogen as the sum of nitrate, nitrite and ammonia-N, and total nitrogen as total organic plus total inorganic nitrogen.

Two-liter volumes of composited euphotic zone water were filtered using 0.45 pm Millipore filters and stored on ice in clean, sterile amber bottles for algal assays. Limiting nutrients were determined by a modification of the standard EPA procedure (New Mexico EID 1981).

During Classification Phase II Rio Cebolla discharge was measured monthly at the inlet and outlet stations using a pygmy current meter or a Marsh-McBirney Model 201 portable water current meter. Discharge was also measured at stream stations above Fenton Reservoir on February 8 and June 22, 1983. These discharge measurements were used to flow-weight the stream nutrient concentrations. Statistical comparisons of the mean stream nutrient concentrations (t-test, by stations) were made using both the raw and flow-weighted nutrient data.

Appropriate volumes of composited euphotic zone water were analyzed for chl a, b, and c using a trichromatic method (EPA 1973). One liter of composited water was preserved and concentrated for phytoplankton identification and enumeration (see Potter 1982). Samples for zooplankton and benthic macroinvertebrate analyses were collected but are not discussed here (see Potter 1982). Percent coverage of the lake bottom by macrophytes and percent shoreline coverage by emergent plants were visually estimated.

The four TSIs used to rank the lakes by averaging each TSI and examining each seasonal result separately were as follows:

(a) The EPA index was computed using total phosphorus, total dissolved phosphorus, total inorganic nitrogen, chl a, and DO concentrations, and Secchi disc visibility depth. Dissolved inorganic nitrogen was substituted for total inorganic nitrogen, and a composite index was determined (EPA 1974). Values less than 420 are in the eutrophic range.

(b) The univariable Carlson index was computed for Secchi disc visibility depth and chl a and TP concentrations (Carlson 1977). Each of the three Carlson TSI Values were evaluated independently. Values greater than 47 are in the eutrophic range.

(c) An index for zooplankton relative abundance (Krieger 1981) was computed as TSI = no. calanoid copepods per unit volume/(no. cyclopoid copepods and cladocera per unit volume).

(d) Generic diversity indices (Shannon-Weaver) were computed for cladocerans and phytoplankton.

Nutrient loading was calculated using appropriate nutrient export coefficients for forested watersheds and bulk precipitation (Reckhow 1979, Beaulac and Reckhow 1982), and nitrogen export data for pine and mixed conifer watersheds in the Tesuque basin (Gosz 1978). The selected coefficients ($g/m^2/yr$) were TP-bulk precipitation, 0.02; undisturbed forest, 0.005; TN-bulk precipitation, 0.620; TIN-bulk precipitation, 0.450; and TN-undisturbed forest, 0.10. (Coefficient term m^2 refers to lake surface or drainage basin area.) Estimates of the annual external loads were calculated as (coeff.) (watershed area)/surface area. A second calculation was made from the observed nutrient concentrations using the Dillon (1974) and Bachmann (1981) models (fig. 1).

The TP and DIN loading rates were calculated for Lake Roberts and Quemado Lake using nutrient concentrations observed during Classification Phase I and R_{LM} (fig. 1). Calculations for Fenton Reservoir were made using nutrient and hydrologic data collected during Classification Phase II and $R_{ex}p$.

The lake outflow volume for Lake Roberts was computed from the long-term average flow over the spillway of 5 cfs and current lake volume was extrapolated as 17% loss of the original volume (Solomon and Kingston 1975). Flushing rate and water retention time were subsequently calculated as indicated in fig. 1.

Because runoff, lake outflow volume and retention time were not known for Quemado Lake, water retention time was estimated by assuming that runoff volume is 5% of precipitation, evaporation is 60 to 62 in/yr (US Weather Bureau 1959) and annual precipitation is 14 in/yr (Tuan et al. 1969). Thus, water retention time was estimated as initial lake volume/net inflow discharge, and flushing rate and outflow volume were calculated.

Hydrologic variables for Fenton Reservoir were determined as follows: precipitation -- available records for Seven Springs (National Weather Service, written comm.) and Fenton Hill (Barr and Wilson 1981) stations were averaged; evaporation -- US Weather Bureau records, 1.22 m/yr; inflowing stream discharge volume -- indirect daily discharges were calculated by linear regression of inlet discharge measurements with USGS discharge data for tributaries in an adjacent watershed (Pat Borland, written comm.); lake outflow volume -calculated from daily outlet discharge obtained by linear regression from daily inlet discharge; lake surface area, volume and mean depth -as shown in Table 1. Finally, the water budget was calculated (see Potter 1983).

Monthly and annual nutrient loading rates were calculated for Fenton Reservoir as observed nutrient concentration (g/m^3) times the sum of the daily discharge volumes (m^3)/lake surface area (m2).

Recommendations for watershed management and lake restoration were developed according to four criteria. First, the nutrient exporting

Dillon P Loading Model:

$$L = \frac{(P)\,\bar{Z}\,\rho}{1-R_p}$$

PARAMETER	**SYMBOL**	**EQUIVALENT EQUATION**	**UNITS**
lake TP concentration	P		mg/l
lake surface area	A_o		m^2
TP retention	R_p, R_{LM}	$1/1+\sqrt{1/\tau_w}$	--
	R_{exp}	1-(outflow L/inflow L)	--
lake volume	V		m^3
lake outflow volume	Q		m^3/yr
flushing rate	ρ	$^1/\tau_w$, Q/A	yr^{-1}
water retention time	τ_w	$^1/\rho$, V/Q	yr
mean depth	$\bar{Z}$	V/A_o	m
phosphorus loading rate	L		$g/m^2/yr$

BACHMANN N LOADING MODEL:

$$TN = \frac{L}{\bar{Z}\,(\alpha+\rho)}$$

N attenuation coefficient	α	yr^{-1}
mean depth = V/A_o	$\bar{Z}$	m
total nitrogen concentration	TN	μg N/l
hydraulic flushing rate	ρ	yr^{-1}
TN loading rate	L	$mg/m^2/yr$

$$\ln\alpha = -0.367 + 0.5541 \ln\rho$$

Figure 1. Nutrient loading models used in Clasification Phase II.

activities that could be most efficiently managed for the greatest water quality improvement were identified. If internal loading was important or flushing rate was slow, consideration was given to in-lake restoration. Second, both long and short-term benefits were considered in relation to selected water quality goals and calculated lake response times (Dillon 1974, Dillon and Rigler 1975). Third, current watershed management practices described by the US Forest Service (E. Beaden, L. Lucas, T. Skinner, A. Smart and J. Williams, written comm.) were compared to best management practices described in the literature. Fourth, the literature was reviewed to assess the applicability of management and restoration programs implemented by other states.

RESULTS AND DISCUSSION

Two graphs representative of the Classification Phase I results are shown in fig. 2. The Carlson SDD index showed little variability between lakes and was considered inapplicable due to high inorganic sediment loads. Alto Reservoir and Morphy Lake were clearly least eutrophic. Alto Reservoir and Morphy Lake were not in the eutrophic range by the Carlson chl a TSI and EPA TSI, respectively. Results for Alto Reservoir were probably due to artificial aeration and copper sulfate addition. Morphy Lake water quality reflects the small drainage area, and therefore a low rate of nutrient loading.

The remaining lakes exhibited high trophic states and specific water quality concerns (see Potter 1982). However, the highest chl a concentrations were observed at Bonito Lake and the maximum TP concentrations were measured at Quemado Lake. Blue-green algal blooms (i.e., concentrations of at least 500 organisms/ml) occurred at Bear Canyon, Fenton, Hopewell, Morphy and Roberts lakes. Phosphorus was limiting or colimiting at all lakes except for Quemado Lake, where N was solely limiting. Hypolimnetic DO concentrations less than 4.0 mg/1 were recorded for all deep water stations, except at Alto Reservoir and Morphy Lake. Finally, macrophytes were densest at Morphy, Quemado, Roberts and Wall lakes.

Lake Roberts, Quemado Lake, and Fenton Reservoir were selected as priority lakes for Classification Phase II, based on the TSI results, aesthetic impairments, and past water quality concerns such as algal blooms, fish kills and sediment accumulation (see Potter 1983).

Results of the nutrient loading rate calculations are shown in Table 2. Quemado Lake has the lowest rate despite the high concentration of TP. For all lakes, loading was primarily a function of the large drainage basins and eutrophic conditions were due to nonpoint sources. However, on-site wastewater disposal does not appear to be an important nutrient source.

For Fenton Reservoir, the combined effects of a perennial stream source, groundwater flow of about 1.0 to 1.5 cfs, and a large drainage basin with steep slopes resulted in a fast flushing rate. However, Lake Roberts and Quemado Lake are fed by ephemeral streams (and a groundwater flow of 5 cfs at Lake Roberts), so that overland flow from low intensity storms may never reach these lakes.

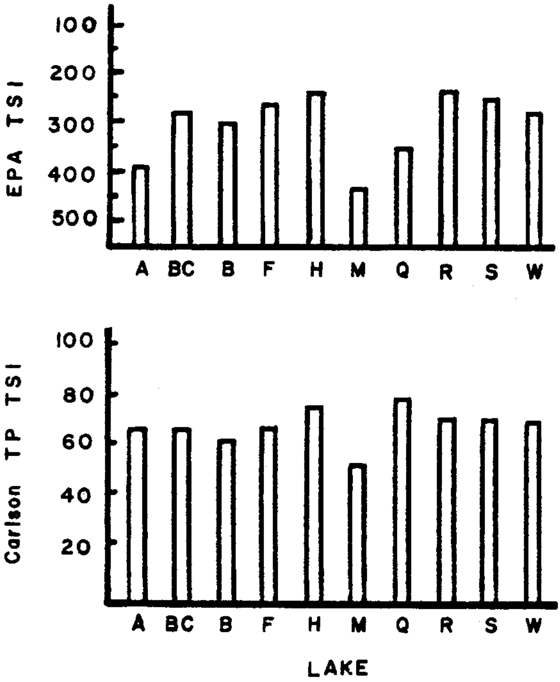

Figure 2. Mean trophic state index (TSI) for each lake using the EPA and Carlson total phosphorus (TP) TSI. EPA TSI values <420 and Carlson values >47 are in the eutrophic range. Lakes are in alphabetical order along the horizontal axis.

Table 2. Results of nitrogen and phosphorus areal unit loading rate calculations for priority lakes. Units for areal loading rates are g/m^2 surface area/yr.

Loading parameter model	Lake Roberts	Quemado Lake	Fenton Reservoir
TP, coefficient method	5.3	1.9	5.7
TP, Dillon model	2.9	2.21	4.2
DIN, Bachmann model	4.8	1.1	28.8
TN, coefficient method	106	37.6	114
TN, Bachmann model	24.6	3.6	86

Due to a rapid flushing rate, phosphorus retention was low (i.e., below 0.02) for Fenton Reservoir. However, a large portion (24%) of Fenton Reservoir's N load was supplied by groundwater and N-fixation, so that a net loss of N to the outflow was observed. Inputs to the TP load were Rio Cebolla, 88%; direct precipitation, less than 1%; and groundwater, 12%. Inputs to the TN load included Rio Cebolla, 84%; direct precipitation, 2%; groundwater, 17%; and N-fixation, 7%. Stream stations below the hatchery and Seven Springs had the highest mean TP concentrations. However, flow-weighted ammonia concentrations were not significantly greater (a= 0.05) than background below Seven Springs, but were significantly above background (l= 0.01) below the hatchery.

RECOMMENDATIONS

The ultimate water quality goal is to reduce the trophic states from eutrophic to mesotrophic by achieving concentrations of 15 ug TP/1 and 3.0 pg chl a/1. These goals were selected to improve the coldwater fishery (see GaFn and Parrott 1977). However, an interim goal is to inhibit nuisance algal blooms by reducing the nutrient concentrations to 25 pg P/1 and 300 pg inorganic-N/1.

Alum treatment was selected as the restoration method to achieve these goals. Alum has successfully controlled P availability for up to five years at Medical Lake, WA (Horwitz 1980), Horseshoe Lake, WI (Cooke and Kennedy 1980), Twin Lake, OH (Welch, Michaud and Perkins 1982), Mirror Lake, WI (Knauer and Garrison 1981) and Annabessacook Lake, ME (Dominie 1981). In addition, macrophyte control was recommended if alum can not yield a significiant water quality improvement. Sediment screens were suggested for macrophyte control, and have been successful at Lake Washington and Chautaugua Lake, NY (Perkins 1980).

Rotational grazing schedules are currently operating on the USFS land in all three watersheds. However, further reduction of cattle access to degraded range is warranted. It was also suggested that any future development of on-site wastewater disposal systems be further analyzed in terms of the P adsorption capacity of the soils.

For Lake Roberts, alum treatment was suggested to reduce TP concentrations and internal nutrient supply due to groundwater movement through reduced sediments. Additional fencing along strategic areas could be used to restrict cattle access and facilitate re vegetation.

Since logging occurs in the Quemado Lake watershed (and N is limiting), it is important that range conditions are periodically inspected using routine erosion monitoring so that problem areas can be identified, protected and improved. Although no private buildings are located in the watershed, future development of on-site wastewater disposal systems could present a water quality concern due to N-limitation. Alum could induce P-limitation, if applied to both the open water and sediments. Since the water residence time for Quemado Lake is about one year, nutrients enter and exit the lake slowly, and long-term nutrient control may be attainable.

No in-lake treatments were recommended for Fenton Reservoir. Watershed management strategies included stabilizing the shoreline, cattle crossings and areas where channels cross the road, and repair of drift fences along the stream. Hatchery effluent could also be reduced during the summer, so that background nutrient concentrations are not exceeded. However, due to the high background loading, water quality goals to inhibit nuisance algal blooms may not be achievable using watershed management.

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REFERENCES

American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1975, Standard methods for the examination of water and wastewater, 14th edition: American Public Health Association, Washington, D.C., 1193 p.

Bachmann, R.W., 1981, Prediction of total nitrogen in lakes and reservoirs, in Restoration of lakes and inland waters: US Environmental Protection Agency, Washington, D.C., pp. 320-324.

Barr, S., and Wilson, S.K., 1981, Meteorological analysis for Fenton Hill, 1979: Los Alamos Scientific Laboratory, Los Alamos, 21 p.

Beaulac, M.N., and Reckhow, K.H., 1982, An examination of land use-nutrient export relationships: Water Resources Bulletin, v. 18, no. 6, pp. 1013-1024.

Carlson, R.E., 1977, A trophic state index for lakes: Limnology and Oceanography, v. 22, p. 361-369.

Cooke, G.D., and Kennedy, R.H., 1980, Phosphorus inactivation: a summary of knowledge and research needs, in Restoration of lakes and inland waters: US Environmental ProtiEtion Agency 440/5-81010, Washington, D.C., pp. 395-399.

Dillon, P.J., 1974, A critical review of the Vollenweider nutrient budget model and other related models: Water Resources Bulletin, v. 10, pp. 969-989.

Dillon, P.J., and Rigler, F.H., 1975, A simple method for predicting the capacity of a lake for development based on lake trophic status: Journal of the Fisheries Resource Board of Canada, v. 31, p. 1519.

Dominie, D.R., 1981, Hypolimnetic treatment of softwater Annabessacook Lake, in Restoration of lakes and inland waters: USEPA 440/5-81010, Wiihington, D.C., pp. 417-423.

Garn, H.S., and Parrott, H.A., 1977, Methods recommended for classifying lake condition, determining lake sensitivity, and predicting lake impacts: US Forest Service, Milwaukee, 49 p.

Gosz, J.R., 1978, Nitrogen inputs to stream water from forests along an elevational gradient in New Mexico: Water Research, v. 12, pp. 725-734.

Horwitz, E.L., 1980, Our nations lakes: US Environmental Protection Agency, Water Regulations and Standards, Washington, D.C., 58 p.

Knauer, D.R., and Garrison, P.J., 1981, A comparison of two alum treated lakes in Wisconsin, in Restoration of lakes and inland waters: USEPA 440/5-81-010,Washington, D.C., pp. 412-416.

Krieger, K.A., 1981, The crustaceans of the southern near shore zone of the central basin of Lake Erie in 1978 and 1979: indications of trophic status: Heidelberg College, Tiffin, Ohio, 41 p.

New Mexico Environmental Improvement Division, Water Pollution Control Bureau, 1981, Procedures for performing limiting nutrient assessments, Santa Fe, 9 p.

Perkins, M.A., 1980, Managing aquatic plants with fiberglass screens, in Restoration of lakes and inland waters: USEPA 400/5-81-010, Wishington, D.C., pp. 245-248.

Potter, D., 1982, New Mexico clean lakes program classification phase I, final report: EID/WPC-82/4, NM Environmental Improvement Division, Santa Fe, 75+ p.

Potter, D., 1983, NM Clean lakes program classification phase II: restoration and management recommendations for selected priority lakes: NM Environmental Improvement Division, Santa Fe, 120+ p. Reckhow, K.H., 1979, Quantitative techniques for the assessment of lake quality: EPA-400/5-79-015, Washington, D.C.

Solomon, R.M. and Kingston, R.L., 1975, An assessment of erosion and sediment yield from the Lake Roberts watershed: US Forest Service, Gila National Forest, Silver City.

Tuan, Y., Everard, C.E., and Widdison, J.G., 1969, The climate of New Mexico: State Planning Office, Santa Fe.

US Environmental Protection Agency, 1973, Biological field and laboratory methods for measuring the quality of surface waters and effluents: EPA-600/4-73-001, Washington, D.C.

, 1974, An approach to a relative trophic index system for classifying lakes and reservoirs: Working Paper No. 24, Pacific Northwest Environmental Research Laboratory, Corvallis, Oregon.

, 1979, Methods for chemical analysis of water and wastes: EPA-600/4-79-020, Environmental Monitoring and Supply Laboratory, Cincinnati.

Welch, E.B., Michaud, J.P., and Perkins, M.A., 1982, Alum control of internal phosphorus loading in a shallow lake: Water Resources Bulletin, v. 18, no. 6, pp. 929-936.

INTENSIVE WINTER SURVEY OF THE RIO HONDO, NEAR TWINING (TAOS SKI VALLEY), TAOS COUNTY, NEW MEXICO

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ABSTRACT

As part of a continuing series of water quality studies in high mountain streams, an intensive survey was undertaken to determine the effects of the Twining wastewater treatment plant discharge on water quality and benthic macro invertebrates (fish food organisms) in the Rio Hondo during critical low stream flow and maximum effluent discharge during late March of 1982. Fifteen water quality parameters were measured eight times during a 40-hour period at seven stream sites and the effluent channel. The most noticeable changes in water quality in the Rio Hondo occurred downstream from the effluent discharge: (1) during the period of discharge, water quality immediately downstream from the mixing zone exceeded the stream standards for total inorganic nitrogen, total phosphorus, and turbidity (increased concentrations were also evident 2.4 miles downstream), and (2) when there was no discharge, water quality was well within or below stream standards. The quality of the macro invertebrate community downstream from the mixing zone was lower than at adjacent stream sites. This was evident by: (1) a nearly 50% reduction in total numbers of organisms; (2) a lowering of the biotic condition index (BCI); and (3) a 50% reduction in total numbers of taxa collected. Results of this and other surveys further substantiate the observation that small high mountain reaches of high quality coldwater fishery streams are extremely sensitive to the discharge of effluent from poorly located or inefficiently operated sewage treatment plants.

INTRODUCTION

The Surveillance and Standards Section of the Water Pollution Control Bureau is responsible for planning and implementing a statewide monitoring program of which intensive surveys play an integral part. Data gathered by such surveys are used to evaluate the water quality of high priority stream reaches which have water quality problems or are subject to significant development. In addition, such information can be used to protect and maintain both water quality and the designated uses of such aquatic ecosystems as required by the water quality standards according to the federal Clean Water Act and the New Mexico Water Quality Act.

Discharge (approximately 80,000 gpd) from the Twining Water and Sanitation District (TWSD) sewage treatment plant has caused stream standards in the Rio Hondo to be exceeded on numerous occasions since the plant was constructed in 1967 (NMEID 1975, NMEID 1981, Jacobi 1982). An Assurance of Discontinuance issued by the New Mexico Water Quality Control Commission in 1980 required the TWSD to meet effluent discharge limits for TSS (total suspended solids), BOD (biochemical oxygen demand), and fecal coliform bacteria. Improvements in effluent quality were observed in some parameters covered in the assurance (NMEID 1981) but not in the macro invertebrate-indicator organism community in the receiving stream in winter (Jacobi 1982). A point source waste load allocation for the TWSD new treatment process (more stringent than secondary) was approved in March 1982. A new privately financed treatment plant was constructed in 1982 with initial operation during the 1982-83 ski season. Disinfection was to be accomplished by ozonation (initial backup chlorination) and total phosphorus was to be reduced to 1.0 mg/1 by advanced treatment methods. Because phosphorus was determined to be the limiting nutrient in the Rio Hondo (NMEID 1981), the NPDES (National Pollutant Discharge Elimination System) permit for the new treatment plant included a variable (seasonal) effluent concentration limit set to meet the stream standard for total phosphorus (0.1 mg/1).

The purpose of this survey was to provide additional information regarding the effect of poorly treated effluent on water quality and the indicator organism community in the Rio Hondo during the last winter of operation of the old TWSD treatment plant.

DESCRIPTION OF STUDY AREA

The Rio Hondo is a major perennial tributary of the Rio Grande and is classified for use as a high quality cold water fishery stream according to the New Mexico water quality standards (NMWQCC 1981). Eight sampling sites were selected for the study; seven were on the Rio Hondo and one was the effluent channel of the TWSD sewage treatment plant. Site numbers using STORET access codes (US EPA computer-based water quality data system), elevations, and location descriptions are as follows: HON-3, 9450 ft, North Fork Rio Hondo adjacent to the Taos Ski Valley parking lot; HON-3.5, 9395 ft, Rio Hondo 0.15 mi NE of the Taos ski lift; HON-4, 9390 ft, Rio Hondo 50 yds upstream from the TWSD treatment plant outfall; HON-6, 9385 ft, TWSD treatment plant outfall; HON-8, 9370 ft, Rio Hondo 300 yds downstream from the TWSD treatment plant outfall; HON-10, 8640 ft, Rio Hondo 2.4 mi downstream from the TWSD outfall; HON-12, 7650 ft, Rio Hondo 1.5 mi upstream from Valdez at the USGS gage (9 mi downstream from the TWSD outfall); HON-18, 6760 ft, Rio Hondo at NM Highway 3 bridge; and HON-20, 6460 ft, Rio Hondo 50 yds upstream from the junction with the Rio Grande.

The Rio Hondo study sites exhibited the following habitat characteristics: HON-3, greater than 3.0% gradient with boulder and rubble substrates; HON-3.5 through HON-12, 1.3 to 3.0% gradient with pea gravel and dominant rubble substrate; HON-18, less than 1.3% gradient with mostly gravel and sand substrate; and HON-20, less than

1.3% gradient with gravel and dominant rubble substrate. Current velocities at each sample site were less than 2 ft/sec and water depths did not exceed 1 ft. Stream discharge this winter was similar to gaged observations from previous years (Jacobi 1982); less than 5 cfs above the treatment plant outfall (HON-4) and 10 cfs at HON-12. At the time of study, air and water temperatures at the upstream sites were around 0 C while downstream at the junction with the Rio Grande they approached 10 C. Snow depths up to three ft were encountered along the stream course from HON-3 downstream to HON-10.

METHODS AND MATERIALS

Eight sets of physical and chemical samples were collected at all stream sites during a 40-hr period beginning on March 29. Only five sets of samples were collected from the effluent channel because there was no discharge from the sewage treatment plant during the first three sampling periods. All samples were preserved and analyzed in accordance with the 14th edition of Standards Methods for the Examination of Water and Wastewater (APHA 1975) and Methods for Chemical Analysis of Water and Wastes (US EPA 1979). Nutrient analyses were performed by the SLD (Scientific Laboratory Division) in Albuquerque.

Three quantitative samples of benthic macro invertebrates (circular sampler, Jacobi 1978) were collected at each stream site at the end of the study. Methods of analyses included invertebrate identification, the Shannon-Weaver diversity index (H), equitability, and percent composition of biota. Significant differences between sites ($P < 0.05$) were based on raw numbers of organisms following methods presented by Elliott (1971) and Cox (1976).

The major method of macro invertebrate analysis was the biotic condition index (BCI), an integration of physical, chemical and biological stream components used to predict the health or biotic potential of a stream site (Winget and Mangum 1979 with modifications by R. N. Winget, pers. comm. 1980 and G. Z. Jacobi, S. J. Oppenheimer, unpubl. data 1980). This aquatic ecosystem inventory involving macro invertebrate analysis was developed for the U.S. Forest Service Intermountain Region to assess the impact of management practices on the aquatic environment. Improper land and water management practices that result in degraded water and habitat quality should be reflected in the composition of the Macro invertebrate community. Management practices designed to improve water and habitat quality should be evident by an improvement in the condition of the macro invertebrate community.

Winget and Mangum (1979) calculated tolerance quotients (TQ) for Rocky Mountain macro invertebrates based on species tolerances to extremes in selected environmental variables (e.g., gradient, substrate size, alkalinity, and sulfate). Tolerance quotients ranged from 2 for sensitive organisms indicative of undisturbed systems to 108 for organisms extremely tolerant of degraded or disturbed environments. Tolerance quotients were assigned to all species or genera and the actual community tolerance quotient (CTQ_a) for the stream biota was calculated using:

$$CTQ_a = \frac{\Sigma\ (\log ni\ TQi)}{\log ni}$$

where ni = number of organisms in the ith taxon
TQi = tolerance quotient for the ith taxon

A community tolerance quotient (CTQp) was then predicted for the biota based on the physical and chemical variables mentioned above using a key provided by Winget and Mangum (1979). The biotic condition index (BCI) thus is a ratio of the expected or predicted biological community (CTQp) to the actual biological community (CTQa): e.g., CTQ_D/CTQ_a x 100.

A high BCI (100) is indicative of a high quality environment; the lower the value, the lower the quality of the environment. A low predicted or actual CTQ (50) is indicative of a high quality macro invertebrate community; the higher the value, the lower the quality of the macro invertebrate community.

RESULTS AND DISCUSSION

PHYSICAL AND CHEMICAL PARAMETERS

Mean concentrations with minimum and maximum values of selected physical and chemical water quality parameters are shown in Table 1. A complete set of water quality data (STORET Retrieval) is available (Jacobi and Smolka 1983). Water quality concentrations at all sites except HON-8 were within numeric criteria established for high quality coldwater fishery streams. Water temperatures were low with concomitant high dissolved oxygen concentrations; dissolved oxygen saturation values consistently approached or exceeded 100%. Conductivity values were low upstream, 119 pmhos at HON-3, and increased steadily downstream to 238 pmhos at HON-20. Total sulfate and bicarbonate concentrations were low at all sites and were similar to observations on another northern New Mexico high mountain stream system, the Rio Costilla (Smolka and Jacobi 1983).

Nutrient concentrations (total phosphorus and total inorganic nitrogen) were low at most sites removed from the immediate impact of the TWSD sewage treatment plant discharge and showed a general increasing trend downstream (Table 1). Unexpected high concentrations of total phosphorus of 0.09 mg/1 at HON-3 and 0.05 mg/1 at HON-3.5 (in the early morning hours) suggest that non-point contributions within the Taos Ski Valley may be occurring at these upstream control sites (Table 1).

When there was effluent discharge from the sewage treatment plant, total inorganic nitrogen, total phosphorus, and turbidity concentrations exceeded stream standards at HON-8 and were significantly higher ($P < 0.05$) than at other stream sites (Tables 1

Table 1. Maximum, mean, and minimum concentrations of selected water quality parameters at Rio Hondo study sites, March 1982.

	Water Temp. (C)	Dissolved Oxygen (mg/l)	Dissolved Oxygen (% sat.)	Conductivity (µmhos @ 25°C)	Total Phosphorus (mg/l)	Total Inorganic Nitrogen (mg/l)	Turbidity (JTU)	Total Sulfate (mg/l)	Bicarbonate Ion (mg/l)
HON-3	0.8	11.00	110.15	132	0.090	0.190	7.5	11.8	85
	0.2	10.52	102.80	119	0.025	0.164	4.8	9.8	84
	0.0	10.03	97.69	93	0.010	0.150	1.0	7.9	81
HON-3.5	0.8	11.00	107.92	135	0.050	0.404	15.0	16.3	74
	0.3	10.58	104.32	127	0.019	0.321	7.2	14.6	74
	-0.1	10.10	98.16	122	0.010	0.275	0.8	13.1	73
HON-4	0.6	11.10	107.86	138	0.020	0.336	32.5	16.9	73
	0.2	10.48	102.54	125	0.012	0.313	11.9	14.4	72
	-0.2	10.03	97.46	108	0.010	0.294	0.8	12.8	71
HON-6	4.9	7.30	80.89	439	3.400	28.060	73.0	33.0	208
	4.3	6.80	74.36	404	3.170	26.706	44.4	29.7	205
	4.0	5.85	63.34	383	2.870	25.150	34.0	27.8	201
HON-8	1.7	11.00	106.88	148	0.230	1.370	36.0	16.9	77
	0.7	10.42	103.31	134	0.136	0.952	18.2	14.5	75
	0.1	10.00	99.87	117	0.010	0.343	1.0	12.8	72
HON-10	2.4	11.30	109.69	148	0.100	1.117	16.0	15.0	75
	1.0	10.59	102.43	140	0.080	0.745	10.6	12.6	73
	0.0	10.25	98.19	129	0.040	0.459	1.0	10.2	72
HON-12	2.5	11.30	108.68	146	0.040	0.549	9.0	17.2	67
	1.5	10.82	102.94	135	0.026	0.430	5.0	15.8	66
	0.2	10.50	98.18	117	0.020	0.368	0.5	14.4	66
HON-18	7.8	11.10	105.51	168	0.030	0.550	17.0	22.7	126
	3.7	10.21	99.43	156	0.022	0.307	10.4	17.7	84
	0.0	9.30	95.47	147	0.010	0.129	0.5	14.4	77
HON-20	10.0	11.00	106.67	260	0.080	0.740	28.0	25.1	132
	5.8	10.15	102.66	238	0.043	0.579	13.0	22.4	120
	2.0	9.50	97.08	226	0.030	0.217	1.5	15.1	78

and 2). The phosphorus-turbidity association, i.e., increased concentrations in both parameters, has been observed by others (Hynes 1960, Wetzel 1975, and Smolka and Jacobi 1983) and is directly related to high concentrations in the sewage treatment plant discharge (Table 1 and 2). Elevated levels of total phosphorus and total inorganic nitrogen were also evident at HON-10, 2.4 miles downstream from the discharge point (Table 1). When there was no discharge from the sewage treatment plant, nutrient concentrations at HON-8 were well below stream standards (Table 2).

BENTHIC MACROINVERTEBRATES

A summary of pertinent benthic macro invertebrate data is presented in Table 3. A complete list and detailed discussion of individual species composition is presented in Jacobi and Smolka (1983). The greatest number of taxa (41) were collected at HON-12, 9 miles downstream from the sewage treatment plant outfall while the fewest taxa (15) were collected at HON-8, 300 yards downstream from the outfall. The low number of total taxa at HON-8 represents a reduction of almost 50% when compared to adjacent stream sites, upstream HON-4 and downstream HON-10 (Table 3). High standing crops (density) of macro invertebrates of 6591/m^2 at HON-10 and 5474/m^2 at HON-12 were significantly different ($P < 0.05$) from low standing crops of 1083/m^2 at HON-3 and 1197/m^2 at HON-8 (Table 3). Diversity indices were generally high and varied from 4.24 at HON-12 to 2.46 at HON-20. Equitability values were also generally high and ranged from 0.81 at HON-3 to 0.33 at HON-20 (Table 3).

Thirteen taxa of stoneflies (Plecoptera) were collected. Between five and 10 taxa were present at HON-3, 3.5, 4, 10, and 12 and comprised between 13% and 27% of the total numbers of organisms at these sites. Numbers of sensitive Plecoptera were reduced to two taxa and 1% of the total number of organisms at HON-8 (Table 3). Low numbers of Plecoptera at HON-18 and 20 were attributed, in part, to sensitive species being replaced by other more tolerant taxa.

Fourteen total taxa of caddisflies (Trichoptera) were collected and sample site numbers varied between five and eight taxa. Composition of the total fauna varied from 57% at HON-10 to 4.6% at HON-18 (Table 3).

Eleven taxa of mayflies (Ephemeroptera) were collected and representation varied from seven taxa at each HON-3 and HON-10 to only one taxon at HON-8. Faunal composition varied from 52% at HON-12 to 1.4% at HON-8 (Table 3).

A total of 19 taxa of true flies (Diptera) were collected; nine taxa consisted of representatives of the Chironomidae, non-biting midges. Fourteen taxa of tolerant dipterans accounted for 22% of the total number of organisms at HON-12 and three taxa represented 3% at HON-3.5. In contrast, five taxa comprised 54% of the macro invertebrate community at HON-8 (Table 3).

Flatworms (Turbellaria: Polycelis coronata) were present at all sites and varied between 24% of the total number of organisms at HON-4 to 2% at each HON-8, 12, and 20 (Table 3).

Table 2. Summary of water quality data from the Twining Sewage Treatment Plant effluent channel (HON-6) and downstream from the mixing zone in the Rio Hondo (HON-8), March 29-31, 1982.

Parameter	concentration at HON-6 (n = 5)	concentration at HON-8		
		without discharge (n = 3)	with discharge (n = 5)	average (n = 8)
Turbidity (JTU)	44.4	5.3	26.0	18.2
Total Phosphorus (mg/l)	3.17	0.03	0.20	0.14
Total Inorganic Nitrogen (mg/l)	27.70	0.40	1.29	0.96

Table 3. Selected biological parameters from Rio Hondo sites, March 31, 1982.

Parameter Sites	3	3.5	4	8	10	12	18	20
Average density (no./m^2)	1083	2475	2062	1197	6591	5457	1381	5050
Diversity Index ($\bar{H}$)	3.92	3.59	3.62	2.80	2.89	4.24	3.35	2.46
Equitability	0.81	0.71	0.64	0.67	0.34	0.68	0.50	0.33
CTQ_p	50	50	50	50	50	50	60	53
CTQ_a	44.0	41.4	46.1	54.1	48.6	46.1	80.9	72.3
BCI	113.6	120.8	108.5	92.4	102.9	108.5	74.5	73.3
Total taxa	27	24	28	15	29	41	30	24
Plecoptera (stoneflies)								
number of taxa	7	7	8	2	5	10	2	1
percent composition of density	26.4	22.3	18.6	1.0	12.5	15.4	3.3	1.0
Trichoptera (caddisflies)								
number of taxa	6	7	5	6	5	8	5	6
percent composition of density	24.0	18.0	29.9	41.6	56.8	23.6	4.6	11.0
Ephemeroptera (mayflies)								
number of taxa	7	6	6	1	7	6	3	3
percent composition of density	32.1	42.4	21.6	1.4	8.3	37.1	6.2	52.0
Diptera (true flies)								
number of taxa	5	3	6	5	9	14	12	9
percent composition of density	6.9	2.5	5.3	53.8	10.1	21.7	64.5	28.9
Turbellaria (flatworms)								
number of taxa	1	1	1	1	1	1	1	1
percent composition of density	9.0	14.7	23.8	2.4	11.8	1.9	2.5	2.1
Other*								
number of taxa	1	0	2	0	2	2	7	4
percent composition of density	1.6	0	1.0	0	1.0	1.0	18.9	5.0

*Coleoptera (beetles), Mollusca (snails), Hydracharina (water mites), Amphipoda (scuds), Hemiptera (true bugs), Oligochaeta (segmented worms), and Lepidoptera (aquatic moths).

Infrequently collected taxa include Mollusca, Hydracharina, Amphipoda, Hemiptera, and Oligochaeta (Table 3). The riffle beetle (Coleoptera: Heterelmis) present at four sites, accounted for 13% of the total number of organisms at HON-18. The aquatic moth (Lepidoptera: Parargyractus) represented 5% of the total number of organisms at HON-20 (Jacobi and Smolka 1983).

The predicted community tolerance quotients (CTQp) based on the physical and chemical criteria established by Winget and Mangum (1979) indicated high quality habitats for all upstream canyon sites, HON-12 to HON-3. The predicted qualities were lower for downstream HON-18 and 20 (Table 3) and were due, in part, to geomorphological and altitudinal differences. These two sites were similar to lower elevation sites on another high quality mountain stream, the Rio Chama (Jacobi and Smolka 1983).

The actual community tolerance quotient (CTQ_a) and biotic condition index (BCI) values for HON-8 were indicative of a high quality environment but were lower when compared to values at the other high elevation sites. Dominant taxa (Diptera - Chironomidae) at this site were more tolerant of perturbation than those dominant (Plecoptera and Ephemeroptera) at sites immediately upstream and downstream (see CTQ_a comparisons for HON-4, 8, and 10, Table 3). Sensitive Plecoptera and Ephemeroptera were virtually absent from HON-8 and the number of total taxa and total number of organisms was reduced by almost 50% when compared to HON-4. Dipterans dominated the biota and faunal composition was almost identical to that of 1979 and reduced numbers were similar to those observed during an over chlorination event in 1981 (Jacobi 1982).

Sites HON-3, 3.5, 4, 10, and 12 all had CTQ_as of less than 50 and BCIs greater than 100 which indicate biota from unstressed high quality systems. HON-18 and 20 had CTQ_as and BCIs indicative of lower quality environments. HON-18 was below a beaver pond and the substrate appeared disturbed at the time of sampling. HON-20, upstream from the junction with the Rio Grande and the lowest elevation site on this high quality stream, contained a more tolerant fauna similar to that of the Rio Chama (Jacobi and Smolka 1983).

Results of previous surveys during the winters of 1979, 80, and 81, have shown degraded water quality and impacted biological communities in the Rio Hondo downstream from the Twining sewage treatment plant discharge (Jacobi 1982). Biota consisted of either increased numbers of tolerant taxa (many Diptera) or reduced numbers of sensitive fauna (Plecoptera and Ephemeroptera); neither condition indicate a high quality environment. This 1982 survey also showed degraded water quality at HON-8 accompanied by a change in composition and abundance of the high quality headwater macro invertebrate community. Though the change may appear subtle it was none the less a degradation of the existing high quality environment which is incompatible with the goal of maintaining or improving the quality of existing surface waters to insure attainment of designated uses in sensitive high mountain streams.

CONCLUSIONS

1. Water quality concentrations were generally well below or within stream standard limits for high elevation (7650 to 9450 ft) sites HON-3, 3.5, 4, 10, and 12. Values for the CTQ_D and BCI for the macro invertebrate community reflected these high quality stream reaches.
2. Water quality concentrations were also well below or within stream standard limits at low elevation (6460 to 6760 ft) sites HON-18 and 20, but the quality of the macro invertebrate community was lower due to the dominance of more tolerant organisms. Tolerant organisms were also dominant at low elevation sites on other New Mexico high quality coidwater streams.
3. During the period of effluent discharge from the Twining STP, water quality in the Rio Hondo below the mixing zone (HON-8) exceeded the stream standards for total inorganic nitrogen, total phosphorus, and turbidity. Increased concentrations were also evident 2.4 miles downstream at HON-10.
4. When there was no discharge of effluent from the Twining STP, water quality was well below or within stream standard limits at HON-8.
5. The quality of the macro invertebrate community at HON-8 was lower when compared to adjacent stream sites. This was evident by: (a) a reduction of almost 50% in total numbers of organisms/m^2; (b) a lowering of the biotic condition index (BCI); (c) a 50% reduction in total numbers of taxa collected; and (d) a loss of sensitive Plecoptera and Ephemeroptera taxa.

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REFERENCES

American Public Health Association, 1975, Standards methods for the examination of Water and Wastewater, 14th edition: American Public Health Association, Washington, D.C., 1193 p.

Cox, G. W., 1976, Laboratory manual of general ecology: Wm. C. Brown Co., Dubuque, Iowa. 232 p.

Elliott, J. M., 1971, Some methods for the statistical analysis of samples of benthic macro invertebrates: Freshwater Biological Association, United Kingdom, Scientific Publication 25, 144 p.

Hynes, H. B. N., 1960, The biology of polluted water: University of Toronto Press, Toronto, Canada, 202 p.

Jacobi, G. Z., 1978, An inexpensive circular sampler for collecting benthic macro invertebrates in streams: Archiv fur Hydrobiologia, v. 83, pp. 126-131.

, 1982, Effect of organic pollution on benthic macro invertebrates in the Rio Hondo, Taos County, New Mexico. New Mexico Environmental Improvement Division, Santa Fe, New Mexico, EID/WPC-82-1, 41 p.

, and L. R. Smolka, 1983, Intensive survey of the Rio Chamita and Rio Chama, near Chama, Rio Arriba County, New Mexico: New Mexico Environmental Improvement Division, Santa Fe, New Mexico EID/WPC-83/l, 39 p.

New Mexico Environmental Improvement Division, 1975, Water quality of the Rio Hondo: New Mexico Environmental Improvement Division, Water Pollution Control Bureau, Santa Fe, New Mexico, 10 p.

____________________, 1981, Point source waste load allocation for the Twining water and sanitation district: New Mexico Environmental Improvement Division, Water Pollution Control Bureau, Santa Fe, New Mexico, 43 p.

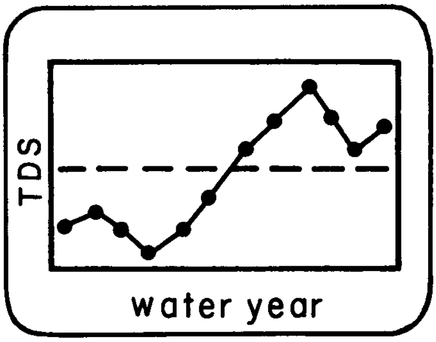
New Mexico Water Quality Control Commission, 1981, Water quality standards for interstate and intrastate streams in New Mexico, 81-1, June 4, 1981: New Mexico Water Quality Control Commission, Santa Fe, New Mexico, 87503, 40 p.

Smolka, L. R., and G. Z. Jacobi, 1983, Water quality survey of Cordova and Costilla Creeks near the Rio Costilla ski area, October 14-16, 1982: New Mexico Environmental Improvement Division, Santa Fe, New Mexico, 35 p.

U. S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, EPA-600/4-79-020.

Wetzel, R. G., 1975, Limnology: W. B. Saunders Company, Philadelphia, Pennsylvania, 743 p.

Winget, R. W. and F. A. Mangum, 1979, Biotic condition index: integrated biological, physical, and chemical stream parameters for management: United States Forest Service, Provo, Utah, 51 pp.



PROTECTION OF SURFACE WATERS: THE AWT PLANT AT RED RIVER, NEW MEXICO

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Culp/Wesner/Culp, Consulting Engineers
John H. Miller
Mayor, Town of Red River

ABSTRACT

The Red River is a high mountain stream having its headwaters in the Wheeler Park Wilderness area of Taos County. The river supports a trout fishery and is the center of the summer tourism in and around the Town of Red River. The New Mexico Environmental Improvement Division (NMEID) established stringent stream standards to protect the aquatic environment and aesthetic quality of the stream. This paper chronicles the events leading to the establishment of the stream standards and effluent limitations and the changes in the state's nitrogen standard for streams. The inappropriateness of the total nitrogen standard is discussed. A description is presented on the selection of the treatment system to meet the effluent limitations, and the individual treatment processes which include RBC's for biological treatment and chemical addition for phosphorus removal, disinfection and pH control. The theory of operation of the treatment processes is explained and the range in effluent quality concentrations for the first few months is included.

INTRODUCTION

The Town of Red River is located in north central New Mexico, along the banks of the pristine Red River. The Red River is one of only two continuously flowing, high mountain streams in the State, and has its origin in the Wheeler Peak Wilderness area, just north of the Taos ski area. The stream discharges into the Rio Grande River, about 7 miles (11.3 km) west of Questa.

The NMEID required the removal of the nutrients ammonia and phosphorus from municipal sewage to protect the river against the growth of periphyton, a small moss-like growth that attaches to stream bed rocks. The ammonia limitation was also intended to protect the aquatic life from the potentially toxic effects of un-ionized ammonia.

The NMEID designated the following beneficial uses for the Red River:

- Domestic Water Supply
- Fish Culture
- High Quality Cold Water Fishery
- Irrigation
- Livestock and Wildlife Watering
- Secondary Contact Recreation
- Industrial Water Supply

The major uses of the Red River in or close to the Town are:

- Trout fishing - Both the Town and State stock the Red River with Rainbow Trout annually. There are native Brown and Cutthroat Trout fisheries, but they are not stocked.

- Camping - there are several private and public campgrounds along the Red River in and near the Town.
- Hiking - people staying at the lodges in town, or at a campground, use the River shoreline for hiking.
- Wildlife watering - the indigenous wildlife use the stream as a water supply.
- Irrigation - a few town residents and/or landowners have rights for water withdrawals for irrigation purposes.

The uses generally reflect the tourist nature of the area. Also, during the summer months, children swim and tube along sections of the river.

EVOLUTION OF EFFLUENT LIMITATIONS

To protect the beneficial uses enumerated above, the NMEID established numerical water quality standards for the Red River. The water quality standards originally proposed are listed in Table 1.

Table 1. Water Quality Standards for the Red River

Constituent	Standard	How Applied
Ammonia-Nitrogen (Total)	0.2 mg/L	Single Sample
Un-ionized Ammonia Nitrogen	0.02 mg/L (as N)	Single Sample
Dissolved Oxygen	The greater of 6.0 mg/L or 85% of saturation	Single Sample
pH	6.6 - 8.8	Single Measurement
Temperature	<20°C	Single Measurement
Total Chlorine	0.002 mg/L	Single Measurement
Conductivity	400 umhos/cm	Single Measurement
Total Organic Carbon	7 mg/L	Single Sample
Nitrate Nitrogen	0.8 mg/L	Single Sample
Total Phosphorus	0.1 mg/L	Single Sample
Turbidity	25 FTU	Single Sample
Fecal Coliform	100/100 mL	Monthly Geometric Mean
	200/100 mL	No more than 10% of Samples

The standards for the first five constituents listed on Table 1 were designated to protect the cold water fishery. Un-ionized ammonia can be toxic to fish. The U.S. EPA publication Quality Criteria for Water (the Red Book), 1977, recommends a criterion of 0.02 mg/L (as N). While some debate still continues in the scientific community as to the appropriateness of this number (e.g., see American Fisheries Society (1979), it is the predominant one in use and appears to be generally accepted. Prior to July 8, 1980, New Mexico had only the total ammonia-nitrogen standard. In an update of their standards the un-ionized standard was added. The amount of um-ionized ammonia is related to the amount of total ammonia, the temperature and the pH. For instance, for a given amount of total ammonia at 15°C,4a pH change from 7.0 to 7.3 will double the amount of ammonia in the un-ionized form. If the temperature is 15°C and the pH is 7.0, a total ammonia of 7.5 mg/L would produce un-ionized ammonia of 0.02 mg/L. A higher concentration would be potentially toxic and a lower concentration safe.

The total ammonia standard was inappropriate for two reasons. First, for certain temperature and pH concentrations it would allow un-ionized ammonia concentrations higher than 0.02 mg/L (e.g., a pH of 8.5 and temperature of 20°C). Second, for much of the time it is unnecessarily restrictive. For example with an average pH of 7.0 and a temperature of 15°C, 0.2 mg/L total ammonia would translate to only 0.00055 mg/L unionized ammonia. Total ammonia per se has no adverse effect on fisheries, and has no effect on this beneficial use. Therefore, from both the point of view of the State of New Mexico and the Town of Red River, it was desirable to base the ammonia effluent limitation on the un-ionized ammonia standard.

The Red River had stream standards for nitrate-nitrogen (0.8 mg/L) and total phosphorus (0.1 mg/L). State of New Mexico staff indicated that these standards were meant to control the growth of undesirable attached algae (periphyton). The results of the EPA standard algal bioassays indicated that phosphorus is the limiting nutrient. The mean Total Nitrogen to Total Phosphorus (TN/TP) ratio is approximately 14. Values greater than 8 have generally been accepted as indicating phosphorus limitations. The State indicated in a letter of August 22, 1980, that only the limiting nutrient (phosphorus) need be controlled.

The reach of the Red River adjacent to the Town is a cold, rapidly moving, mountain stream. It experiences its lowest temperatures and flows in the winter (January and February). Its highest temperatures occur in late summer and highest flows in early summer. Fig. 1 is a plot of observed temperatures for the Red River just upstream of the Town and fig. 2 is a plot of the seven-day-average-two-year-return monthly low flow, which were used to establish the effluent limitations for the plant.

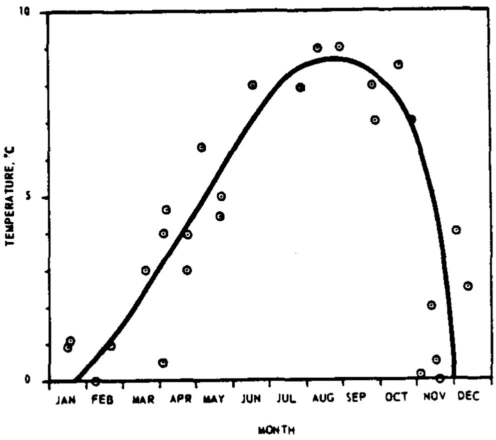

Figure 1. Red River Water Temperatures
Source: STORET Data File

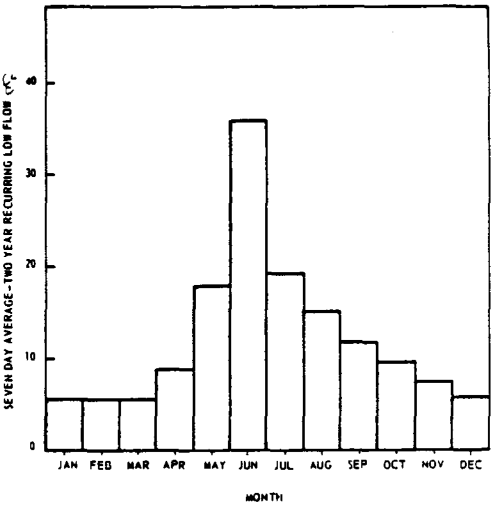

Figure 2. Critical Low Flow Values for the Red River Below the Town
Source: Reiland, Louis J.

INITIALLY PROPOSED EFFLUENT LIMITATIONS BY NMEID

The proposed effluent limitations are summarized in Table 1. CWC was concerned about the impact of these stringent effluent limitations on the construction and operating costs of a wastewater treatment plant. Consequently, CWC offered an alternative set of effluent limitations which would result in lower costs, but maintain the specified beneficial uses. These alternative standards are discussed below.

The effluent limitations in Table 1 were based upon several factors which, if changed, may produce less restrictive effluent limitations without impairing beneficial uses. These factors are:

1. the ammonia-nitrogen stream standard of 0.2 mg/L,
2. the calculation of effluent limitations on an annual basis, and
3. the minimum phosphorus limitation.

Table 2 presents allowable effluent ammonia-nitrogen and total phosphorus concentrations based on:

1. the unionized ammonia stream standard of 0.02 mg/L as N, and
2. the calculation of allowable phosphorus concentrations based on various effluent flow rates.

Table 2. Effluent Limitations Proposed by CWC

Month	7-day, 10-yr flow, cfs Red River Zwergle Dam	Est. @ Outfall	Allowable Total Ammonia In Plant Effluent, mg/L Design Flow	1987 Flow	% Nitrification Required Design Flow	1987 Flow	Allowable Phosphorus In Effluent, mg/L Design Flow	1987 Flow
Jan	3.7	3.9	26.6	33.0	19	0	0.62	0.77
Feb	3.6	3.8	21.9	27.1	34	18	0.61	0.76
Mar	3.6	3.8	14.4	17.9	56	46	0.61	0.76
Apr	5.1	5.3	49.5	61.4	0	0	2.93	3.64
May	11.1	11.6	256.3	317.7	0	0	6.29	7.82
June	12.0	12.6	14.4	17.6	50	39	6.82	8.48
July	8.0	8.4	9.9	12.3	66	58	1.00	1.24
Aug	7.5	7.9	13.4	16.6	54	43	0.94	1.17
Sept	6.8	7.1	69.7	86.4	0	0	3.89	4.84
Oct	5.7	6.0	91.6	113.6	0	0	3.30	4.10
Nov	4.4	4.6	23.8	29.5	0	0	0.71	0.88
Dec	3.4	3.6	20.9	25.9	37	22	0.58	0.72

Monthly allowable effluent concentrations for total phosphorus were calculated. Plant discharge, critical low monthly stream flows, and seasonal ambient upstream constituent concentrations were used to compute the effluent limitations.

Monthly allowable effluent concentrations for ammonia were calculated in a two-step procedure. First, based on maximum observed pH and temperature for the month and the 0.02 mg/L unionized ammonia stream standard, a maximum monthly allowable stream ammonia concentration was calculated. The second step was to complete a mass balance using the highest observed upstream ambient ammonia concentration and the allowable stream ammonia concentration to obtain the required effluent limitations.

Comparison of the State of New Mexico proposed design flow (0.50 mgd) total phosphorus effluent limitation (0.8 mg/L) and Table 2 shows that during the critical part of the year (December through March) that a low phosphorus effluent limitation was required, but that it may be relaxed considerably during the other part of the year. A seasonal effluent limitation was justified.

Comparison of the State of New Mexico design flow limitations for ammonia with the allowable monthly effluent concentrations on Table 2 shows that much less stringent effluent requirements were sufficient to protect the fishery and that seasonal ammonia limitations were also justified.

DISCHARGE REQUIREMENTS RECOMMENDED BY CWC

National Pollution Discharge Elimination System (NPDES) permits are issued for five years. However, facilities have a design life much longer than five years. For Red River, the design life was 20 years, and facilities planning, design and construction should be done on the basis of expected requirements at the time design capacity is reached. The effluent limitations proposed by CWC are shown in Table 3. The recommendations for total phosphorus and ammonia are discussed below.

Table 3. Effluent Limitations Proposed By CWC

Non-Flow Ralated	
Same as shown in Table 2	
Flow-Related	
Total Phosphorus	1.0 mg/L October through April 1.3 mg/L May through September
Ammonia	29 mg/L October through February, May & June 19 mg/L March, April, July, August & September
Total Chlorine Residual	Same as shown in Table 2
Average Daily Flow	0.39 mgd September through May 0.49 mgd June through August

1 mgd = 43.8 liters per second = 3.785 m^3/day

The total phosphorus effluent limitation of 1.3 mg/L for May though September was a direct reflection of the monthly allowable effluent concentration on Table 2 and the higher allowable flows for May and September. The limitation of 1.0 mg/L for October and November reflected the monthly allowable effluent concentration on Table 2 and for October the increased allowable flow. From Table 2 one would expect a total phosphorus effluent limitation for December through April of less than 1.0 mg/L. To reliably meet an effluent limitation of less than 1.0 mg/L total phosphorus, effluent filtration would be required.

The limitation for phosphorus was designed to achieve a 0.1 mg/L in-stream concentration. This value is based on controlling the growth of periphyton in the stream and is the value suggested by the EPA Red Book. The in-stream phosphorus concentration should be based on the available, or soluble, phosphorus discharged from the plant. Particulate phosphorus, and other forms of phosphorus that are tied up with constituents in the wastewater, are not readily available for bio stimulation. Studies using alum for wastewater treatment at the South Tahoe plant have shown that only about 10 to 20 percent of the phosphorus in the treated water is available for bio stimulation. Therefore, limiting effluent concentrations to 1 mg/L phosphorus, would meet the State's requirement for phosphorus control to prevent periphyton growths in the Red River.

The ammonia-nitrogen effluent limitations of 29 mg/L for October through February, May, and June represented a level which provided the necessary protection to the fishery with a margin of safety and a concentration which should easily be met with little or no ammonia removal. The limitation of 19 mg/L for March, April, July, August and September reflects the need for higher effluent ammonia control to protect the fishery.

NPDES PERMIT

The NMEID considered the CWC proposal and accepted the general principles presented above. Based on the analysis completed by CWC, and additional detailed analyses of water quantity and quality, the NMEID developed a revised set of effluent limitations. These are summarized in Table 4. Inspection of this table shows that variable discharge limitations are included, that the minimum phosphorus concentration is 1 mg/L, and that the nitrogen limitation is based on the in-stream unionized ammonia standard of 0.02 mg/L. The NMEID has since changed the state standards to eliminate the total nitrogen standard.

Table 4. Discharge Standards for Red River AWT Plant

pH, Units	6.6-8.6	Phosphorus, mg/L	
Biochemical Oxygen Demand, mg/L		October-April	1.0
30-Day Average	30	May	7.5
7-Day Average	45	June	1.7
Total Suspended Solids, mg/L		July-August	1.2
30-Day Average	30	September	5.0
7-Day Average	45	Ammonia, mg/L as N	
Fecal Coliform, Organisms/100 mL	500	September	30
Chlorine Residual, mg/L	0.02	October	20
		November-February	30
		March-April	20
		May	30
		June	20
		July	14
		August	18

TREATMENT SYSTEM

The Town has about 380 permanent residents, but it has a tourist influx of as many as 3,000 tourists during the summer and winter seasons. The population and flow projections are shown in figs. 3 and 4. Three treatment systems were evaluated in detail as a part of the design report. These were:

- RBC biological system
- Extended aeration biological system
- Bio tower biological system

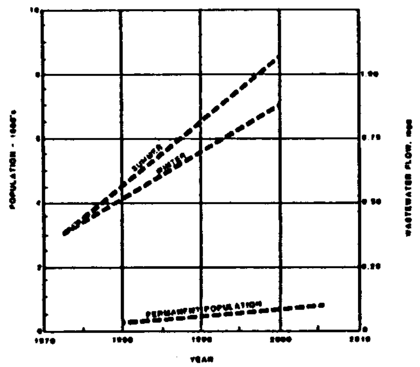

Figure 3. Population Projections
Source: CWC Design Report

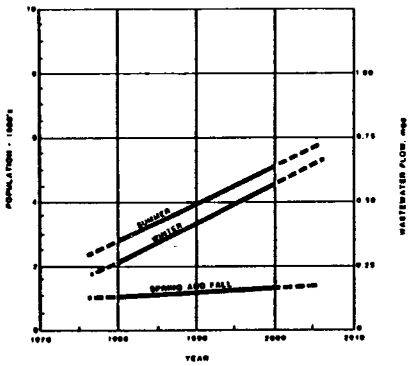

Figure 4. Projected Wastewater Flows
Source: CWC Design Report

Life cycle costs were developed for each system which showed that the RBC process resulted in lower overall costs to the Town. The Red River AWT plant is now operational and the RBC's are performing well.

The major factors considered during the design are as follows:

- wide fluctuations in population due to tourists (10:1)
- wide variations in influent wastewater flow and strength
- high elevation (8,550 ft (2,606 m) above MSL)
- severe climatic conditions, including heavy snowfall, extreme cold, low influent wastewater temperature (8°C)
- low alkalinity in influent wastewater (75 mg/L)
- unreliable power supply, and high power costs in winter
- remote location affecting servicing and supply deliveries The process schematic for the Red River plant is shown in fig. 5, and

the design wastewater flows and characteristics are shown in Tables 5 and 6, respectively. The plant is totally enclosed to protect equipment and operators from the extreme cold in the winter months. The plant is located in a valley which funnels the wind past the plant and causes severe wind chill effects.

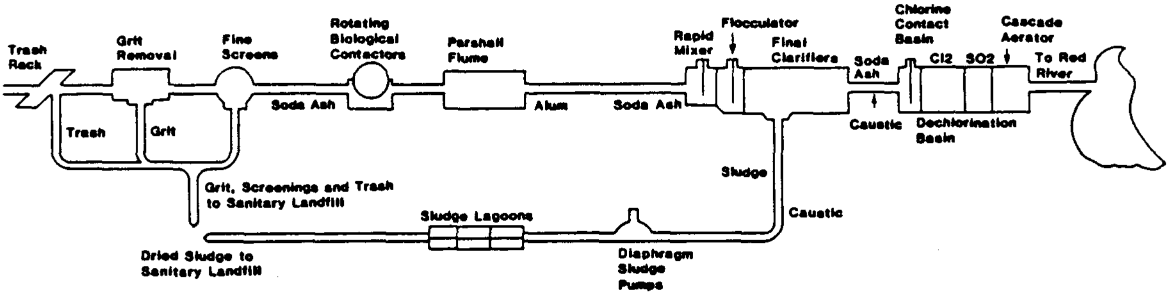

Figure 5. Process Schematic

Table 5. Estimated Wastewater Flows - in MGD

Year		Wastewater Flows, MGD Nov-Mar	Apr-May	June-Aug	Sept-Oct
1980					
	Avg. Daily	0.26	0.13	0.35	0.13
2001*					
	Min. Daily	0.34	0.13	0.37	0.13
	Avg. Daily	0.57	0.16	0.63	0.16
	Max. Daily	1.15	0.32	1.26	0.32
	Max. Month	0.86	0.24	0.95	0.24
	Max. Hour	2.30	0.50	2.50	0.50

*Design Conditions.
1 mgd = 43.8 liters per second = 3.785 m^3/day

Table 6. Design Wastewater Characteristics

Constituent	Constituent Concentrations Nov-Mar	Apr-May	June-Aug	Sept-Oct
BOD_5, mg/L	300	162	300	162
COD, mg/L*	505	281	505	281
TSS, mg/L	300	162	300	162
VSS, mg/L*	321	125	231	125
NH_4-N, mg/L	30	16	30	16
PO_4-P, mg/L*	10	10	10	10
Alkalinity, mg/L*	75	75	75	75
pH	7	7	7	7
Temperature, °C	8	12	15	12

*Estimated Values.

Raw wastewater flows by gravity from the Town to and through the new AWT plant. The plant processes start with a bar rack to remove large debris that could damage downstream equipment. A vortex-type grit removal system follows the bar rack to remove grit, sand, coffee grounds and other similar material. De-gritted wastewater then passes through rotating fine screens in lieu of primary sedimentation tanks. The screens remove suspended solids above 0.10 (2.54 mm) inches in size. The grit and screenings are buried in an adjacent landfill site.

The flow then enters the biological treatment process which consists of the RBC's and clarifiers. The RBC's provide treatment to the waste stream by means of a film of microorganisms which grows on the surface of plastic sheets that are wound around a central shaft to a diameter of about 10 feet (3.05 m). The media is submerged approximately 40 percent in the wastewater. The shafts to which the media is attached are rotated slowly by means of a motor-driven belt drive at one end of the shaft, while the other end rotates freely.

As the media rotates, the microbial growth contacts alternately with the wastewater and air. During passage through the wastewater, the media pick up a thin film of wastewater from which the organic material is synthesized by the biomass. The excess growth of microbes slough off from the disks and flows to the clarifiers to be separated from the wastewater.

The RBC system at the Red River plant consists of three parallel basins, each of which contains four RBC's. The baffle arrangement in each basin is set up to provide three-stage treatment with the first stage containing two shafts of normal density media (100,000 SF/shaft) (9,290 m^2)and the second and third stages each containing one shaft with high density media (150,000 SF/shaft (13,935 m^2).

The phosphorus concentration in the raw wastewater is reduced by chemical precipitation and subsequent clarification. Phosphorus is present in the wastewater in a soluble form and also as finely divided, suspended particles. About 5 percent of the influent phosphorus is insoluble and can be removed by the fine screens.

The phosphorus in the effluent from the RBC process will be in the orthophosphate form, which is the easiest form to precipitate through chemical reactions. The precipitation process is achieved through the addition of alum to the wastewater. The mixture is blended and then gently stirred to aggregate particles into larger particles that can settle, and be removed in the final clarifiers.

Alum reacts with alkalinity and phosphate in water, and according to the stoichiometric equations, 3.13 mg/L of alum reacts with 1 mg/L $P0_4^{3-}$to precipitate 1.29 mg/L $AlPO_4$; and each mg/L of alum decreases the alkalinity concentration (expressed as CaCO3) by 0.50 mg/L while precipitating 0.26 mg/L of $Al(OH)_3$. The Al:P mole ratio is 1:1 and the weight ratio is 0.87:1. Therefore, 9.6 lbs of alum are required to remove 1 lb of phosphorus (P).

The solubility of aluminum phosphate ($A1PO_4$), is pH dependent. To obtain the most effective removal of $AlPO_4$, the pH should be adjusted to minimize the solubility of $AlPO_4$, which occurs at a pH of 6. Therefore, the optimum pH for the removal of phosphorus probably is in the range of 5.5 to 6.5.

Chemical feed systems also are provided in the Red River plant for alkalinity and pH adjustment. These are the soda ash feed and caustic feed systems.

Soda ash can be fed at three locations in the plant: prior to the RBC's; prior to chemical clarification; and prior to chlorination. Soda ash addition is necessary to offset the alkalinity destruction caused by biological nitrification alum reactions, and it also buffers the water in a pH range where the coagulant can be effective. Soda ash addition prior to the chlorination basins is provided as a standby system to the caustic feed.

Caustic may be introduced at three locations in the plant: the RBC split box; the final clarifier split box; and the sludge line leading to the lagoons. Caustic feed to the RBC split box is provided as a standby system to the soda ash. Feeding of caustic prior to chlorination is to control the pH in the pH depression caused by alum and chlorine addition. Caustic feed to the sludge line is used to control odors from the sludge lagoon by raising the pH to 10.0 or greater.

When nitrification occurs in the RBC's, approximately 7.14 mg/L of alkalinity as $CaCO_3$ is destroyed for each 1 mg/L of ammonia-nitrogen oxidized. Furthermore, severe pH depression can occur when the alkalinity in the wastewater approaches depletion by the acid produced in the nitrification process. Therefore, excess alkalinity should always be present in the RBC influent when nitrification is expected to occur.

There are two operating modes for the chlorination system: the disinfection mode, and the breakpoint chlorination mode. In the disinfection mode chlorine is added to the clarifier effluent in sufficient quantity to destroy pathogenic organisms.

Chlorine is delivered to the plant in both 150 lb and 1-ton cylinders. The liquid chlorine vaporizes to pressurize the cylinders and is withdrawn in gaseous form for use in the plant. When chlorine is dissolved in water at temperatures between 49°F and 212°F, it reacts to form hypochlorous and hydrochloric acids. Greater bactericidal efficiency is attained by HOC1 than the other forms of chlorine. Because HOC1 predominates at lower pH's, the addition of caustic or soda ash is carefully monitored to maintain a neutral pH.

The addition of excess quantities of chlorine to wastewater, termed "Breakpoint Chlorination," can remove nitrogen. Because breakpoint chlorination removes all the ammonia, only a portion of the effluent needs to be subjected to this reaction. The final blending of the effluent will meet the discharge limitations. The required chlorine dosage is calculated based on 8 to 10 mg/L of chlorine for each 1 mg/L of ammonia-nitrogen.

Stiochiometrically, the breakpoint reaction requires an atomic ratio of Cl:N of 3:1 or a weight ratio of 7.6:1. Therefore, theoretically 7.6 parts of chlorine are required to chemically oxidize one part of ammonia-nitrogen. In practice the weight ratio is in the range of 8 to 10:1 because of competing reactions. The use of chlorine solutions produces acid, and reacts with the alkalinity present. Stoichiometrically, it requires 14.3 mg/L of alkalinity (as calcium carbonate) to neutralize the acid produced during the oxidation of 1 mg/L of NH_4-N.

The de-chlorination system is provided to reduce the chlorine residual in the treatment plant effluent to a level satisfying the NPDES permit. Chlorine concentrations above 0.002 mg/L in the stream are toxic to fish. De-chlorination is achieved using a sulfur dioxide solution which is added at the end of the chlorine contact basins.

The required sulfur dioxide feed rate is determined by multiplying the chlorine residual value by the stoichiometric sulfur dioxide requirement. Sulfur dioxide reacts with both free and combined forms of chlorine residuals. The predictions of sulfur dioxide dosages required for de-chlorination suggest an $S0_2$:$C1_2$ molar ratio of 1:1. This corresponds to a weight ratio of 0.9:1. In practice, the weight ratio is in the range of 0.9 to 1.0 parts of SO_2 per 1.0 part of chlorine residual (expressed as C12).

SLUDGE HANDLING

Sludge and scum collected in the clarifiers are pumped to storage lagoons. The seven sludge lagoons are of earthen construction with impervious liners and were the basis of the original treatment system. The liners are covered with 6 inches (15.2 cm) of sand for protection.

The waste sludge is pumped continuously into one of the seven sludge lagoons. When the wet sludge depth reaches 9 inches (22.9 cm), the clear surface water decants through the outlet pipe and returns to the plant for treatment. Feed to the selected lagoon continues until alum sludge particles in the decant are visible to the operators. Influent sludge then is diverted to the next lagoon. The sludge retained within the first lagoon settles and the water evaporates allowing the sludge to dry. The sludge is stored in the lagoon for about 1 year before removal. During this period, biological solids digest and are rendered harmless.

In order to control odors from the sludge lagoons, caustic (NaOH) is added to the sludge to raise the pH to above 10.0. The caustic is fed into the sludge line automatically. The dried sludge in the lagoons is removed and hauled to the adjacent sanitary landfill for disposal.

EFFLUENT QUALITY

The plant has operated with a minimum of problems. The effluent quality has met or exceeded all NMEID requirements during start-up and continues to do so. The plant operators have not established formal laboratory procedures as yet, because certain necessary laboratory equipment has not been delivered. However, some tests have been taken by an outside laboratory, and the results are summarized in Table 7.

The plant operators are still experimenting with operational procedures, and the plant has not operated in a steady state condition. Also, the wide variations of influent flows cause operational changes with which the operators are learning to cope.

Table 7. Ranges in Plant Operating Data

Item	Influent	Effluent
BOD_5, mg/L	200-300	15-25
Suspended Solids, mg/L	100-200	9-20
Ammonia-Nitrogen, mg/L	-	<10
Phosphorus, mg/L	-	0.1-1.0
Fecal Coliforms, #/100 mL	-	200
Turbidity, NTU's	-	<1

ACKNOWLEDGEMENTS

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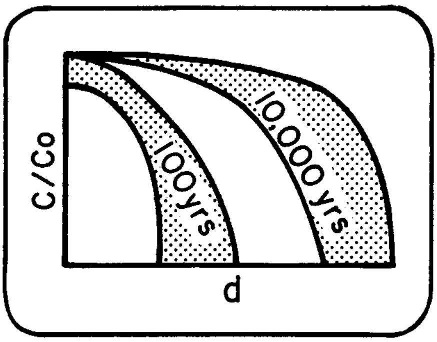
REFERENCES

Culp/Wesner/Culp, Design Report for the Red River AWT Plant, prepared for the Town of Red River, New Mexico, January, 1981.

Culp/Wesner/Culp, Operation and Maintenance Manual, prepared for the Town of Red River, New Mexico, March, 1983.

Reiland, Louis, J., "Low Flow Characteristics for: Red River Below Red River Village, NM, Red River Below Questa, NM, and Rio Honda at Twining, NM," prepared for New Mexico Environmental Improvement Division, no date.

U.S. Environmental Protection Agency, STORET Data Bank.



QUALITY OF URBAN RUNOFF IN ALBUQUERQUE, NEW MEXICO

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ABSTRACT

Data on the quantity and quality of runoff in the Alameda Floodway in Albuquerque, New Mexico, were analyzed to determine if correlations between runoff and water quality could be developed, and to compare the derived characteristics to the characteristics of ten other study areas throughout the United States. This paper presents the results of these analyses. Significant, but not comprehensive, correlations between runoff and several common water quality parameters were observed; and corresponding regression equations were derived. The regression coefficients for the Alameda Floodway were compared to similarly derived coefficients for other study areas. In all cases, the Albuquerque data indicated the highest pollutant generation rates among all of the eleven areas analyzed. Possible explanations for such high rates, and how these rates could be lowered, are also discussed.

INTRODUCTION

The accurate prediction of storm water quality resulting from non-point sources of pollution has recently become a significant area of investigation. In general, storm water quality is a function of the total contaminant accumulation on all paved and unpaved surfaces exposed to rainfall. However, the rainfall intensity and wash-off potential of the contaminants are also important factors. After contaminants have been dislodged from exposed surfaces, overland flow and channel hydraulics determine the contaminant concentrations in the flow. Recent studies have indicated that contaminant accumulation rates are affected by several factors including land use, population density, impervious area, traffic intensity, surface condition, total overland flow length, time since last rain, street sweeping frequency, climate and season.

A water quality prediction strategy, as normally formulated, requires the compilation of a data base, calibration of a predictive model, simulation of existing and future conditions, analysis of these predictions, and use of the results in planning decisions (Young and Terney, 1976). Consequently, the data base provides a foundation on which both the analysis and subsequent decisions will be carried out. Because of the importance of valid data to the overall strategy, numerous investigators have attempted to compile data which could be used to develop predictive correlations between land use, watershed characteristics, runoff, and water quality. The result of these efforts is a comprehensive data base for areas throughout the United States, including Albuquerque, New Mexico. Unfortunately, the data collection and analysis procedures utilized by each investigator are rarely uniform, consequently different sets of data must be carefully processed to be comparable.

DATA SELECTION AND ANALYSIS

Eleven watersheds from eight different regions of the United States were chosen for analysis, and data for a total of 121 runoff events were compiled. Data for the Alameda Floodway in Albuquerque were provided by D. Tague (unpublished data, 1979); this area was particularly chosen to reflect urban runoff quality from cities in semi-arid climatic regimes in the southwestern United States. Table 1 presents characteristic data for the selected watersheds. The analysis of the data base was specifically directed towards the development of a predictive model which, with given parameters of runoff quantity and watershed characteristics, would predict storm water quality.

To compare the quantity-quality relationships between different watersheds, and hence different surface and land use characteristics being studied, it was necessary to reduce the data to a common format. Because each watershed is different in terms of the drainage area, ground slope, soil type, and vegetation, different runoff volume and pollutant quantities may be produced even if other factors such as land use and rainfall were equal. For this reason, runoff volumes and pounds of pollutants were converted to inches of runoff and unit pollutant loading rate (average pounds of pollutant per acre) generated during each storm event.

A previous study (Diniz and Espey, 1979) had identified significant empirical relationships between pollutant loads and runoff volumes. The two quantity-quality statistical models which showed reasonable linear association were found to be logarithmic transforms of:

1. Total runoff volume in inches versus the unit pollutant loading rate in pounds per acre.
2. Cumulative runoff volume in cubic feet versus the cumulative pollutant load in pounds.

The reliability of these relationships was statistically verified by use of the correlation coefficient and the standard deviation for the data sets.

For all storm events and pollutants examined, a reasonably linear relationship was found to exist. This relationship was found to hold true in both the total and cumulative runoff-versus-pollutant comparisons. As a result of this analysis, it was decided that the unit pollutant loading rate relationship would be used as a basis for more detailed statistical studies.

WATER QUALITY PREDICTIVE METHOD

The correlation analysis by Diniz and Espey (1979) suggests that the logarithmic transforms of total runoff volume in inches and total pollutant load in pounds per acre yield the highest degree of correlation with correlation coefficients ranging from 0.77 to 1.00 and having a median value of 0.93. Therefore, best fit equations were generated for total suspended solids, biochemical oxygen demand, chemical oxygen demand, Kjeldahl-nitrogen, ammonia nitrogen and total phosphates for each watershed.

This analysis consisted of first transforming the variables, total runoff in inches and the unit pollutant loading rate in pounds per acre, to their logarithmic values, and then performing a linear regression on the variables. The second correlation, between logarithmic transforms of cumulative pounds of pollutant and cumulative runoff in cubic feet, also proved to be successful.

Table 1. Descriptions of watersheds used for analysis.

	Watershed	Area Acre	Percent Impervious	Number of Events
1.	39th and Holdrege Lincoln, NE	79.0	24.0	18
2.	63rd and Holdrege Lincoln, NE	85.0	22.5*	14
3.	78th and A Lincoln, NC	375.0	15.0*	10
4.	Third Fork Durham, NC	1,069.0	29.0	35
5.	Panther Branch Woodlands, TX	16,050.0	1.0*	4
6.	Panther Branch Woodlands, TX	21,007.0	10.0*	5
7.	Hunting Bayou Houston, TX	1,976.0	23.0	4
8.	K.N. Clapp Basin Lubbock, TX	223.0	30.0	11
9.	Selby Street San Francisco, CA	3,400.0	22.0	7
10.	Alameda Floodway Albuquerque, NM	65,920.0	23.0*	4
11.	Spring Creek Rockford, IL	723.0- 3,225.0	18.0*- 36.0	6

* Estimate based on land-use.

Both correlation equations are in the form of the power function:

$$L = aQb$$

where: L = pounds of pollutant per acre or
cumulative pounds at time, t
O = total runoff in inches or cumulative runoff
in cubic feet at time, t
a , b = coefficients determined by regression analyses

The results of this analysis of the Alameda Floodway data are presented in figures and tables as follows. Figure 1 shows the unit pollutant loading rate as a function of runoff in the Alameda Floodway; correlations between cumulative runoff and cumulative pollutant loads for individual storms are shown in figure 2. Similar analyses were conducted for the other study areas. Table 2 presents the derived regression coefficients "a" and "b" for the total runoff volume and unit loading rate correlations for the eleven study watersheds. Figure 3 graphically depicts the variations in the regression equations for several of the study watersheds. To evaluate the statistical significance of the regression analysis, a test utilizing the standard deviation of the correlation coefficients was performed. The results of this analysis indicate a generally higher degree of significance, with standard deviations ranging from 0.17 to 1.00 and a median value of 0.85.

The derived unit pollutant loading rates for the Alameda Floodway were extremely high in comparison to the other study areas as shown in Table 2. These results suggest that during a relatively wet summer, heavy pollutant loads may be carried into the Rio Grande in and below Albuquerque. This could have serious consequences to Rio Grande water users in the valley below Albuquerque. However, additional storms should be sampled and similar analyses conducted to verify these results. It is postulated that in this case, the definition of runoff volume in inches may be inaccurate because of the non-uniform rainfall patterns typical for this area. Also, the extensive use of retention ponds in the watershed may have resulted in a reduced measurement of rainfall volume at the sampling point. The Alameda Floodway watershed is the largest area investigated in this study; and, in semi-arid areas runoff per unit area may be reduced as the watershed becomes larger, thereby concentrating non-soluble pollutants. Therefore, higher rainfall volumes would elevate these curves and perhaps reduce the extreme differences encountered in this analysis.

In attempting to relate these regression equations to different surface characteristics found in each watershed, a number of previously identified parameters were examined. As may be expected, one parameter which appeared to produce rational association with runoff quantity and quality was "percent imperviousness" of each watershed. In general, as the percent imperviousness of the watershed increased, the pollutant load generated by a specific runoff event was found to increase. Therefore, using percent imperviousness, a statistical analysis was conducted in an attempt relate this parameter to the quantity-quality equations previously developed. The results of this analysis indicate a strong correlation between variations in the imperviousness of a basin and the previously defined coefficient "a". Coefficient "b", on the other hand, exhibits little correlation, and seems to cluster around a value approaching 1.0. A final set of generalized runoff quantity and quality functions stemming from this analysis is presented in Table 3. Given the percent imperviousness of a basin and the runoff volume in inches, this function can be used to generate the unit pollutant loading rate in pounds per acre for a given runoff event.

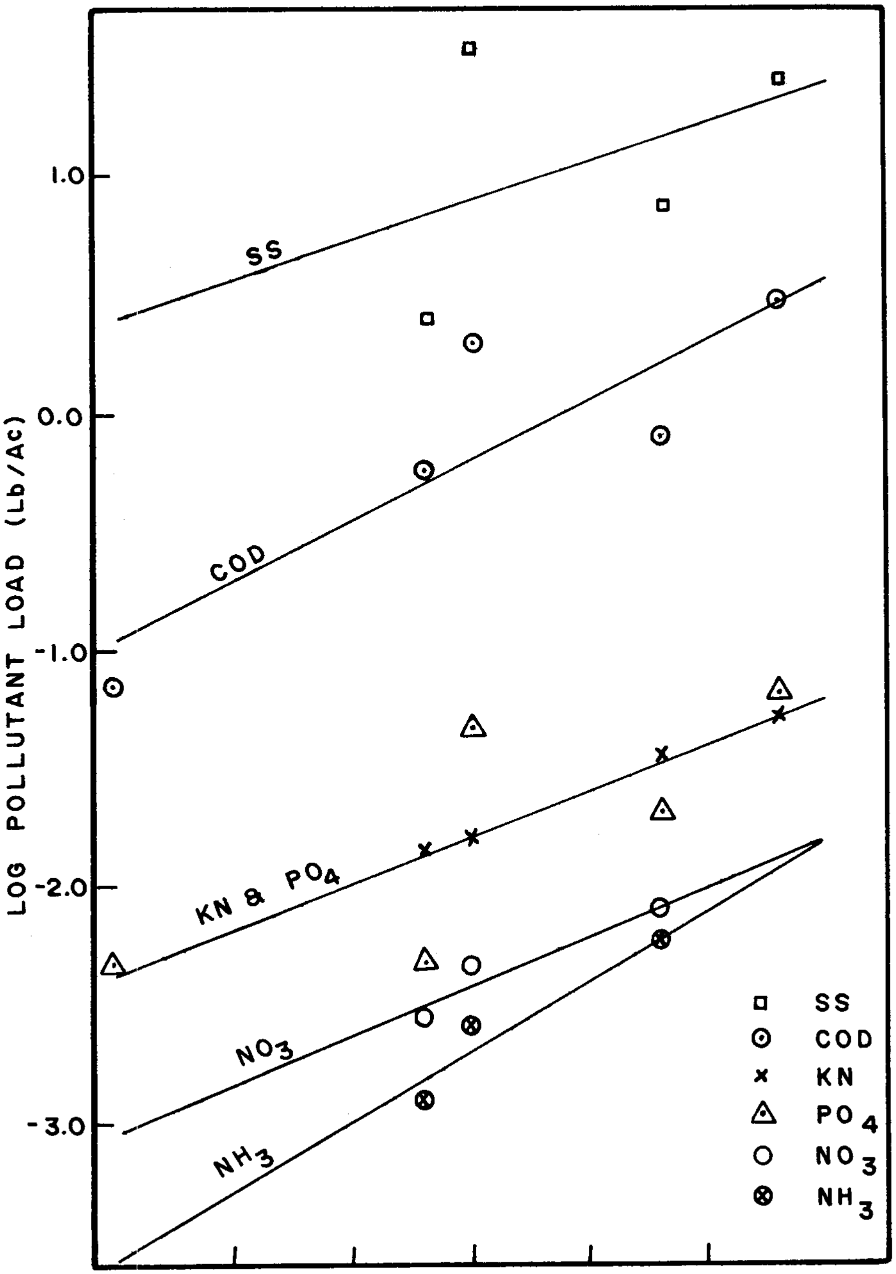

FIGURE I. ALAMEDA FLOODWAY, ALBUQUERQUE, N.M. UNIT POLLUTANT LOADING-RATE CORRELATIONS

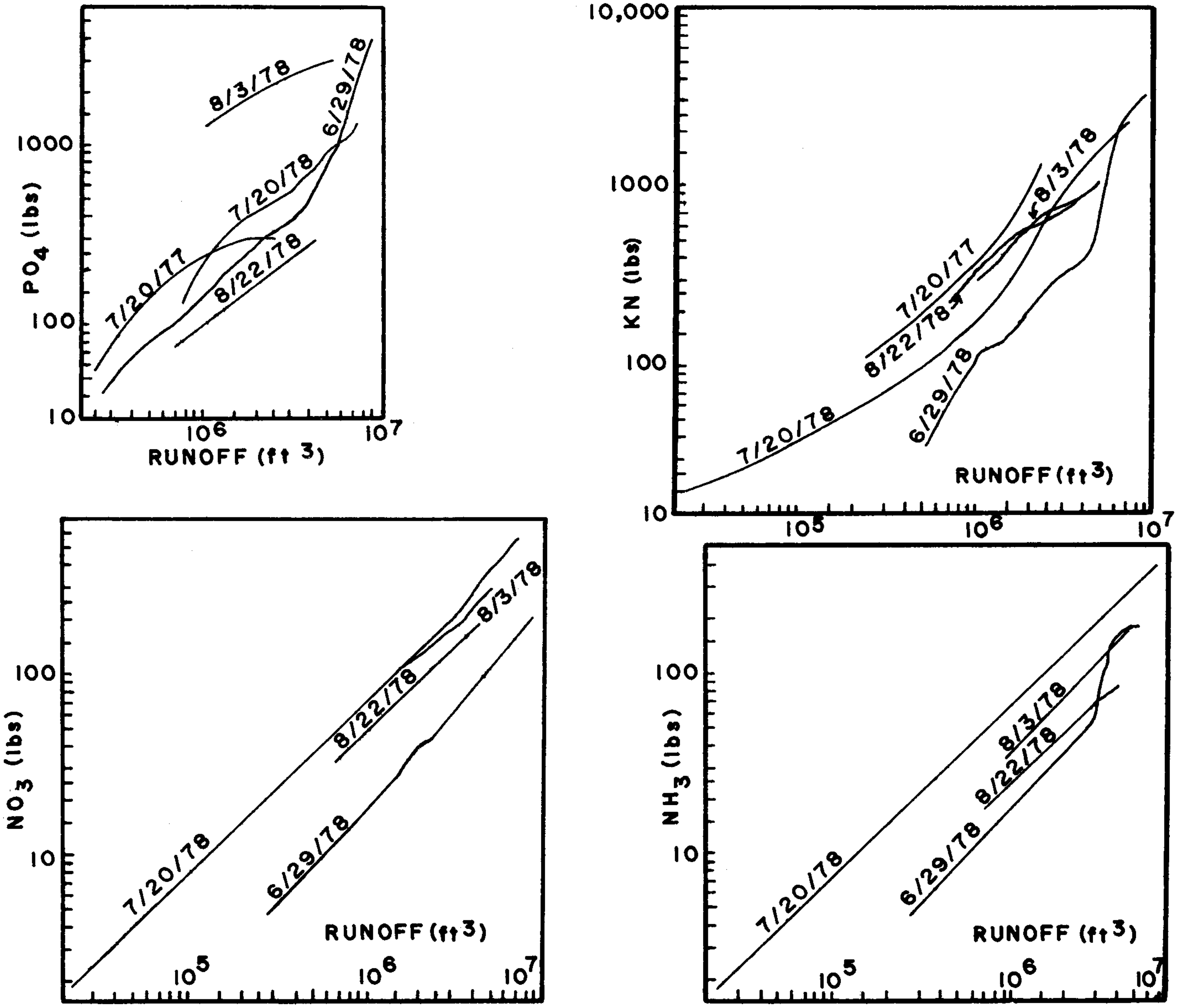

FIGURE 2. ALAMEDA FLOODWAY, ALBUQUERQUE, N.M.
POLLUTANT CHARACTERISTICS OF STUDY STORMS

Table 2. Summary of regression coefficients derived from the quantity/quality analyses, TSS = total suspended solids; B.O.D.(5) = 5-day biochemical oxygen demand, C.O.D. = chemical oxygen demand.

	Watershed	Number of Events	TSS		B.O.D.(5)		C.O.D.	
			a	b	a	b	a	b
1.	39th and Holdrege Lincoln, NE	18	185.88	1.19	3.69	.65	38.81	.84
2.	63rd and Holdrege Lincoln, NE	14	156.26	1.14	2.89	.35	26.24	.64
3.	78th and A Lincoln, NE	10	155.75	.97	1.08	.71	15.46	.95
4.	Third Fork Durham, NC	35	222.66	1.05	13.15	1.18	35.78	.99
5.	Panther Branch Woodlands, TX	4	7.16	.75			18.51	1.14
6.	Panther Branch Woodlands, TX	5	38.94	.77			12.49	.89
7.	Hunting Bayou Houston, TX	4	49.77	1.16			19.85	.87
8.	K.N. Clapp Basin Lubbock, TX	11	763.63	1.54	27.65	1.70		
9.	Selby Street San Francisco, CA	7	51.19	.72	4.77	.31	26.52	.54
10.	Alameda Floodway Albuquerque, NM	4	4,910.2	1.63	741.00	1.73	14,454.00	2.56
11.	Spring Creek Rockford, IL	9	45.7	1.38	2.40	.94	12.6	.94

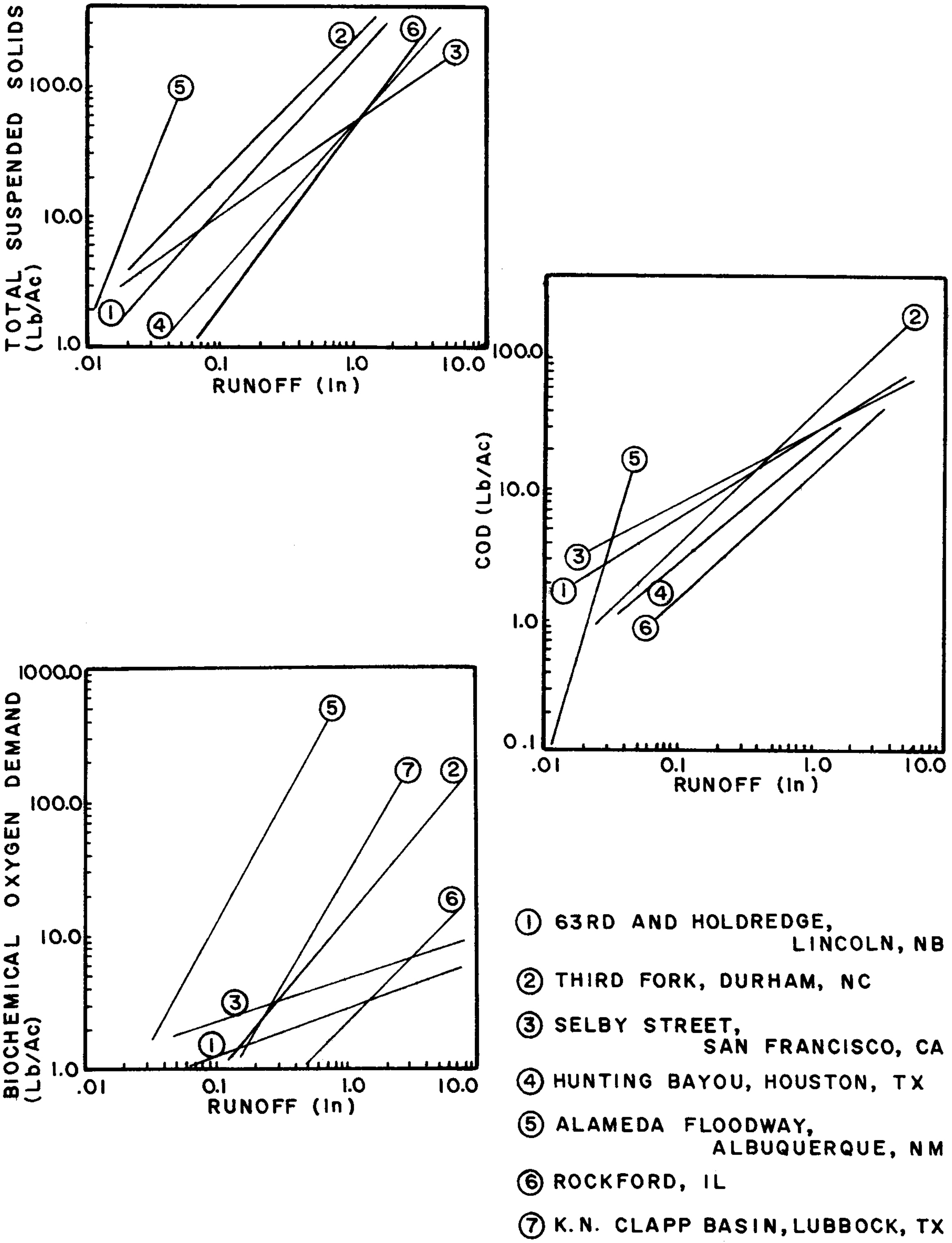

FIGURE 3. COMPARISON OF UNIT POLLUTANT LOADING-RATE CORRELATIONS

Table 3. Summary of unit pollutant loading rate (LB/AC) quantity/quality equations. Q = inches of runoff; I = percent imperviousness of watershed; TSS = total suspended solids; BOD(5) = 5-day biochemical oxygen demand; COD = chemical oxygen demand; KN = Kjeldahl nitrogen; NH_3-N = ammonia nitrogen; T-PO_4 = total phosphates.

$$\text{lbs TSS/acre} = I/(0.1362 + 0.00384(I)\ Q^{1.05}$$

$$\text{lbs BOD(5)/acre} = 7.3971\ (83.0334/I)\ Q^{0.82}$$

$$\text{lbs COD/acre} = 12.71e^{0.0315(I)}\ Q^{0.86}$$

$$\text{lbs KN/acre} = 0.01369e^{0.0888(I)}\ Q^{0.90}$$

$$\text{lbs NH}_3\text{-N/acre} = 0.2437e^{0.0438(I)}\ Q^{0.95}$$

$$\text{lbs T-PO}_4\text{/acre} = 0.09677(I)\ Q^{0.89}$$

At this time, the correlation between watershed parameters and the coefficients of the cumulative runoff-water quality equations has not been sufficiently investigated and defined for acceptable modifications, similar to those made for the unit loading rate relationships.

FUTURE DIRECTIONS

This relatively simple and direct method to predict storm water quality can be very effective in determining total pollutant loads, and in constructing pollutographs for most drainage areas in Albuquerque and throughout the United States. The relationships between runoff and pollutant transport indicate a direct proportionality between pollutant load and urbanization as measured by percent imperviousness of the area.

This storm water quality prediction method has received only limited testing and verification, particularly in the Albuquerque area. Furthermore, only the total load and pollutant relationships have been correlated to impervious area on a multi-regional basis. A similar analysis has to be conducted for the cumulative runoff and pollutant relationships which currently are only available for specific regions.

As more data become available in other geographic areas not previously considered, the correlations developed thus far must be re-evaluated and verified, or revised as necessary. However, major revisions are not anticipated. It must be noted that although statistical models can provide a reasonable degree of accuracy when used to predict pollutant loadings in storm water runoff, no single functional relationship will consistently give the best answer. Therefore, selection of the model most representative of the real system should be based on the judgment of the user.

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REFERENCES

1. Diniz, E. V., and Espey, W. H. Jr., 1979, Maximum utilization of water resources in a planned community -- Application of the storm water management model: Environmental Protection Agency, EPA-600/2-79050c., pp. 63-88.
2. Young, G. K., and Terney, G. F., 1976, Environmental data management: American Society of Cvil Engineers, Journal of the Water Resources Planning and Management Division, v. 102, no. WR2, pp. 255-264.

STATISTICAL ANALYSES AND NUMERICAL MODELING OF SEDIMENT TRANSPORT IN RIO PUERCO, NEW MEXICO

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ABSTRACT

Sediment load in Rio Puerco, New Mexico, is estimated using two approaches; a linear regression analysis, and a deterministic numerical model. Using regression procedures, sediment load, a dependent variable, is related to water discharge, an independent variable. Sediment load is estimated on a daily, monthly, and annual basis. Results of the regression analysis indicate high correlation coefficients for the daily and monthly relationships, and a relatively lower coefficient for the annual relationship. In the second approach, a numerical model is used to estimate sediment load. The continuity equation for sediment transport is applied to each particle type for routing the sediment. Bed load and suspended load are calculated using the Yalin equation and a modified Einstein equation, respectively. The transport capacity of flow is distributed among the various particle types available for transport. Results of the model application to Rio Puerco indicate that, provided accurate estimates of channel flow are available, sediment load can be predicted with a reasonable accuracy.

INTRODUCTION

The Rio Puerco, an ephemeral stream in Central New Mexico, produces one of the highest suspended sediment concentrations in the United States. It is estimated that only about 16 percent of the flow in Rio Grande is contributed by the Rio Puerco; however, more than half the sediment load in Rio Grande is contributed by the Rio Puerco (Brandvold et al., 1981). These sediments have resulted in severe damages in the Rio Grande Valley, particularly from the mouth of the Rio Puerco to Elephant Butte Reservoir (Corps of Engineers, 1973).

The problem is even more complicated when one considers the quality of the sediments. The bed load and suspended load in both Rio Puerco and San Jose were reported to contain some toxic substances (Brandvold et al., 1981). The Rio Puerco and San Jose were found to have elevated heavy metals of As, Hg, and U in the bed load sediments. The trace metals As, Cd, Co, Hg, Mo, U, V, and Zn showed elevated values in suspended sediments of San Jose. These high values do not appear in the Rio Puerco suspended sediments, probably because of extremely high sediment loads in the Rio Puerco. Most of the detected metals were associated with uranium ores. Therefore, it was suggested that these metals may be related to the mining and milling of the uranium ores in the Grants Mineral Belt (Brandvold et al., 1981).

OBJECTIVES. In our study, we utilize two approaches - statistical and deterministic - to estimate the sediment load in Rio Puerco. In the first approach, the sediment load is estimated as a function of water discharge. A linear regression analysis is utilized to relate sediment load, a dependent variable, to the water discharge, an independent variable. In the second approach, the sediment load is estimated using a mathematical model. The continuity equation for sediment transport is applied to each particle type for routing the sediment. Bed load and suspended load are calculated using the Yalin equation and a modified Einstein equation, respectively. The transport capacity of flow is distributed among the various particle types available for transport.

DESCRIPTION OF STUDY AREA

The Rio Puerco has a drainage area of 7340 square miles. The contributing drainage area above the gaging station at Bernardo (fig.l) is 6200 square miles. The stream originates in the San Pedro Mountains, flows southward for about 170 miles, and enters the Rio Grande near Bernardo. The stream channel is 20 to 50 feet deep and 40 to 1000 feet wide. Chico Arroyo and Rio San Jose are the two major tributaries (fig. 1). Chico Arroyo drains about 1340 square miles and the contributing drainage area from Rio San Jose is about 2670 square miles (Corps of Engineers, 1973).

The study area is characterized by an average annual precipitation of 7 inches in the lower elevations and 17 inches in the mountains. Most of the precipitation (about 50 percent of the annual precipitation) occurs in July, August, and September in the form of intense thundershowers (Corps of Engineers, 1973). The flow in Rio Puerco is mostly rainfall-runoff resulting from thunderstorm activity. Runoff from snow melt is of little significance.

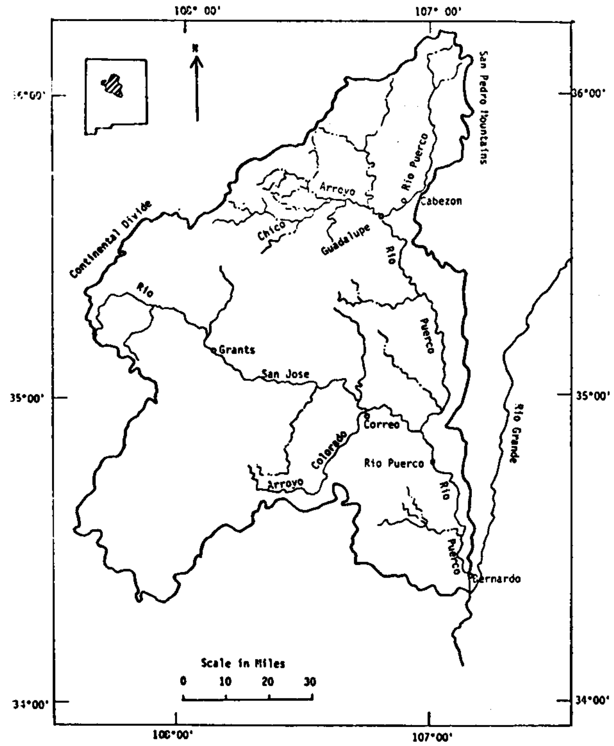

Figure 1. Rio Puerco Drainage Basin, New Mexico (after Corps of Engineers, 1973).

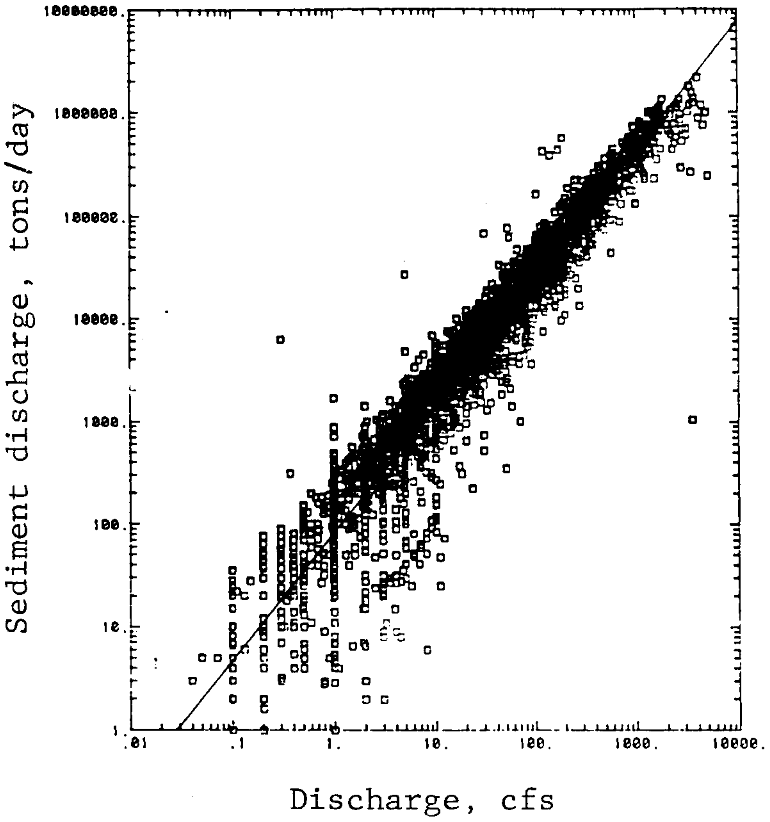

Figure 2. Daily sediment discharge as a function of daily flow.

SEDIMENT COMPOSITION AND SOURCES

The suspended sediment content of samples obtained from the Rio Puerco was frequently found to be in excess of 40 percent by weight (Corps of Engineers, 1973). However, the average sediment concentration for all flows is about 14 percent by weight. According to Nordin (1963), more than 50 percent clay-sized material, on the average, were observed in suspended sediment samples from Rio Puerco at Bernardo. The Corps of Engineers (1973) reported a higher clay content in the range of 43 to 76 percent in stream flows at Bernardo. Obviously, the clay fraction of the suspended sediment has increased in the 10-year period (1963-1973) between the two studies. The statistics provided by the Corps of Engineers (1973) continue to suggest a silt content in the range of 24 to 45 percent, and a variation of 0 to 20 percent in the sand content. The same sequence of distribution of clay, silt and sand contents, in a decreasing order, was reported for many locations in the Rio Puerco. These estimates indicate that clay represents the bulk of the sediment load carried by the Rio Puerco, as previously suggested by Nordin in 1963.

The sources of sediment carried by the Rio Puerco were investigated by Nordin (1963) and the Corps of Engineers (1973). The clays are believed to be derived from the watershed shales, primarily the Chinle Formation (Triassic age), the Mancos Shale (Cretaceous age), and the Rio Puerco Formation (Eocene age). The silts are believed to be produced by the numerous deposits of fine wind-blown materials.

STATISTICAL APPROACH

Linear regression analysis relating sediment load to the flow in a stream, is a common practice in the study of sediment discharge. The procedure is often used to investigate the long-term variability of the sediment discharge at a particular gaging station. The regression equation has the form:

$$Y = a\ X^m \qquad (1)$$

where: Y = sediment load or concentration; X = water discharge; a = a constant; and m = slope of regression line.

Many investigators (e.g., Leopold & Maddock, 1953; Flaxman, 1972; Bhowmik et al., 1980) have employed equations similar to (1) in estimating sediment discharge.

Using equation (1), we estimated Rediment 1 ad as a function of streamflow discharge on a daily, monthly, and annual basis. Data for the gaging station near Bernardo (fig. 1) were obtained from Water Resources Data for New Mexico, published by the U.S. Geological Survey. The Bernardo station is the only active station in the Rio Puerco Basin, and has the largest period of operation (1947 - present). Data used in the regression analysis cover a period of 32 years from October 1947 to September 1979. The analysis was performed using the SPSS program (Norman et al., 1975). Results of the regression procedure are indicated in Table 1.

REGRESSION EQUATIONS. The relationship between sediment load, Y, in tons per day and daily water discharge, X, in cubic feet per second at Bernardo, is shown in fig. 2. It is obvious that the sediment load correlates very well with the discharge (correlation coefficient, r = 0.95). However, the data indicate some deviation from the predictive equation (Table 1) at stream flows less than 10 cfs. For flows greater than 10 cfs, the data match the predictive equation, and very little scattering of data is observed. Furthermore, at low flows the majority of data fall below the regression line. Consequently, use of the regression equations at low flows will result in an overestimation of sediment load.

Similar regression analyses were reported by Leopold and Maddock (1953) for some streams in the western United States (in: Leopold and Miller, 1956). For Rio Puerco at Cabezon, they estimated the value of the slope (coefficient m in equation 1) to be 1.58. It was suggested that typical slope values for the western ephemeral streams lie in the range of 1.09 to 1.58, with a median of 1.29. The value of the slope obtained in this study is 1.22. This value compares very well with the median value obtained by Leopold and Maddock (1953). However, it is to some extent lower than that obtained for the Rio Puerco at Cabezon. Two factors could be responsible for this difference. First, Leopold and Maddock (1953) analyzed the data of an upstream station near Cabezon, whereas the present study deals with a downstream station near Bernardo. Obviously, the sediment yield is affected by many factors, other than discharge, between the upstream and downstream stations. Second, their analysis included data for a 30-day period only, whereas this study includes data for a 3250-day period. In general, results of this study are in good agreement with those of Leopold and Maddock (1953) for the western ephemeral streams.

The relationship between monthly sediment load, Y, in tons per month, and monthly water discharge, X, in cubic feet per second, is shown in fig. 3. The regression equation is indicated in Table 1. The correlation coefficient for the relationship is 0.97. The coefficient is higher than that obtained for the daily sediment dis-

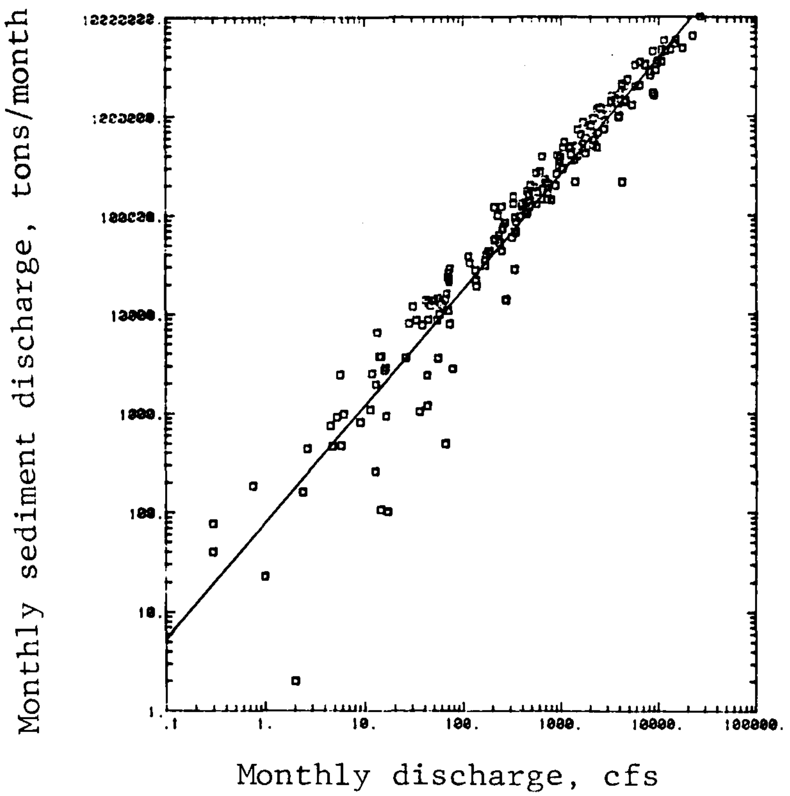

Figure 3. Monthly sediment discharge as a function of monthly flow.

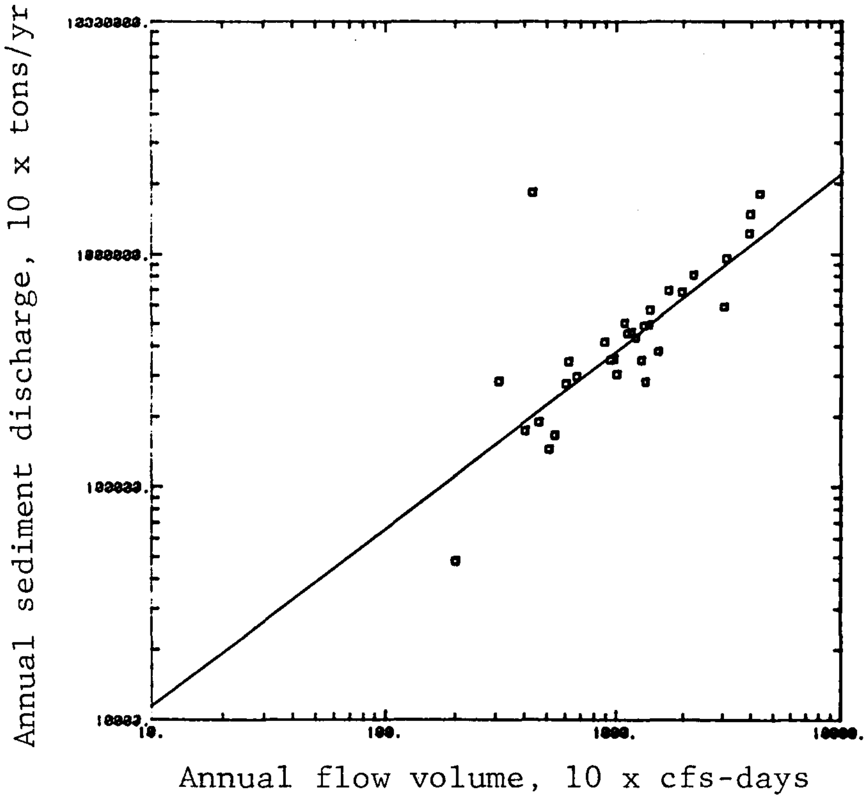

Figure 4. Annual sediment discharge as a function of annual flow volume.

Table 1. Regression Equation Parameters ($Y = aX^m$)

Relationship	a	m	correlation coefficient, r	Standard Error of Regression Coefficient	Standard Error of Estimate
daily sediment load *vs.* daily water discharge	88.24	1.22	0.95	0.007	0.37
monthly sediment load *vs.* monthly water discharge	79.09	1.18	0.97	0.02	0.30
annual sediment load *vs.* annual water discharge	3558.79	0.76	0.76	0.12	0.22

charge. Hence, the relationship is at least as accurate as that obtained with daily data.

Again, scattering of data is observed to occur at low flows (fig. 3). However, the degree of scatter is less than that observed with daily sediment discharge (fig. 2). Scattering of data suggests that the regression equations are not quite representative at low flows for both the daily and monthly sediment discharges.

The relationship between annual sediment load, Y, in tons per year, and annual flow volume, X, in cfs - days, is shown in fig. 4. The correlation coefficient for the annual relationship was 0.76 (Table 1). As expected, this coefficient is lower compared to both daily and monthly coefficients. The low correlation is probably due to vast variations in the hydrologic factors influencing flow throughout the year. It is more likely that these variations occur in shorter periods, e.g., seasonally, rather than annually. The seasonal effect is expected to have a dominating influence since most of the runoff in the Rio Puerco occurs in the summer months (July, August and September), and very little flow occurs in the winter months. Nevertheless, such relationship might be useful in providing some rough estimates of annual sediment yield.

DETERMINISTIC APPROACH

A finite-difference numerical model is used to study the sediment transport in Rio Puerco. The model is essentially similar to that developed by Simons (1977) and Li et al. (1977). Khaleel et al. (1979) employed a modified version of the same model in their study. The model allows overland flow routing as well as sediment routing. However, in this study no water routing is considered due to lack of adequate data. Sediment routing is performed through application of continuity equation for sediment transport. The model accounts for sediment transporting capacity and availability. The bed load and the suspended load transport capacities are calculated, respectively, by the Yalin sediment transport equation (Foster and Meyer, 1972; Neibling and Foster, 1977; Khaleel et al., 1979) and a modified version of Einstein's equation (Li et al., 1977; Simons, 1977; Khaleel et al., 1979). The actual sediment transport rate (i.e. sediment load) is determined by comparing the availability of material with the transport capacity of flow. Runoff is the main controlling factor of sediment detachment in the Rio Puerco Channel, and it is more likely that little is contributed by rainfall. Accordingly, only detachment by runoff is considered in this study, and is estimated using the equation proposed by Meyer and Wischmeier (1969).

CONTINUITY EQUATION FOR SEDIMENT TRANSPORT. Continuity of sediment transport requires (Bennett, 1974):

$$\frac{\partial q_s}{\partial x} + \rho_s \frac{\partial (Cy)}{\partial t} = D \tag{2}$$

where q_s = mass sediment discharge ($ML^{-1}\ T^{-1}$); x = distance (L) alotig a slope length; p_s = mass density of the sediment particles (ML^{-3}); C = sediment concentration in the flow (sediment volume per unit of flow volume); y = flow depth (L); t = time (T); and D = total detachment rate ($ML^{-2}\ T^{-1}$).

To account for the fact that different sediment sizes have different uptake rates of pollutants, the percentages of sediment for each particle type are accounted for in the transport equations. The sediment continuity equation is written for each type:

$$\frac{\partial q_{si}}{\partial x} + \rho_{si} \frac{\partial (C_i y)}{\partial t} = D_i \tag{3}$$

where the subscript i stands for the size fraction.

SEDIMENT TRANSPORT EQUATIONS. The total sediment load can be divided into bed load and suspended load. Bed load sediment moves along the bottom of the channel and is readily deposited when transport capacity decreases to less than the bed load component of the sediment load. The suspended load is more evenly distributed throughout the flow depth and is much less readily deposited. As a consequence, suspended load generally travels considerably further than does bed load before it is deposited when the transporting force is removed (Foster, 1982).

Different transporting capacities are expected for different sediment sizes. The transporting rate for each sediment size is divided into the bed load transport rate and the suspended load transport rate.

We used the Yalin equation to compute the bed load transport capacity. The Yalin equation assumes that sediment motion begins when the lift force of flow exceeds a critical value. Once a particle is lifted from the bed, the drag force of the flow carries the particle downstream until the particle weight forces it out of the flow and back to the bed. The number of particles in motion at a given time is a linear function of S, the dimensionless excess of the tractive force (Foster and Meyer, 1972).

The Yalin equation may be written as:

$$\frac{W_s}{(SG)\rho_w\, dV_*} = 0.635\ \delta\ \{1 - \frac{1}{\sigma}\ \ell n(1 + \sigma)\} \tag{4}$$

where:

$$\sigma = A.\delta \qquad (5a)$$

$$\delta = Y/Y_{cr} - 1 (\text{when } Y<Y_{cr},\ \delta = 0) \qquad (5b)$$

$$A = 2.45(SG)^{-0.4}\ (Y_{cr})^{0.5} \qquad (5c)$$

$$Y = V_*^2/(SG - 1.0)gd \qquad (5d)$$

$$V_* = \sqrt{gyS_\ell} \qquad (5e)$$

where: W_s = the transport capacity of soil particles {mass of sediment/(time • flow width)}; SG = particle specific gravity; p_w = mass density of water; d = particle diameter; V_* = shear velocity;

-cr critical lift force given by the Shield's diagram (Henderson, 1966); g = acceleration of gravity; y = flow depth (assumed to be equal to hydraulic radius); and S_z = slope of the energy gradeline.

The equation requires only two common flow parameters; the depth of flow, y and the slope of the energy gradeline S. Particle specific gravity, particle diameter and the critical lift force (the ordinate from the Shield's diagram) define the transportability of soil particles (Neibling and Foster, 1977). In the derivation of the equation, the constant 0.635 is the only empirically derived factor other than the Shield's diagram. For low particle Reynold number NR, the extended form of the Shield's diagram is used to determine Y (Mantz, 1977; Partheniades, 1978; in: Khaleel et al., 1979).

The sediment is a mixture of particles having various sizes and densities. The Yalin sediment transport equation is modified to accomodate mixtures. Since the sediment is a mixture of different particle types, flow is assumed to distribute its total transport capacity among the different particle types. Where more capacity is available for a given particle type than there is sediment of that type available for transport, the excess capacity shifts to other particle types. The Yalin equation was accordingly modified by Foster and Meyer (1972) to accomodate this shift in transport capacity. This procedure was used by Davis (1978) and Khaleel et al. (1979).

The basis of the Yalin derivation was that sediment transport capacity is equal to the number of particles in transport over a unit area times the mass and velocity of each particle. To modify the equation, a mixture was assumed to reduce the number, but not the velocity, of particles of a given type in transport. Yalin assumed that the number of particles in transport is proportional to 6. For a mixture, the number of particles of a given type i was assumed to be proportional to Si. Values for di for each particle type in a mixture were calculated and summed to give a total:

$$T = \sum_{i=1}^{n} \delta_i \qquad (6)$$

where n = number of particle types. The number of transported particles of type i in a mixture was given as:

$$(Ne)_i = N_i \frac{\delta_i}{T} \tag{7}$$

where N_i = number of particles transported in sediment of uniform type i for a δ_i.

As derived by Yalin, the left hand side of equation (4) is proportional to the number of particles in transport. Let the left side of equation (4) = P (a nondimensional form for transport capacity). Then

$$(P_e)_i = P_i \frac{\delta_i}{T} \tag{8}$$

where: $(P_e)_i$ = the effective P for particle type i in a mixture; and P_i = the calculated P for uniform material of type i. The transport capacity W_{si} of each particle type in a mixture was then expressed by:

$$W_{si} = (P_e)_i \, (SG) \, \rho_w \, d \, V_* \tag{9}$$

This is the bed load transport capacity assuming that the supply of all particle types is either greater than or less than the transport capacity of the respective particle types. However, if supply of some particle types exceeds the transport capacity of those types, transport capacity shifts from those types where supply is less than capacity. The procedure for estimating the shift is discussed later.

We used the Einstein equation as given by Li et al. (1977)(in: Khaleel et al., 1979) to compute the suspended load transport capacity:

$$q_{ssi} = C_a V_* \, a \, \rho_w (SG) \frac{E^{\omega-1}}{(1-E)^{\omega}} \{(\frac{U}{V_*} + 2.5) J_1 + 2.5 J_2\} \tag{10}$$

where: C_a = sediment concentration at distance, a, above the bed; a = 2 d; E = a/y; $\omega = V_s/(0.4V_*)$; V_s = settling velocity of the sediment given by Stokes Law and Rubey's formula (Simons and Senturk, 1977); U = q/y; and q_{ssi} = suspended load transport rate in mass per unit width. The integrals J_1 and J_2 are given by:

$$J_1 = \int_E^1 (\frac{1-r}{r})^{\omega} \, dr \tag{11}$$

$$J_2 = \int_E^1 \ln r (\frac{1-r}{r})^{\omega} \, dr \tag{12}$$

where: $r = \varepsilon/y$; and ε = the distance above the bed. The integrals, J_1 and J_2, can be evaluated by successive integrations of a power series expansion given by Li (1974).

The reference concentration, C_a, is related to the bed load transport by:

$$W_{si} = 11.6\ C_a\ V_* \ a\ \rho_w\ (SG) \qquad (13)$$

In our study, the availability of sediment for transport is given by (Meyer and Wischmeier, 1969):

$$D_F = S_{DF}\ A_I\ S^{2/3}\ Q^{2/3} \qquad (14)$$

where DF = detachment by runoff; SDF = detachability factor, 0.0005 (Meyer and Wischmeier, 1969); AI = area of segment; S = segment slope; and Q = runoff on segment. Only detachment by runoff is considered.

The actual sediment transport rate (i.e. sediment load) is determined by comparing the availability of material with the transport capacity of flow. Since the sediment is a mixture of particle types, flow is assumed to distribute its total transport capacity among the particle types.
Where more capacity is available for a given particle type than there is sediment of that type available for transport, the excess capacity shifts to other particle types. The scheme developed by Davis (1978) was modified and used to estimate the resultant sediment-transport capacities following a redistribution of transport capacity.

First, the procedure outlined by Foster and Meyer (1972) is used to calculate the bed load transport capacity for each particle type (assuming that the amount available for each particle type exceeds their respective transport capacities). This gives a reference concentration that is used in the modified Einstein equation to compute suspended load transport capacity. The sum of the bed load and suspended load transport capacities is the total transport capacity, T_ci, for each particle type (Khaleel et al., 1979). These values for each particle type are then compared with the sediment available for transport for the respective particle types to determine if excess capacity is available for redistribution.

Where T_ci (transport capacity for particle i) > q_si (sediment available for particle i), excess transport capacity exists and shifts to those particle types where T_ci qsi• For those particle types where T_ci > q_si, the average sediment concentration for T_ci, the average concentration for q_si, and the reference concentration for T_ci for the Einstein equation are computed. The reference concentration "required" for T_ci to equal q_si is then obtained by taking the ratio of the q_si concentration to the available Tci concentration times the $T_{c}i$ reference concentration. Given this "required" reference concentration, the suspended load is computed and subtracted from the total load to obtain the "required" bedload for those particle types where $T_{c}i > qsi$•

Next, those bedloads are used to compute the required Pi's (a non-dimensional term for sediment transport capacity) in the Yalin equation for the types where $T_{c}i > q_{s}i$ (Khaleel et al., 1979). These values are divided by the Pi value for uniform sediment of the same type as sediment i, and subtracted from 1.0 to give a measure of the transport capacity to be distributed among the remaining particle types.

This excess is distributed among the remaining types according to their distribution of di (equations 4 and 8). New bed load and total load potential transport capacities are computed. After this redistribution, there may still be some excess. If so, the procedure is repeated until all of the potential transport capacity is used. The technique is illustrated in Khaleel et al. (1979).

MODEL APPLICATION

A finite-difference numerical model was developed based on the deterministic approach. To apply the model, the Rio Puerco (including its tributaries Chico Arroyo and Rio San Jose) was divided into 20 segments. For each segment, the slope, length, and water discharge were determined. The slopes and lengths were obtained from topographic maps of 1:100000 scale. The water discharge for a segment was obtained by weighting the flow at a gaging station with a ratio based on drainage areas. The model was applied to 14 storm dates. Discharge values were obtained from the Water Resources Data for New Mexico for all storms except those for the year 1961. Data for the year 1961 (including particle diameter, percentage, and discharges) were obtained from Nordin (1963). Four particle types were considered in each simulation.

The model was applied without adjusting the exponents for the runoff and slope in the detachment equation (14). Results obtained are indicated in Table 2. The predicted sediment yields are larger compared to the observed yields by one or two orders of magnitude. It is possible that the flow rates used were overestimated, and therefore do not represent actual flows.

For those storms simulated by the model, flows at the gaging station near Bernardo were used to estimate the sediment yield by the regression equation (Table 1) developed for daily flows. The results obtained are also indicated in Table 2. As expected, the predicted yields by the regression equation are nearly identical to the observed yields.

Table 2. Predicted versus Observed Sediment Yields.

		Predicted Sediment Yield (lb)	
Storm Date	Observed Sediment Yield (lb)	Numerical Model	Regression Equation
4/25/80	0.06×10^{9}	0.57×10^{10}	0.16×10^{9}
7/25/76	0.33×10^{9}	0.11×10^{10}	0.21×10^{9}
8/22/74	0.45×10^{8}	0.16×10^{9}	0.76×10^{8}
9/22/74	0.11×10^{9}	0.44×10^{9}	0.12×10^{9}
10/12/74	0.06×10^{10}	0.33×10^{10}	0.06×10^{10}
7/19/61	0.17×10^{9}	0.42×10^{10}	0.30×10^{9}
8/19/61	0.17×10^{10}	0.12×10^{12}	0.26×10^{10}
9/11/61	0.10×10^{10}	0.37×10^{11}	0.10×10^{10}
8/12/54	0.05×10^{10}	0.35×10^{11}	0.10×10^{10}
8/17/54	0.18×10^{10}	0.15×10^{12}	0.30×10^{10}
9/13/54	0.10×10^{10}	0.16×10^{12}	0.15×10^{10}
9/14/54	0.20×10^{10}	0.87×10^{11}	0.28×10^{10}
5/12/49	0.04×10^{10}	0.38×10^{11}	0.10×10^{10}
7/12/49	0.48×10^{9}	0.13×10^{11}	0.49×10^{9}

However, it should be noted that results based on our study may not be generally applicable to the Rio Puerco, since it is based on only 14 arbitrarily selected storms. In any case, the regression equations and the proposed deterministic model are reasonable procedures in estimating sediment yields in Rio Puerco.

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REFERENCES

Bennett, J. P., 1974, Concepts of mathematical modeling of sediment yield: Water Resources Research, v. 10, nO. 3, pp. 485-492.

Bhowmik, N. G., Bonini, A. P., Bogner, W. C., and Byrne, R. P., 1980, Hydraulics of flow and sediment transport in the Kankakee River in Illinois: Illinois State Water Survey, Report of Investigation 98, 170 p.

Brandvold, D. K., Popp, C. J. and Brandvold, L., 1981, Transport mechanisms in sediment rich streams-heavy metal and nutrient load of the Rio San Jose-Rio Puerco systems: New Mexico Water Resources Research Institute, Technical Completion Report No. 132, 34 p.

Davis, S. S., 1978, Deposition of nonuniform sediment by overland flow on concave slopes: Unpublished M.S. Thesis, Purdue University, West Lafayette, IN.

Flaxman, E. M., 1972, The use of suspended sediment load measurements and equations for evaluation of sediment yield in the west, in Present and Prospective Technology for Predicting Sediment Yields and Sources: Proceedings of the 1972 Sediment Yield Workshop, USDA Sedimentation Lab., Oxford, MS, U.S. Agr. Res. Serv., ARS-S-40, pp. 46-56.

Foster, G. R., 1982, Modeling the erosion process, in: Haan, C.T. (ed.), Hydrologic Modeling of Small Watersheds:ASAE Monograph No. 5, ASAE, St. Joseph, MI, pp. 297382.

Henderson, F. M., 1966, Open Channel Flow: The Mac-Millan Co., New York, 522 p.

Khaleel, R., Foster, G. R., Reddy, K. R., Over cash, M. R., and Westerman, P. W., 1979, A nonpoint source model for land areas receiving animal wastes: III. A conceptual model for sediment and manure transport: Transactions of the ASAE, v. 22, No. 6, pp. 1353-1361.

Mantz, P. A., 1977, Incipient transport of fine grains and flakes of fluids - extended Shields program: ASCE J. of Hyd. Div., v. 103, no. HY6, pp. 601-615.

Meyer, L. D., and Wischmeier, W. H., 1969, Mathematical simulation of the process of soil erosion by water: Transactions of the ASAE, v. 12, no. 6, pp. 754-759.

Neibling, W. H., and Foster, G. R., 1977, Estimating deposition and sediment yield from overland flow processes: in Kao, D. T. (ed.), Proceedings of the 1977 International Symposium on Urban Hydrology, Hydraulics and Sediment Control, UKYBU114, Univ. of Kentucky, Lexington, pp.75-86.

Nordin, C. F., 1963, A preliminary study of sediment transport parameters, Rio Puerco near Bernardo, New Mexico: U.S. Geological Survey Professional Paper 462-C, 21 p.

Norman, H. N., Hull, C. H., Jenkins, J. G., Steinbrenner, K. and Bent, D. H., 1975, Statistical Package for the Social Sciences: McGraw-Hill Book Co., New York, 675 p.

Partheniades, E. F., 1978, Discussion on "Incipient transport of fine grains and flakes by fluids - extended Shields diagram" by P. A. Mantz: ASCE J. of Hyd. Div., v. 104, no. HY6, pp. 929-932.

Simons, R. K., 1977, A modified kinematic approximation for water and sediment routing: Unpublished M.S. Thesis, Colorado State Univ., Fort Collins, CO.

Simons, D. B., and Senturk, F., 1976, Sediment Transport Technology: Water Resources Publications, Fort Collins, CO, 807 p.

U.S. Army Corps of Engineers, 1973, Rio Puerco and Rio Salado, New Mexico, Report on Review Survey for Flood ontrol and Allied Purposes, 44 p.

Leopold, L. B., and Maddock, T., 1953, The hydraulic geometry of stream channels and some physiographic implications: U.S. Geological Survey Professional Paper 252, 21 p.

Leopold, L. B., and Miller, J. P., 1956, Ephemeral streams-hydraulic factors and their relation to the drainage net: U.S. Geological Survey Professional Paper 282-A, pp. 11-13.

Li, R. M., 1974, Mathematical modeling of response from small watersheds: Unpublished Ph.D. dissertation, Dept. of Civil Engineering, Colorado St. Univ., Fort Collins.

Li. R. M., Simons, R. K., and Shiao, L. Y., 1977, Mathematical modeling of on-site soil erosion, in Kao, D. T. (ed.), Proceedings of the 1977 International Symposium on Urban Hydrology, Hydraulics and Sediment Control, UKYBU114. Univ. of Kentucky, Lexington, pp. 87-94.

NITROGEN/PHOSPHORUS TRANSPORT IN THE RIO GRANDE

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ABSTRACT

A computer-based simulation model of nitrogen and phosphorus compounds being transported in the Middle Rio Grande Basin was developed. The model was validated using flow data, input loads, and STORET data for river gauging stations. Additional contributions from non-point sources are included. The model studied resulted in kinetic parameters for the postulated reaction kinetics of the nitrogen and phosphorus compounds and allowed prediction studies on loading at Elephant Butte Reservoir.

INTRODUCTION

In the summer of 1973, several citizen groups raised the question of the effect of rapid development in the Albuquerque area and the subsequent increase in nitrogen and phosphorus compounds entering the middle Rio Grande. The Environmental Improvement Division (EID) of the State of New Mexico completed a preliminary study showing the usefulness of a predictive model for the basin. (EID, 1976) Appropriate paperwork was generated and a joint effort of the Water Quality Office, EID, and the Chemical Engineering Department at New Mexico State University was undertaken to produce a computer based simulation model. Basin characteristics were to be supplied by the EID and computer modelling by the University.

The middle Rio Grande Basin covers the region of the state which has the highest population density, e.g. Albuquerque suburban area. This region continues to show rapid growth in population and light industry while continuing small farm operations (25 to 100 acres) in the river valley. Replacement of small farms by suburban development is not expected to reduce non-point source discharges, since much of this rural development operates on septic tanks or small waste collection facilities which discharge to river drains.

In the middle Rio Grande area, the river has been channeled and no major flooding has occurred for a significant period. Jemez Dam and Cochiti Dam make it highly unlikely that the basin will experience major flooding, although high runoffs from within the basin contribute significant flows periodically. During normal (or low) flow the stream meanders within the retaining dikes with flow depths anywhere from several inches to several feet. Sediment loading e.g. nonorganic particulate, is large in this portion of the river both as a result of the river bed and the basin terrain. Several irrigation diversion dams exist within the basin. Associated with each of these diversion dams is a small ponding area. The retention volumes are small and these ponds are not considered in the model. Figure 1 is a schematic of that portion of the Rio Grande included in the 'middle' basin. The major population center is indicated, point-source discharges tributaries and gaging stations are marked. The basin description is completed in Table 1.

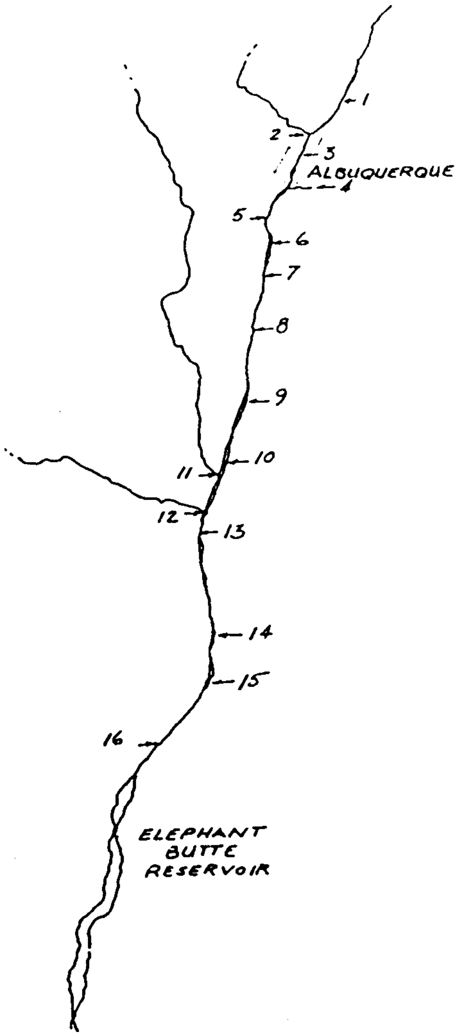


Figure 1. Middle Rio Grande Basin

TABLE 1. BASIN DESCRIPTION CONCENTRATION, mg./ℓ.[b]

SITE	LOCATION	DESCRIPTION	RIVER MILE[a]	CHANNEL DEPTH FT.	FLOW[b] CFS	NITROGEN COMPOUNDS			PHOSPHORUS CMPDS	
						ORG. N.	AMMONIUM	NITRATE	PART.	BAP[c]
1	San Felipe Pueblo	Headwater	1572.7	1.	900.	0.60	0.016	0.08	0.11	0.02
2	Jemez River	Tributary	1566.2	1.	36.[g]	0.60	0.02	0.08	0.11	0.02
3	Bernalillo	WWTP[d]	1555.9	1.	0.5	13.6	11.7	0.12	1.13	8.81
4	Alameda	Floodway	1546.0	1.	7.96	4.11	.55	0.92	5.19	0.15
5	Bridge Blvd	GS[e]	1538.2	1.	-	-	-	-	-	-
6	Albuquerque	WWTP	1533.0	1.	56.4	7.71	22.6	2.0	1.95	7.58
7	Isleta	GS[f]	1527.7	1.	800.	0.90	0.60	0.55	0.60	0.38
8	Los Lunas	WWTP	1516.0	1.	0.34	13.9	11.7	0.12	1.13	8.81
9	Belen	WWTP	1506.1	1.	0.7	13.9	11.7	0.12	1.13	8.81
10	Bernardo	GS[e]	1487.2	1.	-	-	-	-	-	-
11	Rio Puerco	Tributary	1482.0	2.	48.8	8.62	0.6	0.85	10.3	0.06
12	Rio Salado	Tributary	1474.0	2.	15.9	8.62	0.6	0.43	10.3	0.06
13	San Acacia	GS	1472.6	2.	700.	2.2	0.04	0.50	1.4	0.20
14	Socorro	WWTP	1456.0	2.	0.99	13.9	11.7	0.12	1.13	8.81
15	San Antonio	GS	1443.7	2.	-	-	-	-	-	-
16	San Marcial	GS	1425.2	2.	600.	2.5	0.07	0.50	1.1	0.20

a. Measured from Gulf of Mexico
b. Model calibration values - 1978 data
c. Biologically assimilated phosphorus
d. Wastewater Treatment Plant
e. Old Town Bridge - used in model to mark change in velocity flow regime only
f. Gaging station (U.S. Geological Survey)
g. Point-source and tributary data are yearly averages

Nitrogen compounds are classified as organic nitrogen, ammonia and nitrate. Phosphorus is treated as particulate phosphorus (PP) which includes both biological and inorganic phosphorus and biologically available phosphorus (PBA) which includes both dissolved and colloidal. The values shown for each compound in Table 1 are yearly average values for the point sources. For the calibration points (gaging stations), they are an adjust value weighted to the total stream flow. Further detail as to the compound measurement is given with the description of the kinetic model.

Consideration of nitrogen and phosphorus compound transport in this portion of the river requires stream velocities. The values for total flow and compound concentrations shown in Table 1 are 'experience' values provided by the EID. Their familiarity with the several reaches within this stretch of the river resulted in the channel depths shown in the table. Since the river meanders within the retaining dikes, determination of the width of a reach was impossible. Using STORET flow/velocity data, four velocity regimes were calculated for the middle Rio Grande. These expressions are shown in Table 2. The parameter values are least squares values based on a minimum of twenty data sets for each regime.

Table 2. Velocity Regime Equations

Reach Location	Functional Equation
San Felipe to Old Town Bridge	$V_1 = .12\ Q^{.48}$
Old Town Bridge to Bernardo	$V_2 = .13\ Q^{.31}$
Bernardo to San Acacia	$V_3 = .44\ Q^{.29}$
San Acacia to San Marcial	$V_4 = .40\ Q^{.33}$

The river model developed for the simulation is a one-dimensional mass balance. The following assumptions were made:

1. The river system is in steady state flow, i.e. the accumulation term in the general balance is zero;
2. There is only one phase that is considered, the liquid phase. This assumes that
   a. Oxygen transfer is not considered;
   b. Bed-load particles and sediments are fully suspended throughout the river section and their density remains constant over the entire middle Rio Grande, i.e. 11000 ppm;

c. Ammonia loss via volatilization is handled as a simple kinetic loss, i.e. a sink term;

3. The river section is in plug flow, i.e. there are no radial or vertical gradients in concentration, temperature or velocity. The only gradients which occur are the concentrations of the five species identified above, changing along the length of the river. These axial concentration gradients can contribute to solute flow through diffusion. The presence of point and non-point source discharges suggests that axial diffusion be neglected. The variation in the volumetric flow within the river basin is associated with irrigation and/or seepage to ground water;
4. Flow into the river from point-sources are treated as short duration pulses which are instantaneously mixed with the river segment;
5. Non-point sources are introduced in the same manner as point sources but then occur as pulses of finite width;
6. For any given simulation run, water temperature is constant.

The above assumptions may appear to have produced an oversimplified model. The data available for calibrating the model do not warrant a more complex description of the flow in the river. The conservation equation for the i^{th} species for a small (differential) section of the river is

$$\frac{dC_i}{dl} = \sum_{\rho=1}^{r} \nu_{i,\rho}\, k_\rho\, C_i/\bar{v}_k + \left\{ \sum_{j=1}^{p} F_j\, \overset{o}{C}_{i,j}\, \delta(l-j) + \sum_{n=1}^{N} f(l)_n\, T_{i,n} \right\} / \dot{V}_T \qquad (1)$$

Symbolic meanings are:

C_i,	the concentration of the i^{th} species, mg/l
l ,	the length, miles.
$\nu_{i,\rho}$,	the stoichiometric coefficient of the i^{th} species in the ρ^{th} reaction.
k_ρ	the reaction rate constant for the ρ^{th} reaction, $days^{-1}$
$\bar{v}_k$,	the fluid velocity in the k^{th} regime, miles/day
F_j,	jth Point Source, volumetric flow, CFS
C^{o}_{ij},	jth Point Source concentration of i^{th} species, mg/l
$\delta(l-j)$,	Delta function for j^{th} Point Source
$f(l)_n$,	Non-point source function defines reach of river along which non-point source discharge occurs
$T_{i,n}$,	Non-point source pollution, kg/day
and $\dot{V}_T$,	Total volume flow of river, CFS.

The limits on the various indices used are five chemical species, therefore, $i = 1\cdots5$; there are four flow regimes, therefore, k = 1— 4; there are thirteen reactions, therefore, = 1-13 (to be defined later); there are nine point sources, therefore, j = 1•••9; and there are five areas of non-point source discharges, therefore, n = 1•••5 (These are determined by the calibration). The complete model then is five equations with a maximum of twenty-seven terms in each equation.

The kinetics of the reactions of nitrogen compounds in surface streams have been described by Van Kessel (1979). Similar work for phosphorus was not available. There is still much discussion in the literature on kinetic mechanisms for nitrogen and phosphorus compounds in surface rivers. Available data on reaction rate constants is summarized in Table 3 and Table 4. These values are appropriate to provide an initial guess on parameter values and to provide a check on consistency of the model calibration. Because of the lack of agreement about the kinetic mechanisms occurring all reactions were treated as first-order, irreversible.

Table 3. Reaction Rate Constants for Nitrogen Transformation Reactions (Wilson and Babcock, 1979)

Reaction	Rate Equation	Constants	System Studied
Ammonification $ORG\text{-}N \rightarrow NH_4$	$\mu_{ON} = -k_1 C_{ON}$	$k_1 = .111\ hr^{-1}$	1. Urea and casein, chicken manure in cultures
	$\mu_{ON} = -k_1 C_{ON}$	$k_1 = 2.66\ day^{-1}$	2. Empirical fit from Truckee-Carson River
Nitrification Step 1.	$\frac{dNH_4}{dt} = -k_2$	$k_2 = 17.42\ mg/_{liter\ hr}$	3. Same as (1) above; k_2 is a Monod Constant
$NH_4^+ \rightarrow NO_2^=$	$\frac{\Delta NH_4}{\Delta t} = -\alpha C_{NH_4^+}$	$\alpha (\equiv k_2) .325 hr^{-1}$	4. Taken from Clinton River (Michigan)
	$\mu_{NH_4} = -k_2 C_{NH_4^+}$	$k_2 = 1.day^{-1}$	5. Empirical fit from Truckee-Carson River
	$\frac{dc}{dt} = -k_2 MC/(K_s + C)$	$k_2 = 1.7\ day^{-1}; K_s = 3.59 mg/L$	6. C is NH_4^+, M is biological Mass, Laboratory
Step 2. $NO_2^= \rightarrow NO_3^=$	$\frac{dNO}{dt}2 = -k_3$	$k_3 = 25 mg/liter\ hr$	7. Same as (1) above; k_3 is a Monod Constant
	$\frac{\Delta NO}{\Delta t}2 = -\beta C_{NO_2^=}$	$\beta (\equiv k_3) = .35\ hr^{-1}$	8. Taken from Clinton River (Michigan)
	$\mu NO_2 = k_3 C_{NO_2^=}$	$k_3 = 5.0\ day^{-1}$	9. Empirical fit from Truckee-Carson River
Total Nitrification	$\frac{dc}{dt} = -k_3 MC/(K_s + C)$	$k_3 = 4.6\ day^{-1}; K_s = 1.) mg/L$	10. Same as (6)
Unsteady state Mass Balance	$\mu = -k_N N$	$k_N = K_N$ (stream Factors)	11. N local conc. of nitrogenous BOD
	$\mu = -k_N N$	$k_N = 20.5\ hr^{-1}$	12. N as (NH_3-N): sewage effluent in thin film
Dentrification other	$\frac{\Delta NO}{\Delta t}3 = -k_{DN} C_{NO_3^=}$	$k_{DN} = 127\ Liters/m^2 day$	13. Sediment denitrification in drainage channel
	$\frac{\Delta NH}{\Delta t}3 = -k_{NH_3} C$	$k_{NH_3} = .076\ hr^{-1}$ (at 20°C)	14. Loss of gaseous ammonia in laboratory flow system

Table 4. Transformation Rate Constants for Phosphorus

Mechanism	Rate Equation	Value of Transformation Constant	System
1. Adsorption-Desorption	$r_{ads}=k_1PO_4(soln)$	$k_1=.0049$ hr^{-1}	Illinois River, Spoon River
$PO_4(soln)\underset{k_{-1}}{\overset{k_1}{=}}PO_4(ads)$	$r_{des}=k_{-1}PO_4(ads)$	$k_{-1}=.0043$ hr^{-1}	
2. Assimilation	$\Delta PO_4=-k*d*PO_4$	$k=.011$ $mile^{-1}$	South Platte River d is river distance
	$\Delta PO_4=-k*d*PO_4$	$k=.02$ $mile^{-1}$	Pigeon River, North Carolina

Figure 2 is a schematic description of a differential section of the river showing the sources and sinks for each of the nitrogen compounds being considered. The transformations of nitrogen which occur are represented in terms of the four species defined as:

(1) Concentration of organic nitrogen = Kjeldahl Nitrogen - Ammonia
(2) Concentration of Ammonia (NH_4^+ in solution) = NH_3
(3) Concentration of nitrite = 0
(4) Concentration of nitrate = $C_{NO_2} + C_{NO_3}$

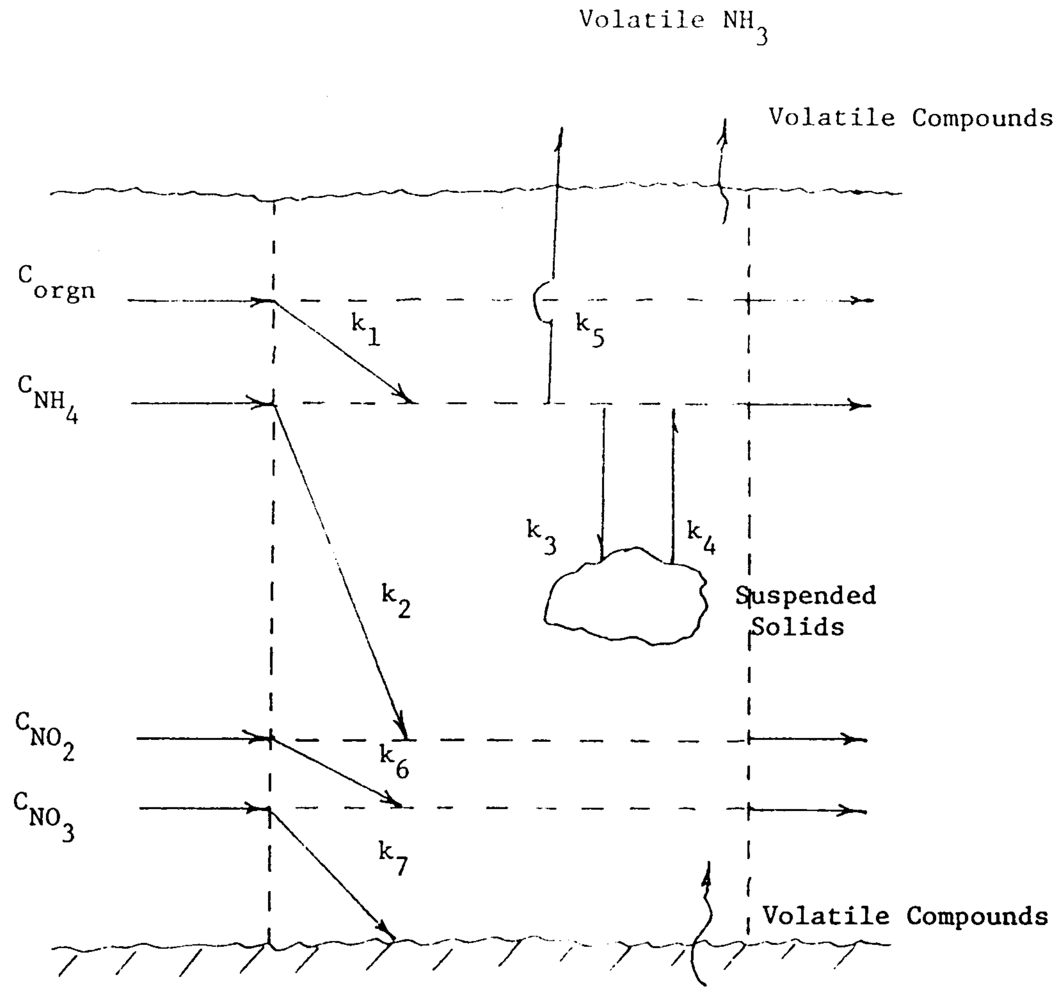
For the mechanisms shown one other compound will be required and this is the concentration of ammonia absorbed on the particulate matter, e.g. suspended solids. The concentration of suspended solids is a constant. The specific reaction (transformation) equations are as follows:

(1) Ammonification

$$R_{orgn} = (dC_{orgn}/dt) = -k_1C_{orgn} \tag{2}$$

(2) Ammonia Oxidation - Step 1 Nitrification

$$R_2 = (dC_{NH_4}/dt) = -k_2\ C_{NH_4} \tag{3}$$



CONSTANT	NAME
k_1	Ammonification
k_2	NH_3 Oxidation - Nitrification Step 1
k_3	NH_4 Adsorption
k_4	NH_4 Desorption
k_5	NH_3 Volatilization
k_6	NO_2 Oxidation - Nitrification Step 2
k_7	Denitrification

Figure 2. Nitrogen Compounds - Kinetic Model

Table 3 indicates that this reaction under laboratory conditions is zero order for ammonium and the reaction constant is better described by a Monod kinetic mechanism. The equation shown will be used and a k_2 empirically determined. This is also the reaction rate equation for production of NO_2,

$$R_2 = (dC_{NO_4}/dt) = k_2\ C_{NH_4} \qquad (4)$$

(3) Adsorption/Desorption of Ammonia
Rate of adsorption is

$$R_{ads} = k_{ads}C_{NH_4}(1-\sigma) \qquad (5)$$

where is the fraction of the available surface for adsorption on the solid particles. $k_{ads}\ (1-\sigma)$ will be calculated as the difference between some maximum concentration, the absorbed concentration multiplied by the concentration of suspended solids and a rate constant,

$$k_{ads}(-\sigma) = k_3\ \rho_{ss}(C_{max} - C_{ss},NH_4) \qquad (6)$$

Rate of desorption is

$$R_{des} = k_{des}\sigma = k_4\ \rho_{ss}C_{ss},\ NH_4 \qquad (7)$$

The overall change of ammonia due to absorption/desorption is

$$dC_{NH}\ /dt = \underset{4}{R}^{ads} - R^{des} \qquad (8)$$

(4) Ammonia Volatilization

$$R_{vol} = (dC_{NH_4}/dt)_{vol} = -k_5C_{NH} \qquad (9)$$

In actual practice the rate of ammonia volatilization would be proportional to the difference of the solution concentration and the partial pressure of ammonia above the river. For all practical purposes the latter is zero. The total rate of change of ammonia due to reaction is

$$dC_{NH_4}/dt = \sum_{\rho=3}^{9} R_\rho \qquad (10)$$

(5) NO_2 Oxidation Step 2: Nitrification

$$dC_{NH_4}/dt = -k_7C_{NO_3} + k_6C_{NO_2} \qquad (11)$$

The limitations of the sampling system and the method of analysis indicate that NO2 - is usually not detected; therefore the equation for $NO_3^=$ would be

$$dC_{NO_3}/dt = k_2C_{NH_4} - k_7C_{NO_3} \qquad (12)$$

PHOSPHORUS TRANSFORMATIONS

The present kinetic model for the phosphorus transformations considers the phosphorus loading of the river in terms of two species: (1) biologically available phosphorus consisting of soluble or colloidal material and equivalent to measured PO_4 (PBA); and (2) particulate phosphorus (PP) consisting of both biological and inorganic particulate material and calculated by subtracting the measured PO_4 concentration from the measured total phosphorus P_{TOTAL}. Figure 3 is a schematic of a river section showing the various phosphorus transformation mechanisms. The specific reaction rate (transformation) equations follow:

(1) Geochemical dissolution

$$dPP/dt = -k_8 PP \tag{13}$$

(2) Biological Assimilation

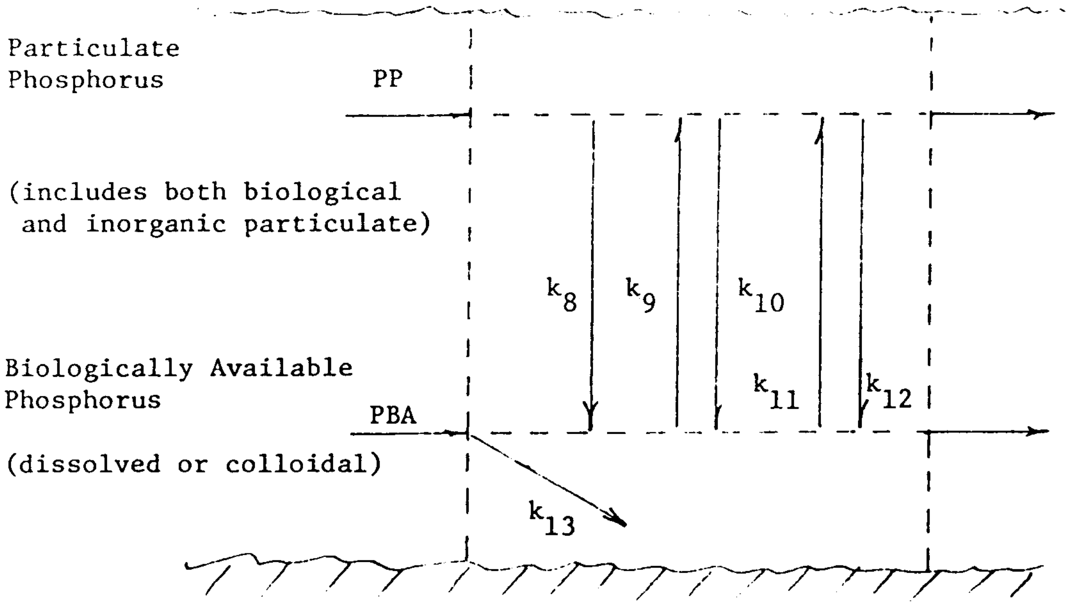
$$dPP/dt = k_9 PBA \tag{14}$$

(3) Mineralization and Biological Release

$$dPP/dt = -k_{10} PP \tag{15}$$

(4) Phosphorus Adsorption/Desorption

$$dPP/dt = k_{11}\ PBA - k_{12}\ PP \tag{16}$$



CONSTANT	NAME
k_8	Geochemical Dissolution
k_9	Biological Assimilation
k_{10}	Mineralization and Biological Release
k_{11}	Phosphorus Adsorption
k_{12}	Phosphorus Desorption
k_{13}	Phosphorus Sink

Figure 3. Phosphorus Compounds - Kinetic Model

Particulate matter for phosphorus adsorption/desorption include biological solids not included in ρss, the concentration of suspended solids.

(5) Phosphorus Sink

$$dPBA/dt = -k_{13}\ PBA \qquad (17)$$

The combined transformation rate equations for PP is

$$dPP/dt = -k_8\ PP + k_9\ PBA - k_{10}\ PP + k_{11}\ PBA - k_{12}\ PP \qquad (18)$$

or

$$dPP/dt = -\ (k_8 + k_{10} - k_{12})\ PP + (k_q + k_{11})\ PBA$$

Should available data not be sufficient to determine the individual reaction rate constants the two parameters of the last equation can be used. The combine transformation rate equation for PBA is

$$dPBA/dt = +k_8PP - l_qPBA + k_{10}PP - k_{11}PBA + k_{12}PP - k_{13}PBA \qquad (19)$$

or

$$dPBA/dt = (k_8 + k_{10} + k_{12})PP - (k_9 + k_{11} + k_{13})\ PBA$$

The combined equation has the additional parameter k_{13} which could be used if warranted. These kinetic expressions for the nitrogen and phosphorus transformations contain thirteen rate constants as model parameters.

EXPERIMENTAL DATA

The computer simulation model is a GEMS program (Babcock, 1977) for solving the set of component equations, Equation 1. GEMS, standing for General Equation Model Solver, is a FORTRAN based computer program for dynamic systems. Its algorithms are based on the system equations being expressed in state-variable form (Sursher, 1976). This type of computer program readily lends itself to solving river simulations such as performed on the middle Rio Grande. Table 5 illustrates the GEMS program statement corresponding to the model equation for organic nitrogen.

In this specific illustration the unknown parameters are K1, RNOFFZ(XO), TRN22, and TRN32. These as well as the other parameters were adjusted by a trial-and-error procedure until the computed component concentrations agreed with the calibration values form Table 1.

RESULTS AND DISCUSSION

The computer model was calibrated and the parameter values are given in Table 6 for the reaction rate constants and the non-point source pollution discharges are in Table 7. Figures 4 and 5 give the river concentration profiles computed. Shown on the figures are the calibration values. One additional adjustment to the model was made in order to obtain reasonable fit to the data.

Table 5. GEMS Program Statement

Define: X2 ≡ state variable for organic nitrogen; point inputs will be a unit pulse, FPJZ, times a volumetric flow, FJZ, times a concentration, CJZX2, etc.

Non-point sources will be a square pulse function, RNOFF1, times a mass flow rate, TRNX6.

$$dC_{orgn}/dt = DX2 \text{ and } L \equiv XO$$

$$V_k = X7$$

$$V_T \text{ Total} = X1$$

```
DX2 = (- K1 * X2/X7)
    + ((FPJZ(XO) * FJZ * CJZX2
    + FPB  (XO) * FB  * CB X2
    + FPAY (XO) * FAY * CAYX2
    + FPAQ (XO) * FAQ * CAQX2
    + FPLL (XO) * FLL * CLLX2
    + FPBN (XO) * FBN * CBNX2
    + FPRP (XO) * FRP * CRPX2
    + FPRS (XO) * FRS * CRSX2
    + FPS  (XO) * FS  * CS X2) * FAC)/X1
    + (RNOFF2 (XO) * TRN2X2 + RNOFF3 (XO) * TRN3X2/X1.
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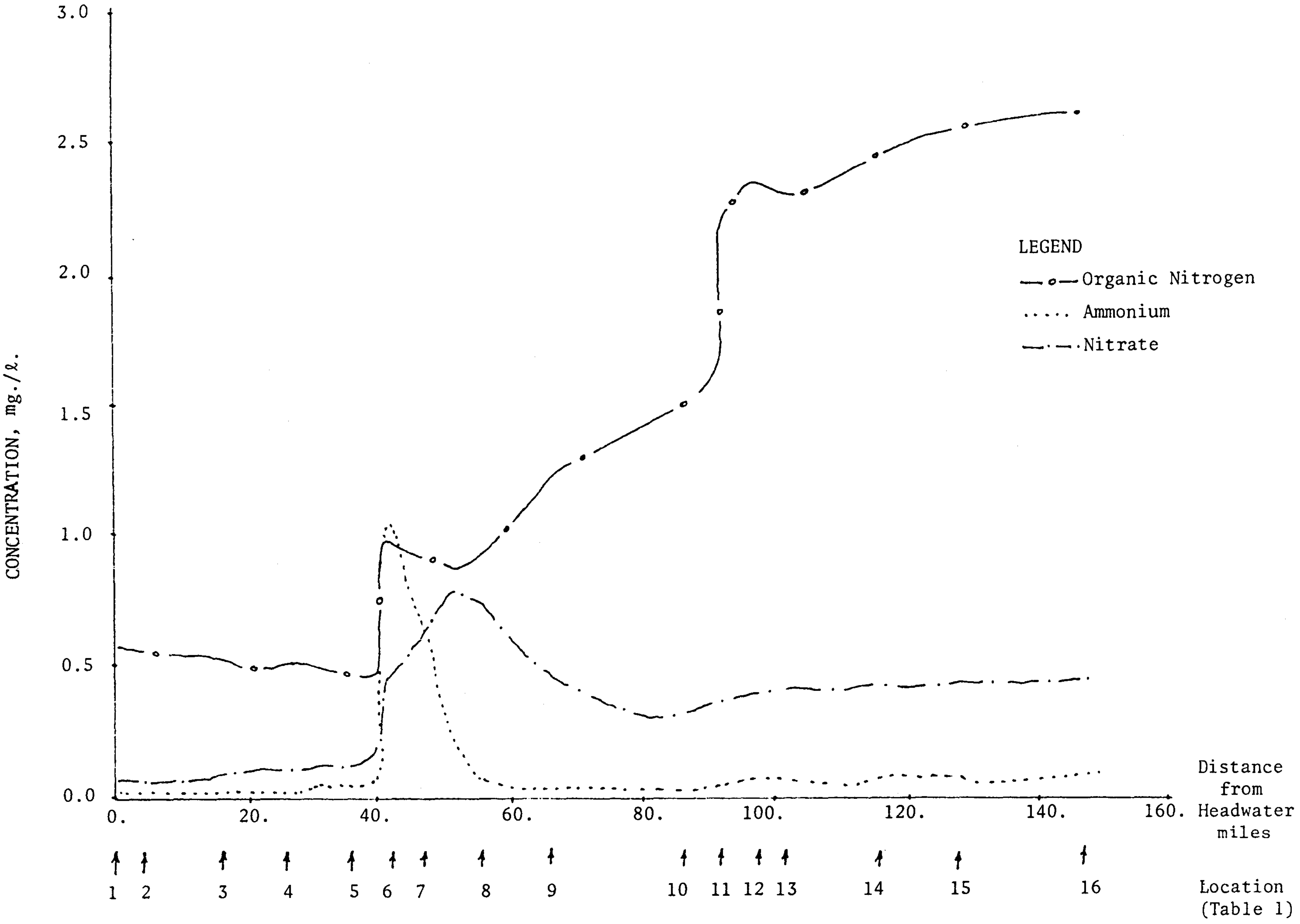

Figure 4. Nitrogen Compounds Concentration Profiles

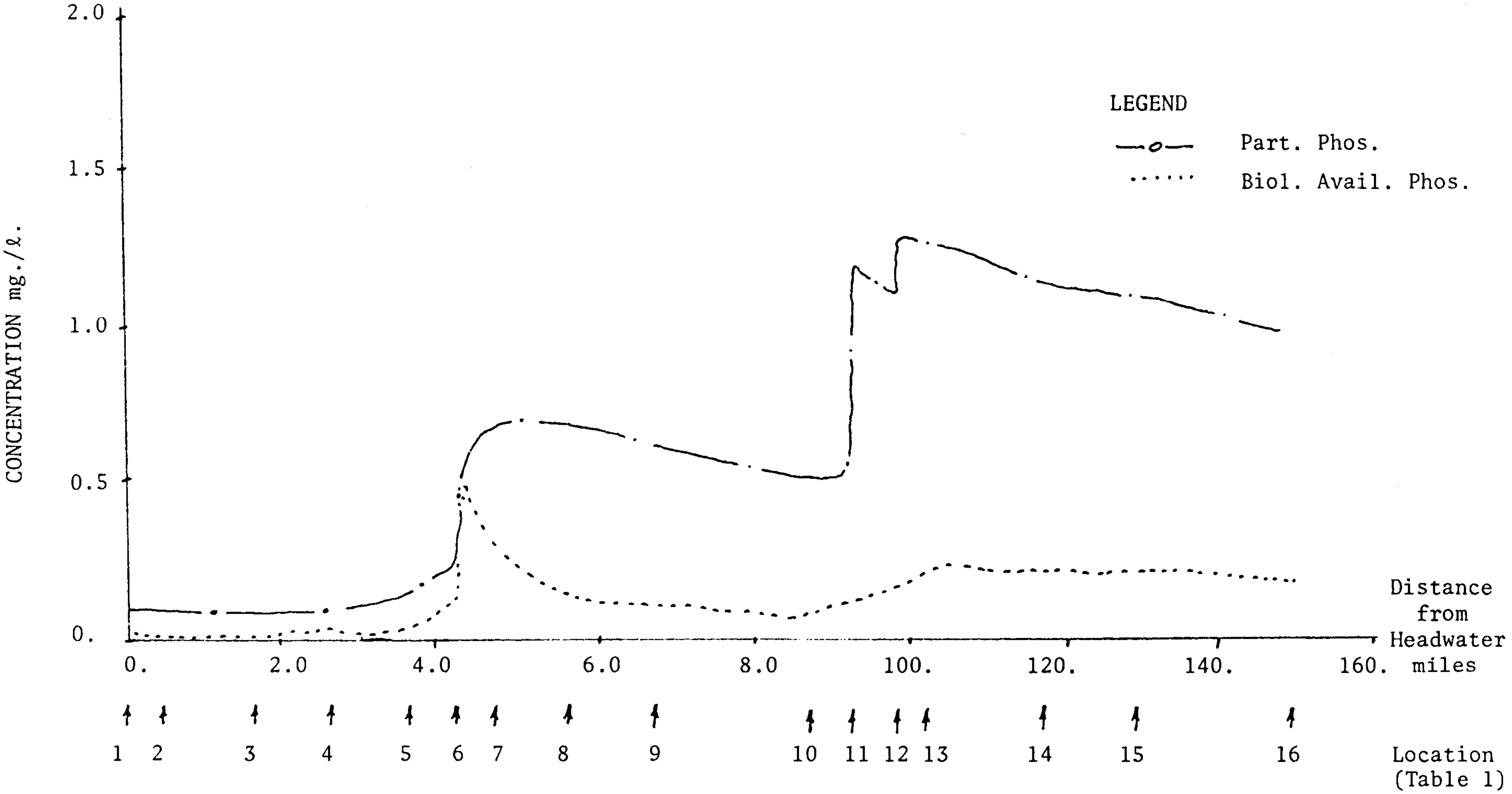

Figure 5. Phosphorus Compounds Concentration Profiles

Table 6. Reaction Rate Constants

K1 = .56 days^{-1}; Ammonification

KK2 = 14.0 ppm^{-1}days^{-1}; Nitrification - Step 1

K3 = 30.0 days^{-1}; NH_4 Adsorption

K4 = 10.0 days^{-1}; NH_4 Desorption

K5 = 3.0 days^{-1}; NH_4 Volitilization

K6 = 8. days^{-1}; Nitrification - Step 2

K7 = 2.5 days^{-1}; Denitrification

K8 = 0.05 days^{-1}; Geochemical Dissolution

K9 = 2.5 days^{-1}; Biological Assimilation

K10 = 0.75 days^{-1}; Mineralization and Biological Release

K11 = 3.50 days^{-1}; Phosphorus adsorption

K12 = 0.75 days^{-1}; Phosphorus Desorption

K13 = 2.0 days^{-1}; Phosphorus Sink

SSP = 11000. ppm^{-1}; Suspended Solids

CX9MAX = .25 days^{-1}; Conc. of adsorbed ammonium on suspended solids

Table 7. Non-point Source Contributions

(1) Ortho-phosphate (PBA); Albuquerque area, Total/year = 0.152 x 10^6kg/yr over river mile

(2) Organic nitrogen; Isleta to San Acacia, Total/year = 0.686 x 10^6kg/yr over river mile

(3) Organic nitrogen; San Acacia to San Marcial, Total/year = 0.55 x 10^6 kg/yr over river mile

(4) Ortho-phosphate (PBA); Socorro area, Total/year = .013 x 10^6kg/yr over river mile

Using the kinetic model for nitrogen compounds as shown in Figure 2 it was not possible to obtain the ammonia calibration concentrations.

It has been suggested (Stratton and McCarthy, 1967) that ammonia nitrification is dependent on available oxygen. It is known that there is oxygen sag in the middle Rio Grande below the Albuquerque waste water treatment pinat discharge into the Rio Grande. a delay function for the first step of nitrification was introduced over the river for a distance of four miles below the effluent point. This brought the nitrogen compound simulation into calibration. All other parameter values were consistent with the available data and non-point source discharge are consistent with the present development of the middle Rio Grande Basin. The simulation satisfactorily described the transport of nitrogen and phosphorus compounds in the middle Rio Grande.

REFERENCES

"Assessment of the Impact of Albuquerque Wastewater on the Trophics Status of Elephant Butte Reservoir", New Mexico Health and Social Services Department, EID Water Quality Division, Santa Fe, New Mexico, Nov. 1976.

Van Kessel, J. F.,"Factors Affecting the Dentrification Rate in Two Water-Sediment Systems", Water Research, Vol.11, pp.259-267, 1977.

Wilson, D. B. and P. D. Babcock, "Nitrogen and Phosphorous Compounds in the Middle Rio Grande", NMSU Engineering Experiment Station, Las Cruces, NM, May 1979.

Babcock, P. D., "General Equation Modelling System", GEMS V2.0, "User Manual", Department of Chemical Engineering, University of Connecticut, May 1977.

Stratton, F. E. and P. L. McCarty, "Prediction of Nitrification Effects on the Dissolved Oxygen Balance of Streams", Environmental Sci. and Tech., Vol. 5, pp.405-410, May 1967.

AN OVERVIEW OF TREATMENT TECHNOLOGY CURRENTLY AVAILABLE FOR WATER POLLUTION CONTROL MANAGEMENT

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ABSTRACT

Water and wastewater treatment technologies constitute a key tool for most water resources management strategies. Because New Mexico is a water-limited state and faces present and future problems related to water pollution, treatment technologies definitely play a major role in meeting any water quality goals. This paper inventories over forty available technologies that are in current use or in research and development at the present time. The thirteen most commonly used unit operations and processes and their potential applications are reviewed briefly. Typical treatment trains for water supply, wastewater discharges and aqueous spills are outlined. The paper finally pinpoints some of the technologies of prime concern for New Mexico.

INTRODUCTION

The purpose of this paper is to describe the most common technical options available for water and wastewater treatment. The technical detail is limited to that needed for defining usefulness and extent of applicability. The reader interested in more specific design details of the technologies reviewed here is encouraged to read beyond this discussion.

Much of the paper describes technologies that reduce the quantity of pollutants from the waste generated, as opposed to those focusing on wastewater reduction. Most of these techniques simultaneously offer the possibility for material or energy recovery. It is important to mention that recovery schemes often permit recycling of the treated effluent or the recovered material or both, thereby diminishing water or material demands or both.

There are several technologies, not discussed in this paper, that with further research might play an important role in future treatment trains. However, it is important to note that the immediate future does not seem to offer significant breakthroughs in treatment technologies; instead, one must expect optimization and refinement of present unit operations and processes (Josephson, 1983).

Water resources in an arid region such as New Mexico are perhaps the most valuable resources the state has due to their scarcity. Kneeze and Brown (1981) in their recently published five-year study on the Southwest emphatically conclude the high priority of water as the most precious resource in the region and the key to immediate and future economic development.

Water is required in large quantities to maintain present living standards. Unfortunately, this marvelous solvent carries organic and inorganic wastes whose concentrations and properties might cause significant degradation of the environment and pose serious health hazards. The management of water resources requires that adequate treatment technologies be applied to attain specific water quality standards for either specific uses or discharge into surface or groundwater reservoirs.

Selection of an appropriate water or wastewater treatment technology depends on the water characteristics, state and federal regulations and cost effectiveness. Table 1 is a list of unit operations (physical treatment) and unit processes (chemical, biological and thermal treatment) that are presently used or are under research and development; starred headings correspond to readily available alternatives. These technologies may be applied to municipal, industrial, hazardous and nonhazardous wastewaters, one-phase (liquid) wastes or two-phase (sludge and water) wastes, water supplies and aqueous spills (Vesilind et al, 1983; Casaveno, 1980; Office of Technology Assessment, 1983; Ghasseni et al, 1980).

CURRENTLY COMMON TECHNOLOGIES

The next sections briefly describe the most common technologies for water and sludge treatment (De Renzo, 1978; Metcalf & Eddy, Inc., 1979; Eckenfelder, 1980). Table 2 lists the operations and processes discussed and identifies applications of each treatment technology to either water supply, wastewater discharges, spills or the resultant sludges. Many technologies or their combinations, that are applicable to the same wastes, compete in the market place.

ADSORPTION

Many organic solutes and a limited number of inorganic solutes can be removed from aqueous streams by adsorption onto activated carbon with a high adsorptive surface area (500-1500 m^4/g). In general, the process works best with chemicals that have a low water solubility, high molecular weight, low polarity, and low degree of ionization. The concentration of adsorbents in the influent should be less than 1%, if recovery is not involved, and up to 50% if recovery is included.

TABLE 1 UNIT OPERATIONS AND PROCESSES IN PRESENT USE OR DEVELOPMENT FOR AQUEOUS STREAMS TREATMENT
(Adapted from De Renzo, 1978, p. 6)

PHASE SEPARATION

- *Centrifugation
- *Coagulation-Flocculation
- Distillation
- Evaporation
- *Filtration
- Flotation
- High Gradient Magnetic Separation
- *Precipitation
- *Sedimentation
- Ultrafiltration

COMPONENT SEPARATION

- Air Stripping
- Ammonia Stripping
- *Carbon Adsorption
- Distillation
- Electrodialysis
- Evaporation
- Freeze Crystallization
- *Ion Exchange
- Liquid Ion Exchange
- *Resin Adsorption
- Solvent Extraction
- Steam Stripping
- Ultrafiltration

CHEMICAL PROCESSES

- Catalysis
- Chorinolysis
- *Disinfection
- Electrolyses
- Microwave
- Neutralization
- Oxidation
- Ozonolysis
- Photolysis
- *Precipitation
- *Reduction

BIOLOGICAL PROCESSES

- *Activated Sludge
- *Aerated Lagoon
- *Anaerobic Digestion
- Composting
- Land Treatment
- Hyacinth Pond
- *Trickling Filter
- *Waste Stabilization Ponds

THERMAL PROCESSES

Calcination:
- *Incineration
- Pyrolysis

---

*Currently common technologies

TABLE 2. CHARACTERIZATION OF CURRENT TECHNOLOGIES

Process	Potential Treatment Applications	Main Treatment of		Component Separation		
		Inorganics	Organics	Physical	Chemical	Biological
1. Adsorption	ws, ww, s_p		●	●	●	
2. Biological Treatment	ww, s_p, s_l		●			●
3. Calcination	ww, s_p, s_l	●	●	●	●	
4. Centrifugation	s_l	●	●	●		
5. Coagulation-Flocculation	ws, ww, s_p, s_l	●	●		●	
6. Chemical Oxidation	ws, ww, s_p, s_l	●	●		●	
7. Chemical Reduction	ws, ww, s_p, s_l	●	●		●	
8. Disinfection	ws, ww,		●		●	
9. Filtration	ws, ww, s_p, s_l	●	●	●		
10.Ion-exchange	ws, ww, s_p	●	●	●	●	
11.Neutralization	ws, ww, s_p, s_l	●	●		●	
12.Precipitation	ws, ww, s_p	●			●	
13.Sedimentation	ws, ww, s_p, s_l	●	●	●		

water supply, ws; wastewater, ww; spill, s_p; sludge, s_l

Suspended solids must be low (< 50 mg/1) and oil and grease less than about 10 mg/i.

Adsorption of organic solutes is commonly followed by thermal regeneration of the carbon and simultaneous destruction of the organics. Thermal regeneration is economical if the carbon usage is above 1,000 lb/day. When there is no regeneration, the spent carbon disposal presents a problem. Regeneration furnaces usually require an afterburner, a scrubber, and perhaps a dust filter.

Recovery may be possible if the adsorbate is easily desorbed from the carbon by treatment with acid, base, steam, or solvent. New methods for combined regeneration and recovery are needed.

There are several variables or alternatives in the design and operation of a carbon treatment unit, all of which can affect the cost-effectiveness: type of carbon (granular or powdered), contact time, flow rate, configuration (series, parallel, or moving bed), number of stages, flow direction (packed or unpacked, upflow or downflow), hydraulic force (pumped or gravity), carbon capacity, and method of regeneration (thermal, chemical, none). It is usually necessary to carry out laboratory tests with several types of carbon before any final decision is made.

Synthetic resins may be used to extract and recover dissolved organic solutes from aqueous streams. Resins with either (or mixed) hydrophobic or hydrophylic natures are available, and can be used to extract, respectively, hydrophobic or hydrophylic solutes. Surface areas of resin adsorbents are generally in the range of 100-700 m^2/g. The operation can be particularly attractive for color and fat removal, and phenols recovery. Great possibilities exist for treatment of munitions facilities wastewaters, and removal of pesticides, carcinogens and chlorinated hydrocarbons. Experience shows that influent concentrations of phenols may be as high as 8%. Suspended solids should not be higher than 50 mg/1 or 10 mg/1 in some cases.

Resins are always chemically regenerated. The weaker attractive forces between the solute molecules and the resin that those present in carbon adsorption allows for easier adsorbent regeneration along with improved recovery of the adsorbed substances. Either caustic or organic solvents are used as regenerants. Both regenerant and solute may be recovered by distillation.

The process variables of resin adsorbents are similar to that of carbon desorption. However, regeneration of the resin is performed in situ. Tests should be run on several resins when evaluating a new application. Important properties are the degree of hydrophilicity and polarity, particle shape (granular versus spherical), size, porosity, and surface area.

BIOLOGICAL TREATMENT

Biological treatment involves the use of microorganisms to convert dissolved and oxidizable organic matter to organic and inorganic end products and to insoluble biomass which can be removed by settling, flotation, and/or filtration. For the treatment of biodegradable organics in an aqueous medium, it is usually the most cost-effective treatment.

The organics amenable to biodegradation may be either dissolved, colloidal or suspended. In aerobic processes (in the presence of oxygen), both simple and complex organics can, in principle, be decomposed to carbon dioxide and water. In anaerobic processes (in the absence of oxygen), mostly simple organics such as carbohydrates, proteins, alcohols and acids can be decomposed. Soluble inorganics should be kept below toxic levels. Trace concentrations of inorganics may be partially removed from the liquid waste stream by adsorption onto or incorporation into the microbial floc.

The most common biological treatment processes are: activated sludge, trickling filters, aerated lagoons, waste stabilization ponds, anaerobic digestion, and composting. Activated sludge, trickling filters and aerated lagoons typically process wastewaters with less than 1% solids. Waste stabilization ponds process wastewaters with less than 0.1% solids. Anaerobic digestion normally operates on sludges with less than 10% solids; and composting operates on sludges of less than 50% solids.

Most processes function best in the mesophilic range (20 to 40°C) except for aerobic digestion and composting that operate within the thermophilic range. Most organisms require a neutral pH, between 6 and 8. Some organisms are more sensitive than others. All the processes, except composting, require equalization due to variation in influent waste characteristics, quality and quantity, often followed by neutralization as pretreatment stages.

Of all the processes, activated sludge leads as the most widely used, and anaerobic digestion as the most sensitive to changes in environmental factors. The latter and composting offer possibilities for recovery of energy (methane) and material (humus). A more advanced version of waste stabilization ponds is the so-called hyacinth pond, whose studied overall performance and expected costs could be more favorable than activated sludge; it also offers the advantage of potential production of methane from the hyacinth crop (aquaculture), or fertilizers. Versions of composting are land application of treated effluents and sludges, and land farming which has been widely used by the petroleum industry in the disposal of oily sludges.

CALCINATION

Calcination may be a continuous process for treating sludge and concentrated waste, which generally operates at high temperature and atmospheric pressure. Volume reduction is of over 90% for liquids and 50-80% for inorganic sludges. The solid residue is generally more suitable for storage or landfilling, although it may still contain toxic metals. The gaseous residue is formed by particulate and gases that require air pollution control system prior to discharge into the atmosphere. Calcination temperatures vary in the 6501400 ^{0}C range.

Several types of calciners are available today to simultaneously concentrate, destroy and detoxify liquids and sludges. Three of the most common kinds are: open hearth, rotary kiln and fluidized bed. Each has advantages and disadvantages that should be identified for each particular application.

CENTRIFUGATION

Centrifugation is one of the unit operations typically used for sludge treatment (liquid-solid separation or sludge dewatering). Centrifugal forces acting on the revolving fluid mass carry the solids to the periphery of the reactor where they are removed. It is particularly suitable for dewatering sticky, gelatinous sludges. In general, it thickens dilute sludges (2 to 5%) to concentrations of 15 to 50%.

Centrifuges are classified in two groups: sedimentation and filtering based on whether the solids cake deposits upon the inner vessel walls or upon a filter medium. Some of the types of centrifuges are: tubular, disc, and conveyor bowl within the sedimentation group, and batch, conical basket and pusher as filtering alternatives.

COAGULATION-FLOCCULATION, PRECIPITATION AND SEDIMENTATION

Coagulation involves the addition of chemicals to promote flocculation of suspended and colloidal particles to enhance settling. Precipitation removes a substance from solution and transforms it into colloidal or suspended sizes. Precipitation and coagulation-flocculation may occur simultaneously. Two categories of coagulants (or precipitants) are recognized, primary coagulants and coagulant aids. The most common primary coagulants are alum, copperas, lime, ferric chloride and ferric sulfate. Coagulant aids are commonly polyelectrolytes (polymeric organics), and may be cationic, nonionic or anionic. Coagulants may act by charge neutralization or inter-particle bridging or both. This train may be applied to either liquid streams or for conditioning of sludge to improve dewatering characteristics.

As the final stage in this train, sedimentation removes and concentrates suspended solids in the liquid stream or sludge by action of gravitational and inertial forces. Sedimentation can be carried out in simple settling ponds, conventional settling basins, or in more advanced clarifiers which are often equipped with built-in flocculation zones and tube-like devices that enhance settling. Settling basins tend to be rectangular and clarifiers are generally circular, although the terms are usually interchangeable.

CHEMICAL OXIDATION & REDUCTION

Oxidation-reduction, or "redox" reactions are those in which the oxidation state of at least one reactant is raised when that of another is lowered. Oxidation is primarily used for detoxification and secondly for metal precipitation.

There are many oxidizing agents; however, only a few are convenient to use. Those most commonly used include: potassium permanganate, chlorine gas, calcium hypochlorite, sodium hypochorite, hydrogen peroxide and chromic acid. Oxidation may also be accomplished by aeration. Most applications are in the oxidation of cyanide effluents, sulfur compounds, phenols, pesticides and other organics.

Chemical reduction is used to reduce metals to their elemental form for recycle or to convert them to less toxic oxidation states. Common reducing agents are: sulfur dioxide, sodium bisulfite, ferrous sulfate and sodium borohydride. Current applications are: reduction of chromium VI to chromium III, mercury, lead, silver, and other metals removal.

DISINFECTION

Disinfection is a unit process that destroys pathogenic organisms. In the water industry, bacteria, virus, and protozoans are the groups of microorganisms of prime concern. Disinfection is mainly accomplished by physical agents (heat and light) and chemical agents (mostly chlorine and its compounds, hydrogen peroxide, and ozone). Other methods include mechanical means (plain sedimentation and filters among others) and radiation (gamma rays).

At present, the most common method of disinfecting waters is by the addition of chlorine. Present problems with this technology are related to the production of carcinogenic chloro-organics. Highly acid or alkaline water can also be used to destroy pathogenic bacteria (above pH = 11 or below pH = 3).

FILTRATION

Filtration is perhaps one of the oldest unit operations for aqueous stream treatment. It is used for liquid-solid separations: removal of suspended solids to purify water or removal of water to concentrate sludges. The operation separates suspended solids from the liquid phase by forcing the fluid to pass through a porous medium, that can be a thick layer of granular material (sand, coke, coal or ceramics) or a thin barrier (cloths or screens).

There are three general kinds of filters: granular media, fixed media and pressure chambers. Granular media filters need to be periodically backwashed (with 1-5% of the filtered water by volume); operational experience suggests influent suspended solids concentrations below 250 mg/1 for effluent solid concentrations less than 10 mg/l. Fixed media include vacuum filters, microstrainers, and disk filters; vacuum filters are the most representative devices with wide use for concentrating sludge up to 10-40% solids by weight. Pressure chambers include leaf filters, horizontal plate filters, tube element filters, and the filter press; the filter press is the most representative device and alternative to vacuum filtration, concentrating sludge up to 15-50% solids by weight.

ION EXCHANGE

Ion exchange is often an effective means of removing metals from waste streams. There are a variety of resins for specific applications. When the resins are saturated, they are currently regenerated with an acid or alkaline medium to remove the ions from the resin bed. In general, mineral acids ae used to regenerate cation resins, and alkalies are used to regenerate anion resins. The regenerant solution is smaller in volume and higher in concentration than the wastewater, but these metal values must then be adequately disposed of or recovered. Ion exchange is particularly applicable for waste streams which, for one reason or another, will not respond to more conventional treatment, or where the metals can be recovered.

Two groups of resins are in use: inorganic crystals (both natural and synthetic) and synthetic organic resins. This last group is the most popular for general use. The process is generally carried out in continuous flow columns or bed operations.

NEUTRALIZATION

Strictly speaking, neutralization is the adjustment of pH to 7. The basic principle behind the process is simply combining an acid with an alkali (NaOH, $Ca(OH)_2$) or an alkali with an acid (HC1, H_2SO_4) to adjust the pH of the product to an acceptable level. Neutralization of aqueous waste streams is necessary among other things to allow effective operation of biological treatment processes, to prevent metal corrosion or material damage, to control chemical reaction rates, and to protect aquatic life.

Neutralization maybe carried out in tanks, in ponds, in absorber columns or in a variety of other types of reaction equipment either in batch or continuous flow operations depending in part upon the volume and rate of flow.

CONCLUSIONS

Because New Mexico is a water-limited state, it must protect its water resources by requiring adequate treatment of wastewaters prior to discharge of effluents into either surface or groundwater streams and reservoirs. Future state industrial growth is dependent upon quantity and quality of water supplies and will require optimal schemes for water recycling and renovation. These challenges can be tackled by applying combinations of the technologies reviewed in this paper. Figures 1 and 2 are general flowcharts for water supply, wastewater, and sludge treatment trains.

Because of liquid hazardous wastes transportation through or within the state, as well as accidents in industrial plants and/or storage facilities, aqueous spills also require treatment trains as part of clean-up operations, either in situ or after collection in treatment facilities, prior to final discharge into surface or ground water bodies, as illustrated in Figure 3.

Some promising technologies that deserve special attention for New Mexico in their search for a better water resources management are a) reverse osmosis and electrodyalisis for reclamation of the large amounts of saline aquifers, b) use of secondary effluents and sludges in reclaiming mine lands and poor agricultural soils, and c) adsorption and oxidation-reduction processes for cleanup of contaminated aquifers.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. Bruce M. Thomson of the Civil & Environmental Engineering Department of the University of New Mexico at Albuquerque and Dr. Fernando Cadena-C of the Civil & Environmental Engineering Department of the New Mexico State University at Las Cruces for their review and comments.

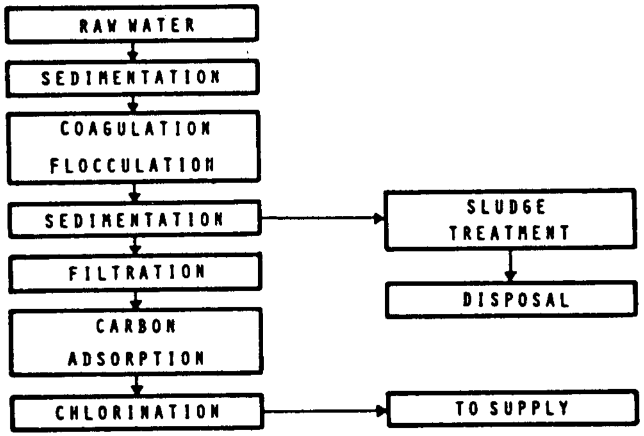


FIGURE 1
A WATER SUPPLY TREATMENT TRAIN

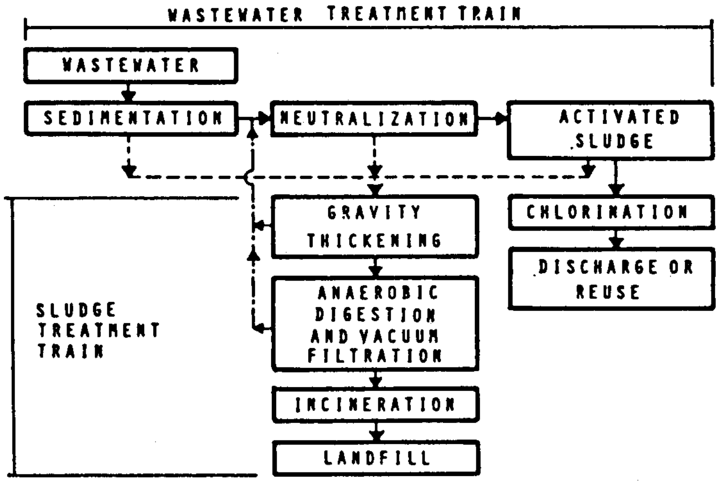


FIGURE 2
A GENERAL WASTEWATER AND SLUDGE TREATMENT TRAIN

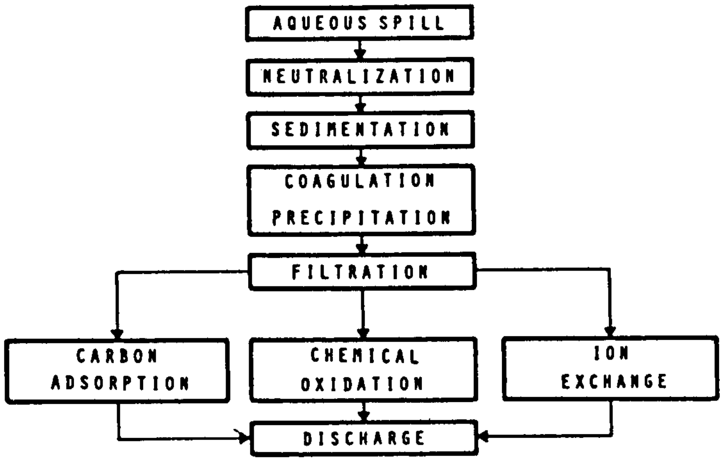


FIGURE 3
AN AQUEOUS SPILL TREATMENT TRAIN

LEGEND

⟶ WATER FLOW
- - - -→ SLUDGE TREATMENT/ DISPOSAL
-·-·-→ RECYCLED WATER FROM SLUDGE TREATMENT

REFERENCES

Cavaseno, V., Industrial Wastewater and Solid Waste Engineering, Chemical Engineering, McGraw-Hill Publications Co, New York, N.Y. (1980).

De Renzo, D.J., Unit Operations for Treatment of Hazardous Industrial Wastes, Noyes Data Corporation, Park Ridge, N.J. (1978).

Eckenfelder, W.W., Principles of Water Quality Management, CBI Publishing Company, Boston, MA (1980).

Ghasseni, M., Ju, K., and Freestone, Frank, J. "Applicability of Commercialized Wastewater Treatment Techniques to the Treatment of Spill-Impacted Waters," Proceedings of the National Conference on Control of Hazardous Material Spills, Louisville, KY (May, 1980).

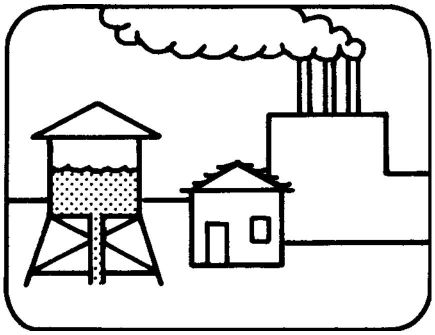
Josephson, J., "Water Research Needs and Trends," Environmental Science and Technology, 17, 2, 69A (1983).

Kneese, Allen V., and Brown, F.L., The Southwest Under Stress, The Johns Hopkins University Press, Baltimore, MD (1981).

Metcalf & Eddy, Inc., Wastewater Engineering: Treatment, Disposal, Reuse, McGraw-Hill Book Company, New York, N.Y. (1979).

Office of Technology Assessment (OTA), "Technologies and Management Strategies for Hazardous Waste Control", Congress of the United States (March, 1983).

Vesilind, P.A., and Pierce, J.J., Environmental Engineering, Butterworth Publishers, Woburn, MA (1982).



DRINKING WATER TREATMENT

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ABSTRACT

The SAFE Drinking Water Act establishes standards for the quality of drinking water. Treatment technology to bring a water supply in compliance with the standards either reduces the total solutes or selectively removes species. Part 1 of this paper describes the operations of reverse osmosis and electro dialysis for total solute reduction and Part 2 describes ion exchange and chemical clarification for selective species removal.

Part 1 of this paper deals with the operational experiences of the author during a project which dealt with the ability of the named processes to remove contaminants from drinking water supplies of small public systems. The towns ranged in size from 300 to 7,000 population. The reverse osmosis and electro dialysis units performed as expected, with the results and design considerations given here.

Part 2 of this paper deals with the fact that many drinking water supplies are good quality except for a single species of contaminant, i.e. arsenic, fluoride, uranium, etc. Rather than reduce the concentration of all solutes, technologies are directed toward removing the specific contaminant. Ion exchange and chemical clarification are appropriate processes for consideration. Ion exchange is a replacement process, frequently replacing anion contaminants with chloride, for example. Regeneration of the exchange resin produces a concentrated contaminant solution for ultimate disposal. Chemical clarification requires chemical addition producing a precipitate with the contaminant either as the precipitate or adsorbing on the precipitate.

Subsequent solid-liquid separation removes the contaminant. A waste slurry is produced for ultimate disposal.

INTRODUCTION - PART 1

In November 1977, New Mexico State University, Chemical Engineering Department, under the auspices of Water Resources Research Institute, began operation of two distinct types of water treating equipment. The objectives of the demonstration unit were:

1) to develop operating conditions and information for an engineering evaluation of the two primary treating methods, i.e. reverse osmosis and electro dialysis, and their associated secondary support processes;
2) to develop specific cost data;
3) to extend available water treatment technology in the area of single solute removal from drinking water containing a large number of ionic and dissolved species;
to provide the necessary material for assimilation of this unit or comparable equipment into the educational activities of water supply and water treating, specifically for engineering and technology students and operator training;
5) to evaluate brine disposal methods in compliance with New Mexico groundwater regulations.

As part of the plan, several New Mexico communities with different contaminant problems were identified as possible sites for location of the water treating equipment. Sites were chosen on the availability of needed resources: i.e. water and electricity; and were evaluated on the amount of exposure the demonstration unit would receive at any given time. Also, the contaminant, or contaminants, which were present were analyzed as to their potential to provide an adequate test of the abilities of each of the types of equipment to remove those specific contaminants.

The types of treatment processes utilized for the demonstration, reverse osmosis and electro dialysis, are by no means new technology. They are however, and have been, undergoing rapid changes in design to widen their respective fields of application. The electro dialysis unit, which was on loan from Ionics, Inc., was one of the first reversal type units to achieve greater than 100% sulfate saturation in the brine stream. This parameter has since been designed into the present units as a feature which enables greater flexibility in operation and maintenance.

Reverse osmosis systems have been commercially available for over twenty years. In that period of time, there has been marked advances of the technology related to membrane material and casting techniques which have enabled reverse osmosis to become widely accepted in many different fields. Not the least of these is the area of water desalination, for both seawater and brackish water. It was with this in mind that the demonstration unit incorporated reverse osmosis into the design as the primary type of equipment to be modeled. The inclusion of electro dialysis came at a later date and proved to be an excellent addition to the overall usefulness of the demonstration.

New Mexico is one of several states that is considered to have critical water problems (1). According to the State of New Mexico Environmental Improvement Division, there are more than 800 communities which are affected by the SAFE Drinking Water Act which sets limits on the amounts of various substances found in water which may adversely affect public health. Of these 800 communities, an extensive list was formulated which could possibly meet the objectives of the demonstration. From this initial list, nine communities were selected as sites for the demonstration unit.

As the project progressed, it became apparent that a need for information dissemination to the general populace should become a focal point of the demonstration unit. Therefore, after the first two or three sites, the physical placement of the unit became a primary concern along with the ability to return the final product back into the community system after being certified as potable. Due to the placement of the unit in many cases, however, return of the final product water to the community was not possible.

In each of the communities visited, a pre-visit by Dr. Gary Kramer, who also performed the bulk of the biological tests on the system, was conducted in order to inform the local community government of the test and its objectives. Also, at that time, the initial site for the location of the demonstration unit was determined. The reason for each visit was to insure that there were no misunderstandings as to the exact nature of the test. During the course of the project, a new design factor involving the reverse osmosis unit was implemented, that being the two-stage system. This system utilized the DuPont membranes as the test unit. The reject (brine) of the first stage was fed to a smaller second stage in order to enhance the recovery of the system. The staged DuPont system achieved approximately 75% recovery versus the 50% of the remaining reverse osmosis units.

The demonstration of the technical and economic feasibility of desalination of brackish water can and will alleviate the predicted shortages we are faced with in this area of the country. Recovery of brackish water via desalting would not only provide additional fresh water otherwise deemed unusable, but would reduce the environmental burden created by decreasing fresh water sources and give greater flexibility in locating water treatment plants.

PROJECT PLANNING - PART 1

To accomplish the objectives of the demonstration project, a 3-phase activity was planned. The phases were as follows:

Phase 1: Preliminary System Cost,
Design and Construction
Phase 2: Demonstration of System Operation
Phase 3: System Performance Analysis

Phase 1: System procurement was performed through the University system of acquiring bids from companies in the area, capable of constructing the system as specified in the Request For Bids (2). The resulting contract went to Saltech, Inc. of El Paso, Texas. They performed the design of the reverse osmosis units, as well as the construction, and the installation of the electro dialysis unit. The initial shakedown of the system consisted of the operation of one bank of the reverse osmosis units for a period of about one week on water drawn from the Ag pond located next to the Ag building on the campus of New Mexico State University. After the preliminary results were considered acceptable, the trailer was returned to El Paso for the inclusion of the Ionics AQUAMITE V unit. The system was then transported directly to the first stop which was the Village of Cuba.

Phase 2: During this time the system was transported from town to town, with the intention of not only demonstrating the ability of the contained equipment, but also to provide as wide a technological base as possible. The contaminants treated varied from Arsenic to Selenium to Fluorides. In each of the sites visited, problems occurred which were both common to the entire run of the project and also unique to each location. In every case, the product water was determined to meet standards. However, not every location permitted the reinjection of the product water back to the distribution system. At various times during the testing period, people were given the opportunity to "sample" the final product. In only two of the locations was the product water returned to the distribution system.

Phase 3: The analysis of the system's ability to remove the contaminants was conducted by means of examining the operating data generated on daily, site-by-site, and an overall basis. The tool used to do this is the water analysis. This is perhaps the most important tool used in the design and operation of water treatment equipment. By inspecting the water analysis produced from the feed source, product of both the reverse osmosis units, and the product of the electro dialysis unit a clear picture of the units ability to handle certain types of water can be developed.

Since both reverse osmosis and electro dialysis are membrane separation techniques, the two can be compared on an equal basis for any given feed source. Even though the driving forces of the two units differ greatly, however, they are both manufactured for much the same use and use a fairly similar material for the desalting aspect. The water analysis in every case was run by the Soil and Water Testing Laboratory located at New Mexico State University. The equipment used was an Atomic Adsorption unit which uses spectrophotometry to do the determinations. These methods are approved by the E.P.A. and are found in the Standard Methods of Analysis Handbook.

TECHNOLOGY - PART 1

Water desalination processes can be divided into four categories, namely: membrane, distillation, crystallization, and chemical process. Presently, plants using distillation provide the most product water. It has been postulated that in the upcoming years, the majority of desalination plants will be either membrane or crystallization technology because these processes are more energy efficient (3). Of the membrane processes, reverse osmosis and electro dialysis represent the most technologically advanced at this time. The crystallization processes which are currently in the developmental stages include: vacuum-freezing, vapor compression secondary refrigerant freezing, and eutectic freezing.

The selection of an optimum water desalination system depends upon many factors as is illustrated in Figure 1. The feed water characteristics, product water requirements, required water recovery ratio, plant utilization, site, performance factor, and brine disposal method all affect the selection of the desalination process.

For example, consider the effect of feed-water salinity upon the product water costs for membrane processes. Figure 2, shows a calculated example. For a given water recovery ratio, the process provides product water at a certain cost. Increasing the water recovery ratio decreases the feed water salinity for which the cross-over in product water cost occurs. As can also be seen, with the increase in the product water recovery ratio, the cost for brine disposal decreases, but the cost for the desalting process increases giving a minimum cost at a given water recovery ratio. This minimum is dependent upon the brine disposal method and the rate at which it takes place; that is, it depends upon the particular site chosen for the plant.

The product water recovery ratio may be dictated by the economics involved, as is seen in Figure 2, or it may be dictated by the relatively small amount of feed water available. The product water recovery, in turn, often dictates the method chosen for scale control, or pretreatment, on the system.

It is often best to remember, that the membrane system chosen for any particular site is only as reliable as the pretreatment that it receives.

SYSTEM DESIGN AND COSTING PARAMETERS - PART 1

The three companies which were contacted for bids are listed below:

1) Saltech, Inc. 11237
   Pellicano El Paso,
   Texas 79926
2) Continental Water Systems Corp.
   12400 Darrington Road
   P.O. Box 20018
   El Paso, Texas 79998
3) El Paso Environmental Systems
   123 N. Concepcion
   P.O. Box 10751
   El Paso, Texas 79978

In accordance with New Mexico State University purchasing policy, the low bidder was selected. Saltech, Inc., began construction on the reverse osmosis units in an 8x40 foot semi-trailer which was supplied by the Chemical Engineering Department of NMSU. The price tag for the reverse osmosis units and the various support equipment was $30,000.00. The equipment provided was in accordance with the specifications submitted.

Under usual circumstances, the design of a reverse osmosis system begins with a careful study of the feed water analysis. When utilizing the feed water analysis for design purposes, the main issue is the tendency for the water to scale when it is concentrated in the reject stream. As the water is forced through the membrane, only water is permitted to flow through, thus leaving the dissolved solids on the reject side. This tendency will occur when the salt which does not pass through the membrane, concentrates on the membrane surface and causes a "scale".

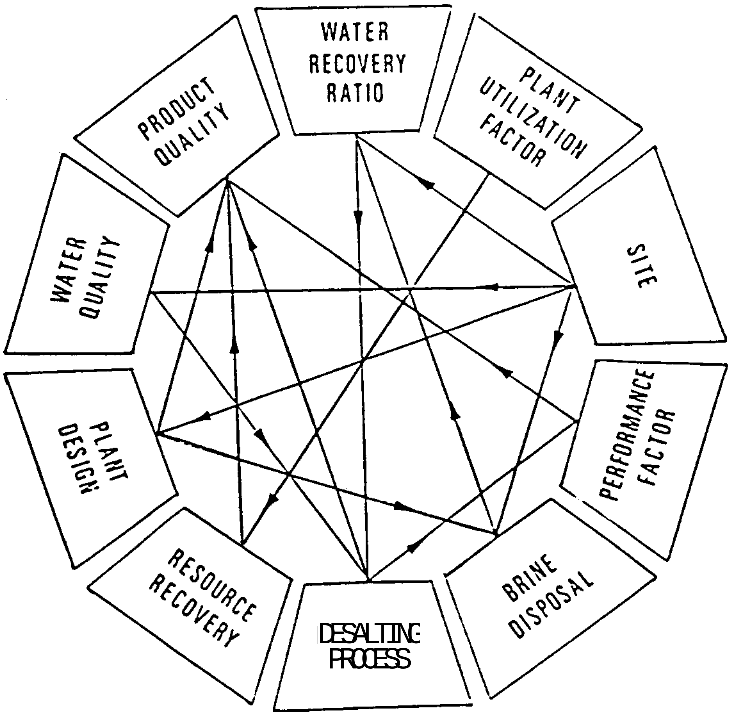
In order to foresee this problem, a tool, known as the Langelier Saturation Index, is used in the determination of a pretreatment scheme. The LSI is used on the reject stream, which will be a calculated value generated from the feed stream analysis.

Numerous other variables are used when determining the best configuration of a reverse osmosis system. Some of these are presented in Figure 3, which shows the interrelationships of the variables.

The electro dialysis unit which arrived from Ionics, was only slightly modified from their standard product. The system was an AQUAMITE V with a single stack that had been modified to process a lower gallonage feed flow, approximately 10,000 gallons per day. The ability of the unit to adjust to such a modification comes from the "modular" design of the entire system. The productivity of the unit depends directly on the number of stages, both hydraulic and electrical, in a given stack. These, along with the number of 'cell-pair', will determine the overall operational capacity of the unit.

The electro dialysis unit also requires pretreatment, which is directly dependent upon the feed water analysis. The membranes used in the desalting process are very susceptible to oxidation and therefore require removal of substances such as iron, manganese and chlorine. Above this consideration, however, the electro dialysis unit is capable of running on a very wide variety of feed waters. Other than the aforementioned criteria, the system requires only pre filtration of the feed water source.

FIGURE 1. FACTORS AFFECTING DESALINATION SYSTEM



SELECTION
(modified from Luft, 1981)

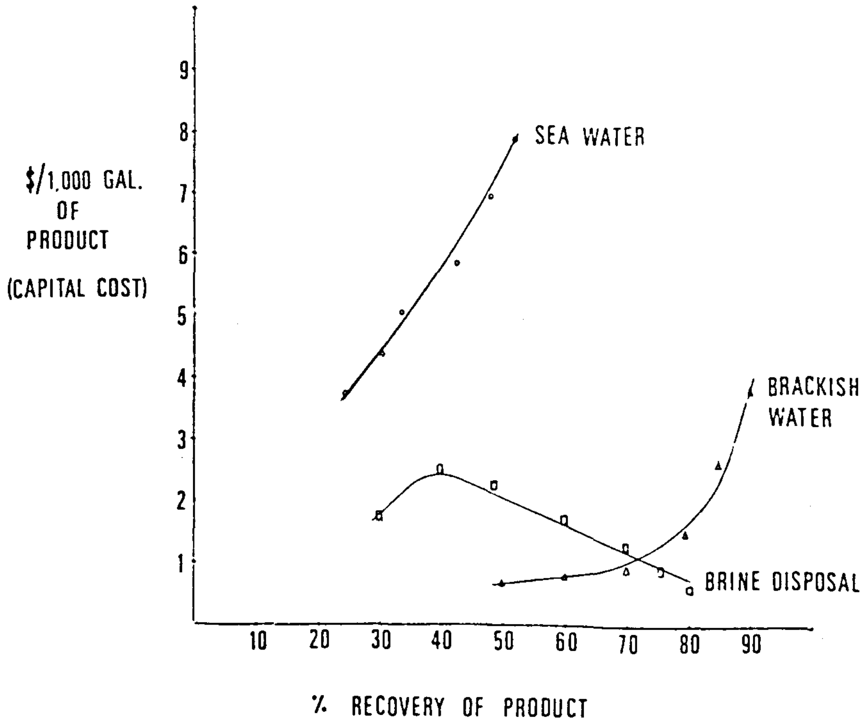


FIGURE 2. CALCULATED COST OF SYSTEM ON 1000 GAL. BASIS

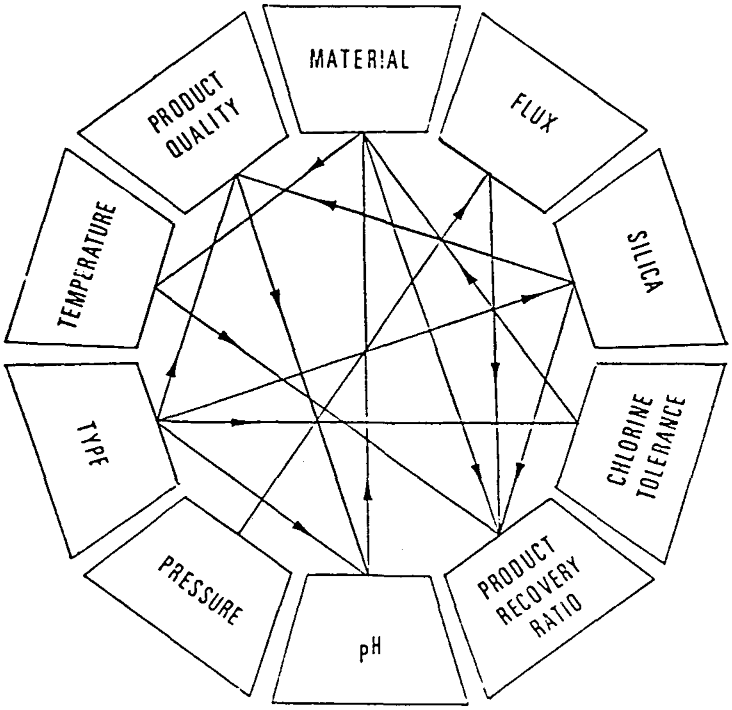


FIGURE 3. FACTORS AFFECTING SYSTEM DESIGN/COST
(modified from Luft, 1981)

SYSTEM OPERATION - PART 1

As previously mentioned, the satisfactory operation of a reverse osmosis or electro dialysis unit depends greatly upon the amount of pretreatment the feed water receives before it enters the unit. In this case, the pretreatment included the following: manganese greensand filters, these units served a dual purpose in that they removed dissolved iron and manganese and served as roughing filters for the removal of sand and sediment; chemical injection, prior to introducing the water to the units, adjustments must be made to the pH and other variables such as chlorination and scaling tendencies through the addition of sodium bisulfite and sodium hexametaphosphate, respectively; pre filtration, the feed water, after a reasonable retention time in an intermediate holding tank, passed through 5 micron pre filters in order to remove any suspended material which may have remained to this point; and, surge tanks, which eliminated any possible surges in the feed water to the high pressure reverse osmosis pumps and the electro dialysis feed pump.

The reverse osmosis units were operated at a feed pressure of 400-450 psi, which is considered the appropriate pressure for maximum operating life. The operating data are given in Table 1. From this table, it can be seen that the feed pressure stayed fairly constant throughout the entire project.

Once the system has been determined for a particular site, pretreatment and all, the operation is fairly straightforward. The reverse osmosis unit will operate fairly well for a long period of time with a minimal amount of supervision. The normal operating parameters can be checked on a once or twice daily routine for consistency. If any abnormal condition appears, then the system can be taken off line for cleaning.

The electro dialysis unit can also be run for long periods of time without any adverse effects. If the parameters indicate that all is as it should be, then the system need only be checked on a daily basis. The electro dialysis unit has been engineered in such a way as to have a periodic cleaning built into the system, about every 15 minutes, which permits extremely long operational runs and service life. This cleaning cycle is known as 'reversal' of the polarity within the stack itself. When the system goes through this operation, the electrical driving force actually becomes an electrical cleaning force. The system goes through an 'off-spec' time of about 45 seconds to 1 minute while the removal of concentrated salts from the unit are flushed to drain.

The comparison between the two types of systems is given in Table 2. This table is comprised of the product water quality from each unit as compared to the initial feed water quality.

TABLE 1. TYPICAL OPERATING PARAMETERS OF RO SYSTEMS

RO PARAMETERS	Cu	Ca	LL	SY	Bl	Mo	Ha	SJ	Al
Feed Conductivity	1020	3500	3300	1350	6000	1360	1100	1340	2200
Product Conductivity	98	390	150	100	300	90	190	70	100
Product Flow	3.0	3.3	3.7	5.0	2.0	1.5	2.0	7.7	6.0
Concentrate Flow	5.0	3.3	1.6	3.3	1.6	1.1	1.4	3.5	4.3
Recycle Flow	3.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Feed Temperature (°F)	56	60	64	78	66	66	73	65	73
ΔP Across Membranes									
HFF	N/A	N/A	10	10	10	15	20	15	15
SW	40	105	35	25	30	N/A	30	30	30
ΔP Across C. Filters	3	2	2	3	2	2	2	6	3
Feed Pressure	32	32	32	32	32	32	32	32	32
Inlet pH	5.6	4.8	5.3	6.9	6.3	6.0	6.8	7.2	6.4
Product pH	5.9	5.4	4.6	N/A	6.2	5.7	6.0	6.8	5.8
ΔP Across GS Filters	4.0	1.0	1.0	3.0	1.0	1.0	7.0	6.0	9.0
ΔP Across Sand Filter	15	3	8	3	4	3	8	7	12
Pump Pressure									
HFF	N/A	N/A	500	500	510	515	515	515	485
SW	420	450	450	410	450	N/A	450	435	440

Cu - Cuba
Ca - Carrizozo
LL - La Luz
SY - San Ysidro
Bl - Bluewater

Mo - Moriarty
Ha - Hagerman
SJ - San Jon
Al - Alamagordo

NOTE: All conductivities are given in micromhos; all flows are given in gpm; all pressures are given in psi. All numbers are averages of total running period data taken.

TABLE 2. RO vs ED ON GIVEN FEED WATERS

SITE	% Recovery		Total Dissolved Solids (ppm)						
	RO	ED	Raw	Reverse Osmosis			Electrodialysis		
				Feed	Prod	Waste	Feed	Prod	Waste
Cuba	40	77	688	688	25	820	688	380	1300
Carrizozo	50	74	2066	2066	130	3000	2066	210	2700
La Luz	70	72	1990	1990	130	4700	1990	520	2690
San Ysidro	60	72	864	864	60	N/A	864	110	1732
Bluewater	56	77	908	908	36	N/A	908	224	1650
Moriarty	58	77	858	858	68	1340	858	228	1796
Hagerman	58	77	1127	1127	48	3312	1127	98	2320
San Jon	75	77	882	812	21	3726	812	76	2452
Alamagordo	58	77	1300	1300	81	3094	1300	74	3668

Both the reverse osmosis and electro dialysis processes are utilized for the reduction of total solutes in a given solution. This characteristic is due to the means of manufacture of the principle desalting barrier which is the membrane itself.

In the case of a reverse osmosis unit, the membrane is cast in one of four physical configurations, these are: plate and frame; tubular; hollow fine fiber; and, spiral wound. The two types tested were: the hollow fine fiber, DuPont and Dow; and the spiral wound, Envirogenics, ROGA Division of U.O.P., Desal Inc., and Osmonics Inc.. The membrane casting technique for the HFF, (hollow fine fiber), is one that has been developed as an off-shoot of the synthetic fabric process. The membrane material is actually extruded and then packaged into a complete unit, pressure vessel and all. The advantage of this type of unit is the area available in a given container. In a housing five inches in diameter, there may be as many as 2.3 million hollow fibers. Because of this large amount of area, this type of unit is able to produce a large volume of product water for a fairly small space requirement. The main disadvantage is one of velocity. At the surface of the fiber, the flow into each is very low. It is because of this low flow that the hollow fiber membrane is considered to have higher scaling tendencies than the spiral wound type.

The spiral wound type of membrane is basically a flat sheet cast on a support backing for structural purposes. The material is then rolled up like a newspaper and sealed in a semi-rigid fiberglass material. This type of membrane takes a separate pressure vessel, which will hold one or more membranes, in order to make the system complete.

It is the physical and electrochemical properties of these membranes which allow them to affect essentially all dissolved solutes. Each membrane or membrane material is classified by its ability to reject solutes. The solution for determining the rate at which membranes will remove solutes varies slightly from manufacturer to manufacturer.

The only manufacturers to market membranes at different rejection levels, i.e. 98%, 97%, 96%, 95% and 90%, are the spiral wound type manufacturers. Because of the relative difficulty in controlling the formation of pores in the extrusion process of the hollow fine fiber, the manufacturers of this type of membrane do not guarantee a rejection rate of greater than 90%. This is to say that at a given solution concentration, the minimum rejection will be 90% of the incoming dissolved salts given as NaCl.

The ability of the electro dialysis unit to effectively remove dissolved solids directly corresponds to the amount of current applied. The membrane material itself is very similar to ion exchange material cast onto a flat sheet. It is through this material that the dissolved ions are pulled by the electrical charge of the poles.

The ability of the electro dialysis unit to handle high concentrations of dissolved solids gives it a distinct advantage in the area of highly brackish waters. Whereas the reverse osmosis membranes are adversely affected by the concentration of salts at the membrane surface at high salinities, the electro dialysis membranes remain relatively constant in their ability to handle these higher concentrations. The primary aspect to watch for, is the development of Calcium Sulfate scale in the brine stream. The formation of scale can, and does, cause problems for the brine pump.

CONCLUSIONS - PART 1

As can be seen by the results of the operation of the two types of equipment, both are very capable of handling the water problems associated with New Mexico. This is apparent as evidenced in Tables 1 and 2. As for a distinct advantage of one over the other, it will suffice to say that each situation must be evaluated on its own merits. The variables presented in Figures 1 and 3, can be used as a guide for evaluating those situations.

INTRODUCTION - PART 2

In June, 1982, the Chemical Engineering Department of New Mexico State University entered into a contract with the United States Environmental Protection Agency to study means of extracting uranium from drinking water supplies. The objectives of this research are:

(1) Process selection and design,
(2) Cost evaluation, and
(3) Process operation experience for removing uranium from drinking water sources.

The two types of extraction processes which are involved are ion exchange and chemical clarification. These processes are designed according to current manufacturing practices in order to test their feasibility for implementation into commercial size plants.

PROJECT PLANNING - PART 2

To accomplish the objectives of the research, the operation of the equipment on-site at the Physical Plant of New Mexico State University began in August, 1983. The ion exchange columns are commercial type units developed specifically for this pilot project. Three of the four units are of the conventional down-flow type, while the fourth is an up-flow unit. The actual design of these units is discussed in the following section.

There are some specific objectives which relate to the ion exchange process. These are:

(1) To demonstrate extended operation (12 months) of four ion exchange units (3-5 gpm capacity each), each utilizing a different resin (with the exception of one down-flow and the up-flow having the same resin). These units are commercially available and include automatic regeneration capabilities.
(2) To assemble the necessary ion exchange equipment and monitoring instrumentation in a self-contained trailer unit.
(3) To prepare a general evaluation of radioactive waste disposal technology which would be appropriate for the ion exchange process.
(4) To prepare the necessary engineering data for process selection, process design and cost evaluation for removing uranium from individual community water supplies.

TECHNOLOGY - PART 2

The ion exchange process has been utilized in the purification of water for centuries (4). The early exchangers were of the inorganic type, usually aluminosilicate products which operated in the sodium cycle. In the mid-30's sulfonated coal exchangers, which could be operated both in the hydrogen and sodium cycle, were developed. These made possible de alkalization and to some extent partial deionization. The development of condensation polymers with sulfonic and amino groups followed shortly and brought about deionization without the ability to remove weak acids. In the mid-40's, sulfonated and aminated copolymers of styrene and divinylbenzene became available. With the quaternization of the amino groups, complete deionization was possible (5).

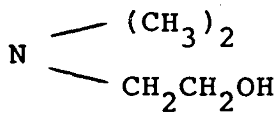
In todays market, many products are available for both general and specific applications. The use of these products adequately, frequently means prior knowledge or evaluation since they can represent a very large capital investment.

The resins utilized in this project have been used in bench tests in E.P.A. laboratories. These resins have shown good promise for the adequate removal of uranium from water. The resins are: 1) Dow SBRP; 2) Dow 21K; and, Ionac A-641. All of these resins are strong base resins which are operating in the chloride form.

As seen in Figure 4, the resin is spherical in shape. The styrene matrix is cross-linked with a certain percentage of divinylbenzene. The amount of cross-linking provides the resin with certain physical properties, i.e. strength, stress resistance, water retention , etc. It is the functional group attached which designates the resin as weak base or strong base. For example, a weak base functional group would be tertiary amine, shown below:

$$R-N-(CH_3)_2$$

a strong base functional group would be quaternary ammonium, shown as:



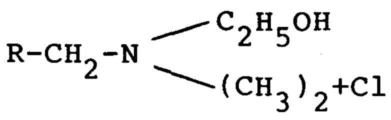
$$N\begin{array}{l}\diagup (CH_3)_2\\ \diagdown CH_2CH_2OH\end{array}$$

The strong base anion exchanger also comes in two types; Type I and Type II. These differ in their relative basic strength and are best described by diagramming their active groups (5):

Type I

$$R-CH_2-N(CH_3)_3{+}Cl^-$$

Type II



$$R-CH_2-N\begin{array}{l}\diagup C_2H_5OH\\ \diagdown (CH_3)_2{+}Cl\end{array}$$

In developing the ion exchange columns for this project, the physical configuration of the down-flow units was copied from commercial units. The up-flow unit was designed according to the engineering data supplied from the resin

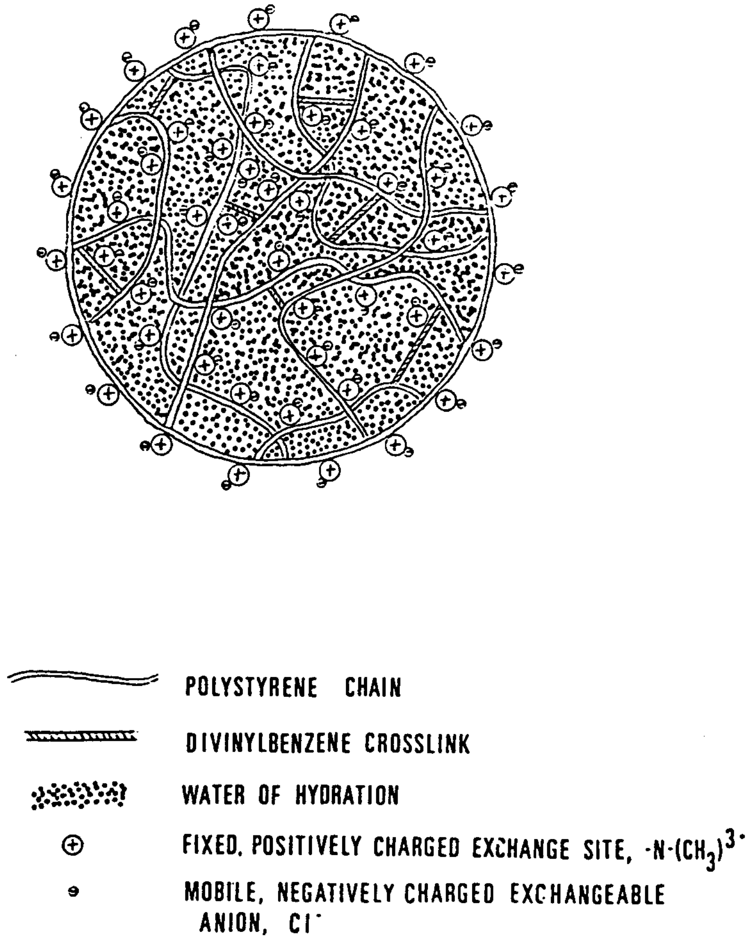


FIGURE 4. RESIN BEAD

manufacturer. Essentially, the fluidized bed is produced by entering the feed water from the bottom of the column and operating in the 'backwash' mode. The amount of bed expansion can be regulated by means of controlling the incoming water rate at a given temperature.

Each manufacturer provides data for their resin which gives expected capacity of anion removal. From this data, then, throughput, or the amount of water that can be processed between regenerations, can be calculated. By using the graphs provided by the resin supplier, the estimated capacity for each of the resins used in the project was on the order of 13 kilograms per cubic foot of resin volume. From this number, the amount of water that can be processed is found to be approximately 5,000 bed volumes, or 10,000 cubic feet (74,810 gallons). At the feed rate of 6 gallons per minute, the expected operating time would be 8.5 days. At this time, regeneration would be required to produce the desired quality effluent.

From the initial E.P.A. bench test results, however, somewhere in the range of 30,000 bed volumes can be expected, which would result in a running time of approximately 2 months.

The postulation as to why this occurs is that the anionic uranium complex has a relatively high valence. This would give preferential removal to that particular ionic species. If this is so, then as the exchanger removes the lower valence ions and becomes 'exhausted' then the reaction is carried out even further with the resin exchanging these removed anions with the higher valence uranium complexed anions. At this time this is merely what is expected to be seen, but has yet to be actually proven.

PRELIMINARY CONCLUSIONS - PART 2

The actual cost of the installation is approximately $1,000 over budget (with budget being $35,000). This relates to a capital cost of approximately $1.11/gal produced. The operational cost of the project has yet to be determined, yet with the regeneration chemical being salt, NaC1, this cost is expected to be quite low on a per gallon basis.

Effluent quality is yet to be determined although the preliminary indications show that the down-flow units will provide a somewhat higher quality, yet lower throughput than the up-flow unit. The reasoning behind this being that the uranium bearing water has a longer contact time with the resin in the down-flow units due to the relative proximity of the resin beads. It is often the bed depth in an ion exchange unit that designates the quality of the effluent. In this case, however, the actual depth of the beds is the same for the down-flow and up-flow units, but the beads in the up-flow unit are separated due to the bed being expanded (fluidized).

CHEMICAL CLARIFICATION - PART 2

The application of chemical clarification to the removal of uranium from drinking water is based upon an extensive literature review (ORNL, 1982) and preliminary testing at Oak Ridge National Laboratory. (Lee and Bondretti, 1983) The objective of the current development is to obtain operational data on a small pilot unit on a continuous basis.

Chemical clarification as an advanced wastewater treatment process has been principally applied for removal of suspended solids. In that application three distinct operations have been identified: (1) coagulation - addition of chemicals resulting in a reduction of the forces tending to keep suspended particles apart; (2) flocculation - agglomeration of suspended material to form particles that will settle by gravity; and (3) sedimentation - the separation of suspended solids from wastewater by gravity.

In applications of chemical clarification for removal of single solutes, e.g., dissolved species, ions, molecules, complexes, a better chemical and physical description would be to consider the three operations as: (1) precipitation (or co-precipitation) and adsorption, (2) coagulation and flocculation, and (3) solid-liquid separation.

PRECIPITATION AND ADSORPTION - PART 2

The addition of iron salts, alum, lime, etc. to water initiates a precipitation of an appropriate species of the salts, e.g. hydroxides, etc. The solute to be removed adsorbs on the precipitate. The chemistry of uranium in aqueous solution results in a uranyl ion complex, the composition a function of pH and ligands present. Table 1 gives the expected complex information.

Table 1. Uranium Ions in Aqueous Solution (Cotton & Wilkenson, 1972)

Ion	Color	Preparation	Stability
U^{3+}	Red-Brown	Na or Zn/Hg on UO_2^{2+}	Slowly oxidized by H_2O, rapidly by air to U^{4+}
U^{4+}	Green	Air or O_2 on U^{3+}	Stable; slowly oxidized by air to UO_2^{2+}
UO_2^+	?	Transient species	Stability greatest at at pH 2-4; disproportionates to U^{4+} and UO_2

UO_2^{2+}	Yellow	Oxidize U^{4+} with HNO_3, etc.	Very stable; difficult to reduce

Adjusted pH (6)
(In the prescence of carbonate)

	4	6	9	10
Uranyl Species	UO_2^{2+}	$UO_2CO_3^{0}$	$UO_2(CO_3)_2^{2-}$	$(UO_2)_3(OH)_5^{+}$

Previous work combined with ease of handling suggested that ferric chloride be used as the precipitate chemical. Fe(III) in solution has solubility as shown in Figure 1. The surface species of the precipitate is geothite, FeOOH. This surface species (solid) undergoes two potential determining reactions with hydronium and hydroxide ions, as follows:(4)

$$FeOOH(s) + H^+ \quad Fe(OH_2)^+ \text{ (surface)}$$

$$FeOOH(s) + OH^- + H_2O \quad Fe(OH)_4^- \text{(surface)}$$

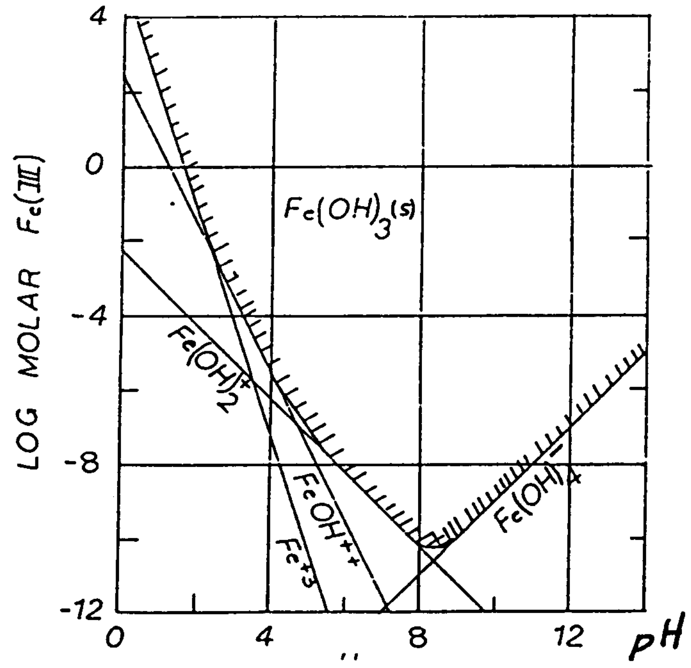


Figure 1. Solubility of Ferric Ion.

This data shows that electrostatic adsorption between $(UO_2)_3(OH)_5^+$ and $Fe(OH)_4^-$ would occur at a pH of 10.

COAGULATION/FLOCCULATION AND SOLID-LIQUID SEPARATION - PART 2

Uranium contamination of drinking waters is anticipated to be less than 50 g/liter and with an anticipated standard of 15 <J/liter the quantity of solids to be handled is small. Therefore consideration was given to alternatives to conventional coagulation/flocculation and sedimentation. In addition ultimate disposal of the uranyl complex required volume reduction and ease of handling.

The initial chemical addition occurs in a rapid-mix device (called a "flash" mixer). To facilitate the exploration of alternative solid-liquid separation processes, a small scale flotation cell (Joy Manufacturing - Model D 110) is used as the contact device. This unit can be operated using mechanically-induced air, pressurized-air or both. The system is supplied with the necessary instrumentation for evaluating power consumption. Residence times are adjusted by inlet flow (the unit is operated in an overflow mode at present). No additional flotation chemicals are being used at present. Liquid waste management systems at Los Alamos National Laboratory have used continuous vacuum filtration as part of their aqueous waste treatment program. (Emelity etial, 1977) Applied to a system for treating drinking water, continuous vacuum filtration (rotary drum) would provide a reduced-volume cake for disposal. Previous work with ferric hydroxide filtration suggested that pre-coat filtration (diatomaceous earth) using continuous addition of filter aid should be used. Although this increased the quantity of solids for disposal, it improves the filtration characteristics of the cake, i.e. reduces cake-blinding of the filter membrane. Operational data is to achieve a minimum cake quantity with a residual moisture of less than 60%. Cake washing is not being applied at present.

EXPERIMENTAL SYSTEM - PART 2

Figure 2 is a schematic of the chemical clarification unit. As mentioned the contact cell was purchased from Joy Manufacturing. The remainder of the system was shop-fabricated at New Mexico State University.

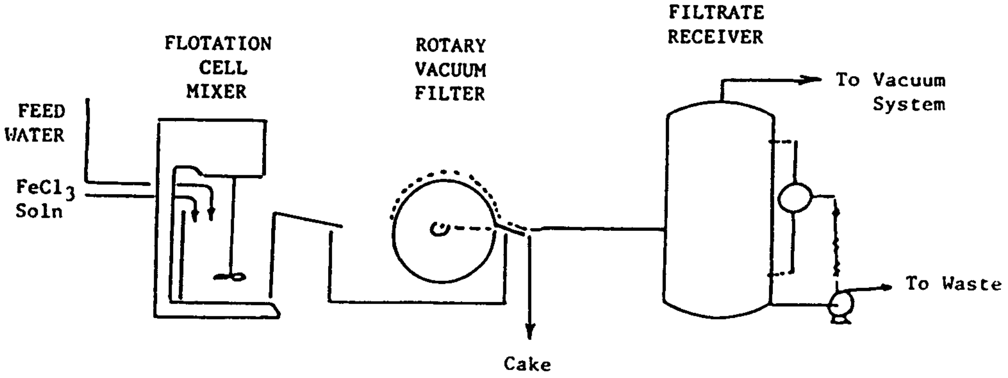


Figure 2. Chemical Clarification Unit

The specific objective is to demonstrate on a continuous basis, the removal of uranium from a drinking water supply. Current operation is summarized in Table 2.

Table 2. Chemical Clarification Operation

Operation	Range
Ferric Chloride Addition	10-50 mg/l as Fe(III)
Contact Time (in Contact Cell)	15-45 minutes
Filtration Aid	0-3 gm/l
pH Adjustment	5-10

At a pH of 10, using 25 mg/1 as Fe(III), a contact time of 30 minutes, no filter aid, better than 98% of the uranium (feed containing 300 g/1 as uranium) has been continuously removed. The product would satisfactorily meet the anticipated drinking water standard.

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REFERENCES

Bahr, T.G., and Herman, R.P., 1981, Water Problems and Research Needs for New Mexico: WRRI Report No. 135, pp. 31-38.

Wilson, *D.B.,* et.al., 1978, Water Treatment For Small Public Supplies: WRRI Report No. 95, pp. 23-25.

Porteous, A., Editor, 1983, Desalination Technology, Developments and Practice: NDC, pp. 1-30.

Calmon, C., and Simon, G.P., 1979, Ion Exchange For Pollution Control: CRC, Volume 1, pp.23-39.

Betz Laboratories, Inc., 1980, Handbook of Industrial Water Conditioning: BETZ, pp. 1, 48-51.

Luft, W., 1981, Water Supply Improvement Association Technical Proceedings from Ninth Annual Conference, adaptation of variable relationship figures.

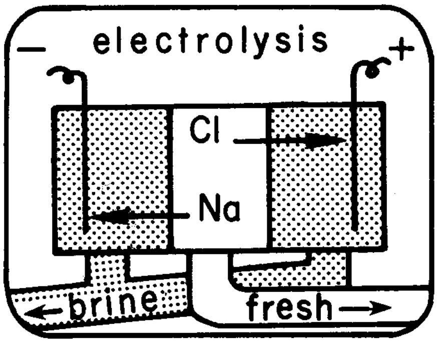
"Methods of Removing Uranium from Drinking Water - A Literature Survey", EPA-570/9-82-003, ORNL, Oak Ridge, Tenn. December 1982.

Lee, S.Y. and E.A. Bondietti, "Removing Uranium from Drinking Water by Metal Hydroxides and Anion-Exchange Resin". Journal AWWA, pp. 536-547, October 1983.

Cotton, F.A. and G. Wilkinson, Advanced Inorganic Chemistry, Interscience Publishers, (John Wiley & Sons) New York, PP. 1086-1096, 1972.

Hohl, H., L. Sigg and W. Stumm, "Characterization of Surface Chemical Properties of Oxides in Natural Waters," in "Particulates in Water" ACS 189, American Chemical Society, Washington, D.C. 1980.

Emelity, L.A., J.R. Buchhoez and P.E. McGinnis, Review of Radioactive Liquid Waste Management at Low Alamos", LA-UR-77-1195, LANL, Los Alamos, NM 1977.



URANIUM INDUSTRY IMPACTS ON GROUNDWATER IN NEW MEXICO

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ABSTRACT

Impacts on groundwater resources have resulted from the mining and milling of uranium in the Grants Mineral Belt, New Mexico. These include contamination of near-surface and deep formations as well as dewatering of bedrock aquifers. Theoretical and empirical approaches are used to evaluate geochemical interactions occurring between acid and alkaline-leach tailings seepage, groundwater, and the soil matrix. Data interpretation is based on numerical analyses, geochemical modeling, and laboratory studies. Groundwater affected by acid-leach tailings seepage is characterized by high concentrations of SO4, Cl, NO3, Fe, Al, Mn, and other metals. Seepage from alkaline-leach tailings Lo groundwater has resulted in elevated concentrations of Na, HCO3, NO3, Se, Mo, SO4, and U. In most cases, there is limited migration of Ra-226 and Th-230 from the tailings impoundments. Chemical elements associated with tailings seepage form soluble oxyanions under oxidizing conditions. Oxidation-reduction potential, pH buffering, and adsorption processes are the dominant variables that control the mobility of many species. Contamination of deeper aquifers may occur from mining activities, subsurface tailings disposal, recharge from impacted alluvial groundwater, and in-situ ore extraction.

INTRODUCTION

Development of New Mexico's uranium resources began shortly after the second world war, with exploration and ore production for Colorado mills. Kerr-McGee Oil company established the state's first mill in 1954 and the state has since become the nation's leading producer of uranium. Mining and milling of uranium in this state has produced nearly 50 percent of this country's yellowcake (U308), the refined oxide of the milling process. New Mexico production peaked in 1978, at 8,560 tons of yellowcake, but has since fallen drastically following a severe drop in world prices (NMEMD, 1981). In the past 15 years, most of this production has been from the Grants Mineral Belt (GMB) of northwestern New Mexico, with the highest concentration of mines located in the Ambrosia Lake mining district (Figure 1). This region is the focus of this presentation.

The chemistry of uranium is strongly influenced by interaction with water. Thus, it is not surprising to find an important relation between the two, both in mining and milling (Thomson and Heggen, 1983a). The surface hydrology of the GMB may be characterized as semi-arid with few perennial streams• Cary and Gallaher (this conference) describe the surface-water quality in the GMB. The groundwater hydrology of the area is complex, consisting of alluvial and several distinct bedrock aquifers, each

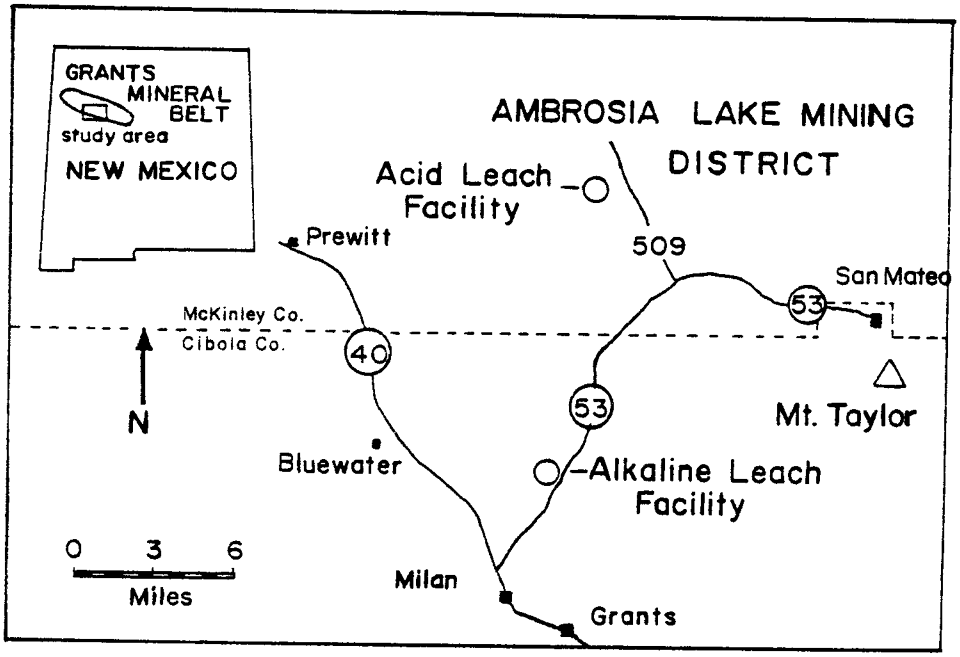

Figure 1. Location of the Grants Mineral Belt

separated by clay and shale-confining layers. Chenoweth (1979) presents stratigraphic sections of the major mining areas. Virtually all current underground mines are located in aquifers and, therefore, must be provided dewatering facilities.

The uranium industry may affect groundwater resources in three ways; drawdown of the groundwater levels, as a result of mine dewatering operations, contamination of near-surface aquifers by surface activities, and contamination of deep aquifers *by* underground activities. Groundwater depletion and drawdown of the potentiometric surface resulting from mine dewatering operations have been addressed in the San Juan Basin Regional Ursinitim Study (U.S. Dept. of Interior, 1980) and found to be significant. However, due to the great depths of these aquifers, there is currently little use of these resources. Consequently, the impacts are negligible. This paper then focuses on the other potential impacts uranium development may have on groundwater resources, including contamination of near-surface and deep aquifers.

GENERAL URANIUM ORE DEPOSITION AND HYDROGEOLOGY

Uranium deposits in the GMB generally are found in aquifers, where ore deposition may be the result of aqueous transport of soluble uranyl carbonate species ($UO2(CO3)i^{-}$, $UO2(CO3)1^{-}$). As reducing conditions are encountered, precipitation of U (IV) minerals may occur. Principal U minerals found in the GMB include coffinite (U(SiO4)1_$_{x}$(OH)4$_{x}$), carnotite ($K2(UO_{2})_{2}(VO_{4})_{6} \bullet 3H_{2}0$), tyuyamunite ($Ca(UO_{2})_{2}(VO_{4})_{2} \bullet 5\text{-}8H_{2}0$), and andersonite (Na2 a(UO2)(C0)3•6H20) (Granger, 1968; Squyres, 1970).

The mineralogy of the host rock (Westwater Canyon Member, Morrison Formation) consists of quartz, K and Na-rich feldspars, kaolinite, montmorillonite, illite, chlorite, mixed-layer clay minerals, hematite, magnetite, and pyrite (Kendall, 1971; Squyres, 1970).

Uranium deposits in the GMB are also enriched with other elements including, As, Mo, Pb, Se, Th, Mn, Fe, Ra, Zn, Cr, Co, V, Ba, and Sr (Spirokis, et. al., 1981; Brookins, 1979).

These species may be further concentrated in the milling process, which involves oxidation and dissolution of the U by either an acid (H_2SO_4) or alkaline (Na2CO3) leach process. After U extraction, the barren tailings and raffinate are sent to a surface tailings impoundment.

The principal aquifers, listed in order of increasing depth, include the alluvial deposits associated with arroyo channels, the Gallup Sandstone, the Dakota Sandstone, the Morrison Formation, and the San Andres Limestone. The bedrock aquifers are used for industrial, agricultural, and domestic purposes. Development of the Morrison Formation is limited due to its depth.

THERMODYNAMIC CONSIDERATIONS

OXIDATION-REDUCTION EQUILIBRIA

The oxidation-reduction chemistry of many of the contaminants found in tailings seepage can be illustrated using Eh-pH diagrams. These diagrams approximate redox conditions of the aqueous environment similar to that found in U ore deposits. They are also useful in describing weathering processes occurring within the vadose and saturated zones adjacent to impoundments.

URANIUM

An Eh-pH diagram for some aqueous species, minerals, and solid compounds of uranium, shown in Figure 2, indicates that primary uranium ore is formed under reducing and slightly alkaline conditions (Brookins, 1979). Note that this zone corresponds to the general redox conditions found in mineralized groundwater and is believed representative of the water chemistry of the Westwater Canyon Member, Morrison Formation. Coffinite is the major crystalline uranium mineral found in the GMB. At activities of Si(OH)4^{u} above 10^{-3}•^{5} molal (30.36 mg/L), coffinite is stable relative to uraninite (UO_2) at 1 atm prepure and 25°C. Kpwever, the reverse is true when the activity of Si(OH)4^{v} is less than 10^{-}-^{7}•'m.

Uranium is oxidized to the (VI) state forming a uranyl species (U02^{2+}) in the milling process. During surface storage of the tailings, the residual U may approach equilibrium with a highly oxidizing and acidic environment. Uranyl sulfate and chloride complexes are also abundant in acid-leach tailings raffinate (Longmire, 1983).

Under initial burial conditions within the tailings impoundment, U(VI) will be concentrated primarily in the pore fluid. Important hydrated uranyl species, such as UO2(OH)$^{+}$, can be adsorbed by diagenetic phases, including geothite and iron oxyhydroxide (Langmuir, 1981; Tripathi, 1982).

IRON

Figure 3 illustrates the aqueous chemistry of important iron-rich species, minerals, and solid compounds found in tailings impoundments and groundwater. The diagram includes the stability fields for jarosite, geothite, pyrite, native sulfur, uranium ore; and aqueous Fe02^{2-}, Fe^{2+}, and Fel^{+}. From previous work (Longmire, 1983), the following observations are made from the diagram:

1. **The stability field for jarosite is substantial under oxidizing,**

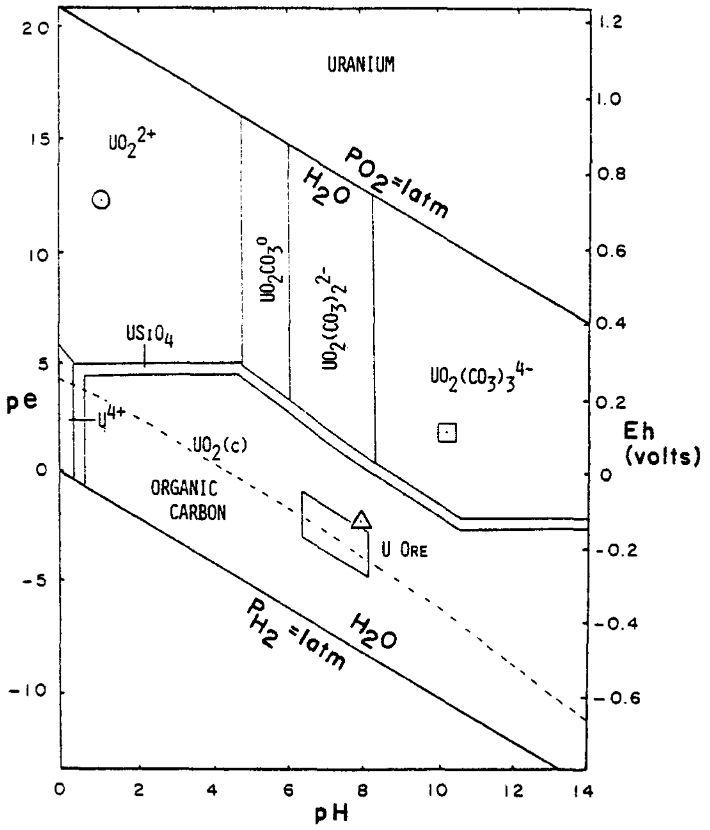

Figure 2 Eh-pH diagram for uranium species at 1 atm pressure and 25°C. Activities of uranium, total dissolved carbon, and silicic acid are 10^{-6}, 10^{-2}, and $10^{-3.5}$ molal respectively (modified from Brookins, 1979). Acid-leach tailings raffinate, alkaline-leach tailings raffinate and groundwater are denoted by ⊙, ⊡, and △, respectively.

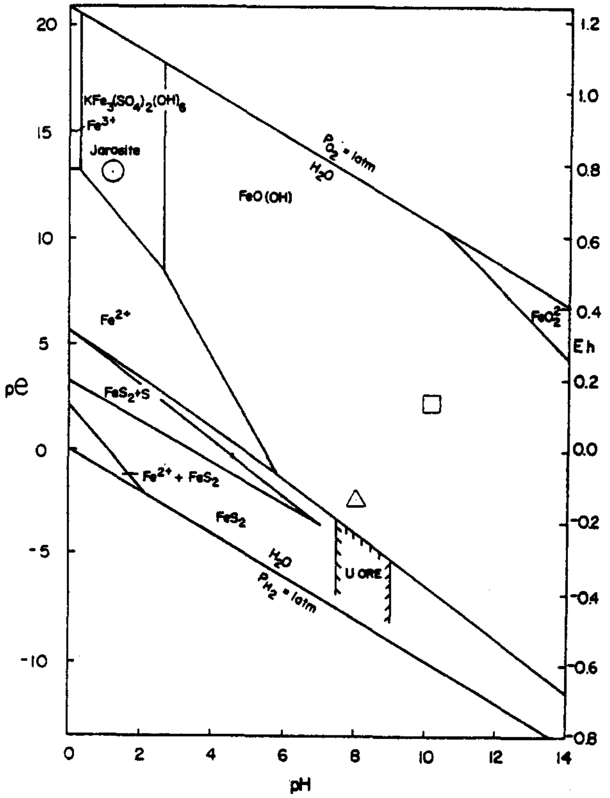

Figure 3 Eh-pH diagram for iron species at 1 atm pressure and 25°C. Activities of sulfate, iron (II), iron (III), and potassium are $10^{-1.8}$, $10^{-4.01}$, $10^{-3.76}$, and $10^{-2.94}$ molal, respectively. Activities are calculated using WATEQFC. Acid-leach tailings raffinate, alkaline-leach tailings raffinate, and groundwater are denoted by ⊙, ⊡, and △, respectively.

acidic conditions. It is an important salt, which is metastable under initial burial conditions and undergoes incongruent dissolution to goethite and iron oxyhydroxide in the subsoil.

2. The pH of the Westwater Canyon Member aquifer in the Ambrosia Lake mining district ranges from 7.1 to 8.6 (Longmire, 1983) and is conducive to the precipitation of pyrite under reducing conditions. Pyrite is a trace constituent of the mineralized Westwater Canyon Member (Hicks, 1981; Della Valle, 1981).

3. Goethite is commonly associated with amorphous ferric hydroxide and other iron oxyhydroxides in the GMB and is stable over a wide range of Eh and pH conditions. Amorphous ferric hydroxide is insoluble (K*10^{-37}' at 25°C) (Sillen and Martell, 1971) and may be a scavenger^{sp} for many of the metals associated with tailings seepage (Benjamin and Bloom, 1981; Leckie and others, 1980).

4. Migration of several Fe species, including Fe^{2+}, Fe^{3+}, $Fe0H^{2+}$, $FeSO_4^{\circ}$, and $Fe(OH)_2^{+}$, is likely to occur in groundwater, if acidic and oxidizing conditions are present.

SELENIUM-IRON

The stability fields for some Se and Fe species are shown in Figure 4,$_e$ The activity of dissolved Se in ground water is assumed to be equal to 10^{-}' molal (0.08 mg/L). From previous work (Howard, 1977), the following observations are made from the selenium-iron Eh-pH diagram:

1. Small concentrations of aqueous Se produce a large stability field for native Se.

2. Ferroselite (FeSe2) is stable under reducing, acidic to alkaline pH conditions (Howard, 1977). Both ferroselite and native Se have been reported in the GMB (Granger, 1968). Some Se could be present in jordisite (MoS2) and pyrite, due to S-Se diadochy.

3. Soluble aqueous species, including H_2Se03, HSe03, $Se03^{2-}$, $Se04^{2-}$, and HSe04, are stable at higher Eh values. Some of these species may exist in equilibrium with tailings raffinate. Migration of Se species may occur under oxidizing and alkaline conditions.

MOLYBDENUM

An Eh-pH diagram for some Mo species is shown in Figure 5. Molybdenum occurring in the GMB, as jordisite, may be a cryptocrystalline precursor for molybdenite (Kendall, 1971). Pyrite and jordisite are stable (Figures 3 and 5) under similar Eh and pH conditions. Migration of molybdenum is possible if oxidizing, alkaline conditions are encountered. This condition requires that reducRd sulfur, occurring as pyrite or jordisite, becomes oxidized to form SO_4^{4-}, with iron possibly forming jarosite and iron oxyhydroxide. However, $HM004^{-}$ can be effectively adsorbed by iron oxyhydroxide under oxidizing conditions (Kaback and Runnells, 1980).

PRECIPITATION AND DISSOLUTION EQUILIBRIA

Dissolution and precipitation reactions are expected to occur in the subsoils beneath tailings impoundments, based on thermodynamic considerations described previously. However, it is not presently possible to determine the rates of these reactions. Equilibrium relationships between gypsum ($CaSO_4 \bullet 2H_20$) and calcite (CaCO3), expected to occur at the tailings-subsoil interface, are discussed below.

The stability of gypsum and calcite at 25°C, at a partial pressure 2f CO2 equal to 10^{-4} atmosphere, is shown in Figure 6. Activities of SO4

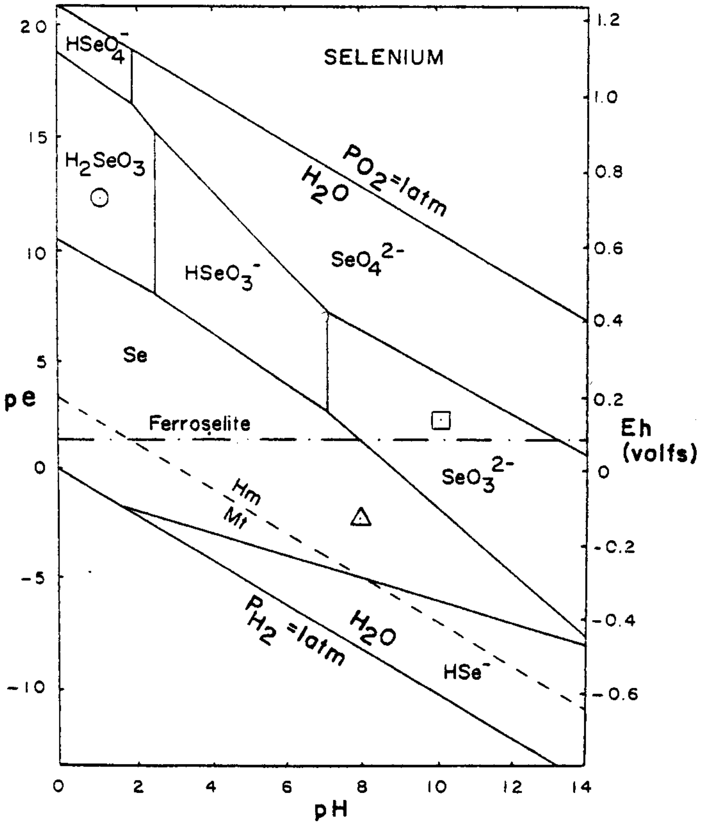

Figure 4 Eh-pH diagram for selenium and iron species at 1 atm pressure and 25°C using 10^{-6} molal selenium and 10^{-6} molal iron. Acid-leach tailings raffinate, alkaline-leach tailings raffinate, and groundwater are denoted by ⊙, ⊡, and △, respectively.

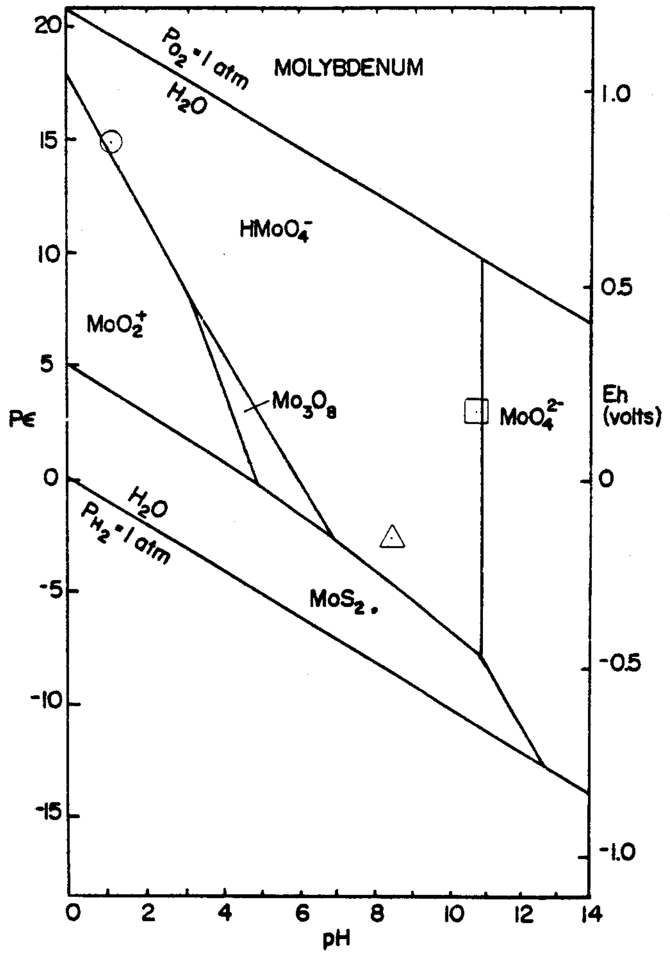

Figure 5 Eh-pH diagram for molybdenum species at 1 atm pressure and 25°C using 10^{-6} and 10^{-3} molal molybdenum and sulfur, respectively (after Brookins, 1979). Acid-leach tailings raffinate, alkaline-leach tailings raffinate and groundwater are deonted by ⊙, ⊡, and △, respectively.

vary from 10^{-1}, to 10^{-4} molal. Calcite is a common mineral in the alluvial and bedrock aquifers. Gypsum has also been observed in soils adjacent to tailings impoundments. Seepage from an acid-leach tailings impoundment may cause incongruent dissolution of calcite and re precipitation of gypsum, illustrated by the following equation:

$$2H^+ + H_2O + CaCO3 + S0_4^{2-} = CaSO_4 \cdot 2H2O + CO_2(_g).$$

Calcite coexists with gypsum beneath the base of the tailings impoundments, where remnant calcite cores are mantled by authigenic gypsum. Sub soils adjacent to tailings impoundments within the GMB, in most cases, are well-buffered and have neutralized acidic-tailings seepage. Groundwater monitoring data support the occurrence of these reactions within the sub soils (EID, 1983).

AQUIFER CONTAMINATION FROM SURFACE

SOURCES CHEMISTRY OF MILL TAILINGS RAFFINATES

The milling process involves three generalized steps: (1) ore handling and preparation, (2) mill concentration, and (3) product recovery (De Carlo and Shortt, 1970). Uranium tailings produced in the GMB consist of numerous chemical constituents, including unrecovered U, disaggregated host rock, and high ionic strength solutions (0.69 M). Table 1 summarizes the concentrations of selected parameters in acid and alkaline-leach tailings raffinates. Although these data are limited,several points are noteworthy:

1. Gross radioactivity is higher in acid-leach tailings raffinates than in alkaline-leach tailings raffinates;
2. Molybdenum, Se, and U concentrations are higher in alkaline-leach tailings raffinates than in acid-leach tailings raffinates;
3. Sulfate concentration are greater than 5,000 mg/L in both types of tailings raffinates; and
4. The TDS of acid-leach tailings raffinates is approximately 1.5 times greater than that of alkaline-leach tailings raffinates.

Migration of contaminants from tailings impoundments, through the subsoil to ground water, will occur to a varying degree at each site in the GMB. The effect of tailings seepage on groundwater quality at two different mill facilities, including an acid-leach operation and an alkaline-leach operation, is described below.

ACID-LEACH MILL SITE

The acid-leach mill site selected for study is located approximately 17 miles north of Grants, New Mexico (Figure 1). The Mount Taylor volcanic complex, consisting of Tertiary andesitic and basaltic flows, is located 8 miles southeast of the site. Several tailings impoundments are situated on alluvial deposits, overlying the Mancos Shale and intercalated beds of the Tres Hermanos Sandstones. Major aquifers in the mill area include the Dakota Formation and the West water Canyon Member, Morrison Formation. The alluvial aquifer is produced from surface discharges, including mine dewatering and tailings seepage, and is of limited areal extent. This aquifer has been affected by tailings seepage to a greater degree than the other aquifers. The mill uses a sulfuric acid-leach process. The tailings raffinate displays a low pH (1.2) and a TDS of 45,500 mg/L. Prior to January 1981, approximately 28,500,000 tons of U tailings had been disposed

TABLE 1

CONCENTRATIONS OF SELECTED CONSTITUENTS NEW MEXICO MILL TAILINGS POND RAFFINATES ANALYSES OF UNFILTERED SAMPLES COLLECTED BY NMEID PERSONNEL, 1978 TO 1981. (All concentrations in mg/L unless noted.) (Thomson and others, 1982)

	4 Acid Mills (14 samples)			1 Alkaline Mill (5 samples)		
Constituent	Minimum	Median	Maximum	Minimum	Median	Maximum
Gross alpha Radioactivity (pCi/L)	3,200	38,000	73,000	3,400	6,700	10,000
Ra-226 (pCi/L)	15	70	1,800	56	58	90
As	0.18	1.3	5.6	2.1	5.0	7.2
Mo	0.20	0.90	29.5	72	98	105
Se	0.006	0.21	6.97	22.1	29.5	51.2
SO_4	300	29,700	56,000	5,500	8,400	16,700
U	1.1	15	69	4.2	53	70
V	39	74	107	1.2	14	16
NH_3 (as N)	3.3	400	3,960	1.1	16	335
TDS	17,900	39,800	72,800	17,000	25,400	39,700
pH	0.3	1.05	2.15	9.9	10.1	10.3

Table 2

Water Quality Analysis of Alluvial Monitor Well Sampled on 5-17-83 (All concntrations in mg/L unless noted)

Constituent	Concentration
Mg	1849.0
HCO_3	539.0
Ca	411.0
Cl	3280.1
Na	2339.0
SO_4	10270.0
NO_3 + NO_2	86.68
NH_3	245.3
As	0.087
Fe*	63.6
Pb	0.01
Mn*	12.9
Mo	0.01
Se	0.06
U	0.39
pH	6.81
DOC	26.0
TDS	19224.0
Eh (volts)	+0.160

*These values probably include dissolved and colloidaliron and manganese produced by corrosion of the steel casing, in addition to concentrations present in groundwater.

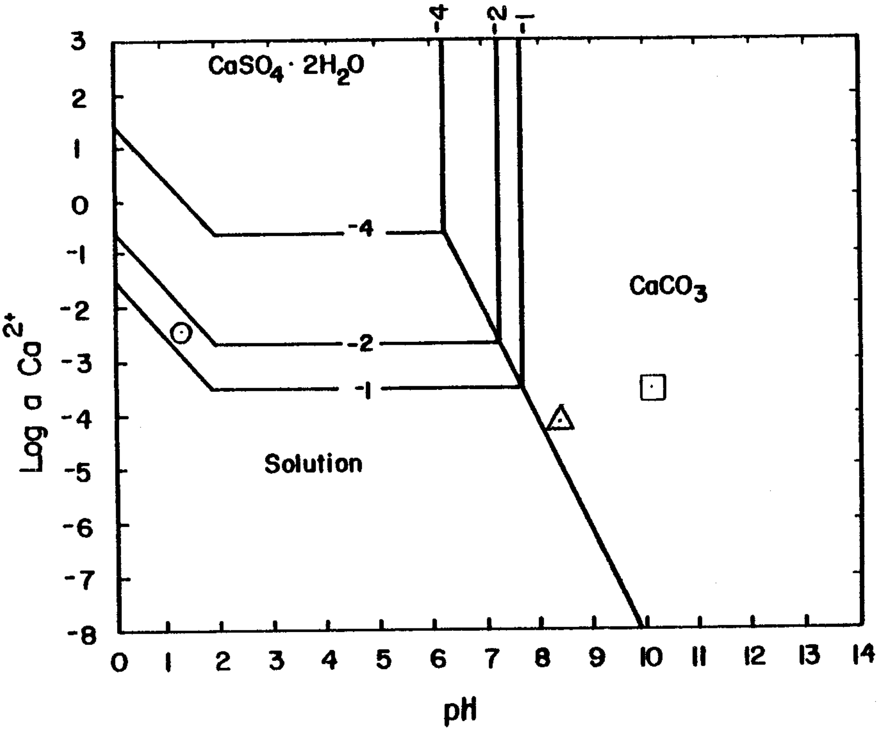

Figure 6 Activity diagram of gypsum-calcite system at 1 atm pressure and 25°C using 10^{-1}, 10^{-2}, and 10^{-4} molal sulfate. Acid-leach tailings raffinate, alkaline-leach tailings raffinate and groundwater are denoted by ⊙, ⊡, and △, respectively.

Table 3

AVERAGE RESULTS 7101 STOPE 9/18/81 SEC 36 MINE
(all units mg/L unless noted)
(Thomson and Heggen, 1983b)

Constituent	Mine Water	Slurry Liquor	Sandfill Decant	Surface Discharge
pH (pH units)	8.2	7.15	7.2	8.0
alkalinity (mg $CaCO_3$/L)	266	179	185	--
TDS	544	2723	2890	1230
As	0.006	0.012	0.015	0.011
Ca	44	548	808	--
Mo	0.004	1.11	0.86	0.99
Na	115	263	245	--
Se	0.017	0.213	0.340	0.12
SO_4	188	1680	1720	680
V	<0.003	<0.003	<0.003	<0.003
^{238}U	0.043	0.832	8.9	0.79
^{226}Ra(pCi/L)	2.67	26.7	25.0	--

in surface impoundments (EID, 1983).

Groundwater flow in the alluvium is generally to the southeast, where the tailings impoundments and the Arroyo del Puerto act as areas of recharge. The seepage velocity has been estimated at 22 feet per year (2.1 x 10^{-} cm/sec), which is indicative of the Mancos Shale (Hydro Geo Chem, 1982).

Alluvial groundwater, in general, is enriched with Ca and SO_4. In areas adjacent to the tailings impoundments, Na is the dominant cation and there are also high concentrations of other major cations and anions. The TDS of alluvial groundwater, near the tailings impoundments, is approximately 10,000 mg/L, whereas the TDS is roughly 1000 mg/L down-hydraulic gradient along the boundaries of the alluvium. Table 2 shows a typical water quality analysis of ground water obtained from a monitor well located near one of the tailings impoundments. Trace element concentrations, including U, Se, Mo, and As, are less than 0.5 mg/L. This aquifer contains high concentrations of dissolved organic carbon (DOC) (Table 2), which may be the result of both naturally occurring organic substances (humic material) present in the weathered shale and tailings seepage.

Geochemical modeling, using the WATEQFC code (Runnells and Lindberg, 1981), has been used to estimate speciation of soluble constituents and to predict stabilities of minerals and solid components that may be present in alluvium. The calculations show that groundwater obtained from the monitor well is supersaturated with respect to hematite, goethite, kaolinite, amorphous iron hydroxide, microcline, smectite, and gypsum. Calcite, quartz, chalcedony, and albite are predicted to dissolve and would then release sorbed and constituent ions to groundwater. These predictions are consistent with observations made at this site.

The quality of tailings raffinate is significantly different than seepage detected in down-gradient monitor wells. These changes in water chemistry are due to interactions between the soil and the raffinate including: (1) dilution, (2) pH buffering, (3) chemical precipitation by reaction with components of the solid porous medium, (4) hydrolysis reactions, (5) precipitation resulting from oxidation and reduction, (6) sorption, (7) biological transformations, and (8) radioactive decay. Redox potential, pH buffering, and adsorption are considered the most important variables.

The most critical factor in controlling contaminant migration at this site is buffering of pH. The pH of groundwater samples taken from the alluvial aquifer range from 6.5 to 8.1, indicating that the acidic pH front has not yet significantly affected this aquifer. The natural buffering capacity, which depends on silicate, carbonate and clay minerals present in the alluvium, greatly reduces contaminant mobility. The alluvial aquifer also serves as a recharge zone for portions of the underlying Tres Hermanos Sandstones, where tailings seepage is further neutralized.

A potential process for removal of many of the contaminants associated with tailings raffinate is sorption onto iron oxyhydroxides (Benjamin and Bloom, 1981; Langmuir, 1981, Leckie et al., 1980). Evidence to support this has been obtained by examining leachates from a corroded steel well casing. Leaching the corroded iron at low pH produced several trace elements including U, Se, Pb, Cd, Ba, and As (Longmire, 1983).

Anion retention in alkaline and oxidizing groundwater, within the GMB, is generally poor. Several anions, including Cl^{-}, $S04^{2-}$, $NO3^{-}$, and NO_2^{-}, readily move through alluvial and bedrock aquifers. Chloride and the N species are probably derived from tailings seepage, whereas SO4 concentrations in groundwater may represent the combined effects of mineral dissolution and tailings seepage. Determination of the amounts of SO4 derived from mine-dewatering via the Arroyo del Puerto, inflow from the Tres Hermanos Sandstones, and tailings seepage was recently investigated by Hydro Geo Chem (1982), through the use of sulfur isotopes.

Prior to 1980, the company had installed approximately 70 monitor wells in the alluvial and bedrock aquifers, including the Tres Hermanos Sandstones, the Dakota Formation, and the West water Canyon Member. Neutralization of the acidic seepage by soils and alkaline, alluvial groundwater is generally complete within a few hundred feet of the tailings impoundments.

ALKALINE-LEACH MILL SITE

The alkaline-leach mill site is located approximately 5 miles north of Milan, New Mexico (Figure D. The mill site contains two tailings impoundments, one of which is currently used. The mill site is located in the San Mateo drainage on the San Mateo Alluvium that unconformably overlies the Triassic Chinle Formation and Permian San Andres Limestone. Tailings seepage from both impoundments have impacted water quality in the San Mateo Alluvium and the upper Chinle Sandstone. The mill utilizes an alkaline-leach caustic precipitation process for uranium recovery, with the use of $Na2CO_3$ and NaHCO3 solutions. Ore extraction takes place in a two-stage circuit at pH 11. The spent solutions, unrecovered U, and host rock are discharged to the active tailings impoundment. Prior to 1982, the active tailings impoundment contained approximately 20,000,000 tons of tailings material (EID, 1983).

Geochemical modeling (WATEQFC, Runnells and Lindberg, 1981) has been applied to tailings raffinate from this facility to speciate dissolved constituents. The raffinate is shown to be supersaturated with respect to hematite, magnetite, goethite, amorphous iron hydroxide, smectite, strontianite, calcite, microcline, and sepiolite under oxidizing and alkaline conditions (Eh + 0.12 volts, pH 9.9). The solution is under saturated with respect to quartz, albite, chalcedony, illite, kaolinite, gypsum, thenardite, and RaSO4.

The alluvial aquifer has been impacted by tailings seepage to a greater extent than the upper Chinle Sandstone aquifer. Groundwater flow in the alluvium is generally to the south-southwest, whereas groundwater flow in upper Chinle Sandstone and underlying San Andres Limestone is generally to the north-northeast, perpendicular to the strike of the formations.

Approximately 75 gallons per minute of tailings seepage, with a TDS of 10,000 mg/L, infiltrates to the sub soils (EID, 1983). Concentrations of NO3, Cl, Mo, Se, U, SO4, and TDS exceed the New Mexico Water Quality Control Commission (NMWQCC) standards for groundwater. Contaminated alluvial groundwater has moved down gradient to the south and southwest of the active-tailings impoundment. The range of average seepage velocities for the alluvial aquifer is 50 to 260 feet per year (4.8×10^{-3} to 2.5×10^{-4} cm/sec) (Hydro-Engineering, 1981). The maximal saturated thickness of the alluvium is 40 feet near the base of the active-tailings impoundment.

Monitor wells, installed and maintained by the company, show concentrations of U, Se, and Mo on the order of 70, 1, and 50 mg/L, respectively, in the alluvium near the base of the active-tailings impoundment. Concentrations of these elements are generally less than 0.1 mg/L down-hydraulic gradient, within 2 miles of the impoundment.

Uranium, in the form of anionic carbonate complexes, is poorly attenuated under alkaline, oxidizing conditions found at the mill site. Again, some of the uranium may be absorbed by iron oxyhydroxides and clay minerals. The chemistries of Mo and Se are complex and it is difficult to predict the mobility of these species under the present set of circumstances. Both elements form soluble oxyanions under alkaline, oxidizing conditions. Molybdenum and Se may be attenuated through the precipitation of several minerals, including ilsemannite (Mo308), ferrimolybdate (Fe203, 3.52 Mo03 10.414$_2$0), native selenium, and ferroselite ($FeSe_2$).

$^-$Concentrations of NO3 in the alluvial aquifer, at the base of the active-tailings impoundment are generally less than 25 mg/L. Nitrate concentrations decrease to approximately 10 mg/L,within 2 miles down-hydraulic gradient from the active-tailings impoundment. Under these field conditions ,the $NO3^-$ ion is a conservative species and has probably migrated the furthest from the tailings impoundment.

At this site sulfate is another conservative species, whose concentration at the base of the active tailings impoundment is typically 7,000 mg/L and decreases to approximately 700 mg/L, within 2 miles down-hydraulic gradient. The high SO_4 concentrations are probably the result of tailings seepage and gypsum dissolution.

Activity of Ra-226 in the alluvial aquifer at the mill site is less than 10 pCi/L. This radionuclide is effectively adsorbed/absorbed by barite, which has been reported in sulfate-rich soils within the GMB. Further attenuation of Ra is achieved by adsorption onto the fine grained soils.

The company has initiated a groundwater protection program to reduce contaminant concentrations in the alluvium. The program involves the use of collection/injection wells to collect seepage as it enters the aquifer near the active tailings impoundment, reduce hydraulic gradients to the north and south of the tailings impoundment, and inject high-quality water to dilute and disperse contaminated groundwater south of the company's property boundary. A similar aquifer restoration program is proposed for the upper Chinle Sandstone.

AQUIFER CONTAMINATION FROM UNDERGROUND ACTIVITIES

UNDERGROUND MINING

As noted, most present mining operations are located in aquifers, usually the West water Canyon Member of the Morrison Formation. Processes responsible for uranium deposition, require strongly reducing conditions (Figure 2). Underground mining operations introduce strongly oxidizing conditions in the form of ventilation shafts, extensive exploratory drilling, both from the surface and from access drifts, and explosives used in mining. Oxidation of exposed material in the mine may result in formation of soluble species that will degrade groundwater flowing into the mine. Contaminants that are observed in mine water at elevated concentrations include As, Mo, S, Se, Th, V, and U. Each of these elements, except Th, has chemical behavior similar to that of U in that reduced phases are insoluble and oxidized phases are soluble. Tetravalent Th is the only oxidation state of this actinide. Following treatment of mine water for removal of suspended solids, U and Ra, most discharges are of high quality, though some discharges in the Ambrosia Lake mining district contain Se in excess of NMWQCC groundwater standards (Thomson and Matthews, 1981). Gallaher and Goad (1981) discuss the impact of mines on surface waters. Cary and Gallaher (this conference) present additional data on surface-water quality.

Mines in New Mexico use the room and pillar method for recovering ore, which leaves large empty underground stopes with little or no roof support.

Roof collapse results in the propagation of fractures towards the surface that provides hydraulic connection with overlying aquifers,resulting in greatly increased mine dewatering requirements (Thomson and Heggen, 1983b). A technique proven to be of value in reducing this interconnection of aquifers involves the backfill of mill tailings into empty stopes. A slurry comprised of tailings (70 percent by weight) and treated-mine water is hydraulically placed in the stopes. Bulkheads are constructed to retain the sands, yet allow drainage of the slurry decant, which then commingles with mine water, flows to the mine sump and is pumped to the surface where it is treated and discharged. Current backfill practice is limited to disposal of the sand fraction of the tailings in the interest of providing rapid drainage of the filled stope.

Investigations of the impacts of backfilling on groundwater quality have separated potential problems into short and long-term impacts. Short-term effects occur while the mine is still being dewatered. Drainage from backfilled stopes commingles with mine water and flows rapidly to the mine sump and is pumped from the mine. In mines investigated by Thomson and Heggen (1983b), the backfill-decant liquor was a small fraction (less than 5 percent) of the total mine water flow. Aquifer contamination was, therefore, considered negligible due to dilution as well as rapid removal from the underground system. A summary of water-quality monitoring data from a backfill event is contained in Table 3. Long-term impacts on the aquifer may occur after dewatering operations cease and groundwater is allowed to flood the mine. Predictions based on hydraulic and geochemical considerations indicate that such effects will be negligible (Thomson and Heggen 1983b, Longmire, 1983). Due to the fact that only the sand fraction of the tailings are backfilled, there is little retained slurry water remaining in the fill. It is estimated that flooding of the backfilled stope with native groundwater will immediately result in dilution of soluble contaminants by a factor of four. Furthermore, conditions within the aquifer are strongly reducing and flooding of the mine will restore reducing conditions. Geochemical calculations suggest that most contaminants will become insoluble, or coprecipitate with one of the insoluble phases under such conditions (Longmire, 1983).

In many regions of the GMB,the water quality of overlying strata is significantly poorer than that of the ore body. Backfilling, therefore, presents an interesting dilemma in groundwater-quality management; whether to allow a onetime introduction of contaminated water with the backfill slurry that is quickly removed from the mine, or to prohibit backfilling and allow future hydraulic connection between two or more aquifers, some of very poor quality. The issue currently has not been resolved.

IN-SITU LEACH MINING

An alternative to conventional mining procedures is in-situ leaching of the U ore. In-situ leaching is basically a reversal of the ore deposition process in that an oxidizing solution is injected into the ore body where oxidation and dissolution of reduced U phases occur. The pregnant solution is then recovered and processed for U removal in a small surface facility. In-situ leaching for U recovery has been practiced elsewhere for many years with great success, most notably in south Texas. A commercial scale pilot test operation is presently nearing operation near Crownpoint (TVA, 1979) and will, when completed, involve approximately 50 acres, 200 injection wells, 260 monitor wells, and 80 monitor wells.

Uranium oxidation and dissolution is achieved by introducing a slightly alkaline solution containing a mild oxidant; $02_{(g)}$ is presently planned, through injection wells. Following oxidation from the (IV) to (VI) state, U will dissolve as a carbonate complex and will be pumped to the surface. Other minerals associated with U ore such as pyrite, ferroselite, and jordisite may undergo oxidation and dissolution as well, producing increased concentrations of Fe, SO_4, Se, and Mo. Preliminary results suggest that decreasing Mo and Se concentrations may be difficult, due to complexation and formation of soluble oxyanions. Aquifer restoration may be accomplished by flushing the ore body with groundwater or introducing chemical reducing agents such as H_2S and FeSO4.

There are numerous potential advantages of the in-situ leach process over conventional mining techniques including:

1. minimal physical disturbance of the aquifer;
2. no production of uranium mill tailings;
3. greatly reduced aquifer dewatering demands;
4. smaller milling facilities; and
5. minimal physical disturbance of the surface environment.

The success of the process depends on the ability to recover a significant fraction of the deposited U, and then to restore the aquifer to its original quality. Both of these questions should be resolved by the current pilot testing.

CONCLUSIONS

1. In most cases, groundwater contamination caused by tailings seepage in the GMB is localized. Oxidation-reduction reactions, adsorption, and buffering of pH leading to precipitation of sulfate, oxide, silicate, hydroxide, and carbonate phases enhance attenuation of many elements associated with tailings seepage.

2. Groundwater affected by acid-leach tailings seepage is characterized by high concentrations of SO4, Cl, NO3, Fe, Al, Mn, and other metals. Groundwater affected by alkaline-leach tailings seepage is characterized by high concentrations of SO4, HCO3, NO3, Na, Se, Mo, and U. There is limited migration of Ra-226 and Th-230 in groundwater contaminated by acid and alkaline-leach tailings seepage.

3. Short-term groundwater contamination, resulting from dissolution of gypsum and pyrite, in areas adjacent to backfill material is expected. Geochemical interactions occurring within the backfill material and dilution of backfill decant by mine water are the main processes contributing to aquifer restoration.

4. Backfill disposal of uranium mill tailings sands has virtually no impact on groundwater in the vicinity of operating mines, and is predicted to have negligible impacts on abandoned mines. Backfill disposal may in fact be of benefit by preventing hydraulic connection and subsequent mixing of aquifers of differing water quality.

5. In-situ mining of U appears to have numerous advantages over conventional practices, from a groundwater perspective, in that underground disturbance and dewatering are greatly reduced and there is no production of mill tailings and associated raffinate solutions. However, the formation of soluble oxyanions, including species of Se and Mo, during U extraction by in-situ leaching may present problems for aquifer restoration operations.

6. Thermodynamic calculations are useful for determining the stabilities of numerous minerals, solid phases, and aqueous species in tailings raffinate, subsoil, and groundwater.

ACKNOWLEDGMENTS

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REFERENCES

Benjamin, MX, and Bloom, N.S., 1981, Effects of strong binding of anionic adsorbates on adsorption of trace metals on amorphous iron hydroxide: Tewari, P.H. (ed.), Adsorption from Aqueous Solutions, Plenum Press, New York, NY, pp. 41-60.

Brookins, D.G., 1979, Study of drill cores from the East Chaco Canyon Area, San Juan Basin Geochemical Studies: U.S. Department of Energy open-file report, 106 p.

Chenoweth, W.L., 1979, Stratigraphic sections and idealized cross section in Grants Uranium Region, prepared for field trip symposium, U.S. Dept. of Energy, Grand Junction Office, CO, 18 p.

DeCarlo, J.A., and Shortt, C.E., 1970, Mineral facts and problems, 1970 Edition: U.S. Department of the Interior, Bureau of Mines Bulletin 650, pp. 219-242.

Della Valle, R.5., 1981, Geochemical studies of the Grants Mineral Belt, New Mexico; Ph.D. Dissertation, University of New Mexico, Albuquerque, NM, 667 p.

Environmental Improvement Division, 1983, Open file information, Santa Fe, NM.

Erickson, J.W., 1978, Underground in-situ mining - a new mining method: Mining Engineering, v. 30, pp. 1532-1534.

Gallaher, B.M., and Goad, M.S., 1981, Water-Quality aspects of uranium mining and milling in New Mexico, in Environmental geology and hydrology in New Mexico, Wells, S.G. and Lambert, W. (eds.), New Mexico geological society, special publication no. 10, pp. 85-91.

Goad, M.S., Nylander, C.L., Gallaher, B.M., Dudley, J.G., and Perkins, B.L., 1980, Water quality data for discharges from New Mexico uranium mines and mills in New Mexico: Environmental Improvement Division, Santa Fe, New Mexico, 87 p.

Hicks, R.T., 1981, Diagenesis of the Westwater Canyon Member, Morrison Formation, east Chaco Canyon drilling project, New Mexico: unpublished M.S. thesis, The University of New Mexico, Albuquerque, NM, 128 p.

Howard, J.H., III, 1977, Geochemistry of selenium: formation of ferroselite and selenium behavior in the vicinity of oxidized sulfide and uranium deposits: Geochimica et Cosmochimica Acta, v. 41, pp. 1665-1678.

Hydro-Engineering, 1981, Groundwater discharge plan for Homestake's Mill near Milan, New Mexico: Consulting report submitted to Homestake Mining Company, 600 p.

Hydro Geo Chem, 1982, Use of sulfur isotopes to trace uranium mill pond seepage: Consulting report submitted to Pueblo of Laguna, Laguna, New Mexico, 33 p.

Kaback, D.S. and Runnells, D.D., 1980, Geochemistry of molybdenum in some stream sediments and waters: Geochimica et Cosmochimica Acta, v. 44, pp. 447-456.

Kendall, E.W., 1971, Trend ore bodies of the Section 27 mine, Ambrosia Lake uranium district, New Mexico: Ph.D. Dissertation, University of California, Berkeley, 167 p.

Langmuir, D., 1981, The power exchange function: a general model for metal adsorption onto geological materials: in Tewari, P.H. (ed.), Adsorption from Aqueous Solution, Plenum Press, New York, pp. 1-18.

Leckie, J.0., Benjamin, M.M., Hayes, K., Kaufman, G., and Altmann, S., 1980, Adsorption/coprecipitation of trace elements from water with iron oxyhydroxide: Electric Power Research Institute, CS-1513, project 910-1, 197 p.

Longmire, P.A., 1983, Geochemistry, diagenesis, and contaminant transport of uranium tailings, Grants Mineral Belt, New Mexico: unpublished M. S. thesis, The University of New Mexico, Albuquerque, NM, 182 p.

Merritt, R.C., 1971, The Extractive Metallurgy of Uranium: Colorado School of Mines Research Institute, Golden, Colorado, 576 p.

New Mexico Energy and Minerals Department, 1981, Uranium resources and technology, a review of the New Mexico uranium industry: 1980, Santa Fe, NM, 242 p.

Runnells, D.D., and Lindberg, R., 1981, Hydrogeochemical exploration for uranium ore deposits: Use of the computer model WATEQFC, In. Rose, A.W. and Gundlach, H. (eds.), Geochemical exploration 1980: Journal of geochemical exploration, v. 15, pp. 37-50.

Sillen, L.G. and Martell, A.E., 1971, Stability constants of metalion complexes: Special Pub. No. 25: The Chemical Society, Burlington House, London, 865 p.

Spirokis, C.H., Pierson, C.T., and Granger, H.C., 1981, Comparison of the chemical composition of mineralized and unmineralized (barren) samples of the Morrison Formation in the Ambrosia Lake uranium area, New Mexico: U. S. Geological Survey, Open File Report 81-508, 43 p.

Squyres, J.B., 1970, Origin and depositional environment of uranium deposits of the Grants region, New Mexico: Ph.D. Dissertation, Stanford University, Stanford, 228 p.

Tennessee Valley Authority, U.S. Department of Interior, 1979, Final environmental statement, Crownpoint uranium mining project: Norris, TN, pp. 27-42.

Thomson, B.M., and Matthews, J.R., 1981, Water and wastewater treatment alternatives for the uranium mining industry in New Mexico: Report No. Ce-56(81)NMEID-7 80-1 to EID, University of New Mexico, Albuquerque, NM, 155 p.

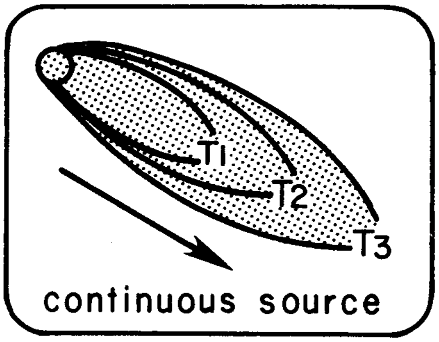
Thomson, B. M., Longmi re, P. A., and Gallaher, B. M., 1982, The hydrologic environment and uranium production in New Mexico: in Proceedings of Water and Energy Conference, American Society of Civil Engineers, pp. 525-531.

Thomson, B.M., and Heggen, R.J., 1983a, Uranium and water: managing related resources, Chemtech, v. 13, pp. 294-299.

Thomson, B.M., and Heggen, R.J., 1983b, Uranium mill tailings backfill management: Report No. EMD-2-69-1107 to NM Energy Research and Development Institute, University of New Mexico, Albuquerque, NM, 110 p.

Tripathi, V. S., 1982b The adsorption of uranium (VI) onto goethite and the effect of carbonate, fluoride, and phosphate labs.): Geological Society of America, annual meeting, v. 14, pp. 633-634.

U.S. Dept. of Interior, 1980, San Juan basin regional uranium study, a report on environmental issues, Abuquerque, NM, pp. V-32 - V-38.



CHARACTERIZATION OF GROUND WATER QUALITY NEAR A URANIUM MILL TAILINGS FACILITY, AND COMPARISON TO BACKGROUND LEVELS AND NEW MEXICO STANDARDS

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ABSTRACT

Historical water quality for the Gallup Sandstone is reviewed on the basis of proximity to a uranium mill tailings facility in Sec. 2, T16N, R16W, N.M.P.M. 115 water quality samples from 68 wells and two springs located in the San Juan Basin were used to derive ranges and mean concentrations for major chemical constituents. Data compiled by state and federal agencies and the uranium milling company define ground-water quality in two distinct aquifers affected by seepage from unlined evaporation ponds at the site. Concentrations of most major constituents, metals and radionuclides in selected site monitoring wells exceed both mean background water quality levels and New Mexico ground water standards, in some cases by thousands of times.

INTRODUCTION

A uranium mill and tailings disposal facility owned by UNC Mining and Milling Division (also known as United Nuclear Corp.) is sited in Sec. 2, T16N, R16W, N.M.P.M., at the far southwest end of Pipeline Canyon about 15 miles (24.2 km) northeast of Gallup, N.M. Seepage of tailings waste water with an initial pH of at least 1.5 (see Table 3, column 5) from unlined evaporation ponds at the mill has been the focus of regulatory action since 1979 (Shuey, 1982) due to the existence of a violation of New Mexico's standards for ground water protection. Sec. 3101.A.2. of the state standards (NMWQCCR, 1982) provides that if the natural quality of waters affected by discharges is higher than the numeric standards then the existing quality becomes the standard. This study was conducted to help determine background water quality in the Gallup Sandstone for comparison to state standards and the quality of waste liquids seeping from the UNC site.

PHYSICAL AND HYDROLOGIC CHARACTERISTICS OF THE GALLUP SANDSTONE

Raymondi and Conrad (1983) have described the geologic sequence in the canyon as (in descending order) a thin veneer of alluvium derived from erosion of the surrounding sediments, the Point Lookout Sandstone, the Crevasse Canyon Formation (including the Gibson Coal Member, Upper Dalton Sandstone Member, Lower Mulatto Tongue of the Mancos Shale, and Dilco Coal Member), the Gallup Sandstone (including the Torrivio Sandstone Member and Zones 3, 2 and 1 of the Upper Gallup Sandstone), the Mancos Shale (including the Upper D-Cross Member), the Lower Gallup Sandstone, and the Lower U-Cross Member of the Mancos Shale. Lone 2 of the Upper Gallup is an intervening shale layer confirmed by borehole geophysics data (Raymondi and Conrad, 1983, fig. 3).

, Reported transmissivities in the Gallup Sands^{-}We range from 59 ft /d near the center of the Basin to 250 to 300 ft /d in the Yah-Ta-Hey well field north of Gallup (Stone et al., 1983,, p. 37). Specific capacities range from .03 gal/d/ft (0.000375 m^{L}/d) in he northwest part of the Basin to 1.0 to 2.0 gal/d/ft (0.0125 to 0.025 mL/d) in the southwest corner of the Basin west of Gallup (Stone et al., 1983, fig. 61). Raymondi and Conrad (1983) computed transmissivities between 110, and 323 ft^{L}id for Zone 3 of the Upper Gallup and between 25 and 70 ft^{L}/d for Zone 1 of the Upper Gallup at the UNC site.

Mercer and Cooper (1970) found that the Gallup Sandstone was capable of delivering up to 80U gpm to city of Gallup wells. Hiss (1975, p. 8) reported sustained yields of 500 to 800 gpm (31.6 to 50.48 1/s) were expected from wells completed in the Gallup. Davis et al. (1963) reported yields of 2 to 45 gpm (0.13 to 2.84 1/s) in Gallup Sandstone wells in the Tohatchi area and yields of 2 to 300 gpm (0.13 to 18.93 1/s) in wells in and a few miles north of Gallup.

SUMMARY OF GALLUP SANDSTONE WATER USAGE

The ability of the Gallup Sandstone to carry and deliver water throughout the San Juan Basin has been described *by* many investigators. Mercer and Cooper (1970) noted that the Gallup Sandstone is the major aquifer of the Gallup-Tohatchi area and the major source of water for the city of Gallup. Hiss (1975, p. 37) called the Gallup "one of the most dependable and productive aquifers in western and northwestern New Mexico..." Thiele (1966, p. 9) showed that in the area around Gallup, the Gallup Sandstone ranked behind only the Dakota-Morrison aquifer system in water stored and available for use.

Water uses were reported for 28 of the 68 wells reviewed in this study (Table 1). Of the 28, six were "public supply," 13 were "domestic," 13 were "stock watering," one was used for irrigation, one was a test well, and six (those closest to the UNC facility) were "industrial ground-water monitoring." Sixteen of the 28 had multiple uses.

SOURCES OF WATER QUALITY DATA FOR THE GALLUP SANDSTONE

This study used published and unpublished data to show chemical quality of water in the Gallup Sandstone. Table 1 lists the wells and springs reviewed, their identification number(s), distances from the UNC site, reported TDS concentrations, and references. Data was taken from publications of the Arizona State Land Department, the Navajo Tribe, the U.S. Geological Survey and the New Mexico State Engineer and others (Table 1).

Six ground-water monitoring wells installed by UNC in Sec. 36, T17N, R16W were included in the list of background wells to show existing water quality in the Gallup Sandstone at the UNC site. While contamination is believed to have reached the Navajo Reservation north

Table 1. Gallup Sandstone wells of northwest New Mexico, showing locations, distances from a uranium mill tailings site, major uses and total dissolved solids concentrations (abbreviations in notes section at end of table).

USBIA, Navajo Tribal No., or local name	USGS Well Identification No.	Quadrangle Location No.	Appx. Dist.* from 16.16.2	Use(s) of Water	TDS (mg/l)	References
12R-98		33-4.90x9.45	69N (111.3)		954.	Th6
12R-100		33-2.15x11.30	67N (108.1)		992.	Th66
12R-148		18-8.20x15.95	80.5N (129.8)		912.	Th66
12T-564		32-10.60x10.60	65N (104.8)		3170.	Th66
14K-300		107-1.45x2.90	16W (25.8)	D,PS,S	464,2580.	Da63, Ki63, Ra83
14K-313		106-3.85x5.70	4W (6.25)	D,S	1390.	Da63, Fr81, Ki63, LI80, Ra83
14M-1		87-10.75x15.55	14NW (22.6)	D,I,S	366.	Da63, Ki63, Ra83
14N-102		87-12.0x16.45	14.75NW (23.8)	D,S	1020.	Da63, Ki63, Ra83
14T-501		107-1.20x3.00	16.5W (26.6)	D,S	517.	Li80, McG66, Ra83
14T-505		107-7.40x0.0	23.25NW (37.5)		388.	Li80
14T-514		88-1.20x10.05	21.5NW (34.7)		362.	Th66
14T-531		107-app:1.6x3.1	16.5W (26.6)		452.	Ra83
15B-2		105-1.45x2.0	13.75NE (22.2)			Ki63
15K-335		104-8.65x5.20	20E (32.3)		681.	Ki63
15T-303 (14K-303**)		105-12.87x5.47	2.5NE (4.0)	S	2624.	Fr81, NMEID file data
15T-505	16.11.17.4322	104-1.10x9.90	27.5E (44.4)	D	1107.	Fr81, Li80, McG66, Th66
15T-513		103-9.25x13.10	34E (54.8)		1080.	Th66
15T-529		86-3.95x17.20	12.5NE (20.2)			Fr81, Li80
16A-260	15.19.11	107-4.25x14.85	19W (30.6)	D,S	554.	Da63, Li80
16K-321	14.18.8.43	123-0.35x3.40	21SW (33.9)	D,S	1010.	Da63, Li80, Th66
16K-338	14.19.17.14	123-8.75x5.50	27.5SW (44.4)	D,S	560.	Da63, Li80
16T-339 (16K-339)		107-8.55x16.70	24.5SW (39.5)	D,S	613.	Da63, Ki63, Li80, Th66
16T-530		123-2.30x8.40	25.5SW (41.1)		522.	Th66
18K-329		107-12.75x3.95	27.5W (44.4)		424.	Ki63, Li80, Th80
18K-551		108-app:0.5x6.0	29W (46.8)		455.	Ra83
	12.18.28.44		30SW (48.4)		254.	Li80
	14.18.9.3		18SW (29.0)		340.	Li80
	14.18.30.14	123-1.30x4.10	21SW (33.9)		454.	Ki63, Li80
	14.19.11.41		23SW (37.1)			Li80
	14.19.22.34		25SW (40.3)		343.	Li80
	15.10.4.1311		34E (54.8)		1110.	Fr80
	15.18.8.32		17SW (27.4)		1250.	Li80
	15.18.9.31		16.5SW (26.6)		603.	Li80
(City of Gallup)	15.18.13.1134a		14SW (22.6)	PS	854.	Da63, Li80
(City of Gallup)	15.18.13.1144		14SW (22.6)	PS	792-968.	Da63, Sh71
(Shamrock Oil Co. No.1)	15.18.13.324	106-11.15x15.25	14SW (22.6)	PS	DR(4140.)	Da63, Ki63, Sh71
(City of Gallup)	15.18.14.222	106-11.85x14.95	14.5SW (23.4)	PS	808.	Da63, Sh71
(City of Gallup)	15.18.14.2244	106-12.15x14.90	14.5SW (23.4)	PS	807.	Da63, Li80
(City of Gallup)	15.18.24.230		15SW (24.2)	D	507.	Sh71
	15.18.30.3232	107-	19SW (30.6)		454.	Ki63, Li80
	15.19.24.43	107-	19.5SW (31.45)		294.	Li80
	15.20.6.33		29WSW (46.8)		484.	Li80
	16.4.36.2321		76E (122.6)			Li80
	16.5.19.414		62E (100.0)	S	2190.	Co68
	16.7.26.221		66E (106.45)	S		Co68
	16.20.3.3		25W (40.3)		1238.	Li80
	16.20.9.4.		26W (41.9)		680.	Li80
	17.12.33.244		22E (35.48)		654.	Fr81
	17.16.36. (TWQ-140***)		<1N (<1.6)	IM	971.	NMEID file data
	17.16.36. (TWQ-141)		<1N (<1.6)	IM	965.	NMEID file data
	17.16.36. (TWQ-142)		<1N (<1.6)	IM	1053.	NMEID file data
	17.16.36. (TWQ-143)		<1N (<1.6)	IM	957.	NMEID file data
	17.16.36. (TWQ-144)		<1N (<1.6)	IM	1058.	NMEID file data
	17.16.36. (TWQ-147)		<1N (<1.6)	IM	1044.	NMEID file data
	21.13.6.1121		33.5NNE (54.0)		1600.	Li80
	24.13.9.1343		44NNE (70.98)			Li80
		105-1.80x1.68	13.75NE (22.2)	D,S	427-811.	Da63, Fr81, Ki63, Li80
		105-2.25x3.01	12.5NE (20.2)		780.	Fr81, Li80
		105-2.50x3.27	12NE (19.4)		400.	Li80
		105-2.65x1.42	12.5NE (20.2)		576.	Fr81
		105-3.40x1.50	12NE (19.4)			Li80
		105-5.02x2.74	10NE (16.1)		125.	Li80
		108-0.29x5.88	28.5W (45.97)		353.	Li80
		108-0.80x6.15	29.5W (47.6)		398.	Li80
		108-1.00x5.94	29.5W (47.6)		341.	Li80
Alison, N.M.		107-2.05x15.55	19SW (30.6)	NR	738.	Da63, Ki63
Blackwater Spring		49-13.20x0.30	60N (6.8)		879.	Th66
Munoz-1	15.18.	106-	14SW (22.6)	T	413.	Me70
Tohatchi Boarding Sch.		88-0.6x9.6E	20.5NW (33.1)	D	209.	Li80
Vernon Washburn Spring		49-12.65x2.85	57N (91.9)		2080.	Th66

Notes: * -- Distances and directions given first in miles and second (in parentheses) in kilometers. ** -- NMEID and United Nuclear Corp. (UNC) records list well 15T-303 as 14K-303 (R. Raymondi, pers. comm., Jan. 5, 1984). *** -- UNC monitoring well numbering system. Use categories: D (domestic), I (irrigation), IM (industry ground water monitoring), NR (no record), PS (public supply), S (stock watering), T (test well). TDS concentrations for selected wells also found in fig. 1. DR -- Anomalous data rejected from calculations of ranges and mean concentrations in Table 2. References: Co68 (Cooper and John 1968), Da63 (Davis et al., 1963), Fr81 (Frenzel et al., 1981), Ki63 (Kister and Hatchett, 1963), Li80 (Link and Kelly, 1980), McG66 (McGavock et al., 1966), Me70 (Mercer and Cooper, 1970), NMEID file data (New Mexico Environmental Improvement Division facility monitoring reports), Ra83 (Raymondi and Conrad, 1983), Sh71 (Shomaker, 1971), Th66 (Thiele, 1966).

of the tailings site (a distance of approximately 3,100 ft [945.1 m]) in Zone 3 of the Upper Gallup Sandstone (R. Raymondi, New Mexico Environmental Improvement Division, memorandum, Oct. 24, 1983), Zone 1 wells at the reservation boundary are not believed to have been affected by seepage flows. We note, however, that these six Zone 1 wells lie within a few hundred feet of the Pipeline Canyon Arroyo (fig. 2) and may be influenced by recharge of fair-to-good quality mine-discharge water through an intervening alluvial ground-water system (Raymondi and Conrad (1983).

RANGES AND MEANS OF MAJOR CONSTITUENTS IN GALLUP SANDSTONE WATER

We recorded all available chemical concentrations for major constituents (cations and anions and some metals) for each of the wells listed in Table 1; that data is available from the authors. Table 2 summarizes this data and reports ranges, mean concentrations and standard deviations for all wells at various distances from the UNC site. The period of record, the number of wells, and the number of samples used for calculations for each distance category are reported. Constituents listed are specific conductance, pH, TDS, sulfate, chloride, nitrate as nitrogen, iron, calcium, magnesium, potassium, sodium and bicarbonate.

The data show that Gallup Sandstone ground-water quality is good for all distance Categories except the 1-to-5-mile range. The ranges shown in Table 2 generally agree with those of Thiele (1966, p. 52), Shomaker (1971, p. 82), and Cooley et al. (1969, p. A52).

To illustrate the comparisons, we use mean TDS shown in part in figs. 1 and 2. The six Sec. 36 monitoring wells averaged 1,017.1 mg/1 TDS on a range of 860-1,691 mg/1, with a low standard deviation indicating consistent water quality. TDS 5 to 15 miles and 15 to 20 miles away was 658.6 and 750 mg/1, ranging from 125-1,020 mg/1 and 2942580 mg/l. Standard deviations showed consistency in quality in the 5to-15-mile zone and variability in the 15-to-20-mile zone.

Table 2 shows water quality deterioration with increasing distance from Gallup Sandstone recharge zones. Water quality is particularly poor toward the center of the Basin and particularly good near Gallup. Fig. 1 shows BS concentrations of selected wells to demonstrate this point. Despite including the poorer quality water away from Gallup, however, the mean concentration of TDS in wells more than 20 miles from the site remains under 1,000 mg/1 and the standard deviation is less than the mean concentration (858.97 mg/1 +626.6 mg/1).

Of the 65 samples for which IDS concentrations were reported, 48 were under 1,000 mg/1, 12 were between 1,000 and 2,000 mg/1, and five were greater than 2,000 mg/l. Thus, approximately 74 percent of all reported TDS concentrations in Gallup Sandstone wells were under the 1,000-mg/1 standard of the state regulations. If two anomalously high, and therefore rejected, TDS concentrations are included, 72 percent of samples reporting TDS concentrations remain under 1,000 mg/1, while the number of samples greater than 2,000 mg/1 increases from about 8 percent to about 10 percent.

Table 2. **Ranges and means of major chemical constituents in ground water in the Gallup Sandstone at distance from the United Nuclear Corp. Church Rock Uranium Mill, Sec. 2, T16N, R16W, N.M.P.M. (all concentrations in milligrams per liter except as noted)[a].**

Range/Mean Concentrations	Per. of Record	No. of Wells	No. of Samples	Spec. Cond. (umhos)	pH (units)	TDS	SO4	Cl	NO3-N	Fe	Ca	Mg	K	Na	HCO3
				Wells within 1 mi (1.6 km) of 16.16.2.											
Ranges of concentrations for all reported data	1980-83	6	35	825.- 1970.	6.9- 8.1	860.- 1691.	198.2- 798.	15.9 22.8	<.005- 1.22	<.01- .92	.56- 140.	12.- 71.	2.3- 5.95	276.4- 341.8	233.8- 351.
Mean concentrations and standard deviations				**1125.97** ±226.8	**7.6** ±.3	**1017.1** ±140.95	**523.0** ±109.3	**19.4** ±1.8	**.54** ±.56	**.14** ±.19	**45.97** ±36.0	**20.4** ±19.0	**3.9** ±2.9	**311.7** ±33.0	**274.1** ±45.2
				Wells 1 mi (1.6 km) to 5 mi (8.1 km) from 16.16.2.											
Ranges of concentrations for all reported data	1955-82	2	9	1780.- 3120.	7.2- 8.1	1390.- 3170.	840.- 2160.	11.- 16.	.0- .6	.0	160.- 396.	89.- 154.	5.07- 6.6	72.- 171.4	209.9- 300.
Mean concentrations and standard deviations				**2450.** ±947.5	**7.7** ±.3	**2469.8** ±636.3	**1597.** ±472.3	**12.96** ±2.1	.22 ±.26		283.8 ±112.0	**118.8** ±30.1	**5.8** ±1.1	121.1 ±49.7	**259.4** ±42.4
				Wells 5 mi (8.1 km) to 15 mi (24.2 km) from 16.16.2.											
Ranges of concentrations for all reported data	1944-77	16	20	565.- 1670.	7.3- 8.8	125.- 1020.	32.- 514.	3.- 153.	.0- 11.	.02- 8.	1.- 148.	.5- 56.	2.- 10.9	6.- 270.	135.- 458.
Mean concentrations and standard deviations				**1055.3** ±326.0	**7.9** ±.4	**658.6** ±260.2	**281.4** ±144.9	**16.4** ±34.8	**.69** ±.53	**1.49** ±2.7*	**52.4** ±50.95	**17.49** ±17.3	3.5 ±2.8*	165.6 ±86.49*	283.3 ±90.
				Wells 15 mi (24.2 km) to 20 mi (32.3 km) from 16.16.2.											
Ranges of concentrations for all reported data	1953-68	11	12	645.- 1120.	7.6- 8.8	294.- 2580.	59.- 310.	4.5- 96.	.0- .8	.01- .02	1.2- 42.	.0- 22.	7.7	87.- 997.	182.- 752.
Mean concentrations and standard deviations				**885.8** ±229.8	**8.3** ±.49	**750.** ±625.1	**152.** ±79.98	**26.45** ±28.8	.23 ±.27	**.02** ±.01*	11.49 ±12.7	4.8 ±6.4	7.7	329.6 ±375.7*	300.3 ±146.7
				Wells greater than 20 mi (32.3 km) from 16.16.2.											
Wells and springs north of Sheep Springs, N.M.	1948-64	6	6	2160. ±1242.3	7.95 ±.2	1497.8 ±939.4	675.3 ±565.1	108.8 ±99.6	.95 ±1.4		34.8 ±33.7	14.7 ±14.5		467.7 ±341.8	361.7 ±139.3
Wells east and northeast of Crownpoint, N.M.	1974-78	9	12	1618.9 ±609.9	7.8 ±.4	1227.3 ±442.7	776.8 ±565.8	60.4 ±106.3	.3 ±.56	.09 ±.13	73.9 ±47.99	22.2 ±13.2	3.2 ±1.3	316.3 ±222.8	294.45 ±118.3
Wells south, west and north of Gallup, N.M.	1952-73	20	21	858.2 ±353.45	8.3 ±1.0	502.1 ±247.2	116.9 ±83.2	15.5 ±16.3	.7 ±1.1	.07 ±.06	40.3 ±20.8	9.8 ±5.49	12.5 ±25.4	123.45 ±106.98	299.1 ±95.4
Ranges of concentrations for all wells >20 mi	1948-78	35	39	410.- 4310.	7.- 11.7	209.- 3170.	6.2- 2322.	2.- 215.	.0- 3.7	.0- .32	1.2- 140.	.3- 39.	.8- 70.	37.- 1040.	145.- 587.
Mean concentrations and standard deviations for all wells >20 mi				**1524.45** ±901.1	**8.1** ±.8	**858.97** ±626.6	**393.5** ±484.7	**42.2** ±75.1	**.63** ±.99	.08 ±.1*	**48.1** ±36.3	**13.9** ±11.2	**7.7** ±18.0*	258.98 ±250.7*	**306.8** ±108.1

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[a] -- Data based on 115 samples from wells listed in Table 1; * -- Total Fe and K + Na concentrations not calculated in ranges or means.

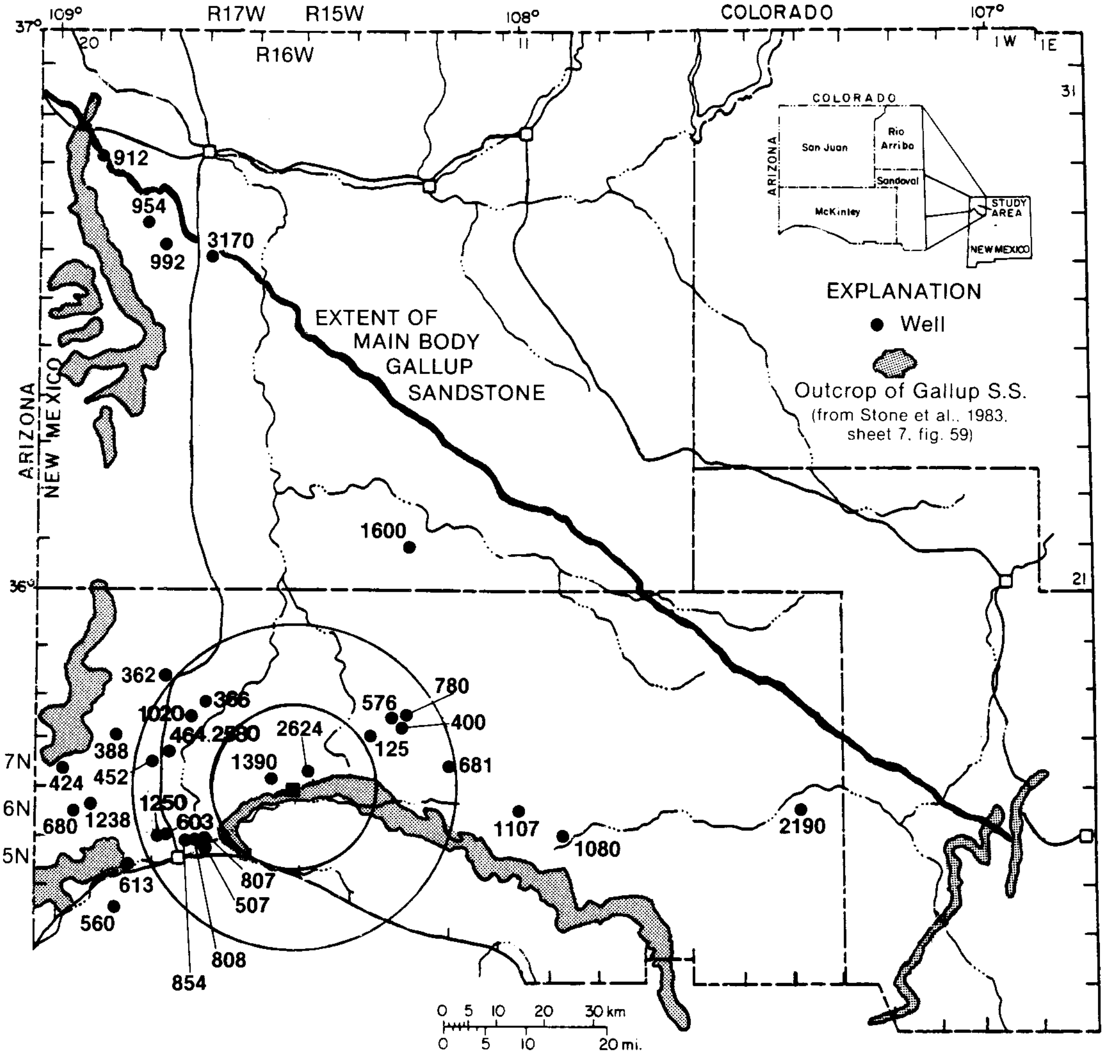

Figure 1. Study area in northwest New Mexico showing total dissolved solids concentrations (in mg/l) in Gallup Sandstone wells and their proximity to a uranium mill tailings facility in Sec. 2, T16N, R16W. Wells used to derive background water quality that are within 1 mile of the facility are listed in Table 1 and shown in fig. 2 (base map modified from Stone et al., 1983, fig. 1).

CHARACTERIZATION OF CONTAMINATED GROUND WATER AT THE UNC SITE AND COMPARISON OF SITE GROUND WATER TO BACKGROUND AND STATE STANDARDS

Water quality in Zones 1 and 3 of the Upper Gallup Sandstone and in the alluvium of Sec. 2, T16N, R16W, and Sec. 36, T17N, R16W, is portrayed in Table 3, columns 7-13. Reported here are recent samples from six contaminated monitoring wells in and around the UNC evaporation ponds (see fig. 1). We have assembled water quality data over time for approximately 25 percent of the more than 250 site monitoring wells, but chose to report only a small amount of that data here because of space limitations. The concentrations for most major constituents, metals and

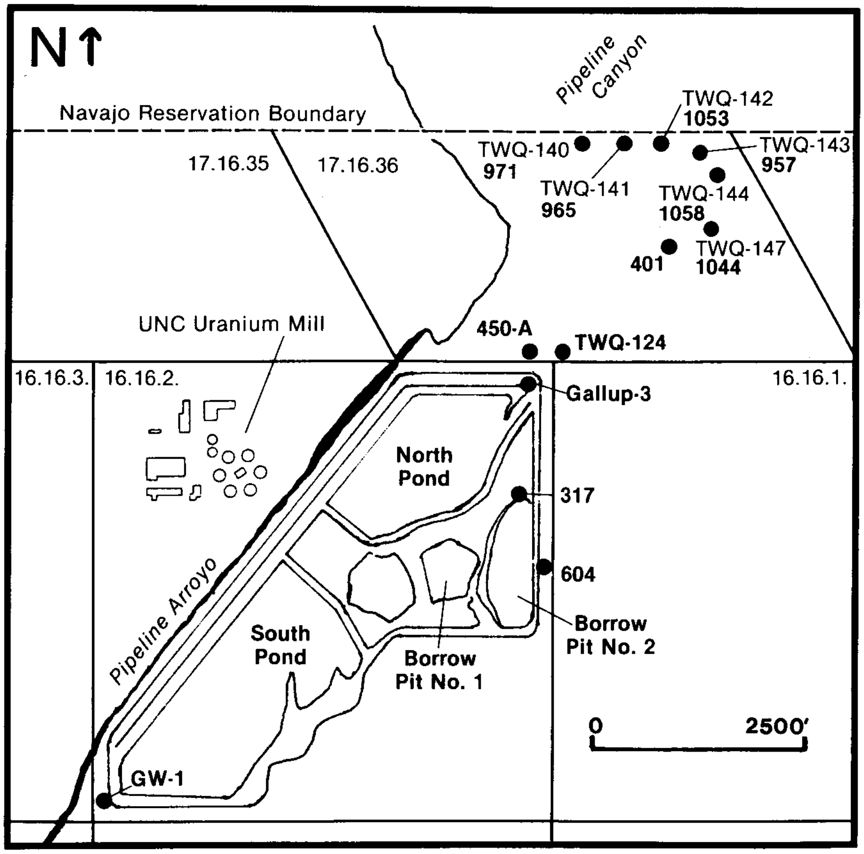

Figure 2. Map of United Nuclear Corp. uranium tailings facility, showing evaporation ponds, seven site monitoring wells (see Table 3 for chemical analyses), and six Upper Gallup Sandstone (Zone 1) wells used to derive background water quality. Sec. 36 wells used in the background study are shown with total dissolved solids concentrations (in mg/l) and are listed in Table 1.

radionuclides reported here are consistent with the variability of chemical quality in the majority of monitoring wells closest to the UNC site. Table 3 reports the chemistry of three evaporation ponds in 1979, 1980, and 1983. The data show the effects of neutralization of ponded waste liquids and show that nearby monitoring wells exhibit chemical qualities consistent with tailings liquors.

Table 3 shows vividly that most major constituents, some metals, and the radionuclide thorium-230 are grossly elevated when compared with the background concentrations reported in Table 2 and New Mexico groundwater standards shown in Table 3, column 14. Some exceedances for major indicators such as TDS and sulfates are on the order of tens to thousands of times background. Compared with the fair water quality of well 15T-303, the closest "background" well greater than a mile from the UNC site, tailings-influenced water quality in Sec. 2, T16N, R16W, and Sec. 36, T17N, R16W, remains elevated, at least for water in Zone 3 of the Upper Gallup Sandstone.

From the standpoint of health concerns, data for nitrates, thorium-230, aluminum, manganese and arsenic, among others, around the tailings facility are particularly disturbing. Development of formerly high-

Table 3. Chemical quality of evaporation pond liquids and contaminated ground water, United Nuclear Corp. Church Rock Uranium Mill, Sec. 2, T16N, R16W, and comparison to New Mexico ground water standards (concentrations in milligrams per liter except as noted).

	CHEMICAL QUALITY: EVAPORATION PONDS[a]					CHEMICAL QUALITY: SELECTED SITE GROUND WATER MONITORING WELLS[b]							
	BP-1	BP-2	BP-2	N-Pond	N-Pond	TWQ-124	Gallup-3	604	450-A	317	401	GW-1	**NMWQCC Standards**
Sampling date(s):	11/01/79E	10/03/80E	03/09/83U 08/01/83E	06/20/80U	03/09/83U 03/17/82E	10/25/82E 10/05/82U	08/02/83E	10/25/82E 01/12/83U	10/25/82E 09/28/82U	10/04/82U	08/02/83E 03/03/83U	01/18/83U 04/21/82E	
Major constituents													
Cond. (umhos)	40788.		12300.		4900.	15000.		6500.	9300.	9500.	3790.	4100.	
pH (units)	1.33		4.17	1.5	7.44	2.15	2.25	3.62	2.37	3.5	6.1	6.24	6-9B
TDS	39043.	64820.	16663.	148100.	5058.	28845.	47460.	9234.	18955.	14386.5	6844.	5255.	1000.0B
SO4	28876.	46010.	12001.	144900.	3260.	15165.	27780.	6014.	12543.	10743.4	3961.	2104.	600.0B
Cl	296.8	583.	279.22	104.	89.23	179.8	292.9	47.4	152.1		92.4	223.37	250.0B
NO3-N	2.03		.328		.365	13.1	4.61	22.58	19.	8.6	58.5	164.68	10.0A
NH3	3.32		3.26		1.464	223.	237.	1.36	152.	14.	4.17	1.29	
Ca	544.	570.	495.5		423.	492.	505.	436.	469.	87.4	494.	752.	
Mg	1205.	650.	476.		101.	960.	275.4	1348.	771.	1182.	706.	256.	
K	82.5		64.4		53.	6.82	3.5	12.48	2.73		10.	3.1	
Na	549.7		738.		472.	363.4	536.		271.4		347.	136.	
HCO3			.0		90.09	.0		.0	.0		250.6	739.2	
Metals (add. sampling dates:)			11/15/82EP		11/15/82EP	11/15/82EP	11/15/82EP	11/15/82EP	04/28/81U	04/09/81U	09/10/81U	02/26/81E	
Al	1220.	1740.	59.92	7400.	.06	1450.	2300.	140.	990.	2180.	<.25	<.25	5.0C
As	1.87	2.4	.098	.1	.059	3.9	7.6	.12	2.63	5.2	<.005		0.1A
Ba	.372	.02	.37	.7	.065	.25	.4	.08					1.0A
B		.88	ND	3.7	ND	ND	ND	ND					0.75C
Cd	.014	.12	.011	.23	.004	.04	.03	.004	.06	.11	<.001		0.01A
Cr		1.7	.019	5.5	.045	16.	24.	.012	.86	.94		<.005	0.05A
Cu		1.7	ND	12.	ND	2.09	37.4	.57	1.41	2.6	<.05		1.0B
Co		1.8	.56	5.3	.067	.05	4.7	3.54	1.92	1.15	.296	<.005	0.05C
Fe		12040.	463.	12000.	.052	1500.	3340.	4.	9.8	1417.5	<.1	<.50	1.0B
Pb		.875	.049	15.9	.048	.28	.45	.014	.53	.131	.005	<.005	0.05A
Mn		190.	68.	380.	5.5	78.9	96.4	21.8	70.	60.	2.8	.11	0.2B
Mo	1.659	1.2	.013	18.7	<.001				.19	<.01	1.34	.014	1.0C
Ni		2.2	.37	3.5	.11	20.4	80.5	.7	2.45	1.83	.39		0.2C
Se	.45	.69	<.002	.1	ND	ND	ND	.0014	.35	.032	.021	.066	0.05A
Ag		.07	.002	.07	.002	.013	.018	ND					0.05A
U	11.4	12.7		54.5	3.011*	3.846*	6.19*		2.27*	.50*	.33		5.0A
V	56.63	49.	.14	180.	.06	18.5	34.	.07	16.	28.2	<.01		
Zn	8.25	12.	2.66	49.	.2	15.4	18.	1.32	11.28	12.8	.38		10.0B
Radionuclides (add. sampling dates:)				06/23/80U	03/03/83U	03/03/83U	03/03/83U		03/03/83U	03/03/83U		09/12/80U	
Th-230 pCi/l				25800.	3.34+0.31	32609+600	83298+5829		12915+817	1875+183		26.2	2000.0**
Ra-226	27±8			148.4	8.39±0.75	5.55±0.7	18.86±1.18		3.37±.59	8.85±.84		.4	30.0A
Ra-228				94.2								1.2	
Pb-210				33100.	3.62±2.38	3.28±6.29	9.82±3.36		.02±.06	1.44±2.13		.0	100.0**

Notes and abbreviations: [a]See fig. 2 for evaporation pond locations; BP-1 (Borrow Pit No. 1), BP-2 (Borrow Pit No. 2), N-Pond (North Pond). [b]See fig. 2 for monitoring well locations; monitoring wells identified by their UNC monitoring-system numbers. Screened intervals for site monitoring wells are Upper Gallup Sandstone (Kgu) Zone 3 (TWQ-124 and Gallup-3), Zone 1 (604 and 450-A), Zones 1, 2 and 3 (317 and 401) and alluvium (GW-1). E (NMEID sample), U (UNC sample), EP (U.S. EPA sample). * -- UNC sample, 03/03/83. NMWQCC Standards -- New Mexico Water Quality Control Commission Regulations, Part 3, Sec. 3-103.A. (Human Health Standards), B. (Standards for Domestic Water Supply), and C. (Standards for Irrigation Use). ** -- New Mexico Environmental Improvement Board, "Standards for Protection Against Radiation," Part 4, Appendix A, Table II, Column 2 (for "unrestricted" areas). ND (not detectable).

quality water supplies within 150 to 250 ft of the surface appears to be precluded near the tailings due to the presence these toxic materials.

CONCLUSIONS

This study shows that ground water in the Gallup Sandstone ranges from fair to good quality throughout the San Juan Basin with the best water available near the recharge zones shown in fig. 1. Background water quality compares favorably with New Mexico's ground-water protection standards; 72-74 percent of background TDS concentrations in the Gallup Sandstone are less than the 1,000-mg/1 state standard.

Upper Gallup ground-water chemistry near the UNC mill is grossly distorted when compared with background and state standards. The existence of the tailings facility near an outcrop area in a recharge zone compounds the severity of the contamination problem. Greatly elevated nitrate, arsenic and thorium-230 levels represent potential public health concerns.

ACKNOWLEDGEMENTS

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REFERENCES

Cooley, M. E., Harshbarger, J. W., Akers, J. P., and Hardt, W. F., 1969, Regional hydrogeology of the Navajo and Hopi Indian Reservations, Arizona, New Mexico and Utah: U.S. Geological Survey, Prof. Paper 521-A.

Cooper, J. B., and John, E. C., 1968, Geology and ground-water occurrence in southeast McKinley County, New Mexico: New Mexico State Engineer, Tech. Rept. 35.

Davis, G. E., Hardt, W. F., Thompson, L. K., and Cooley, M. E., 1963, Geohydrologic data in the Navajo and Hopi Indian Reservations, Arizona, New Mexico, and Utah, pt. I -- records of ground-water supplies: Arizona State Land Department, Water Resources Rept.12-A.

Frenzel, P. F., Craigg, S. D., and Padgett, E. T., 1981, Preliminary data report for the San Juan Basin-Crownpoint Surveillance Study: U.S. Geological Survey, Open-file Rept. 81-484.

Hiss, W. L., 1975, Evaluation and proposed study of potential groundwater supplies, Gallup area, New Mexico: U.S. Geological Survey, Open-file Rept. 75-522.

Kister, L. R., and Hatchett, J. L., 1963, Geohydrologic data in the Navajo and Hopi Indian Reservations, Arizona, New Mexico, and Utah, pt. II -- selected chemical analyses of the ground water: Arizona State Land Department, Water Resources Rept. 12-B.

Link, R. L., and Kelly, T. E., 1980, Aquifers associated with strippable coal, San Juan Basin, New Mexico: prepared for Mining and Minerals Division, Energy and Minerals Department, State of New Mexico, by Geohydrology Associates, Inc., Albuquerque, New Mexico.

McGavock, E. H., Edmonds, R. J., Gillespie, E. L., and Hal penny, P. C., 1966, Geohydrologic data in the Navajo and Hopi Indian Reservations, Arizona, New Mexico, and Utah, pt. I-A, supplemental records of ground-water supplies: Arizona State Land Department, Water Resources Rept. 12-E.

Mercer, J. W., and Cooper, J. B., 1970, Availability of ground water in the Gallup-Tohatchi area, McKinley County, New Mexico: U.S. Geological Survey, Open-file Rept.

New Mexico Environmental Improvement Division, 1976-1983, Ground-water quality monitoring files for United Nuclear Corp. Northeast Church Rock Uranium Mill, Ground Water Quality and Hazardous Waste Bureau.

New Mexico Water Quality Control Commission, 1982, New Mexico Water Quality Control Commission Regulations, rev. Sept. 20, 1982.

Raymondi, R. R., and Conrad, R. C., 1983, Hydrogeology of Pipeline Canyon, near Gallup, New Mexico: Ground Water, v. 21, no. 2.

Shomaker, J. W., 1971, Water resources of Fort Wingate Army Depot and adjacent areas, McKinley County, New Mexico: U.S. Geological Survey, Open-file Rept. MK-32.

Shuey, C., 1982, Accident left long-term contamination of Rio Puerco, but seepage problem consumes New Mexico's response: Mine Talk (Southwest Research and Information Center), v. 2, nos. 1-2.

Stone, W. J., Lyford, F. P., Frenzel, P. F., Mizell, N. H., and Padgett, E. T., 1983, Hydrogeology and water resources of San Juan Basin, New Mexico: New Mexico Bureau of Miners and Mineral Resources, Hydrologic Rept. 6.

Thiele, H. J., 1966, Navajo water resources, supplies and management, and the proposed Navajo Tribal Water Authority (NTWA): prepared for Navajo Tribal Council.

OIL-FIELD BRINE CONTAMINATION - A CASE STUDY, LEA CO., NM

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ABSTRACT

Salt-water disposal practices in the Moore-Devonian oil field near Caprock, NM produced a plume of contamination approximately one mile long in the Ogallala aquifer near Caprock, NM. Maximum chloride concentrations are nearly 26,000 mg/l. The plume heads in the vicinity of an abandoned brine pit and an operating salt-water disposal well which injects brine underground at a depth of about 10,000 feet. There are also numerous pipelines, operating oil wells, and extensive areas scarred from brine spills. A court of law found that the abandoned pit and the injection well contributed to the contamination problem.

Ground-water monitoring near injection wells is not required by State regulation; however, such observation wells emplaced when injection begins and monitored routinely would provide data necessary to protect fresh water resources. In areas of multiple potential sources of seepage, ground-water monitoring may also protect owners and operators of disposal facilities from liability.

INTRODUCTION

The Ogallala aquifer is the sole source of potable ground water in much of southeastern New Mexico. The Ogallala is composed mostly of unconsolidated sand and gravel, and well yields are high. The availability of such an abundant supply of fresh ground water at shallow depths makes possible large-scale irrigated agriculture. In parts of eastern New Mexico this aquifer is underlain by oil reservoirs. Large quantities of brine are often produced along with oil.

The purpose of this article is to briefly describe a case of contamination of the Ogallala aquifer caused by brine seepage from oil-field activities, and to discuss existing legislation designed to protect aquifers from underground injection. It is not our intent to focus on one possible source of contamination or another, nor do we want any personal bias to be read into our description of the case study; instead we want to use this example to demonstrate that ground-water monitoring could be an effective addition to salt-water disposal practices and regulations. Thus, we have omitted discussion of technical details which, although important, do not pertain directly to the question of ground-water monitoring near salt-water disposal wells.

SITE DESCRIPTION

The study area is located in southeastern New Mexico, about 50 miles east of Roswell, just south of Caprock in northern Lea County. The topography is nearly flat, but slopes very gently eastward. Native vegetation consists mostly of sparse grasses. The mean annual precipitation is about 15 inches (38 cm) (Ash, 1963). The Ogallala Formation underlies the area and is about 100 feet (30 m) thick. The upper 20 feet (6.1 m) contains caliche which appears highly fractured in outcrops. The middle section of the Ogallala consists mostly of sand, and the lower 5 to 20 feet (1.5 to 6.1 m) contains sand with gravel in most parts of the study area. Ground water generally flows to the southeast, but the water table is influenced by irrigation pumping (Figure 1).

The Ogallala Formation was deposited during the Late Tertiary by ancestral streams from mountains to the west. The streams cut channels into underlying shale and claystone of the Triassic Chinle Formation, forming an unconformity with a very irregular surface. The very low permeability of the Chinle, also referred to as "the redbeds," makes an excellent hydraulic barrier at the base of the Ogallala. The Chinle Formation is approximately 1600 feet (490 m) thick in this area (Sweeney et al., 1960). Underlying the Chinle is a thick sequence of Paleozoic sedimentary rocks, many of which bear hydrocarbons. Notable among these is a Devonian dolomite approximately 10,000 feet (3000 m) below land surface. Within the study area this oil-bearing formation is called the Moore Devonian Pool.

BRINE CONTAMINATION

In the 1950's, oil wells were drilled at approximately one-quarter mile (400 m) intervals in the Moore Devonian Pool. The proportion of saline water produced with the oil gradually increased with continued development. From about January 1953 to May 1958, approximately 752,000 barrels (119,500 m^3) of produced salt water were disposed into an unlined surface pit (Figure 1) in the northeast corner of section 23 (Runyan 1978a). The State banned the use of pits for saline water disposal in 1969, because of associated wide-spread problems of aquifer contamination. To handle the produced saline water in the Moore Devonian field, an oil well in the southwest part of section 15 (Figure 1) was converted to a salt-water disposal well. From 1966 to 1972 approximately 20 million barrels of salt water were collected from the Moore Devonian field and injected through this well, designated BO-4, back into the Devonian strata (Evelyn Downs, personal communication, N.M. Oil Conservation Div. [NMOCD], 1984). In 1972, it was discovered that the BO-4 injection well was so corroded that a repair of the well was not practical; the well was plugged and abandoned. The oil well one-

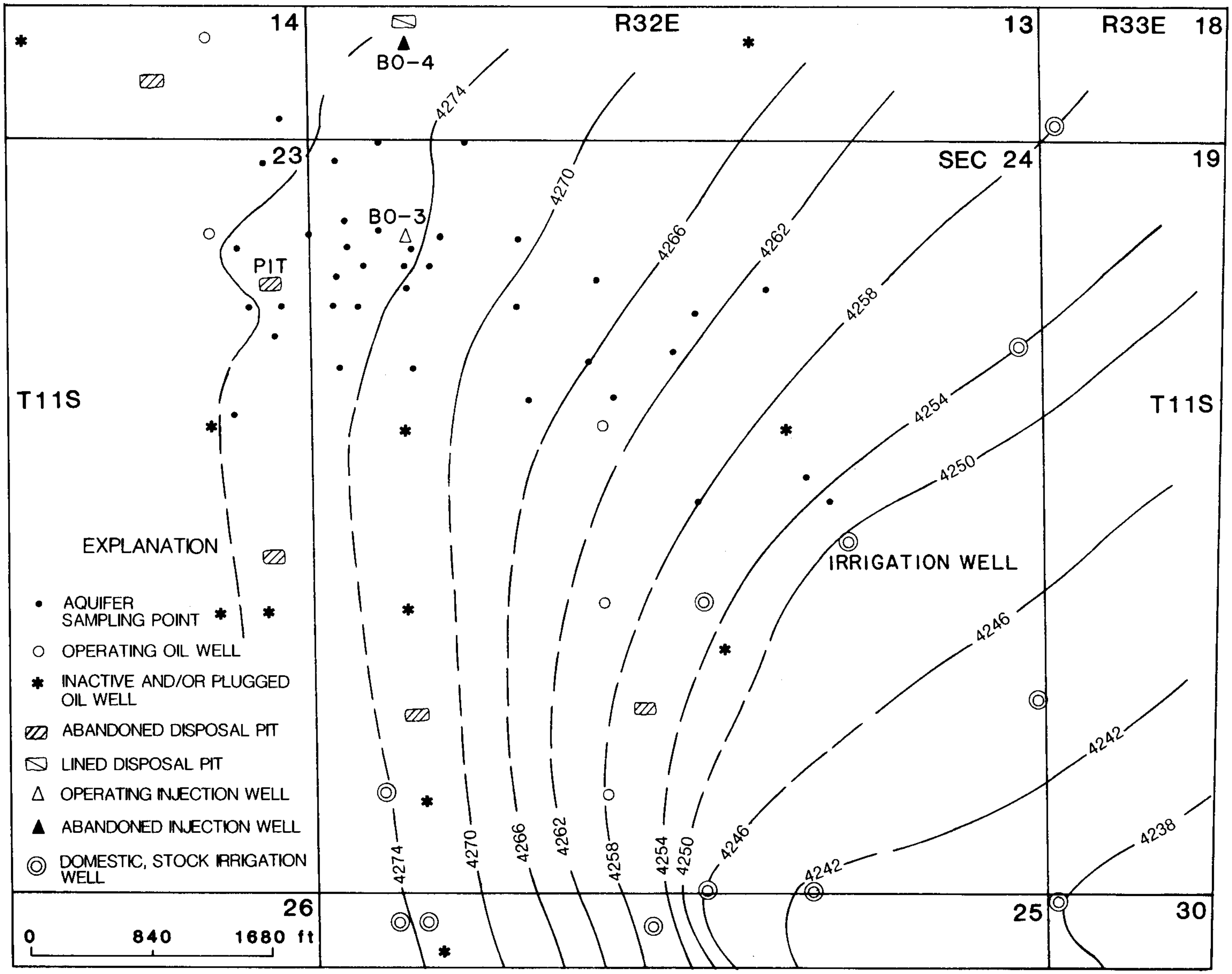

Figure 1. Water table contour map May 27, 1978 and well locations (modified from S.E. Galloway, NM State Engineers Office, Roswell)

quarter mile to the south, B0-3, in the northwestern corner of section 24, was then converted to a salt-water disposal well (Figure 1). Construction details of the converted oil well BO-3 are given in Figure 2; these are essentially the same as B0-4. From October 1972 through July 1977, approximately 20 million barrels of salt water were injected through BO-3 into the Devonian formation at a depth exceeding 10,500 feet (Evelyn Downs, personal communication, NMOCD, 1984).

An irrigation well, completed in 1973, approximately 3900 feet (1190 m) southeast of BO-3 injection well began producing water from the Ogallala with a chloride concentration exceeding 1200 mg/1 in July 1977. Crops irrigated from this well were severely damaged and the bank soon foreclosed on the farm property. There was no evidence of crop damage prior to 1977, and it is assumed that ground water quality at this well was near background, which is less than 100 mg/1 chloride.

Test drilling and sampling from 1977-1978 (Runyan, 1978a,b) showed that there was a plume of saline water which appeared to originate in the northwest corner of section 24 and the northeast corner of section 23 (Figure 3). The highest concentrations of chloride occurred around the BO-3 injection well and southeast of the abandoned brine disposal pit; in places these concentrations were more than 100 times the recommended drinking water standards. The hydraulic gradients indicated in Figure 1 suggest that the probable source of contamination was either the old pit or the BO-3 injection well. Average ground-water flow velocity is on the order of at least a few hundred feet per year, on the basis of hydraulic conductivity and effective porosity data obtained from an aquifer pumping test near BO-3 (Water Resource Associates, Phoenix, written communication, 1982), irrigation well performance data (NM State Engineer Office, Roswell, NM, open file records), and hydro geologic reports (Ash, 1963; Haven, 1966; Nicholson and Clebsch, 1961). Assuming a simple solute-transfer model, saline water from the pit which may have entered the Ogallala shortly after 1958, should have travelled well beyond the irrigation well in question by 1977.

A ground-water monitor well completed in 1978, near the base of the Ogallala, 60 feet southeast of BO-3,was sampled and analyzed. Figure 4 shows that in this well, sampled over a two year period, ground water had a chloride concentration which was generally similar to the injection water, except for the obvious peak. Moreover, the chloride concentration in this observation well was relatively unchanged over nearly a three to five year period when compared with data in Figure 3. Unless there was a subsurface barrier inhibiting saline ground-water movement, or a continuous source of saline water introduced to the aquifer, fresh ground water should have displaced much of the contamination from the vicinity of BO-3.

On the other hand, there is also evidence which suggests

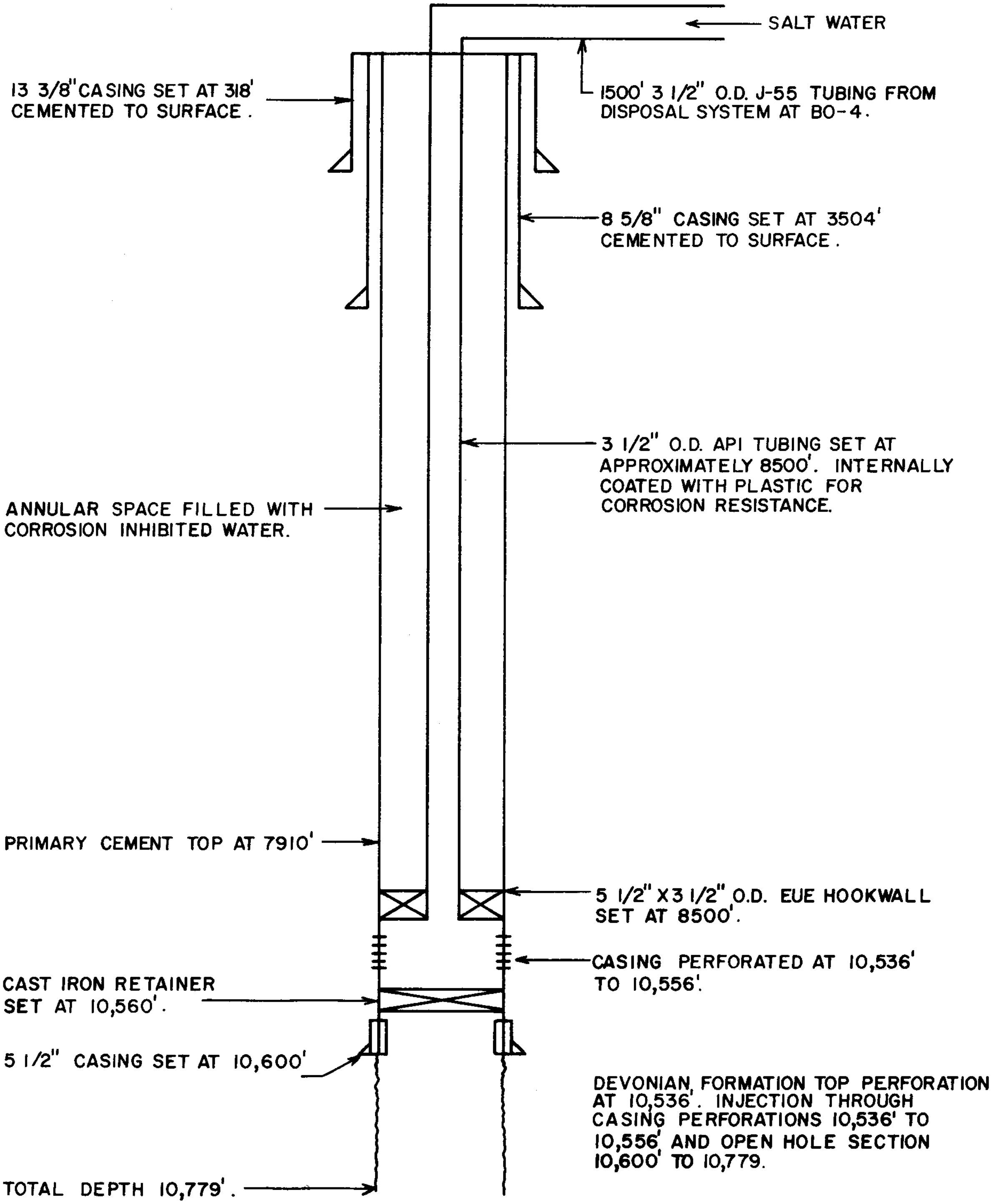

Figure 2. Injection well construction (Modified from Texico, Inc. SWD Well proposal)

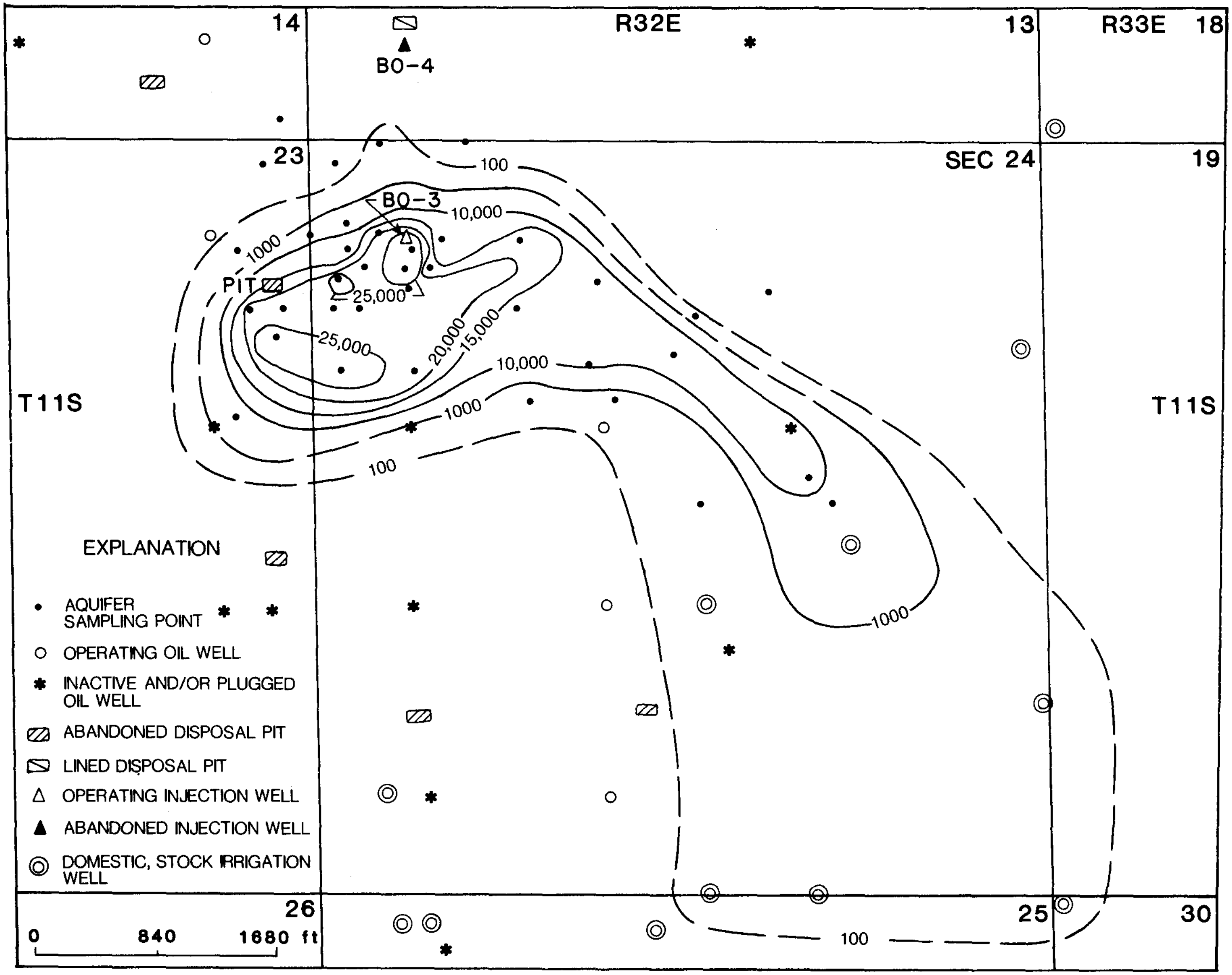

Figure 3. Chloride concentration contour map May 25, 1978 (modified from J. Runyan, NM Oil Conservation Division)

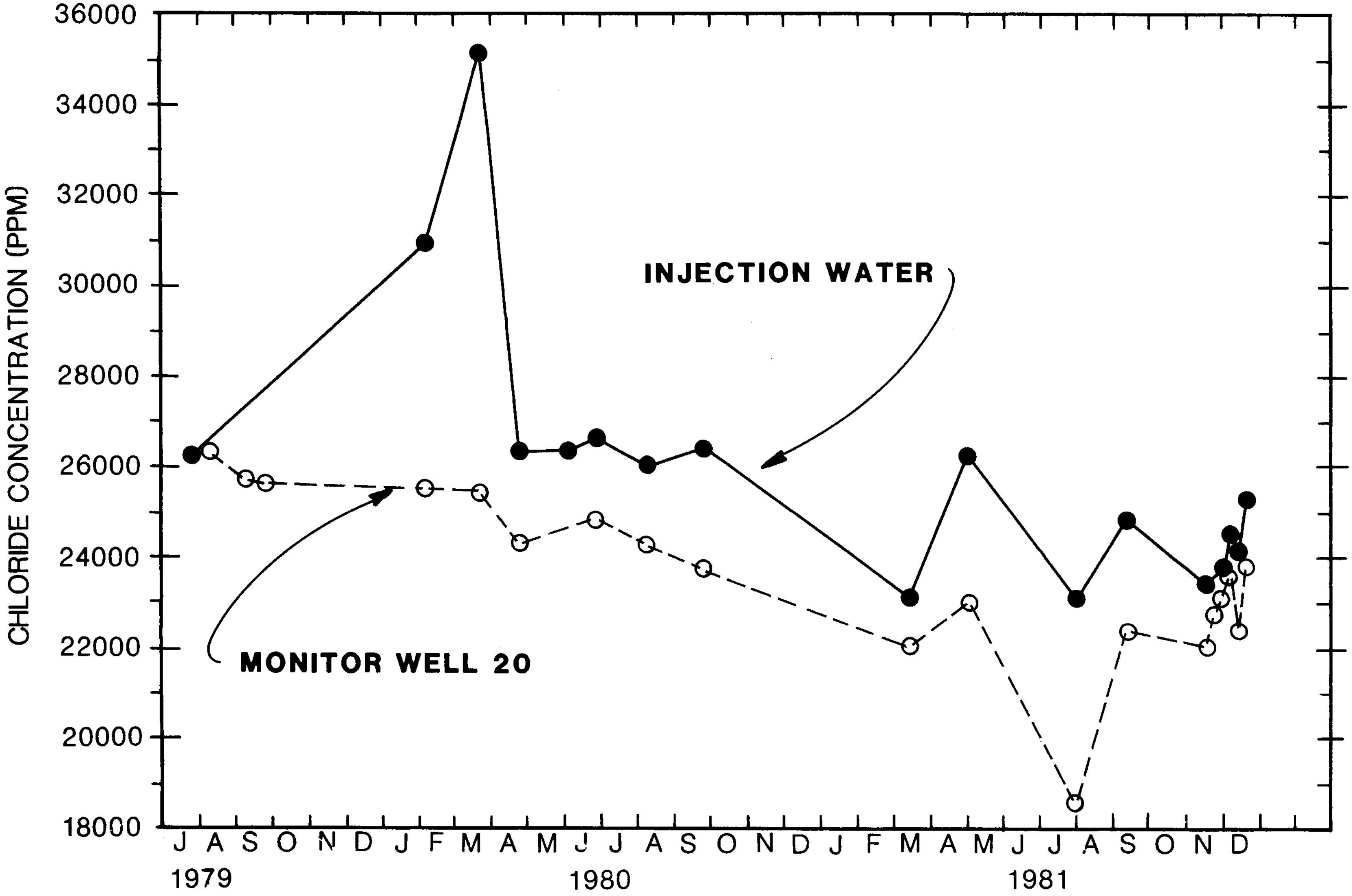

Figure 4. Chloride concentration of injected water and ground water in the Ogallala aquifer. (Analyses by New Mexico Oil Conservation Division)

that BO-3 may not have been leaking. Figure 2 shows that BO-3 was designed to insulate injection fluid from the Ogallala with four steel casings, two of which were cemented to the surface; furthermore, the saline water is being injected nearly two miles below the bottom of the Ogallala. Mechanical integrity tests, which consist of applying and/or monitoring pressure on the casing or injection tubing annuli, were ordered by the N.M. Oil Conservation Division to detect leakage. Radioactive tracer surveys were also conducted. Mr. Richard L. Stamets (OCD, written communication, 1984) indicates that on the basis of "the numerous hearings conducted on this matter before the Oil Conservation Division, the expert witnesses appearing, the expert testimony presented, and the findings of the Commission,... there was no definitive evidence that the salt-water disposal well in question was the source of the contamination."

In 1982, a jury found that both the pit and the injection well contributed to ground-water contamination which reached the irrigation well, on the basis of the above described, and many other, technical issues (Hamilton v. Texaco, US District Court, Santa Fe).

DISCUSSION

In 1981, the OCD assumed responsibility for enforcing the federal Underground Injection Control (UIC) Program which was set forth under the Safe Drinking Water Act (PL 93-523, as amended). According to these regulations, monitoring for Class II injection wells is only required in the injection well unless otherwise stipulated in the permit by the NMOCD. Monitoring essentially consists of a mechanical integrity test at least once every five years; however, since 1978 New Mexico has performed bradenhead tests to check mechanical integrity annually on all salt-water disposal wells in southeast New Mexico (R. L. Stamets, NMOCD, written communication, 1984). According to regulations, the injection well also needs to have facilities available to make measurements of injection and annulus pressure, and monthly injected fluid volume. Other tests may also be required, as ordered by the Director of NMOCD. In reference to the case study of underground injection of saline oil-field water in northern Lea County, no ground-water monitoring in the Ogallala aquifer was required, according to existing regulations. The following discussion will illustrate some of the arguments in favor of ground-water monitoring for the protection of injection well operators and potable ground-water users.

In a typical oil field there are numerous potential sources of saline seepage to shallow aquifers besides injection wells and pits. According to the Petroleum Engineer journal (July, 1967, p. 35) "oil field pollution occurs from ... overflowing waste pits, leakage from broken lines, improperly plugged wells, improperly cased and cemented wells, salt water production from an exploratory core hole, and many other surface and subsurface forms". Many of these potential sources of contamination may be owned and operated by different companies. On the basis of this case study, it might be prudent for the owner of a newly completed salt-water disposal well to install monitor wells to establish baseline conditions before injection begins, as well as a ground-water monitoring-well network surrounding the injection well in order to detect encroaching salt water from other sources. That is, if it is true that the injection well did not ever leak and that all saline water is attributed to the pit, then a few shallow ground water monitor wells drilled prior to converting BO-3 would have shown that the aquifer was already contaminated; this conclusive finding probably would have prevented the costly litigation just described.

Ground-water monitoring of underground injection beneath highly vulnerable and valuable aquifers such as the Ogallala, is crucial to protecting the agricultural economy of the area described in this report. In this case study, 160 acres of farm land was rendered un irrigable, owing to the brine contamination. (However, the present landowner, Mr. Jess Tolton [Caprock NM, personal communication, 1984], reported that he has used an irrigation well located south of the affected irrigation.well, apparently just beyond the plume, for small-scale irrigation.) If one assumes, on the basis of hydrologic evidence, that the injection well actually had a leak when the mechanical integrity tests were performed, then the mechanical integrity tests alone may not be a sufficiently reliable means of protecting aquifers. Part of the problem in interpreting mechanical integrity tests may be in detecting leaks which are quite small. A continuous, slow rate of leakage comprising only a few percent of the total injection rate could have accounted for contamination near BO-3, for example. Without ground-water monitor wells, extensive aquifer contamination is possible during the five-year period between mechanical integrity tests. At rates of groundwater flow on the order of a few hundred feet per year, typical of high permeability aquifers, the number of contaminated agricultural and domestic wells would soon be appreciable. Annual testing of Class II wells in New Mexico which began in 1978, is a step toward minimizing impacts to ground water, and annual mechanical integrity tests on all injection wells (including Class I and III) completed near fresh-water sources should be encouraged. Depending upon the magnitude of the leak and the time when the leak first develops, even annual mechanical integrity tests may not be adequate to avoid extensive brine contamination. It is reported that annual testing in New Mexico reveals about two percent failures (U.S. EPA, 1983, p. 5).

Injection well BO-3 continues to operate as the saltwater disposal well for the Moore Devonian Pool. There has been no effort to date to clean-up the contamination described in this case study, owing in part to litigation which was pending in 1982. More importantly perhaps, the cost of restoring the Ogallala would be quite substantial, inasmuch as the volume of aquifer contamination is on the order of 50 million cubic feet. Valuable irrigated farm land is located east and southeast of the case study area, in the direction of the contaminant plume described in Figure 3. A few shallow ground-water monitor wells at strategic locations near injection wells, drilled at a cost of approximately $15 per foot of depth, would be a relatively inexpensive means of monitoring injection wells and protecting ground-water resources.

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The authors would like to thank the reviewers of drafts of this paper for their comments, in particular Mr. R. L. Stamets and staff of the N. M. Oil Conservation Division. The cooperation of Mr. John Gannon of Texaco Inc., Mr. Paul Hamilton, Mr. Jim Wright and Mr. Sherman "Pinky" Galloway of the State Engineer's Office is also acknowledged.

REFERENCES

Anonymous, 1967, Crack Down on Oilfield Pollution, Petroleum Engineer, July, pp. 33-36.

Ash, S. R., 1963, Ground-water conditions in northern Lea County, New Mexico: United States Geological Survey, Hydrologic Atlas, HA-62, 2 sheets.

Havens, J. S., 1966, Recharge studies in the High Plains in northern Lea County, New Mexico: United States Geological Survey Water Study paper 1819-F, 52 p.

Nicholson, A. Jr., and Clebsch, A. Jr., 1961, Geology and ground-water conditions in southern Lea County, New Mexico: State Bureau of Mines and Mineral Resources, Ground-water Report 6.

Runyan, J. W., 1978a, Paul Hamilton water contamination study Moore Devonian Pool: New Mexico Oil Conservation Division, Report I, 42 p.

Runyan, J. W., 1978b, Paul Hamilton water contamination study Moore Devonian Pool: New Mexico Oil Conservation Division, Report II, 96 p.

Sweeney, H. N., Dietrich, E. S., Dunn, D. A., Fay, R. L., Holt, R. D., McCampbell, W. G., and Stipp, T. F., 1960, The oil and gas field of southeastern New Mexico: Roswell Geological Society, pp. 25-32.

U. S. Environmental Protection Agency, 1983, Mechanical Integrity Workshop, February 1-2, Dallas, Tx, 9 p.

NITRATE CONTAMINATION OF GROUNDWATER IN ALBUQUERQUE

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ABSTRACT

Groundwater contamination by nitrates (NO3) in the Mountain view community of the south valley region of Albuquerque has been noted in domestic wells for over 20 years. Potential sources of the contamination include naturally occurring geological deposits, past disposal of nitrogenous wastes, or current surface activities, either agricultural or on-site wastewater disposal practices. A discussion of the chemistry of nitrogen and related species indicative of groundwater characteristics is presented. This information is then used to examine current knowledge of the contamination problem. Available data include a plethora of recent analytical data as well as limited historic records of groundwater quality. While present data is not sufficient to identify the source of the contamination it appears unlikely that it is the result of on-site wastewater disposal. The evidence against this source includes: 1) the very high levels of NO3 present in many of the wells which is shown to be theoretically unlikely, 2) lack of correlation between NO3 and other parameters normally associated with domestic wastewater, 3) preliminary evidence which may indicate a moving contaminant plume. Better characterization of the problem requires implementation of a groundwater monitoring program along with the development of an understanding of the groundwater flow regime. This knowledge is essential in developing remedial action measures for the problem.

INTRODUCTION

Contamination of groundwater in Albuquerque, NM is a long standing problem that is receiving increasing public attention as a result of several instances of severe and acute problems. The types of contamination include industrial chemicals in municipal water supply wells, leaks of organic liquids from tanks including leakage of gasoline from buried tanks, spills of organic and inorganic liquids onto the land surface and subsequent infiltration into the soil column, and continued seepage from various types of disposal facilities. McQuillan (1983) has provided a summary of groundwater contamination problems in the south valley area of Albuquerque. Unquestionably the largest, in terms of areal extent, and perhaps the most serious of all of the contamination problems in the city are the high nitrate (NO3) concentrations found in the Mountain view community. This problem is also arguably the least understood of all of the groundwater problems in the region.

This paper discusses the history of nitrogen contamination in the Albuquerque area and summarizes previous theories as to its origin. The chemistry of nitrogen and related species is presented and used in the context of evaluating these theories and identifying constraints on the cause of the problem. Finally, a brief discussion is presented on the type of information needed to resolve the question of origination of the problem and potential remedial actions.

BACKGROUND INFORMATION

DESCRIPTION OF THE PROBLEM

A map of the Mountain view community (Figure 1) reveals a relatively isolated community of approximately 3,000 people located on the former alluvial flood plain of the Rio Grande. The area was platted and developed between 1946 and 1949 with a density of slightly over 3 lots per acre. Subsequent land owners have further divided many of the existing lots so that the average density is just under 4 lots per acre. The community is bounded by the Barr Main Canal on the south and west, and the Tijeras Arroyo on the north. The area to the east of 2nd Street consists of light industry and vacant land.

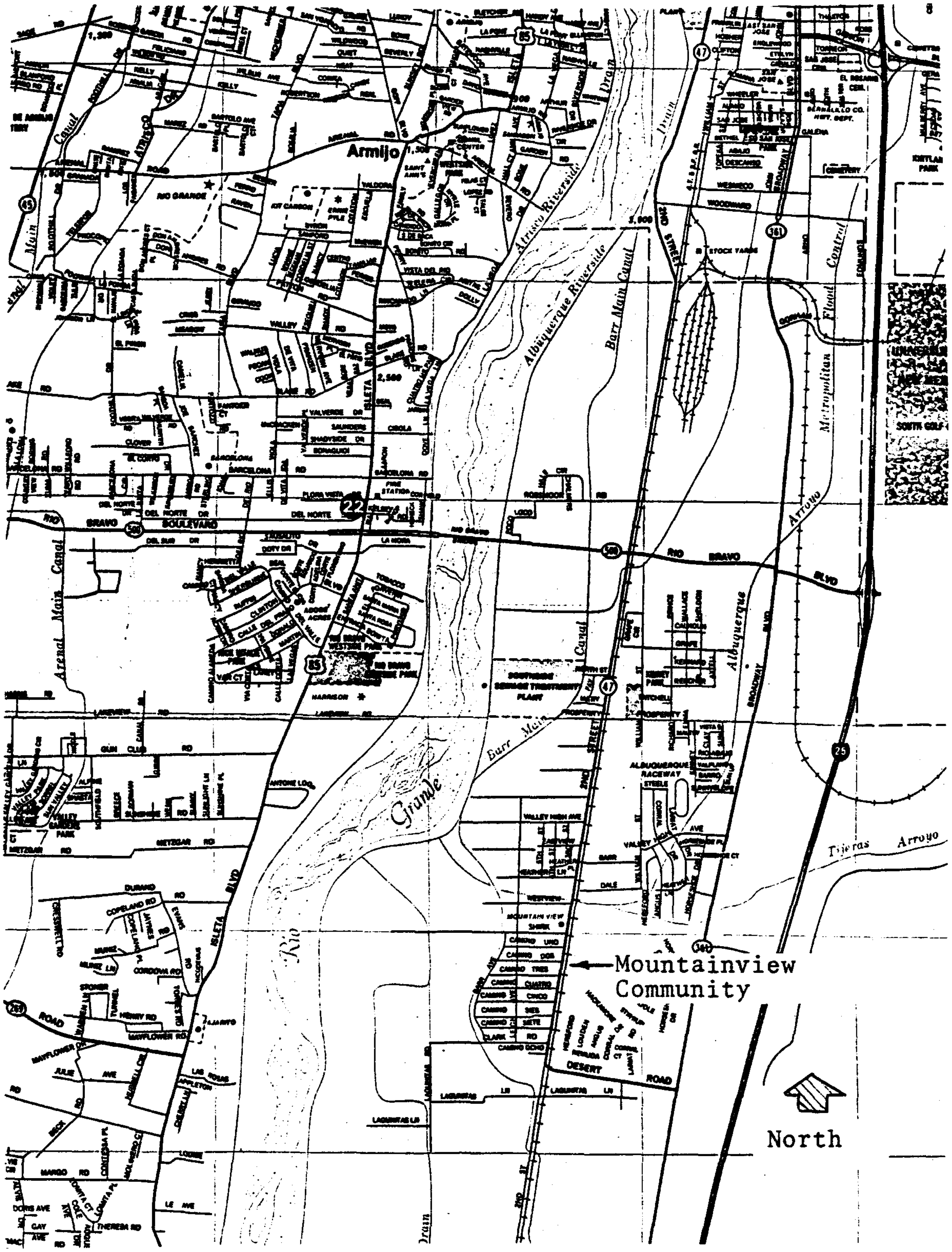
Groundwater quality data for the South Valley prior to 1961 is scarce, however NO5 levels in excess of the drinking water standard of 10 mg N/L as NO$^-$ were documented at this time, appearing in samples taken from the 3 Mountain view Elementary School (NMHED files, 1961). It is apparent that there was a groundwater quality problem many years prior to this based on elevated Total Dissolved Solids (TDS) and electrical conductivity measurements in wells immediately northwest of the present community (Scofield, 1938).

In recent years there have been a number of studies of the groundwater quality in the area, (Alb. City Liq. Waste Div. and Bern. Co. Env. Health Dept., 1978, Bern. Co. Env. Health Dept., 1980, Thomson, 1983). These investigations have found elevated NO3 levels in many of the wells being used for domestic water supply by residents, the highest value reported to date being 522 mg N/L from a well located on Camino Cinco (NMHED files, 1982). Two results of these monitoring programs have been particularly baffling; first is the observation that there is little contamination in areas immediately adjacent to the Mountain view community, and second is the wide variability in NOi concentration neighboring lots within the community. This second observation has made it difficult to display graphically the contaminated zone since it is not possible to reliably construct isopleths of constant concentration. Figure 2 presents results of the Bernalillo County Environmental Health Department study (1980). Investigations to date suggest little or no correlation between elevated NO3 concentrations and well depth, however, due to the uncertain knowledge of well construction it is not possible to exclude such a relation.

One of the difficulties that has been encountered in recent attempts to analyze the problems faced in this area is that most previous studies have only focused on one parameter, NO3, thus it has not been possible to correlate elevated NO3 levels with other parameters. There is, however, one unmistakable conclusion that can be reached and that is that this water resource, in its present form, should not be utilized for human consumption. This conclusion is based on the documented NO3 contamination prevalent in the community.

NITROGEN CHEMISTRY

Nitrogen may exist in solution in five forms; nitrate (NO3), nitrite (NOD, ammonium and ammonia (NH4 and NH3), organic nitrogen (measured as total kjeldahl nitrogen or TKN), and molecular nitrogen (Nzi$_{an}$)). Groundwater systems usually only contain measurable levels of NO3, NH4-NH3 and N2($_{aq}$). For the most part N2($_{aq}$) is biologically inert, leaving only NOi



Mountainview Community

North

Figure 1 - Location of Mountainview Community

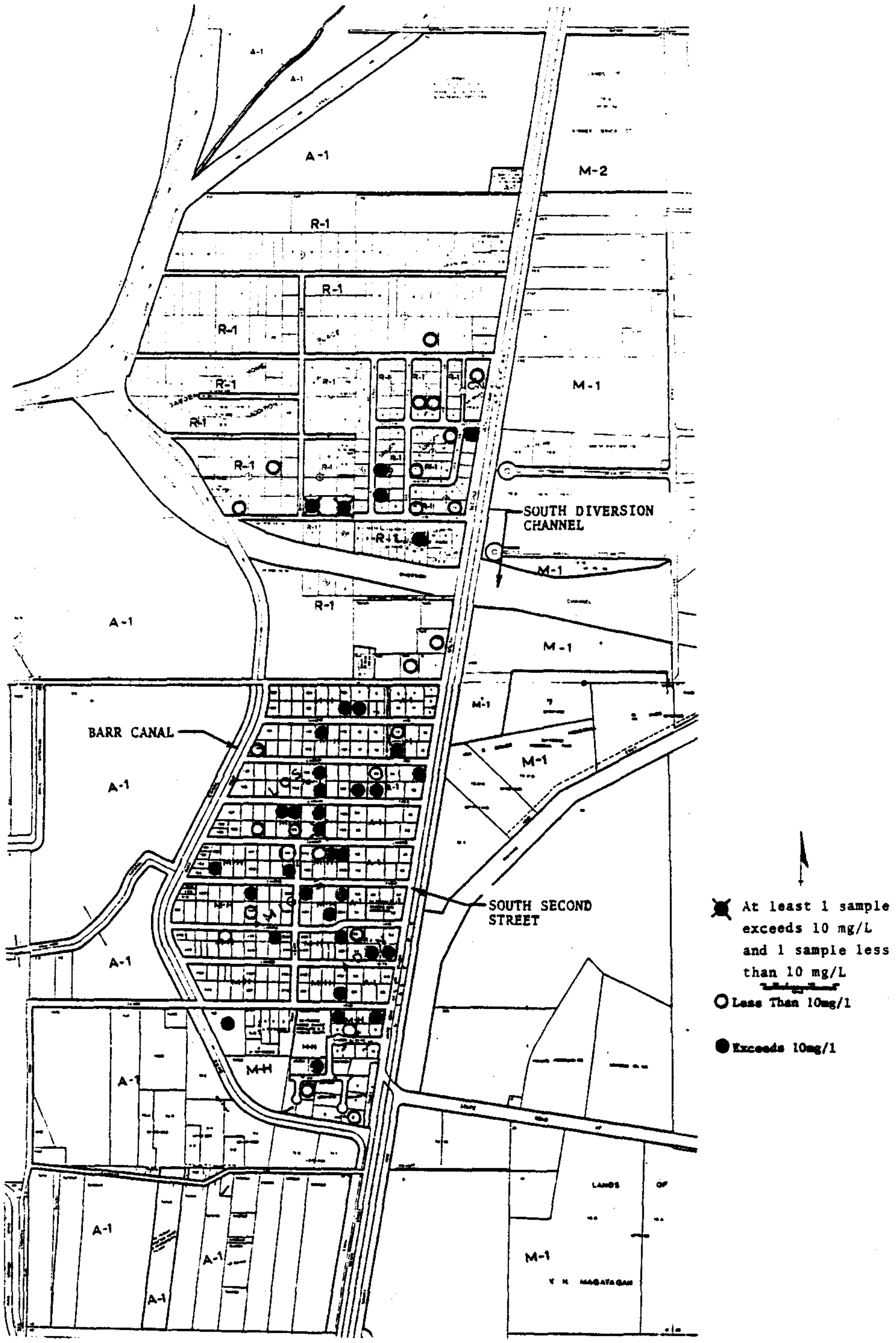


Figure 2 Summary of Bernallilo County Environmental Health Department NO_3^- Sampling Programs

and NH-NH3 as dominant forms of nitrogen in groundwater. The chemistry of these species can be summarized graphically using a pe-pH diagram where pe and pH are defined as:

$$pe = -\log\{e^-\}$$
$$pH = -\log\{e\}$$

pe is proportional to the oxidation potential (Eh) and is a measure of the oxidation-reduction (redox) conditions in a solution. For example a large positive value of pe (greater than 10 at pH 7) indicates strongly oxidizing conditions as would be found in water saturated with $02(_n)$ while a negative value of pe (or Eh) is indicative of reducing conditions as might be present in an anaerobic environment.

A pe-pH diagram for the principal nitrogen species is presented in Figure 3 and shows that under oxidizing conditions NO3 is the dominant species. Under reducing conditions the $NH4-NH_3$ system predominates, with ammonium (NH4) being the major species below pH 9.1. Virtually all redox transformations of nitrogen are biologically mediated and therefore require conditions conducive to growth of the appropriate organisms. Biological oxidation of nitrogenous wastes resulting in NO is called nitrification. Biological reduction of NOi to $N_2(_n)$ is calleardenitrification and requires, in addition to anaerobic conditions, an organic carbon source.

Common sources of nitrogen in the environment include fertilizers which often contain both NH_4 + and NO^-_3 feedlot operations, landfills, and domestic wastewater. Feedlot operations, landfills, and domestic wastewater generally have nitrogen present as TKN and NH4. Usually TKN is quickly hydrolyzed to NH4. NO is not generally associated with the wastes directly but is instead the consequence of biological oxidation of TKN and Niii; Note that oxidizing conditions must be present for this transformation to occur. The increase in concentration of common constituents of septic tank effluents is listed in Table 1 (EPA 1977, Brandes, 1978).

CHEMISTRY OF RELATED SPECIES

Sulfur and iron species are of interest in evaluating groundwater quality in that they may serve as valuable indicators of subsurface redox conditions. The dominant forms of sulfur present in solution consist of sulfates (S0:4) or sulfides (H_2S-HS^-). A pe-pH diagram summarizing sulfur chemistry is presented in Figure 4. Under oxidizing conditions SO; is stable while under reducing conditions $H2S-HS^-$ is expected. As with nitrogen, most redox reactions for sulfur compounds are biologically mediated.

Iron is somewhat different from nitrogen and sulfur in that near neutral pH only one species, ferrous iron (Fe L*), is soluble. Reference to a pe-pH diagram reveals that Fe^{2+} should precipitate as an hydroxide under oxidizing conditions, therefore, high concentrations of iron in a groundwater sample is indicative of reducing conditions (Figure 5).

Finally, one other indicator of groundwater quality which is of interest in the present study is chloride (Cr). Chloride is inert in most aquatic environments and exhibits little or no interaction with soil particles. It is therefore often used as a conservative tracer of groundwater flow. Chloride is also an indicator of human contamination in that domestic use increases its concentration by approximately 50 mg/L (Table 1).

Taken together, these parameters, sulfur, iron and Cl^- can be used to provide an indication of the subsurface aqueous environment and whether there is evidence of direct human waste contamination.

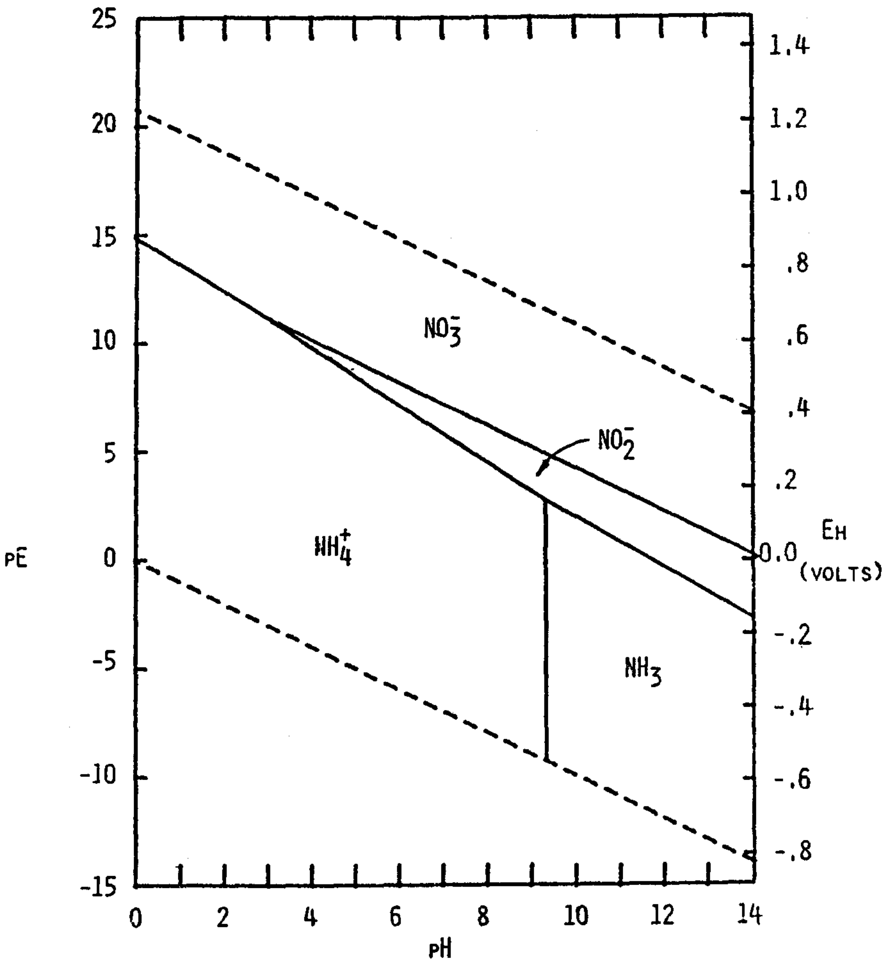


Figure 3—pE-pH diagram for nitrogen species.

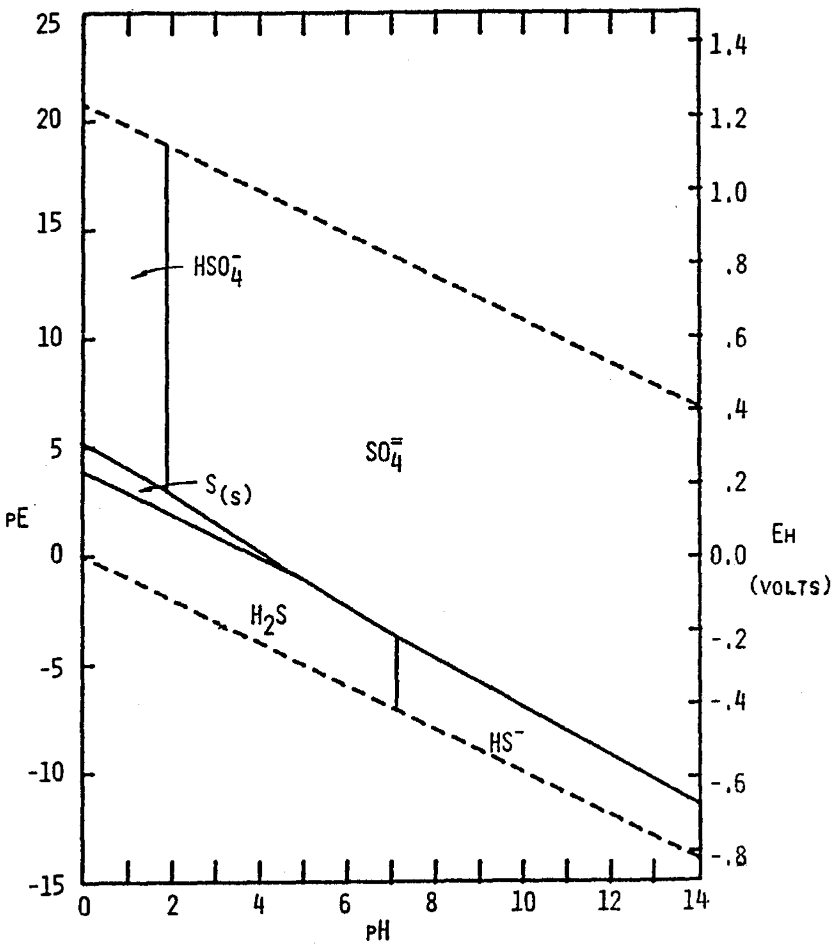


Figure 4—pE-pH diagram for sulfur species. Total sulfur concentration = 10^{-3} M.

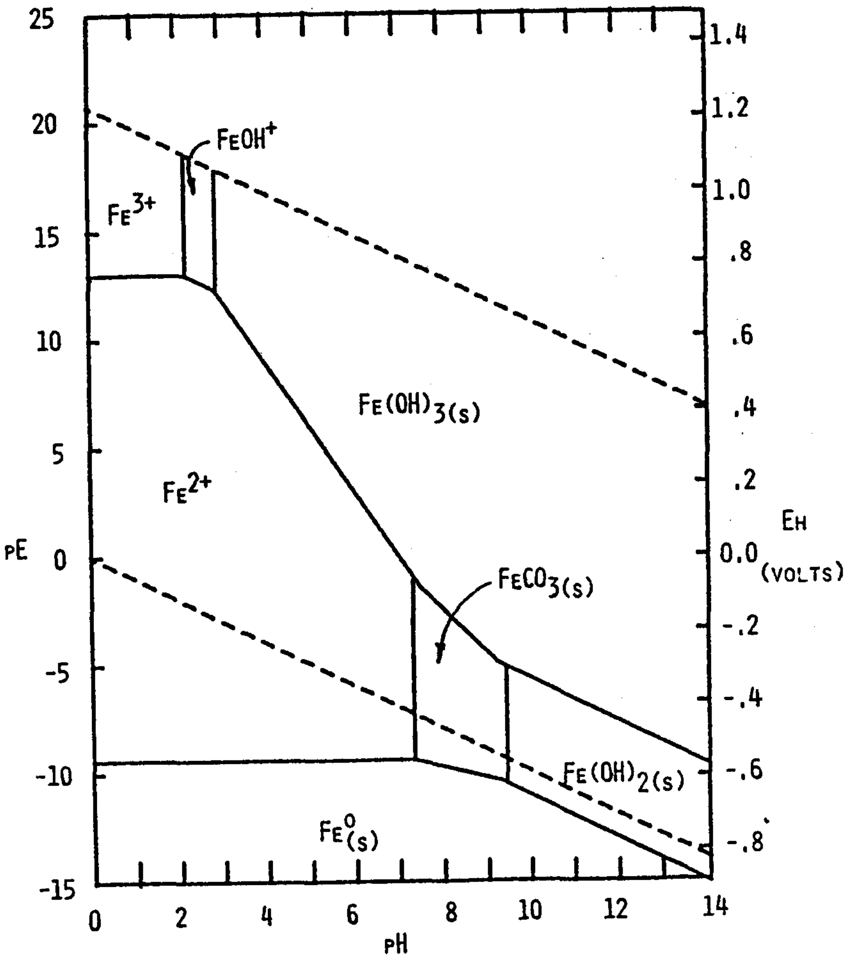


Figure 5 pE-pH diagram for iron species, closed system. Total iron concentration = 10^{-5} M and total dissolved carbon dioxide concentration = 10^{-3} M.

Table 1

Summary of Septic Tank Effluent Quality (EPA - 625/4-77-011) (All units mg/L except as noted).

Characteristic	Mean	Range
BOD_5	158	20-480
TSS	54	11-695
Fecal Coliform Bacteria (no. of orgs./100ml)	4,210	5-180,000
Total Nitrogen	55.3	9.7-124.9
NH_4^{+}[1]	38.7	.9- 90.7
NO_3^{-}[1]	.56	0-74.5
Total P	14.6	3.8-90
Cl^-	48[2] (98)	20-88[2] (86-128)

Notes: [1] Units are mg N/L

[2] Concentration in Grey Water systems (concentration in black water systems) (Brandes, 1978)

ANALYSIS OF NITRATE CONTAMINATON

THEORIES RELATING TO ORIGIN

There has been much discussion about the origin of the Mountain view NO3 contamination problem, unfortunately little of it has been formally presented and reviewed. These theories can be separated into three categories; naturally occurring sources, past disposal of an anthropogenic waste high in nitrogen content, or elevated NO3 concentrations resulting from current surface activities. Identifying the source of the contamination is important because it will determine the nature and effectiveness of future remedial actions.

Based on present knowledge of the geology of the Albuquerque Basin it seems very unlikely that a naturally occurring phenomena, such as an evaporite deposit, could be the source of the NOi. Speculation has therefore focused on mans activities, both past and present. Past activities which have been mentioned as a possible source of the contamination include animal feedlot operations, and solid or liquid waste disposal facilities. There have been accusations leveled by residents of the community of unrecorded dumping of military wastes, possibly including munitions or hazardous wastes, in the Tijeras Arroyo. To date there is no proof of an abandoned disposal site of any type which could account for contamination of the magnitude seen in the Mountain view community.

The alternative to historic dumping of a waste high in nitrogen content is continued introduction of nitrogen to the soil; the most likely activities being wastewater treatment and disposal, and agricultural activities. Most local speculation has focused on on-site wastewater treatment and disposal practices. Hines (1981) has proposed that groundwater levels resulting from the unique surface layout of drainage and irrigation channels as well as subsurface flow of water down the Tijeras Arroyo have created a hydraulic barrier, resulting in stagnation of groundwater below the community. Domestic use of this aquifer would therefore result in a closed loop as groundwater was pumped to the surface and then returned through on-site wastewater treatment and disposal systems. High NOi concentrations would then be the result of increases with each pass through the cycle. This hypothesis can be at least qualitatively tested based on present data and an understanding of chemical conditions within the aquifer.

OTHER INDICATORS OF AQUIFER QUALITY

The uniqueness of NO3 contamination to the Mountain view community is puzzling. Wells sampled in the north valley and other areas of the south valley with similar housing densities has found almost no evidence of elevated NOi concentrations (Alb. City Liq. Waste Div. and Bern. Co. Env. Health Dept. 1978).

Heggen et al. (1979) conducted an investigation on wells in the north valley which has provided a basis for an explanation of the observed lack of NO3. In addition to NO3, H2S-HS^-, phosphates and Nif4-NH_3 were measured in all samples, and a spectrum of 10 metals was measured in 12 of the samples. The results of the findings are summarized in Table 2. The results lead the investigators to conclude that reducing conditions are present in the aquifer. These are the result of a combination of high water table conditions and the discharge of organic wastes to the soil column through on-site wastewater disposal systems. The lack of NO3 is consistent with this conclusion in that reducing conditions prevent the oxidation of TKN and NH4 (Figure 3). Significant concentrations of NHi were not found, however, which was attributed to the high affinity of soi particles for this species, due to adsorption and ion exchange reactions. Evidence in support of these findings include measureable concentrations of H2S-HS^- and FeL^+ (Figures 4 and 5). Indeed high Fe^{2+} concentrations have plagued many residents of the region for years with stained plumbing fixtures, taste problems and extremely hard water, in many cases over 500 mg/L as CaCO3.

Table 2
Summary of North Valley Groundwater
Study (Heggen et al., 1979)

1. Low NO3 and NH4 concentrations
2. High Fe, Mn, and H_2S-HS^- concentrations
3. Reducing conditions
4. Oxidation of TKN and NI inhibited by reducing conditions, nitrogen sorbed onto soil particles

A similar investigation in the Mountain view community and surrounding area produced sharply contrasting results (Table 3) indicative of an oxidizing subsurface environment (Thomson, 1983). These included high concentrations of N05 and negligible concentrations of Fe^{2+} and H2S-HS^-. Recent analyses of samples collected by the NMHED have found measureable concentrations of uranium and selenium in solution, findings which also support the conclusion of oxidizing conditions (NMHED files, 1983, for a discussion of the aqueous chemistry of uranium and selenium see Longmire et al., this conference). In addition, analyses for Cl^- were performed to determine if a correlation exists between it and $NO3^-$. Specifically, recycle of the groundwater as proposed by Hines (1981), should result in a commensurate increase in Cr. The results show at best a weak correlation.

Table 3
Summary of Mountain view Groundwater
Study (Thomson, 1983)

1. High NO3 concentrations
2. Low Fe, Mn, and H_2S-HS^- concentrations
3. Oxidizing conditions
4. Weak correlation between NO3 and Cl^-

Analysis of the limited amount of historic data available from NMHED files and other sources suggests that water quality in wells peripheral to the Mountain view community is changing with time. This evidence takes two forms: changing water quality parameters, most notably TDS, along with anecdotal reports of residents of the community. This information suggests that water quality north of the community is improving while that in the southern edge of the area is declining. If such phenomena can be documented the most likely explanation is that the contaminant plume is moving.

DISCUSSION

ORIGIN OF NITRATE CONTAMINATION

At present there is not sufficient information to identify the origin of the Mountain view community NOi contamination, however, in light of recent observations and a consideration of the theoretical constraints it is possible to all but eliminate on-site domestic wastewater disposal systems as the principal source. This conclusion is based principally on the observed oxidizing conditions in the Mountain view area in contrast to the reducing conditions which would be expected from a sufficiently high density of such systems to cause a problem of the magnitude experienced here. The hypothesis that recycling of groundwater in the area is responsible for NO3 concentrations much greater than the total nitrogen content of domestic wastewater can be countered by noting that in septic tanks, cesspools and soils saturated with domestic wastewater, conditions are ideal for biological de nitrification, reduction of NO to N2($_{0}$). The conditions necessary for biological de nitrification are; a biodegradable carbon source, anoxic conditions and a reasonably long hydraulic detention time (Gaudy and Gaudy, 1981). Most on-site wastewater disposal therefore should actually remove NO3 by converting it to N2().

It is important to note that although it $^{-}$if unlikely that on-site wastewater disposal systems are the major source of the NO contamination, they may contribute to the problem. The NH$_{i}$-NH3 and TKN content of domestic wastewater will be unaffected by denitrification processes occurring in on-site wastewater treatment systems (i.e. septic tanks and cesspools), and instead may pass into the soil. If oxidizing conditions are present in the soil column, as has been found in the Mountain view community, these species may subsequently undergo biological nitrification (i.e. oxidation to NO3) however the concentration will reflect that in the original wastewater which is roughly one order of magnitude lower than found in many of the contaminated wells.

Further evidence that on-site disposal systems are not the principal source of the problem is the historic well data which seems to indicate a moving contaminant plume. If the plume is moving, the contamination most likely is the result of past discharge(s) of a nitrogenous waste, and not a continuous infiltration of contaminated wastewater. Evidence which supports the theory that the NO3 in the Mountain view community is the result of past discharge of a material with a high nitrogen content includes the following:

1. The improbability that on-site wastewater disposal systems can generate extremely high (>100 mg/L) NO3 concentrations.

2. The correlation between high NO3 concentrations and high (>1,000 mg/L) TDS concentrations.

3. Changing water quality in numerous wells; improving water quality in northern wells and declining water quality in southern wells. At present there is no physical evidence of such a disposal of nitrogenous wastes. The apparent correlation between NO3^{-} and TDS, as well as the very high levels of both constituents, may be attributable simply to the high molecular weight of NO3; for example 100 mg N/L as NO3 results in a TDS of 443 mg/L.

ADDITIONAL INFORMATION NEEDED

To fully quantify the Mountain view groundwater contamination problem, including identification of the source, additional information must be developed in three areas; a knowledge of the historic land use of the south valley, a thorough delineation of the contaminant plume, and information on the groundwater flow regime in the area. However, in planning remedial actions to address the problem, a reasonable understanding of the origin and extent of the plume as well as a thorough knowledge of aquifer characteristics will probably suffice.

Delineation of the contaminant plume most likely will require sampling the aquifer at numerous locations in the south valley, as well as collecting groundwater samples at several depths within the aquifer. In conducting the study it is important to be certain that other contaminants are not also present, problems which should be detected by complete analysis of future samples for all regulated contaminants. $NO3^-$ is a conservative constituent in that it does not interact with soil particles, therefore, if the contaminant plume is indeed moving, it will be necessary to confirm that other parameters such as metals or organics are not migrating slower to appear as contaminants in the future, in other words a chromatographic effect. An investigation of stable isotopes including C, 0, and N associated with contaminated and uncontaminated groundwater may assist in determining the origin of the contamination. It is recommended that wells developed for sample collection and determination of water table elevations be permanently placed to allow sample collection into the future to monitor progress of the plume.

To determine the rate of movement of the contaminant plume requires an understanding of groundwater flow patterns. This information must be developed from a knowledge of the aquifer characteristics. Specifically, information is needed on groundwater elevations and hydraulic conductivity of the formation. Groundwater elevations can be readily determined by measurement of water elevations in monitoring wells. Determination of hydraulic characteristics of the aquifer will require pumping tests. Together this information can be used to construct a model of the regime which can be utilized for mapping groundwater flow velocities. Procedures for determining aquifer characteristics are well defined and discussed in most groundwater hydrology texts (see for example Todd, 1981).

REMEDIAL ACTIONS

The proper course of action to alleviate NO3 contamination depends on whether the contamination is the result of continuing surface activities in the area or a onetime disposal of a highly nitrogenous waste. If the NO3 is the result of surface activities, the most effective remedial action will be elimination of those activities and mitigation of damages. For on-site wastewater disposal systems this will most likely mean installation of a sewer system for affected areas, an expensive alternative which has received limited support. However, if, as present evidence seems to indicate, the NO3 contamination is the result of past disposal of a nitrogenous waste material, sewering the area will have virtually no effect on the magnitude of the problem.

Remedial actions for the second case are far less clearly defined than for the first case. Until a long range aquifer restoration project is implemented contaminated groundwater should not be used for human consumption, thus requiring either an alternative potable water source or drinking water treatment. The City of Albuquerque, with funding assistance from the State of New Mexico, is in the process of connecting the Mountain view and surrounding communities to the city's water supply system. O'Brien (1983) has evaluated control options for NO removal from drinking water supplies, concluding that ion exchange and activated alumina adsorption are the most promising techniques. Both are relatively expensive processes and are not likely to be of much use in this area because of the presence of alternative uncontaminated sources. The possibility of long term aquifer restoration will depend on the size of the contaminant plume and the potential for intrusion of contaminated water into uncontaminated strata.

CONCLUSIONS

There is significant groundwater contamination by NOi in the Mountain view community of the south valley region of Albuquerque. Water quality records show significant NOi contamination dating back over 20 years, however indirect evidence of high TDS levels suggests the problem may be over 50 years old. Though on-site wastewater disposal systems have long been believed responsible for aquifer contamination, groundwater quality indicators suggest that they are not the principal source of nitrogenous contaminants. Additional support for this conclusion comes from historic data which may show movement of the contaminant plume.

In developing remedial action plans it is necessary to first generate a better understanding of the contamination problem. This should include implementation of a groundwater sampling program to delineate the extent of the contaminant plume, determination of groundwater elevations in the contaminated region, and a pump test and modeling program to determine the hydraulic characteristics of the aquifer. Future management of the groundwater resources, including implementation of a remedial action program, of the region will depend on whether the contamination is the result of a past disposal of a nitrogenous waste or the result of continued mismanagement of nitrogenous materials through the past two decades.

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REFERENCES

Albuquerque City Liquid Waste Division and Bernalillo County Environmental Health Department, 1978, Special sampling project for nitrate-nitrogen concentration in private household wells: Albuquerque, NM.

Bernalillo County Environmental Health Personnel, 1980, Nitrate as nitrogen, groundwater quality report of the Mountain view community, Albuquerque, NM.

Brandes, M., 1978, Characterization of effluents from gray and black water septic tanks: Journal, Water Pollution Control Federation, pp. 25472559.

Environmental Protection Agency, 1977, Alternatives for small wastewater treatment systems, On-Site Disposal/Septage Treatment and Disposal: EP-625/4-77-011.

Gaudy, A.F., Jr., Gaudy, ET., 1980, Microbiology for Environmental Scientists and Engineers: McGraw-Hill Book Company, New York, NY, pp. 556-567.

Heggen, R.J., Thomson, B.M., Matthews, J.R., Tefera, A., 1979, Groundwater quality study, City of Albuquerque, north valley: Report No. CE-49812-1, University of New Mexico, Albuquerque, NM, 34 p.

Hines, W.G., 1981, Preliminary evaluation of nitrate pollution in shallow groundwater of the Mountainview community: Bernalillo County, New Mexico, Silver City, NM, 16 p.

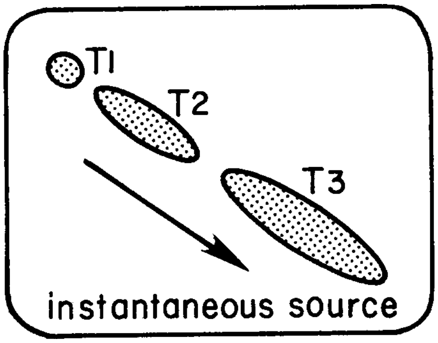
McQuillan, D.M., 1983, Ground water quality in the south valley of Albuquerque: Proceedings of the 28th Annual New Mexico Water Conference, WRRI Report No. 169, Las Cruces, NM, pp. 48-59.

O'Brien, W.J., July 1983, Control options for nitrates and fluorides: Water/Engineering & Management: pp. 36-38.

Scofield, C.S., 1938, Quality of Water of the Middle Rio Grande Valley and its relation to drainage: U.S. Geological Survey water supply-supply paper 839, 294 p.

Thomson, B.M., 1983, Groundwater contamination by nitrate in Albuquerque, New Mexico: Report No. CE83-1, University of New Mexico, Albuquerque, NM, 31 p.

Todd, D.K., 1980, Groundwater hydrology: John Wiley & Sons, New York, NY, 535 p.



Organic Contamination of Ground and Surface Waters: A Selected Bibliography

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ABSTRACT

The Environmental Improvement Division (EID) of the New Mexico Health and Environment Department conducted a literature search on petroleum-distillates (e.g. gasoline) and other potentially-toxic organic substances (e.g. 1,1,2-trichloroethene), in response to the increasing frequency of incidents involving organic contamination of New Mexico's ground waters. The literature search resulted in a selected bibliography containing information on the physical and chemical properties of toxic organic substances (e.g. benzene, polycyclic aromatics and chlorinated aliphatic) in ground and surface waters relevant to contamination problems in New Mexico. This selected bibliography consists of approximately 180 references separated into the following categories: (1), chemical and physical properties; (2), contaminant migration characteristics in soil and ground water; (3), detection, sampling and analytical techniques; (4), soil and water restoration; (5), health effects; and (6), general.

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BIBLIOGRAPHY

4 Abrams, I.M., 1969, Removal of organics from water by synthetic resinous adsorbents: Chemical Engineering Progress Symposium Series 65, 106 p.

4 Adams, A.B. 1973, Air and water pollution control in crude tall oil manufacture in the pulp and paper industry: Journal of the American Oil Chemist's Society, v. 50, pp. 498-500.

6 Afgan, B.K. and Mackay, D. (eds.), 1980, Hydrocarbons and halogenated hydrocarbons in the aquatic environment: International Symposium on the Analysis of Hydrocarbons and Halogenated Hydrocarbons, Plenum Press, New York, 588 p.

4 Alexander, M., 1981, Biodegradation of chemicals of environmental concern: Science, v. 211, pp. 132-138.

1 Alexander, H.C., McCarty, W.M., Bartlett, E.A. and Syverud, A.N., 1982, Aqueous odor and taste threshold vaues of industrial chemicals: Journal of the American Water Works Association, v. 74, pp. 595-599.

2 Alfoldi, L., 1978, Movement of oils in ground water and rocks, in Muzikar, R. (ed.), International symposium on ground-water pollution by oil hydrocarbons: International Symposium on Ground-Water Pollution, Prague, pp. 93-105.

4 Althoff, W.F., Cleary, R.W. and Roux, P.H., 1981, Aquifer decontamination for volatile organics: A case history: Ground Water, v. 19, pp. 495-504.

4 American Petroleum Institute, 1969, Proceedings of the joint conference on prevention and control of oil spills: API Publication 4040, Washington, D.C.

4 American Petroleum Institute, 1973, Conference on the prevention and control of oil spills: API Publication 4172, Washington, D.C.

4 American Petroleum Institute, 1975, Conference on prevention and control of oil pollution--proceedings: API Publication 4245, Washington, D.C.

4,2 American Petroleum Institute, 1977, Proceedings of the 1977 oil spill conference: Prevention, behavior, control and cleanup: API Publication 4284, Washington, D.C.

6 American Petroleum Institute, 1979, Proceedings of the 1979 oil spill conference: API Publication 4308, Washington, D.C.

2 American Petroleum Institute, 1979, The migration of petroleum products in soil and ground water: API Publication 4149, Washington, D.C., 32 p.

4 American Petroleum Institute, 1980, Underground spill cleanup manual: API Publication 1628, Washington, D.C., 34 p.

6 American Petroleum Institute, 1981, Proceedings of the 1981 oil spill conference: API Publication 4334, Washington, D.C.

4 Anderson, C.T. and Maier, W.J., 1979, Trace organics removal by anion exchange resins: Journal Water Technology/Quality, American Water Works Association, pp. 278-283.

1,4 Anderson, J.E., 1972, Factors influencing reverse osmosis rejection of organic solutes from aqueous solution: Journal Physical Chemistry, v. 76.

1,2 Belfort, G., 1979, Selective adsorption of organic homologues onto activated carbon from dilute aqueous solutions: Environmental Science and Technology, v. 13, pp. 939-946.

6 Beynon, L.R. and Oldham, G.F., 1971, Prevention of contamination of water resources by oil: Eighth World Petroleum Congress Proceedings, v. 6, pp. 77-83.

1,4 Blakebrough, N., Garner, P.J., Knap, A.H., Raisbeck, J.M. and Hepple, D., 1976, Aerobic degradation of hydrocarbons in soil: Significance of an initial rise in oxygen uptake rate following contamination with oil: Journal of Applied Chemistry and Biotechnology, v. 26, pp. 550-558.

2 Bouwer, E.J., McCarty, P.L. and Lance,J.C., 1981, Trace organic behavior in soil columns during rapid infiltration of secondary wastewater: Water Research, v. 15, pp. 151-159.

6 Brassell, S.C., Eglinton, G., Maxwell, J.R. and Philp, R.P., 1978, Natural background of alkanes in the aquatic environment, in Hutzinger, 0., Van Lelyveld, L.H. and Zoeteman, B.C. (edsi, Aquatic Pollutants: transformation and biological effects, pp. 69-86.

Buchannan, D., 1972, Decontamination of oil from non-tidal waters: Institute of Water Pollution Control and Petroleum, Seminar Proceedings, pp. 103-112.

6 Burmaster, D.E. and Harris, R.H., 1982, Synthetic organic chemicals are contaminating ground water in many parts of the nation, possibly posing unacceptable risks to human health: Technology Review, v. 85, pp. 51-62.

4 Byer, H.G., Jr.Blakenship,W. and Allen, R., 1981, Groundwater contamination by chlorinated hydrocarbons: Causes and prevention. American Society of Chemical Engineers, v. 51, pp. 54-55.

2,4 Callahan, M., 1979, Water-related environmental fate of 129 priority pollutants, Volume I: U.S. Environmental Protection Agency, EPA-440/4-79-029b, various pagination.

1 Chiou, C.T., Peters, L.J. and V.H. Freed, 1979, A physical concept of soil-water equilibria for nonionic organic compounds: Science, v. 206, pp. 831-832.

1 Clayton, G.D. and Clayton, F.E. (eds.), 1981, Patty's industrial hygiene and toxicology, v. 2B-toxicology, Third edition , WileyInter-Science, New York, pp. 3368-3431.

4 Concawe, 1974, Inland oil spill clean-up manual: CONCAWE Report No. 4/74, The Hague, Netherlands.

6 Concawe, 1977, Strack model to establish optimum locations for a drain to collect oil-polluted ground water: CONCAWE Report No. 12/77, The Hague, Netherlands.

6 Concawe, 1979, Protection of ground water from oil pollution: CONCAWE Report No. 3/79, The Hague, Netherlands.

2 Convery, M.P., 1979, The behavior and movement of petroleum products in unconsolidated surficial deposits: published M.S. thesis, University of Minnesota, 175 p.

2 Copenhaver, E.D. and Wilkenson, B.K., 1979, Movement of hazardous substances in soil: A bibliography, Volume 2, Pesticides: U.S. Environmental Protection Agency, EPA-600/0-79-024b, 228 p.

6 Council on Environmental Quality, 1981, Contamination of ground water by toxic organic chemicals: U.S. Government Printing Office, 84 p.

2,4 Davis, J.B., Farmer, V.E., Kreider, R.E., Straub, A.E. and Reese, R.M., 1972,The principles and counter-measures: American Petroleum Institute Publication 4149, Washington, D.C., 36 p.

3 Dellacqua, R., Bush, B. and Egan, J., 1976, Identification of gasoline contamination of ground water by gas chromatography: Journal of Chromatography, v. 128, pp. 271-280.

4 Dennis, D.M., 1977, Effectively recovering oil spills to ground water, in Proceedings of the joint conference on prevention and control of oil spills: Proceedings of the Oil Spill Conference--Prevention, Behavior, Control and Cleanup, Washington, D.C., pp. 255-258.

3 Dewalle, R.B. and Chion, E.S.K., 1981, Detection of trace organics in well water near a solid waste landfill: Journal of Research and Technology.

2 Dietz, D.N., 1971, Pollution of permeable strata by oil components: Institute Water Pollution Control & Petroleum Seminar Proceedings, pp. 127-139.

2 Deitz, D.N., 1973, Behavior of components from spilled oil on their way through the soil: Journal Petroleum Technology, v. 25, pp. 1045-1046.

1 Dilling, W.L., 1977, Interphase transfer processes - II: evaporation rates of chloromethanes, ethanes, ethylenes, propanes and propylenes from dilute aqueous solutions: Comparisons and theoretical predictions: Environmental Science and Technology, v. 11, pp. 405-409.

1 Dilling, W.L., Tefertiller, N.B. and Kallos, G.J., 1975, Evaporation rates and reactivities of methylene chloride, chloroform, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene and other chlorinated compounds in dilute aqueous solutions: Environmental Science and Technology v. 9, pp. 833-838.

2 Dracos, T., 1978, Theoretical considerations and practical implications on the infiltration of hydrocarbons in aquifers, in Muzikar, R. (ed.), International symposium on ground-water pollution by oil hydrocarbons: International Symposium on Ground-Water Pollution, Prague, pp. 127-137.

1,2 El-Dib, M.A. and Badawy, M.I., 1979, Adsorption of soluble aromatic hydrocarbons on granular activated carbon, Water Research (UK), v. 13, pp. 255-258.

1 Faulkner, D.J, 1980, Natural organohalogen compounds, in Hutzinger, O. (ed.), The handbook of environmental chemistry,,¯v. 1, part A: The natural environment and biogeochemical cycles, pp. 229-254.

4 Federal Ministry of the Interior, Germany, 1970, Evaluation and treatment of oil- spill accidents on land with a view to the protection of water resources: Bonn, Germany.

6 Ferguson, D.P., 1979, Petroleum contamination of wells: Ground Water Age, v. 14, pp. 67-74.

1,4 Fochtman, E.G., 1981, Biodegradation and carbon adsorption of carcinogenic and hazardous organic compounds - Project summary: U.S. Environmental Protection Agency, EPA-600/52-81-032, 2 p.

2 Fried, J.J. and Zilliox, L, 1978, The dispersion scheme in the general mechanisms of ground-water pollution by hydrocarbons, in Muzikar, R. (ed.), International syposium on ground-water pollution by oil hydrocarbons: International Symposium on Ground-Water Pollution, Prague, pp. 139-147.

2 Fried, J.J., Muntzer, P. and Zilliox, L., 1979, Ground-water pollution by transfer of oil hydrocarbons: Ground Water, v. 17, pp. 586594.

6 Geraghty, J.J. and Miller, D.W., 1978, Status of groundwater contamination in the U.S.: Journal of the American Water Works Association, v. 70, pp. 162-167.

6 Giger, W. and Molnar-Kubica, E., 1978, Tetrachloroethylene in contaminated ground and drinking waters: Bulletin of Environmental Contamination and Toxicology, v. 19, pp. 475-480.

6 Giger, W., Molnar-Kubica, E. and Wakeham, W., 1978, Volatile chlorinated hydrocarbons in ground and lake waters, in Hutzinger, O. (ed.), Aquatic pollutants transformatiorii and biological effects: Pergamon Press, Oxford, pp. 101-123.

4 Giusti, D.M., Conway, R.A., and Lawson, C.T., 1974, Activated carbon adsorption of petrochemicals: Journal Water Pollution Control Federation, v. 46, pp. 947-965.

3 Gonzalez-Vila, F.J., Saiz-Jimenez, C. and Martin, F., 1982, Identification of free organic chemicals found in composted municipal refuse: Journal of Environmental Quality, v. 11, pp. 251-254.

6 Greenberg, M., Anderson, R., Keene, J., Kennedy, A., Page, G.W. and Schowgurow, S., 1982, Empirical test of the association between gross contamination of wells with toxic substances and surrounding land use: Environmental Science and Technology, v. 16, pp. 14-19.

3 Guard, H.E., DiSalvo, L.H. and Ng, J., 1980, Determination and identification of hydrocarbon pollutants by thin-layer chromatography, in Albaiges, J. (ed.), Analytical techniques in environmental chemistry: Pergamon Press, New York, pp. 63-68.

6 Guenther, K., 1972, Ground-water pollution caused by gasoline: Wasserwirt, Wasser Technology, v. 22, pp. 158-161.

6 Guerrera, A.A., 1981, Chemical contamination of aquifers on Long Island, New York: Journal of the American Water Works Association, v. 73, pp. 190-199.

6 Harrison, R.M., Perry, R. and Wellings, R.A., 1975, Polynuclear aromatic hydrocarbons in raw, potable and waste waters: Water Research, v. 9, pp. 331-346.

6 Hathaway, S.W., 1980, Sources of toxic compounds in household wastewater: U.S. Environmental Protection Agency, EPA-600/2-80128, 84 p.

6 Hellman, H., Holeczek, M. and Butz, H., 1974, Hydrocarbons in spring waters-oil pollution or natural substances: Tenside Detery., v. 11, pp. 197-201.

1,2 Herbes, S.E., 1977, Partitioning of polycyclic aromatic hydrocarbons between dissolved and particulate phases in natural waters: Water Research, v. 11, pp. 493-496.

2 Hoffman, B., 1969, The spread of hydrocarbons in ground water, unpublished Ph.D. dissertation, University of Hanover.

2 Holzer, T.L., 1976, Application of ground-water flow theory to a subsurface oil spill: Ground Water, v. 14, pp. 138-145.

1,2 Houzim, V., 1978, Alterations of the petroleum substance in rock-water systems, in Muzikar, R. (ed.), International symposium on groundwater polTiltion by oil hydrocarbons: International Symposium on Ground Water-Pollution, Prague, pp. 279-288.

4 Hubbard, E.H., 1975, Inland oil spill clean-up: Ninth World Energy Conference Transactions, v. 3, pp. 392-413.

1,6 Hunt, J.M., 1979, Petroleum geochemistry and geology: Freeman and Company, San Francisco, 617 p.

3 Hunter, L., 1975, Quantification of environmental hydrocarbons by thin- layer chromatography--gravimetry and densitometry comparison: Environmental Science and Technology, v. 9, pp. 241246.

1,2,4 Hutzinger, 0., VanLelyveld, I.H. and Zoeteman, B.C.J., 1978, Aquatic pollutants: Transformation and biological effects: Proceedings of the Second International Symposium of Aquatic Pollutants, Amsterdam, September 26-28, 1977: Pergamon Press, Oxford, 519 p.

6 Ineson, F. and Packham, R.F., 1967, Contamination of water by petroleum products, in Hepple, P. (ed.), The joint problems of the oil and water in¯Estries: Institute of Petroleum: Elsevier Publishing Company, London, pp. 97-116.

1,4 Jamison, V.W., Raymond, R.L. and Hudson, J.0., 1974, Biodegradation of high-octane gasoline in ground water: Developments in Industrial Microbiology, v. 16, pp. 305-312.

4 Jercinovic, D.E. 1982, October 13, 1982 memorandum to Charles Nylander (EID) regarding projected costs of a groundwater-recovery program to mitigate gasoline contamination.

6 Jercinovic, D.E., 1982, Assessment of refined petroleum-product contamination problems in surface and ground waters of New Mexico: Environmental Improvement Division, Santa Fe, EID/WPC82-5, various pagination.

2,6 Jercinovic, D.E., 1983, Hydrocarbon fuels in ground water - increased awareness and concern in New Mexico: in 28th Annual New Mexico Water Conference, Albuquerque, New MeiTEo, Water Quality in New Mexico, Water Resources Research Institute, April 5-6, 1983, pp. 35-47.

3 Johnansen, N.G., Ettre, L.S. and Miller, R.L., 1983, Quantitative analysis of hydrocarbons by structural group type in gasolines and distillates-1: Gas chromatography: Journal of Chromatography, v. 20, pp. 393-417.

1,2 Josephson, J, 1983, Subsurface organic contaminants: Environmental Science and Technology, v. 17, pp. 518A-521A.

4 Kaess, W., 1972, Consequences and treatment of ground-water pollution by crude oil: Advances in organic geochemistry: Proceedings of fifth international meeting: Pergamon Press, Oxford, pp. 665680.

1,4 Kappler, T.H. and Wuhrman, K., 1978, Microbial degradation of the water-soluble fraction of gas oil-I: Water Research (UK), v. **12,** pp. 327-333.

1,2 Karickhoff, S.W., Brown, D.S. and Scott, T.A., 1979, Sorption of hydrophobic pollutants on natural sediments: Water Research. v. **13,** pp. 241-248.

1 Kilzer, L., Scheunert, I., Geyer, H., Klein, W. and Korte, F., 1979, Laboratory screening of the volatilization rates of organic chemicals from water and soil: Chemosphere, v. 8, pp. 751-761.

4 Klecka, M.E., 1977, The sandfarm--a means for disposal of chemical plant and refinery biosolids waste: Shell Development, TPR 212- 76.

4 Knowlton, H.E. and Rucker, J.E., 1978, Landfarming shows promise for refinery waste disposal: The Oil and Gas Journal.

6 Kolpack, R.L. and McKee, J.E., 1970, Long-term spill effects called minimal by experts: Oil and Gas Journal, v. 68, pp. 105-106. 2,6 Kramar, W.H., 1982, Ground-water pollution from gasoline: Ground Water Monitoring Review, v. 2, pp. 18-22.

5 Kraybill, H.F., 1981, Carcinogenesis of synthetic organic chemicals in drinking water: Journal of the American Water Works Association, v. 73, pp. 370-372

3 Kuo, P.P.K., Chian, E.S.K., DeWalle. F.B. and Kim, J.H., 1977, Gas stripping sorption and thermal desorption procedures for preconcentrating volatile, polar and water-soluble organics from water samples for analysis by gas chromatography: Analytical Chemistry, v. 49, pp. 1023-1029.

4 Law Engineering Testing Company, 1982, Literature inventory - treatment techniques applicable to gasoline-contaminated ground water: Report to American Petroleum Institute, Washington, D.C., 60 p.

2 Lehotsky, J., 1978, Dynamics of motion and alterations in quality of petroleum hydrocarbons in soil and water environment, in Muzikar, R. (ed.), International symposium on ground-water pollaion by oil hydrocarbons: International Symposium on Ground-Water Pollution, Prague, pp. 289-301.

6 Longmire, P.A., 1983, Petroleum product contamination of ground and surface water: A literature review: Environmental Improvement Division, Santa Fe, EID/WPC-83/7, 56 p.

1 Mackay, D. and Matsugu, R.S., 1973, Evaporation rates of liquid hydrocarbon spills on land and water: Canadian Journal of Chemical Engineering, v. 57, pp. 434-439.

1 Mackay, D. and Leinonen, P.J., 1975, Rate of evaporation of low-solubility contaminants from water bodies to atmosphere: Environmental Science & Technology, v. 9, pp. 1178-1180.

5 Majeti, V.A. and Clark, C.S., 1981, Health risks of organics in land application: Journal of Environmental Engineering, American Society of Civil Engineers, v. 107, pp. 339-357.

6 Manitoba Clean Environment Commission, 1976, Preliminary report on contamination of underground-water resources by refined-petroleum products: Ground Water, v. 14, pp. 36-44.

4 Mathes, G.M., 1982, Spilled petroleum recovered from atop water table of Mississippi aquifer: Civil Engineering, v. 52, pp. 58-59. 6

Matis, V.R., 1971, Petroleum contamination of ground water in Maryland: Ground Water, v. 9, pp. 57-61.

4,6 McCarty, P.L., 1980, Organics in water-an engineering challenge: Journal of the Environmental Engineering Division, American Society of Civil Engineers, v. 106, pp. 1-17.

6 McCarty, P.L., Reinhard, M. and Rittmann, B.E., 1981, Trace organics in groundwater: Environmental Science and Technology, v. 15, pp. 40-49.

4 McGill, W.B., 1976, Calm and practical restoration shows oil spills do not impair soil permanently: Oilweek, v. 27, pp. 100-101.

4 McGill, W.B., 1977, Soil restoration following oil spills--a review: Journal of Canadian Petroleum, v. 16, pp. 60-67.

6 McKee, J.E., Laverty, F.B. and Hertel, R.M., 1972, Gasoline in groundwater: Journal Water Pollution Control Federation, v. 44, pp. 293-302.

6 McNulty, D.C. and Todd, D.K., 1974, Polluted ground water--a review of the significant literature: U.S. Department of Commerce, NTIS Publication 235-556, 221 p.

1,2 Means, J.C., Wood, S.G., Hassett, J.J. and Banwart, W.L., 1980, Sorption of polynuclear aromatic hydrocarbons by sediments and soils: Environmental Science and Technology, v. 14, pp. 15241528.

6 Mellan, I, 1977, Industrial solvents handbook: Noyes Data Corporation, Park Ridge, N.J., 567 p.

2,4 Metry, A.A., 1977, The fate of pollutants in subsurface environments: Journal of Environmental Sciences, pp. 27-31.

6 Mudallal, U. and Najjar, I., 1974, Effect of oil-refinery effluent on the shallow gravel aquifer in Zerqa area--Jordan: Water Hum. Environment, First Proceeding World Congress Water Resources, pp. 248-272.

2 Mull, R., 1971, Migration of oil products in the subsoil with regard to ground-water pollution by oil: Advances in Water Pollution Research, Fifth Proceedings International Conference, Pergamon, Oxford, pp. 1-8.

4 Naaris, N. and Schneider-Rotel, M., 1978, Evaluation of ozone induced biodegradability of wastewater treatment plant effluent: Water Research (UK), v. 14, pp. 929-938.

1 Nathwani, J.S. and Phillips, C.R., 1977, Adsorption-desorption of selected hydrocarbons in crude oil on soils: Chemosphere, v. 6, pp. 157-162.

6 National Fire Protection Association, 1977, Underground leakage of flammable and combustible liquids: NFPA No. 329, Boston, 57 p.

6 National Fire Protection Association, 1982, Basic classification of flammable and combustible liquids: NFPA No. 321, Boston.

3,4 National Water Well Association, 1983, Proceedings of the third national symposium on aquifer restoration and ground water monitoring, May 25-27, 1983, Columbus, Ohio (in press).

4 Nielsen, D.M. (ed.), 1982, Aquifer rehabilitation and ground water restoration-a light at the end of the tunnel: Proceedings of the second national symposium on aquifer restoration and ground water monitoring, May 26-28, 1982, Columbus, Ohio: National Water Well Association, Worthington, Ohio, 374 p.

4 Ohneck, R.J. and Gardner, G.L., 1982, Restoration of an aquifer contaminated by an accidental spill of organic chemicals: Ground Water Monitoring Review, v. 2, pp. 50-53.

2 Osgood, J.0., 1974, Hydrocarbon dispersion in ground water: Significance and characteristics: Ground Water, v. 12, pp. 427436.

6 Pelikan, V., 1975, Increase in the contamination with petroleum products in rocks and surface water: Geol. Pr. Spravy, v. 62, pp. 227-233.

6 Petura, J.C., 1981, Trichloroethylene and methyl chloroform in groundwater: A problem assessment: Journal of the American Water Works Association, v. 73, pp. 200-205.

4 Quince, J.R. and Gardner, G. L., 1982a, Recovery and treatment of contaminated ground water: Part I: Ground Water Monitoring Review, v. 2, pp. 18-22.

4 Quince, J.R. and Gardner, G.L., 1982b, Recovery and treatment of contaminated ground water: Part II: Ground Water Monitoring Review, v. 2, pp. 18-25.

3 Raymond, A.J., 1975, Determination of individual gasoline boiling range hydrocarbons in ground water by gas chromatography: Conference on analytical chemistry and applied spectroscopy: American Chemical Society.

4 Raymond, R.L., Hudson, J.D. and Jamison, V.W., 1975, Assimilation of oil by soil bacteria, Proceedings--Division of Refining: American Petroleum Institute Report 24-75, Washington, D.C., pp. 429-455.

4 Raymond, R.L., Hudson, J.D. and Jamison, V.W., 1977, Bacterial growth in and penetration of consolidated and unconsolidated sands containing gasoline: Final Report to American Petroleum Institute, Washington, D.C., 20 p.

4 Raymond, R.L., Jamison, V.W., Hudson, J.0. and Mitchell, R.E., 1978, Field application of subsurface biodegradation of gasoline in a sand formation: Final Report to American Petroleum Institute, Washington, D.C., 137 p.

4 Raymond, R.L., Jamison, V.W., Hudson, J.0., Wilkins, G.W. and Gray, C., 1980, The use of biostimulation in mitigating the effects of gasoline in ground water: National Conference and Exhibition on Control of Hazardous Material Spills, Louisville, Kentucky.

4 Reinhard, M., Dolce, C.J., McCarty, P.L. and Argo, D.B., 1979, Trace organics removal by advanced waste treatment: Journal of Environmental Engineering, pp. 675-693.

4 Rittmann, B.E., McCarty, P.L. and Roberts, P.V., 1980, Trace-organics biodegradation in aquifer recharge: Ground Water, v. 18, pp. 236-243.

1,2,3 Roberts, P.V., Schreiner, J. and Hopkins, G.D., 1982, Field study of organic water quality changes during groundwater recharge in the Palo Alto Baylands: Water Research, v. 16, pp. 1025-1035.

6 Robertson, J.M., 1976, Organic leachate threatens groundwater quality: Water and Sewage Works, v. 123, pp. 58-59.

1,2 Rogers R.D., McFarlane, J.C. and Cross, A.J., 1980, Adsorption and desorption of benzene in two soils and montmorillonite clay: Environmental Science and Technology, v. 14, pp. 457-460.

1 Rossini, F.D., Pitzer, K.S., Taylor, W.J., Ebert, J.P., Kilpartick, J.E., Beckett, C.W., Williams, M.G. and Werner, H.G., 1947, Selected values of properties of hydrocarbons: National Bureau of Standards C461.

1 Rossini, F.D., Mair, B.J. and Streiff, A.J., 1953, Hydrocarbons from petroleum: American Chemical Society Monograph, no. 121, 556 p, variouis pagination.

6 Roux, P.H. and Althoff, W.F., 1980, Investigation of organic contamination of ground water in South Brunswick township, New Jersey: Ground Water, v. 18 pp. 464-471.

1,2 Rubelt, C., 1978, Chemical relations in the interaction system rock-ground water - oils, in Muziker, R. (ed.), International symposium on ground-witer pollution by oil hydrocarbons: International Symposium on Ground-Water Pollution, Prague, pp. 231-233.

3 Saxena, J., Kozuchowsky, J., and Basil, D.K., 1977, Monitoring of polynuclear aromatic hydrocarbons in water: Environmental Science and Technology, v. II.

6 Schmidt, K.J., 1983, Ground water quality studies in California, in Procedings of American Society of Civil Engineers, Irrigationd Drainage Division, National Specialty Conference, Jackson, Wyoming, July (in press).

1 Schwartz, F.G., Whisman, M.L., Allbright, C.S. and Ward, C.C., 1964, Storage stability of gasoline: U.S. Bureau of Mines Bulletin 626, 44 p.

2 Schwarzenbach, R.P., Giger, W., Hoehn, E. and Schneider, J.K., 1983, Behavior or organic compounds during infiltration of river water to ground water: Field studies: Environmental Science and Technology, v. 17, pp. 472-479.

2,6 Schwille, F., 1967, Petroleum contamination of the subsoil - a hydrological problem, in Hepple, P. (ed.), The joint problems of the oil and water industries: Institute of Petroleum; Elsevier Publishing Company, London, pp. 23-54.

2 Sellberg, B., 1978, Rate of spread of petroleum products, in Muzikar, R. (ed.), International symposium on ground-water pollition by oil hydrocarbons: International Symposium on Ground-Water Pollution, Prague, pp. 183-207.

3 Simard, R.G., Hosegawa, I., Brandaruk, W. and Headington, C.W., 1951, Infrared spectrophotometric determination of oil and phenols in water: Analytical Chemistry, v. 23, pp. 1384-1387.

2,4 Singhal, A.K., 1981, Tying up TCE: Water/Engineering and Management, v. 128, pp. 56-63.

2 Somers, J.A., 1975, The fate of spilled oil in the soil: Hydrological Science Bulletin, v. 19, pp. 501-521.

3 Spiker, E.C. and Rubin, M., 1975, Petroleum pollutants in surface and ground water as indicated by the carbon-14 activity of dissolved organic carbon: Science, v. 187, pp. 61-64.

4 Stover, E.L., 1982, Removal of volatile organics from contaminated ground water: Ground Water Monitoring Review, v. 2, pp. 57-61.

3 Suffet, I.H., Brenner, L. and Cairo, P.R., 1980, GC/MS identification of trace organics in Philadelphia drinking waters during a 2-year period: Water Research, v. 14, pp. 853-867.

4 Svigar, L., 1978, Vopex - a new sorbent protecting environments and water against pollution by oil products, in Muzikar, R. (ed.), International symposium on ground-water 01-lution by oil hydrocarbons: International Symposium on Ground-Water Pollution, Prague, pp. 83-89.

6 Sylvester, K.A. and Landon, R.A., 1982, Subsurface oil contamination: Ground Water Monitoring Review, v. 2, pp. 54-56.

6 Talts, A., Bauer, J., Martin, C. and Reeves, D., 1977, Discovery, containment and recovery of a jet fuel storage-tank leak: A case history, in Proceedings 1977 oil spill conference: American Petroleum-Tnstitute Publication 4284, Washington, D.C., pp. 259264.

2,4 Texas Research Institute, Inc., 1979, Large-scale model gasoline spill surfactant treatment study: Interim report to American Petroleum Institute, Washington, D.C., 41 p.

2,4 Texas Research Institute, Incorporated, 1979, Underground movement of gasoline on ground water and enchanced recovery by surfactants: American Petroleum Institute Report 4317, Washington, D.C., 48 p.

4 Texas Research Institute, Incorporated, 1980, Examination of venting for removal of gasoline vapors from contaminated soil: Report to American Petroleum Institute, Washington, D.C., 25 p.

4 Texas Research Institute, Incorporated, 1980, Laboratory-scale gasoline spill and venting experiment: Report to American Petroleum Institute, Washington, D.C., 30 p.

4 Texas Research Institute, Incorporated, 1980, American Petroleum Institute venting study: Final report to American Petroleum Institute, Washington, D.C., 25 p.

4 Thiel, R., 1982, Diesel fuel: Crisis in quality: Water Well Journal, v. 36, pp. 64-66.

2,4 Thornton, S., 1980, Underground movement of gasoline on ground water and enchanced recovery by surfactants: National Conference and Exhibition on Control of Hazardous Material Spills, Louisville, Kentucky.

4 Tischler, L.F., Marc, D., Malina, J.F. and Garrett, J., 1979, Evaluation of the potential for air stripping of hydrocarbons during activated sludge waste water treatment: Engineering-Science, Report to the Gulf Coast Waste Disposal Authority.

2,3,4 Thomson, M.B., Dauchy, J., Hutchins, S., Curran, C., Cook, C.J. and Ward C.H., 1981, Groundwater contamination by trace level organics from a rapid infiltration site: Water Research, v. 15, pp. 1109-1116.

6 U.S. Congress, 1980, Toxic chemical contamination of ground water: EPA oversight: Hearing before a subcommittee of the committee on government operations House of Representatives 96th Congress 2nd session, U.S. Government Printing Office, Washington, D.C., 410 p.

4 U.S. Environmental Protection Agency , 1979, A guidance for protection of ground-water resources from the effects of accidential spills of hydrocarbons and other hazardous substances: EPA 570/9-79-017,various pagination.

3 U.S. Environmental Protection Agency, 1982, Handbook for sampling and sample preservation of water and wastewater: EPA 600/4-82-029, 402 p.

2 van Dam, F., 1967, The migration of hydrocarbons in a water-bearing stratum, in Hepple, P. (ed.), The joint problems of the oil and water indUitries: Institute of Petroleum, Elsevier Publishing Company, London, pp. 55-96.

2 Van der Waarden, M., Groenewoud, W.M. and Bridie, A.L., 1977, Transport of mineral oil components to groundwater - II: Influence of lime, clay and organic soil components on the rate of transport: Water Research, v. 11, pp. 359-365.

2 Van der Waarden, M., Bridie, A.L. and Groenewoud, W.M., 1971, Transport of mineral oil components to ground water: Water Research, v. 5, pp. 213-226.

6 Vanloocke, R., DeBorger, R., Voets, J.P. and Verstraete, W., 1975, Soil and ground-water contamination by oil spills: Problems and remedies: International Journal of Environmental Studies, v. 8, pp. 99-111.

1 Verschueren, K., 1977, Handbook of environmental data on organic chemicals: Van Nostrand Reinhold Company, New York, 659 p.

6 Verweij, A., 1979, Pollution of the soil by aviation gasoline: National Aeronautics and Space Administration, Washington, D.C., 26 p.

6 Vindyukov, P.M., Sardarova, G.L. and Kutakov, K.V., 1973, Sources of contamination of artesian-well waters with carcinogenic hydrocarbons: Gig. Sanit., v. 11, pp. 98-99.

6 Vonhof, A., 1976, Contamination of shallow aquifers by refined petroleum products: Proceedings of Third Annual Engineering International Canada Western Regional Conference, Calgary, Alberta.

6 Wakeham, S.G., Davis, A.C., Witt, R.T., Trip, B.W. and Frew, N.M., 1980, Tetrachloroethylene contamination of drinking water by vinyl-coated asbestos-cement pipe: Bulletin of Environmental Contamination and Toxicology, v. 25, pp. 639-645.

1 Weast, P.C. (ed.), 1975, CRC handbook of chemistry and physics, 56th edition: CRC Press, Cleveland, various pagination.

4 Weber, J., Jr., Pirbazari, M. and Melson, G.L., 1978, Biological growth on activated carbon: Environmental Science and Technology, v. 12, pp. 817-822.

6 Williams, D.E. and Wilder, D.G., 1971, Gasoline pollution of a ground-water reservoir - a case history: Ground Water, v. 9, pp. 50-54.

4 Willmoth, B.M., 1978, Procedures to reduce contamination of ground water by hazardous materials: Proceeding 1978 National Conference on Control of Hazardous Material Spills, pp. 293-295.

2 Wilson, J.T., Enfield, C.G., Dunbar, W.J., Cosby, R.L., Foster, D.A. and Baskin, L.B., 1981, Transport and fate of selected organic pollutants in a sandy soil: Journal of Environmental Quality, v. 10, pp. 501-506.

4 Wood, P.R., 1980, Removing potential organic carcinogens and precursors from drinking water, volume I and appendix A., U.S. Environmental Protection Agency, EPA 600/2-18-130a, 367 p.

4 Yaniga, P.M., 1982, Alternatives in decontamination for hydrocarbon-contaminated aquifers: Ground Water Monitoring Review, v. 2, pp. 40-49.

4 Yazicigil, H. and Sendlein, L.V., 1981, Management of ground water contaminated by aromatic hydrocarbons in the aquifer supplying Ames, Iowa: Ground Water, v. 19, pp. 648-665.

6 Wise, H.E. and Fahrenthold, P.D., 1981, Predicting priority pollutants from petrochemical processes: Environmental Science and Technology, v. 15, pp. 1292-1304.

4 Zeff, D., Thrasher, J.D. and Smith, M.M., 1981, Application of UV-Ozone (ULTROX) treatment to industrial wastewaters: 13th Mid-Atlantic Industrial Waste Conference, Newmark, Delaware.

2 Zilliox, L. and Fried, J.J., 1978, The dispersion scheme in the general mechanisms of ground water pollution by hydrocarbons: in Muzikar, R. (ed.), International Symposium of ground water pollution by oil hydrocarbons: International Symposium on Ground Water Pollution, Prague, pp. 139-147.

6 Zilloix, L., Muntzer, P. and Fried, J.J., 1978, An estimate of the source of a phreatic aquifer pollution by hydrocarbons, in Muzikar, R. (ed.), International symposium on ground-watiF pollution by oil hydrocarbons: International Symposium on Ground-Water Pollution, Prague, pp. 209-227.

6 Zoeteman, B.C.J., Harmsen, K., Linders, J., Morra, C. and Sloof, W., 1980, Persistent organic pollutants in river water and ground water of the Netherlands: Chemosphere, v. 9, pp. 231-249.

LOCALIZED FRESH GROUND-WATER BODIES-- A SPECIAL CONSIDERATION IN SITING LANDFILLS ALONG THE RIO GRANDE VALLEY

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ABSTRACT

Considerable quantities of fresh ground water (<1000 mg/L total dissolved solids content) occur in localized bodies or tongues along the margins of the Rio Grande Valley. Three major processes are responsible for their formation: 1) recharge on piedmont slopes, 2) discharge from elevated side basins (isolated alluvial *basins* lying above and adjacent to the valley), and 3) underflow along ephemeral Rio Grande tributaries not associated with piedmont slopes. All of the resulting ground-water bodies may be recognized by flow directions perpendicular or diagonal to those in the central valley and by total-dissolved-solids concentrations an order of magnitude less than those of central valley ground water.

Such fresh ground-water bodies will be valuable resources as the population of the valley continues to grow. However, they are susceptible to pollution from landfills often located on the valley margins because of lower land values and easier excavation there than in the central valley. Special consideration of these fresh-water bodies in landfill siting and construction is essential to their protection.

INTRODUCTION

The Rio Grande Valley is the location of a number of New Mexico's major population centers. Disposal of waste generated by such municipalities is generally accomplished by means of landfills (sanitary and otherwise) located on the valley margins. Siting of landfills there solves the problems of shallow water table, hard or clayey soils, and high price of land often associated with the central part of the valley. However, such landfills may result in pollution of considerable quantities of fresh ground water occurring in localized bodies or tongues along the valley margins. The purpose of this paper is to provide an awareness of the existence, source, and recognition of such water bodies so that their protection may be assured in future landfill siting.

FRESH GROUND-WATER BODIES

Three major processes result in the formation of fresh ground-water bodies along the Rio Grande Valley margins: 1) recharge on piedmont slopes, 2) discharge from elevated side basins, and 3) underflow along ephemeral Rio Grande tributaries not draining piedmont slopes (fig. 1). The resulting fresh ground-water bodies may be recognized by flow directions perpendicular or diagonal to those in the central valley and by total-dissolved-solids concentrations an order of magnitude less than those of central valley ground water.

PIEDMONT-SLOPE RECHARGE

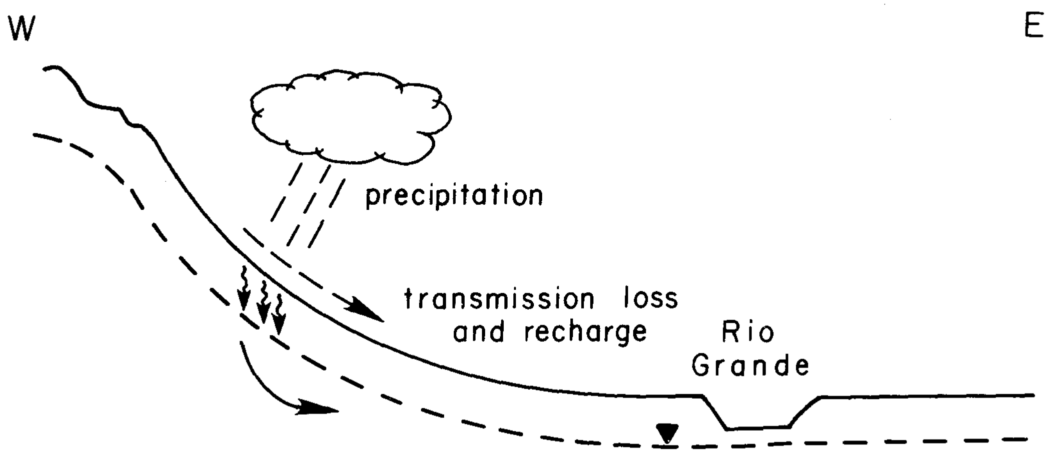
The most obvious source of fresh ground water along the valley margins is recharge on alluvial fans and other geomorphic surfaces that extend from the mountain ranges to the river channel (fig. la) These features cover large areas and thus intercept a considerable portion of the precipitation falling on the region. Piedmont slopes consist of two geomorphically and hydrologically distinct elements: ephemeral distributary channels and un dissected inter-channel divides. 'The opportunity for recharge in the two elements is quite different.

Ephemeral Stream Channels

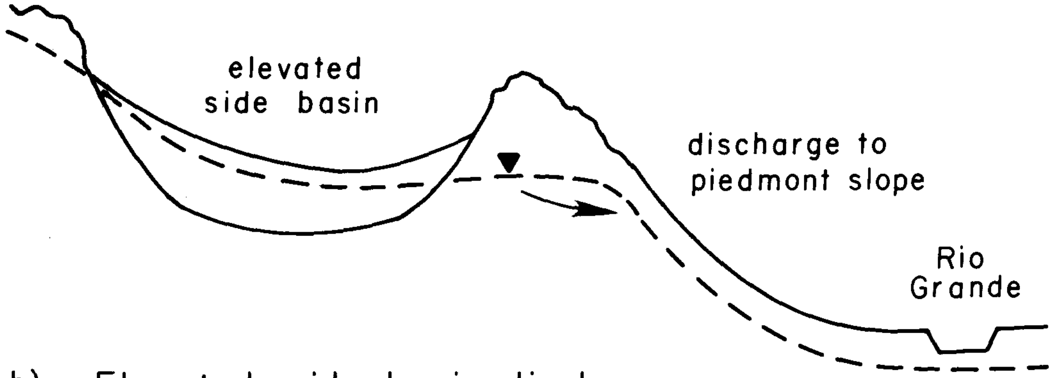
The ephemeral streams have fairly steep gradients and provide a means of conveying integrated runoff down the slope. Along the channels where runoff is concentrated, the sediments are coarse and porous, making the potential for recharge high. Because water is concentrated in the channel, the wetting front can move deep enough to escape evapotranspiration and some water is added to the groundwater reservoir below.

A study of Ropes Draw, an ephemeral stream crossing the western piedmont slope of the San Andres Mountains approximately 25 mi (40 km) northeast of Las Cruces, provided data on rainfall/runoff relationships of such settings (Stone and Brown, 1975). As little as 3% of the precipitation falling on a watershed may show up as runoff in the channel of the main stream. Although 97% of the precipitation enters the ground, most is soon lost to evapotranspiration. Some recharge nonetheless occurs.

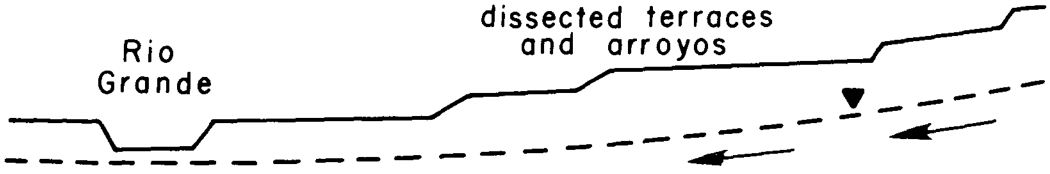
Such recharge is accomplished through transmission loss or downward leakage during flow events. Transmission loss is one of the most important processes in ephemeral-stream hydrology (Renard, 1970). Its effectiveness depends on antecedent moisture or the amount of water remaining in the



a) Piedmont-slope recharge



b) Elevated side-basin discharge



c) Tributary underflow

Figure 1. Schematic cross sections showing source of fresh ground-water bodies, Rio Grande Valley margins; dashed line marked by solid triangle is water table.

unsaturated zone from the last wetting event. In other words, the amount of transmission loss depends on the dryness of the channel sediments at the time a flow event occurs. This is controlled jointly by precipitation characteristics (frequency, intensity, volume) and evapotranspiration. These components of the hydrologic cycle, and thus the potential for transmission loss, may be evaluated by means of two similar factors: climatic index and net water balance.

Climatic index is a dimensionless factor defined by the relationship, $CI = 100\ Pa/(Ta)^2$, where Pa = mean annual precipitation (inches) and Ta = mean annual temperature (°F). According to Mockus (1964), transmission loss can be significant where the climatic index is <1. Based on climatic index calculations for six stations along the Rio Grande Valley (Table 1), transmission loss, and thus recharge potential, should be significant in ephemeral channels throughout the region.

Net water balance is simply the mean annual precipitation minus the potential evapotranspiration. A positive value indicates a surplus, whereas a negative value indicates a deficit. In parts of the valley, annual lake evaporation is as much as 10 times the annual precipitation (Bureau of Reclamation, 1976). As might be expected, water-balance calculations for the six stations in the valley yielded deficits (Table 1), corroborating the conclusion based on climatic index that transmission loss and recharge potential should be significant.

Recharge along ephemeral stream channels results in the formation of underlying bodies of fresh ground water. Such bodies are part of the regional ground-water system, but may be distinguished by slight mounding of the water table and by lower total-dissolved-solids content than in adjacent areas. The position and shape of these bodies coincide roughly with those of the channels beneath which they develop. However, they may extend well beyond the edges of the channel that produced them.

Inter-channel Divides

The interstream divides may have gentle to moderate slopes and are areas of nonintegrated overland flow or sheet runoff. Rain water soaking into the ground on these divides is not concentrated, so does not penetrate very deep, and is soon lost to evapotranspiration. The shallow infiltration depth is documented by the presence of a calcrete or caliche layer (a calcium carbonate soil horizon) within a few feet (lm) of the surface. On slopes that have been stable for a considerable period of time, the calcrete is well developed (Gile and others, 1981) and becomes a semi pervious barrier to recharge. During unusually intense rain events, the interval above such hard pans may become totally saturated, such water

Table 1. Climatic data for selected stations in Rio Grande Valley; precipitation, temperature, and water balance values from Gabin and Lesperance (1977).

Station	Mean Annual Precipitation (inches)[1]	Mean Annual Temperature (°F)[1]	Climatic Index[2]	Net Water Balance (inches)[3]
Taos	12.46 (73)	47.3 (59)	0.56	-19.29*
Espanola	9.35 (47)	49.4 (27)	0.38	-27.12*
Albuquerque (WSO airport)	8.61 (89)	55.7 (83)	0.28	-39.14
Socorro	9.35 (76)	56.8 (69)	0.29	-36.81*
T or C (FAA airport)	8.53 (25)	59.6 (25)	0.24	-40.64
Las Cruces (NMSU)	8.57 (92)	60.1 (80)	0.24	-41.24

[1] based on yearly means; numbers in parentheses below indicate years of record

[2] = $\frac{100 \; (\text{mean annual precipitation, inches})}{(\text{mean annual temperature, °F})^2}$ (Mockus, 1964)

[3] = mean annual precipitation - potential evapotranspiration; negative values indicate a deficit

* surplus occurs some months of the year; value shown represents deficit and surplus

being perched on the calcrete layer. The bulk of this water is ultimately lost to evapotranspiration, but some may get through the calcrete, via fractures, to recharge the groundwater reservoir below.

Based on a study of isotopes and chloride in the unsaturated zone, recharge through a calcrete surface in a semiarid region of South Australia was found to range from 0.05 to 74 mm/yr (0.0019 to 2.91 inches/yr), depending on degree of fracturing (Stone and others, 1982). The maximum value was associated with a sinkhole caused by solution and collapse of underlying limestone and thus is not applicable to most piedmont slopes. A value of <1.0 mm/yr (<0.03937 inches/yr) would be reasonable, suggesting fresh ground-water bodies will not develop as well beneath divides as beneath ephemeral stream channels.

ELEVATED-SIDE-BASIN DISCHARGE

The fresh water underlying a piedmont slope is not necessarily all derived from recharge on that slope. In areas where an isolated alluvial basin lies above and behind the valley-bordering piedmont slope, much of the ground water flowing beneath the surface may result from leakage from the isolated 'basin. Such elevated side basins occur where another mountain range lies behind the valley-bordering mountain range and the intervening depression has been filled to a position above that of the Rio Grande Valley floor (fig. lb). In such a setting, ground water from the elevated side basin moves through fractures in the valley-bordering mountain block.

This source of fresh ground-water bodies was documented during a study of the hydrology of a now abandoned landfill north of Socorro (Stone and Foster, 1977). As noted by Hall (1963), ground water from La Jencia Basin leaks through the Socorro-Lemitar mountain range and flows beneath Nogal Arroyo toward the Rio Grande in the vicinity of Escondida, New Mexico. The fresh ground-water body produced by this leakage is lobate in shape, more or less parallels Nogal Arroyo but extends beyond it, and penetrates the more saline ground water of the Rio Grande Valley (Stone and Foster, 1977, figs. 4 and 5).

In 1977, the city of Socorro simultaneously established a municipal landfill and a municipal water well adjacent to Nogal Arroyo, west of 1-25 at the Escondida interchange. Unfortunately, the main consideration in siting both the landfill and the well was city ownership of the land. Partly in response to public concern over pollution of the fresh ground-water in the area, the landfill was abandoned shortly thereafter.

Based on data presented by Clemons (1979), the Nutt-Hockett basin southwest of Hatch, New Mexico, would be another example of an elevated side basin. Brief inspection of the state geologic map (Dane and Bachman, 1965) suggests other examples may occur on the west side of the valley, northwest of Truth or Consequences, New Mexico. A hydrologic study of these areas would be required to confirm this.

TRIBUTARY UNDERFLOW

Most large tributaries of the Rio Grande are characterized by saline underflow. Examples would include the Rio Salado and Rio Puerco. However, fresh ground-water bodies may be associated with the underflow of other tributaries draining non gypsiferous bedrock or alluvium and not fed by saline ground-water discharge (fig. lc). Examples are not documented at present and landfills are not likely to be sited in such areas. Nonetheless, this source of fresh ground-water bodies is included for completeness.

IMPLICATIONS FOR LANDFILL SITING

Water of any kind is limited in semiarid regions like New Mexico, but fresh water is even more scarse. As communities in the Rio Grande Valley grow in response to the general population shift to the Sunbelt, the need for fresh water supplies will increase. The current trend of residing on the rural outskirts of population centers will no doubt prevail. The localized fresh ground-water bodies described here will be of considerable use to such homeowners.

Unfortunately, the growth of Rio Grande communities will also increase the need for sanitary landfills. Undesirable materials from landfills may mix with ground water through the formation of leachate (a fluid consisting of residual liquid draining from the waste and precipitation or ground water moving through the landfill). the composition of the leachate depends on the nature of the waste and not only varies from landfill to landfill, but also varies with time and place within the same landfill (Turk, 1970, Tables 3, 4, and 5).

In regions of low precipitation, little leachate is generally formed (Flawn, 1970, p. 149). However, intense precipitation events do occur. For example, on 29 August, 1935, the following record intensities were recorded at Las Cruces: 2.5 inches (63.5 mm) in 30 minutes, 4 inches (101.6 mm) in 2 hrs, 5 inches (127.0 mm) in 3 hrs, and nearly 6 inches (152.4 mm) in 4 hrs (Houghton, 1972). Such occasional but intense events are not only capable of producing a slug of leachate but presumably are also capable of moving it toward the water table.

Ideally, migration of leachate may be limited by siting landfills in areas of deep water table or where impermeable material lies between the surface and the water table; ground-water recharge and discharge zones should also be avoided (Bergstrom, 1968). If natural barriers do not exist, artificial barriers (such as clay layers) should be constructed.

In practice, however, siting may be based solely on economic considerations: price or ownership of land, transportation costs, ease of excavation, etc. This is especially true in small communities where budgets are small and technical expertise is either limited or not sought. The location of fresh ground-water bodies can be reasonably predicted and easily checked. It is hoped that future landfill siting will include some consideration of their protection.

The fresh ground-water bodies should obviously also be protected in the disposal of more toxic materials. Although the Rio Grande Valley has not been targeted for study as to its suitability for high-level radioactive waste disposal, a study of possible sites for low-level waste disposal has recently been completed (Hawley, 1983). Sites for nonradioactive hazardous-waste disposal facilities have yet to be located. Criteria given by Longmire and others (1981) for selecting hazardous-waste disposal sites in New Mexico should be consulted when such facilities are finally located.

ACKNOWLEDGEMENTS

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REFERENCES

Bergstrom, R. E., 1968, Disposal of wastes -- scientific and administrative considerations: Illinois Geological Survey, Environmental Geology Notes, no. 20, 12 p.

Clemons, R. E., 1979, Geology of Good Sight Mountains and Uvas Valley, southwest New Mexico: New Mexico Bureau of Mines and Mineral Resources, Circular 169, 32 p.

Dane, C. H., and Bachman, G. 0., 1965, Geologic map of New Mexico: U.S. Geological Survey, scale 1:500,000.

Flawn, P. T., 1970, Environmental geology: Harper and Row, Publishers, New York, 313 p.

Gabin, V. L., and Lesperance, L. E., 1977, New Mexico climatic data -- precipitation, temperature, evaporation, and wind; monthly and annual means 1850-1975: W. K. Summers and Associates, 436 p.

Gile, L. H., Hawley, J. W., and Grossman, R. B., 1981, Soils and geomorphology in the Basin and Range area of southern New Mexico -- guidebook to the Desert Project: New Mexico Bureau of Mines and Mineral Resources, Memoir 39, 222 p.

Hall, F. R., 1963, Springs in the vicinity of Socorro, New Mexico: New Mexico Geological Society, Guidebook 14th field conference, pp. 160-179.

Hawley, J. W., 1983, Site identification for low-level radioactive waste disposal in New Mexico: New Mexico Bureau of Mines and Mineral Resources, Open-file report 189, 37 p.

Houghton, F. E., 1972, Climatic guide, New Mexico State University, Las Cruces, New Mexico, 1851-1971: New Mexico State University Agricultural Experiment Station, Research Report 230, 20 p.

Longmire, P. A., Gallaher, B. M., and Hawley, J. W., 1981, Geological, geochemical, and hydrological criteria for disposal of hazardous wastes in New Mexico: New Mexico Geological Society, Special Publication no. 10, pp. 93102.

Mockus, Victor, 1964, Estimation of direct runoff from storm rainfall: Soil Conservation Service, National Engineering Handbook, Chapter 10, Section 4 - Hydrology, pp. 10-1-10-24.

Renard, K. G., 1970, The hydrology of semiarid rangeland watersheds: U.S. Department of Agriculture, Agricultural Research Service, Report ARS 41-162, 26 p.

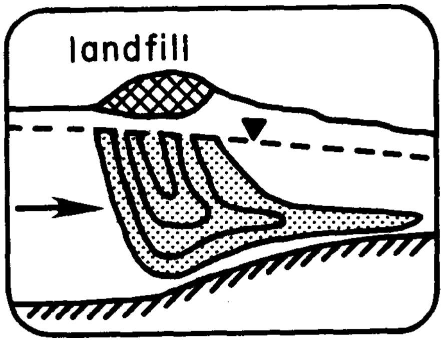
Stone, W. J., Allison, G. B., and Hughes, M. W., 1982, Environmental changes in a calcrete surface (South Australia) from isotopes and chloride in the unsaturated zone (abs): Abstracts, Fifth International Conference on Geochronology, Cosmochronology, and Isotope Geology, Nikko, Japan, p. 356.

Stone, W. J., and Brown, D. R., 1975, Rainfall-runoff relationships for a small semiarid watershed, western flank San Andres Mountains, New Mexico: New Mexico Geological Society, Guidebook 26th field conference, pp. 205-212.

Stone, W. J., and Foster, R. W., 1977, Hydro geologic studies of the Socorro landfill site by the New Mexico Bureau of Mines and Mineral Resources: New Mexico Bureau of Mines and Mineral Resources, Open-File Report 86, 66 p.

Turk, L. J., 1970, Disposal of solid wastes -- acceptable practice or geological nightmare?, in Environmental Geology, American Geological Institute, short course lecture notes (pages not consecutively numbered).

U.S. Bureau of Reclamation, 1976, New Mexico Water Resources -- assessment for planning purposes: U.S. Bureau of Reclamation, southwest region, in cooperation with New Mexico Interstate Stream Commission and the New Mexico State Engineer's Office, 218 p.



EXPERIMENTAL EVALUATION OF LEACHATE ATTENUATION FROM AN IN-SITU COPPER MINE

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ABSTRACT

Laboratory rock-column experiments were used to evaluate pollution attenuation processes at a proposed in-situ copper mine near Santa Fe NM. The experiments simulated the migration of a potent leachate through country rock containing native ground water; and the subsequent flushing out of leachate by a fresh ground-water sweep. The experiments demonstrate that the passage of leachate would cause a marked deterioration in ground-water quality, but that essentially complete aquifer restoration could be accomplished by flushing with fresh water and removal of the displaced leachate. Dilution, pH buffering (neutralization), ion exchange, absorption and/or precipitation are apparent attenuation processes. pH would be the definitive parameter for monitoring water quality near the mine. A secondary leaching phenomenon was observed: migrating leachate dissolved out increased amounts of iron-alumina silicate minerals at the same time as attenuation led to reduced dissolved solids content.

INTRODUCTION

In the early 1970's, a subsidiary of Occidental Petroleum Corporation proposed in-situ chemical extraction of a low-grade (less than 0.5%) copper deposit which occurs in the Cerrillos Hills about 30 km SW of Santa Fe, New Mexico. The project would have involved: 1) blasting to fracture the ore zone, which is an oxidized cap on a copper sulfide deposit associated with a series of Tertiary monzanite intrusions; 2) leaching via percolation of surface-applied sulfuric acid; 3) collection of the leachate in tunnels, drains and/or wells; and 4) precipitation of copper through exchange with scrap iron. The project has yet to be implemented, in part due to the depressed price of copper.

Environmental impacts of the project were evaluated by ROMCOE, the Rocky Mountain Center on Environment (now known as ACCORD). The potential impact of primary concern was the possibility that if some leachate were to escape collection, it could migrate through the aquifers which surround the mine and cause contamination of scarce local water supplies. Even though the risk of such an escape was considered small, it was essential to determine the environmental consequences should a leachate excursion occur; a particular objective was to identify water-quality parameters which might *be* diagnostic of a pollution episode.

METHODS

It is common industry practice to use laboratory studies to evaluate the potential mineral extraction that may result from acid leaching. Consultants to Occidental performed numerous experiments in which dilute sulfuric acid was percolated through vertical pipes (columns) containing core samples of ore-body rock. Analyses were made of the leachate collected at the column bottom; models of solution kinetics were used to predict the amount of copper which would be obtained from a full-scale project. Although field data for in-situ copper mining are limited, it is believed that, with proper adjustments for factors such as rock particle size, the laboratory data provide a basis for reasonably accurate forecasts of actual mining conditions (Dr. Ron Roman, personal communication).

ROMCOE elected to take the same laboratory approach to evaluate potential ground-water impacts of a leachate excursion. ROMCOE performed two experiments in which leachate from the ore-body experiments was percolated through columns containing core-samples fragments from. country rocks (i.e. non-ore bearing material from areas near the ore body). One test had the following characteristics: 1) a single column of PVC pipe, 3 feet (0.9 m) high and 3 inches (7.6 cm) in diameter, was packed with a country rock (a non-oxidized monzonite) having a bulk density of 90 pounds per cubic foot (1.44 g/cm^3); 2) the rock was saturated with native ground water; 3) leachate was dripped onto the top of the column for 24 hours, to simulate the relatively brief migration of fluid which might escape control at the mine site; 4) native ground water was passed through the column for approximately 150 hours, to simulate the effects of a 'ground-water sweep', in which good-quality water is used to flush out contaminated water; 5) periodic water samples taken at the column bottom were analyzed for a broad array of parameters, using standard laboratory methods.

A separate test involved: 1) three columns, the first containing unsaturated, oxidized monzonite (representing a vadose zone) and the others containing saturated, non-oxidized monzonite; 2) leachate was applied to the first column for 100 hours; this was followed by 71 hours of flushing by native ground water; 3) effluent from the first column was applied to the top of the second and effluent from the second column was applied to the third; 4) periodic water samples were collected at the bottom of all three columns, and analyzed as in the other test.

The leachate used in the tests was obtained from Occidental's consultants and had a specific conductance (SC) of about 100,000 micromhos/cm, with a pH of about 1. Copper and sulfate were the dominant ions, occurring at 6,000+ mg/1 and 30,000+ mg/1 respectively. (For comparison, the drinking water standard for copper is 1 mg/1!) Concentrations of major cations such as aluminum, calcium, iron, and magnesium typically exceeded 400 mg/1; other than sulfate, the only important anion was phosphate at 3,500 mg/l. Metals such as arsenic, cadmium, chromium, cobalt, molybdenum, antimony and tin were present in concentrations of a few tenths to a few mg/l. Leachate concentrations of nickel and lead reached 23.4 mg/1 and 6.1 mg/1 respectively.

Native ground water used for flushing had a pH of 7.5 and a SC of about 2,300 micromhos/cm. It was a calcium sulfate water (Ca = 350 mg/1 and SO4 = 1000 mg/1) The copper concentration of the ground water was 0.1 mg/1 and other metals were found in concentrations of less than 0.05 mg/l.

All of ROMCOE's laboratory work was supervised by Dexter Reynolds of Controls for Environmental Pollution, a Santa Fe NM firm specializing in laboratory analyses of environmental media. The laboratory report provided to ROMCOE is available from the author of this article. The report notes that at times the leachate drip was interrupted (pump malfunctioned, or otherwise turned off); and that near the beginning of the single column experiment, the column plugged and it was necessary to clean and repack the rock fragments. Despite these problems, the overall consistency of the results (see below) indicates that the experiments accomplished the objective of simulating attenuation processes, at least with respect to overall character and magnitude.

RESULTS

The most informative results from the ROMCOE tests were the variations in pH and SC. Figure 1 plots pH and conductivity values obtained during the single column test; Figure 2 plots pH and conductivity for each column in the three-column test. The following discussion summarizes the basic data obtained from the tests; these data are interpreted in the subsequent section.

1. In the single column experiment (Figure 1), since the column was originally saturated by ground water, the initial effluent draining from the column was close to natural, background quality, with pH = 6.3 and SC = 2,300. (SC values are in micromhos/cm.)

2. The impact of leachate migration through the column was detected quickly by pH and conductivity monitoring. pH fell

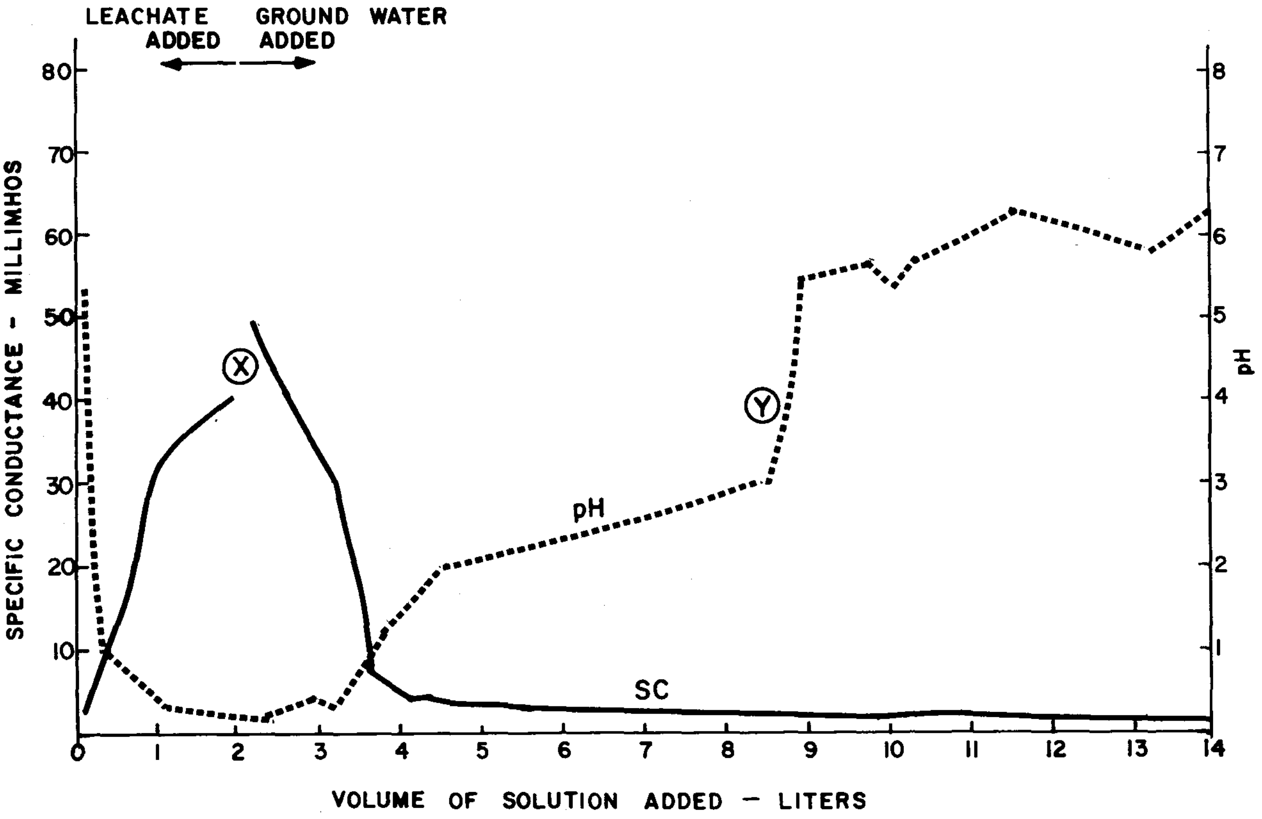

FIGURE 1. pH AND SPECIFIC CONDUCTANCE VALUES DURING SINGLE-COLUMN TEST.

X = column cleaned and replaced
Y = pump off over weekend

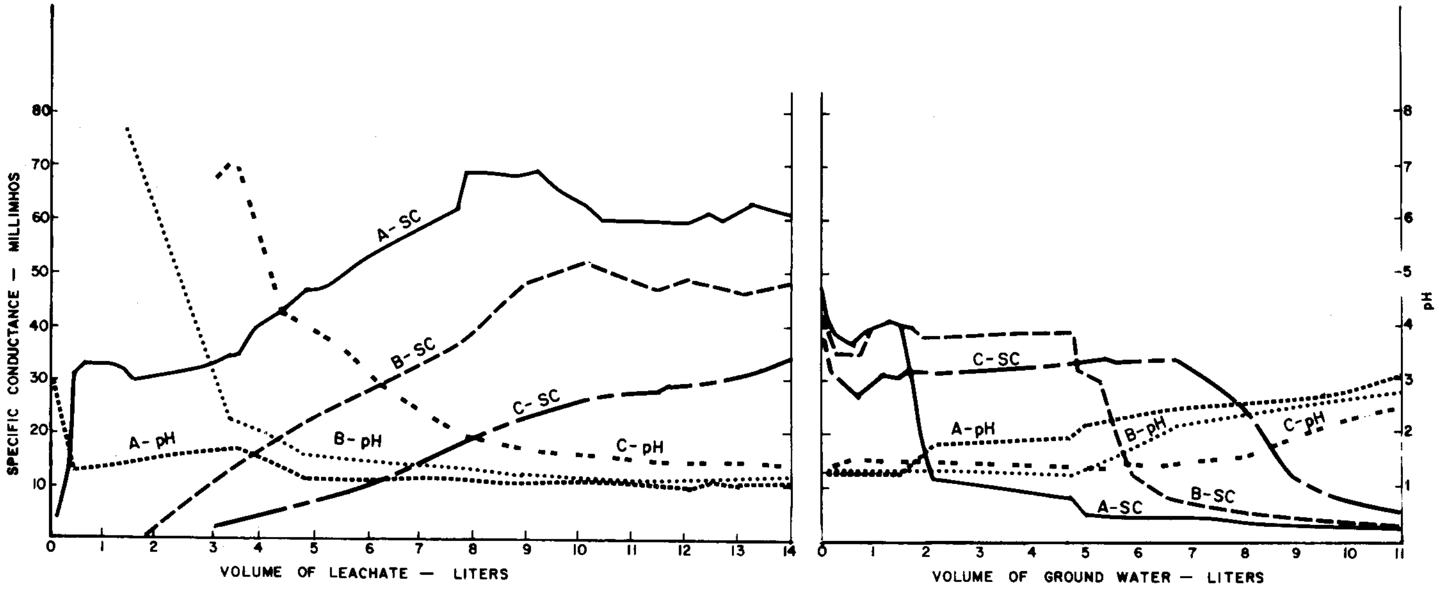

FIGURE 2. pH AND SPECIFIC CONDUCTANCE VALUES DURING THREE-COLUMN TEST.

(A-SC means the specific conductance values observed in effluent from column A.)

rapidly to less than 2 and eventually stabilized at 1.2. SC rose to about 50,000.

3. Shortly after the ground-water sweep began, water quality started to recover. pH rose to 3, then more slowly to 4, then rapidly to 6. By the end of the test, pH was nearly 8, a value higher than for the applied ground water. SC decreased rapidly to about 3,000, then slowly to less than 2,000; again, by the end of the test SC was lower than in the water used for flushing.

Most of the major and minor elements and compounds varied over time in the same manner as specific conductance. These constituents were present at background levels (or not at all) in native ground water; became considerably elevated once leachate appeared at the column bottom; and declined rapidly after flushing began. Specifically, when flushing began to cause a pH rise, the corresponding changes in metal concentrations were rapid, with reductions of 10x or more with a pH increase of a few tenths. Parameters such as potassium, silica, sodium, and boron were reduced in concentration by as much as 2-fold with a pH change of about 0.5.

The three-column experiment provided additional information on the way a leachate plume would evolve as it moves away from the source (Figure 2). In particular, water-quality changes in the third column were smaller and less rapid than in the second column, which in turn was characterized by changes which were less sharply defined than in the first column. For example, during leachate addition the SC of effluent from column 1 peaked at 70,000; while the SC in effluent from column three peaked at 38,400. Minimum pH levels were 1.0 in the first column, 1.1 in the second and 1.3 in the third.

Not all constituents showed a marked decrease as migration occurred. Calcium and magnesium concentrations were relatively low at first, then increased as the pH rose. Most interesting was the observation that some constituents displayed "delayed leaching" behavior in the three-column test. During the time when the effluent from final column was acid and saline, indicating leachate contamination, concentrations of iron, aluminum and silica (and to a lesser extent arsenic, manganese, lead) were considerably higher than concentrations found in original leachate. For example, aluminum reached a concentration of 1260 mg/1 in final column effluent, but was found only at 580 mg/1 in the leachate applied to the first column.

After completion of the experiments the rocks were removed from the columns; a residue or precipitate was observed. Limited data indicate that the precipitate was dominantly calcium sulfate (gypsum).

INTERPRETATION

INDICATOR PARAMETERS FOR MONITORING

While several parameters might be potentially useful for the monitoring of leachate migration (e.g. copper, cobalt), by far the best indicator of pollution and aquifer restoration would be pH. Advantages of pH monitoring include:

1. pH is measured easily and accurately by inexpensive real-time field equipment;

2. pH values as low as observed in leachate do not occur in native ground water in the Cerrillos area; thus observation of low pH values in monitoring wells would be diagnostic of a leachate excursion;

3. a relatively small drop in pH, to less than 6, would be suggestive of a leachate excursion; at this pH other potential indicators probably would still be at background levels and would provide no evidence of a potential problem;

4. toxic metals were typically observed to be at safe concentrations in water with a pH of 3 - 4 or higher, and at unacceptable levels where the pH was 1 or 2; thus pH is a good measure of the potential toxicity of a Cerrillos leachate.

In summary, pH would change sooner and more rapidly than any other parameter in the event contamination occurs, and thus would provide a reliable, sensitive early warning of a possible pollution problem. pH monitoring would be a logical primary component in any environmental program at an in-situ mine of the type proposed for Cerrillos.

LEACHATE ATTENUATION

Figures 1 and 2 show that a change in the type of fluid added at a column top was reflected almost immediately by a change in the chemistry of the column effluent. Thus observed changes in water quality reflect in part the simple physical displacement of one type of water by another.

However, the data also indicate that other phenomena were acting to change water quality and to attenuate the potency of the initial leachate. For example, using SC as a measure of dissolved solids, column A retained two-thirds of all dissolved solids contained in the leachate added at the column top. About 15 percent of the dissolved solids in the leachate reached the end of column 2. A few percent of the "missing" dissolved solids can be accounted for as still being in solution in the water which had not yet drained from the columns; however most of the minerals contained in the initial leachate must have been removed by some physical or chemical process related to rock-water interactions. Attenuation is also shown by the fact that, in the three-column experiment, water-quality changes in each succeeding column were smaller and less rapid than in the preceding columns. Speculations about the chemical dynamics of the migrating leachate are given below.

1. Although physical displacement of leachate occurred in response to ground-water flushing, changes in SC and pH occurred gradually over a period of several hours. This indicates that there was no sharply defined interface between the native ground water and the leachate it was displacing. Dilution and dispersion are processes which probably operated to mix the two types of water and to erase any "ground-water front".

2. Leachate neutralization is indicated by the acid consumption which was measured by the fact that the pH in water from column 3 was never as low as the pH in the leachate dripped onto column 1. Neutralization of leachate would be limited in the Cerrillos area due the lack of carbonates and other rock materials capable of contributing to pH buffering.

3. The delayed leaching phenomenon is an indication of complex solubility relationships. Ion exchange is presumably involved, since the increase in iron, aluminum et al. was accompanied by a decrease in the concentration of less soluble ions, especially copper and other metals.

4. The rise in calcium concentrations with leachate migration probably reflects the neutralization process noted above, and the fact that gypsum solubility would increase as copper and other ions are removed from solution and sulfate ions become more available.

5. The decrease in dissolved solids can be accounted for in part by precipitation, as evidenced by the residue observed on the country rock. No direct evidence was obtained regarding absorption, but metals such as copper presumably were impacted by this process to some extent (limited by the texture and mineralogy of the country rock).

The above processes appear sufficient to account for the bulk of the experimental observations. Thus other potential attenuation mechanisms (e.g. oxidation, reduction, filtration, hydrolysis, volatization) probably were of minor importance.

ROLE OF GROUND-WATER SWEEP

Although leachate attenuation is indicated, it remains clear that physical displacement played a major role in the observed water-quality changes. Thus the simple flushing of an aquifer with good-quality water would have the effect of pushing polluted water away from the site, but in itself would not fully mitigate the effects of a leachate excursion. If a leachate loss were to occur, aquifer restoration would require that the ground-water sweep be designed to displace leachate to collection wells where the contaminated water could be removed for treatment.

CONCLUSION

Based on the ROMCOE study of the Cerrillos site, laboratory experiments have considerable value in simulating a potential pollution episode. An escape of leachate from the Cerrillos mine would be quickly reflected by a marked deterioration in water quality; local water supplies (which are already marginal) would be polluted and unusable.

The data indicate that while rock-leachate interactions may provide some attenuation of pollutants during leachate migration, the principle means for restoring water quality must be the physical displacement of escaped leachate by a fresh ground-water sweep which includes collection and treatment of the escaped leachate.

All major changes in water quality were accompanied by readily measured changes in pH, indicating that pH is an especially useful monitoring parameter for any in-situ mine which uses an acidic leaching solution. The solution dynamics of the delayed leaching phenomenon represent an interesting research problem for future analysis.

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APPLICATION OF THE KONIKOW AND BREDEHOEFT SOLUTE TRANSPORT MODEL TO WATER-QUALITY PROBLEMS IN NEW MEXICO

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ABSTRACT

Computer modeling of solute transport and dispersion of ions in ground water is a valuable tool in many New Mexico aquifer systems. A program written by L. F. Konikow and J. D. Bredehoeft in 1978 has proven to be effective in projecting long-range effects.

Most of the model assumptions are adaptable to water-table aquifers in the State. The assumptions require a conservative contaminant; hydrocarbons may be excluded by fluid density, viscosity, and temperature assumptions.

Two case studies are presented. The model was successfully used to project the plume of waste products from a chemical plant discharging into a shallow alluvial aquifer. An analysis of nitrate movement from the Santa Fe River to the underlying aquifers was made.

INTRODUCTION

The contamination of a ground-water resource is a serious problem in New Mexico and throughout the nation. Such problems can have long-term economic and physical consequences which may not be easily remedied. While the prevention of contamination should be the ultimate goal of all water users, the capability to predict the movement of dissolved chemicals in moving ground water is also needed in order to: (1) plan and design projects to minimize potential contamination; (2) estimate variations of chemical concentrations in time and space; (3) estimate time-of-travel for a contaminant from one point to another; (4) design an effective and efficient monitoring system; (5) design reclamation plans and/or systems to prevent contaminants from spreading.

The chemical concentration within a dynamic groundwater system may change as a result of four distinct processes: (1) mixing of fluid types; (2) convective transport; (3) hydrodynamic dispersion; (4) intra-aquifer reactions. Most of the ground-water contamination problems in New Mexico involve the first two processes; the latter two processes are of lesser importance.

Convective transport and hydrodynamic dispersion depend on the velocity of ground-water flow, the mathematical simulation model must solve two simultaneous partial differential equations. One is the equation of flow, from which groundwater velocities are obtained, and the second is the solute-transport equation which describes the chemical concentration in the ground water.

The method of studying transient two-dimensional areal flow by digital computer was described by Pinder and Bredehoeft (1968). The application of areal transport and dispersion of a chemical constituent in ground water was described by Reddell and Sunada (1970), Bredehoeft and Pinder (1973), and Konikow and Grove (1977).

PROCESSES AND ASSUMPTIONS

In 1978 Konikow and Bredehoeft made a comprehensive presentation of their computer model which was capable of calculating transient changes in the concentration of a non-reactive solute in flowing ground water. Thus it was possible to compute the concentration of a dissolved chemical constituent in an aquifer at any specific place and time. This model has widespread application to water-quality problems in New Mexico.

In order to integrate the flow equation with the transport equation, it was necessary for Konikow and Bredehoeft (1978, p. 4) to make a number of assumptions. They are as follows: (1) Darcy's law is valid and hydraulic-head gradients are the only significant driving mechanisms for fluid flow; (2) the porosity and hydraulic conductivity of the aquifer are constant with time, and porosity is uniform in space; (3) gradients of fluid density, viscosity, and temperature do not affect the velocity distribution; (4) no chemical reactions occur that affect the concentration of the solute, the fluid properties, or the aquifer properties; (5) ionic and molecular diffusion are negligible contributors to the total dispersive flux; (6) vertical variations in head and concentration are negligible; (7) the aquifer is homogeneous and isotropic with respect to the coefficients of longitudinal and transverse dispersivity.

Very rarely are all of these assumptions completely valid in a specific field problem. Consequently the degree to which field conditions deviate from these assumptions will affect the applicability and reliability of the model for that problem.

Virtually all ground water flow models are based on Darcy's law and assume that the aquifer is homogeneous, isotropic, and infinite. Since these are standard assumptions commonly made in ground-water assessments, their limitations on a conventional analysis are understood and accepted.

One of the more important assumptions to be considered is that the vertical variations in head and concentration are negligible. Since most contaminants are assumed to intersect the water table from above, three-dimensional dispersion will occur. However in most hydrologic systems, the horizontal permeability is many times greater than the vertical, and the vertical mixing will be limited. Therefore it is necessary to assume that a contaminant injected into the upper 10 or 20 feet of the aquifer in a uniform concentration, and all movement is assumed to be horizontal within the zone of contamination.

Under steady-state conditions, most ground-water flow is parallel with the phreatic surface and there is very little mechanism for vertical mixing of solutes. However a pumping well provides a strong vertical flow component.

Hydrocarbons are a common contaminant which generally do not meet these assumptions, and the applicability of the Konikow and Bredehoeft model may not be valid when studying this contaminant. Due to the low density and the immiscibility of most hydrocarbons with ground water, the contaminants stratify in the upper few inches of the aquifer system and virtually no mixing occurs. Also, their relatively high viscosity will retard the movement by convective transport and the viscosity will change with time as the volatiles are released.

CASE STUDIES

Two different case studies are cited as examples of the suitability of the Konikow and Bredehoeft model to water-quality problems in New Mexico. In one case seepage from the discharge pond of a chemical company entered a relatively uniform shallow aquifer system. A large amount of available field data produced a good calibration and enabled the chemical company to make long-term projections of the impacts under different discharge scenarios. In the second case very little field data were available. Nevertheless it was possible to make a worst-case assessment of the effects of seepage from a river channel by treated sewage.

SINGLE-POINT INJECTION INTO A UNIFORM AQUIFER

Geo hydrologic conditions

Much of southeastern New Mexico is underlain by relatively unconsolidated deposits of silt, sand, and gravel. The Ogallala Formation is a major water-bearing deposit, and locally younger geologic processes have reworked these deposits. Although the aquifer characteristics may vary locally, in general the uniform lithology results in aquifer parameters which are within the same order of magnitude. These alluvial aquifer deposits generally overlie thick sequences of relatively impermeable shale and siltstone.

In 1962 a chemical manufacturer began discharging waste products into unlined pits that had been excavated into Ogallala-like deposits. Only minimal records of the quantity and quality of discharge were kept. In 1980 the manufacturer undertook a study to determine the effects of its discharge on the area. The Konikow and Bredehoeft model proved to be an invaluable tool during this investigation.

Subsurface information was obtained from about 30 test holes that had been drilled in the area. Aquifer thickness, configuration of the water table, water quality, and transmissivity were determined at a number of sites (fig. 1). An area of dry alluvium was identified immediately northwest of the disposal site; elsewhere the thickness generally increased from about 5 feet (1.5 m) to more than 30 feet (9.1 m) from northwest to southeast. The direction of ground-water flow was also from northwest to southeast, but there was some evidence of mounding at the facility prior to 1980.

A total of 16 aquifer tests were conducted using the method described by Bouwer and Rice (1976). The results of these tests were quite varied with a range in transmissivity of 1 ft^2/d (0.09 m^2/d) to 1,081 ft^2/d (100.4 m^2/d). The only pattern in distribution of the transmissivity values was a general increase in value from west to east. There was no obvious explanation for this trend.

As a result of a water-quality sampling program between 1953 and 1955, prior to beginning operations of the chemical plant, Nicholson and Clebsch (1961, p. 100) described the water as ". . . generally high in silica (65 to 82 ppm), moderately high in calcium-plus-magnesium, low in sodium-plus-potassium, moderately low in sulfate and chlorides, and moderately high in dissolved solids." Waste products from the plant were characterized by high acid content plus high levels of sulfate and chloride. A number of water samples were collected from wells and test holes near the plant, pH was measured in the field. It was found that the pH was generally above 7.0 and acid in the discharge was being neutralized by caliche in the soil. Chloride levels ranged from 154 mg/1 (milligrams per liter) to 28,4000 mg/1, and concentrations greater than 1,000 mg/1 were found in all samples south and east of the plant. Inasmuch as oil-field brines are discharged extensively throughout the region (Nicholson and Clebsch, 1961, fig. 25), it was found that these high-chloride brines could not be differentiated from those of the chemical plant. In most cases, sulfate is a conservative (non reacting) anion in ground water.

Calibration

The model is based on a square, block-centered, finite-

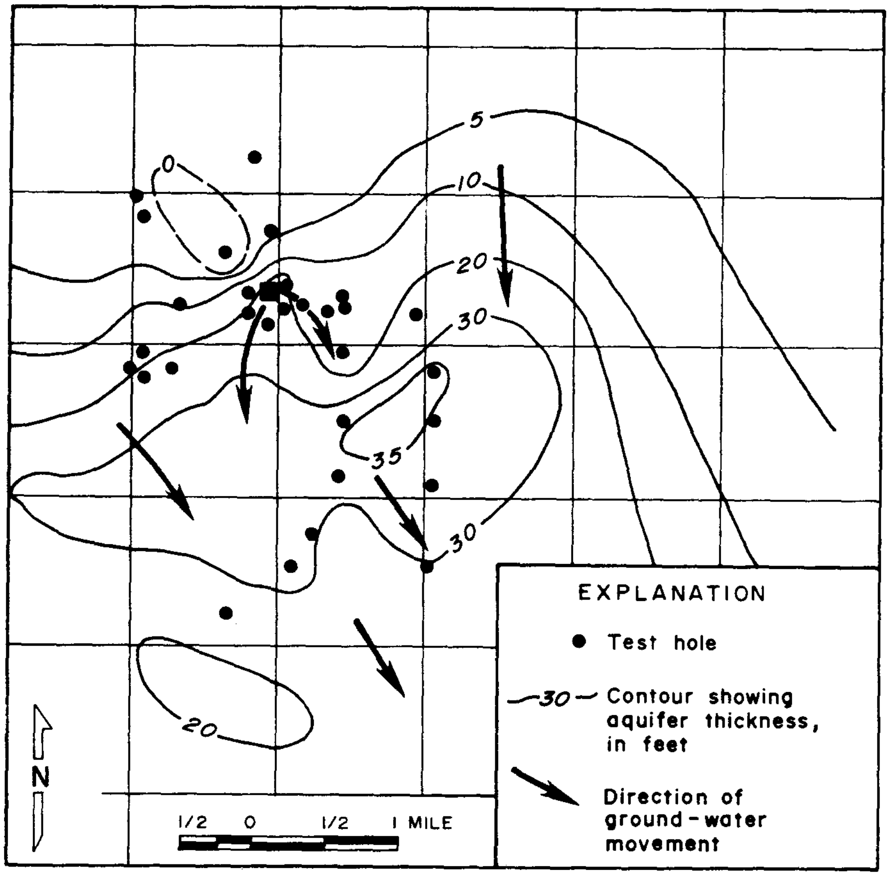


Figure 1. Map in vicinity of chemical plant showing subsurface control and hydrologic data.

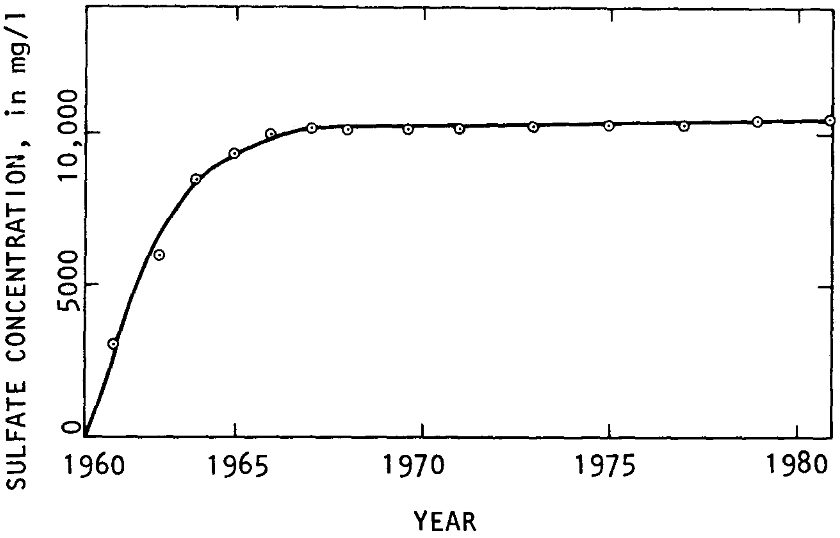


Figure 2. Plot of sulfate concentration versus time for hypothetical well near disposal pond.

difference grid. Constant-flux and constant-head conditions can be simulated in the model and are used to represent the real or artificial boundaries. Use of the latter can help to minimize data requirements and the areal extent of the modeled part of the aquifer. Four hundred nodes with an equidimension of 1,320 feet (0.65 km^2) were used. The waste discharge was simulated by a hypothetical injection well at the disposal pond node. Four observation wells were selected for showing the concentration increase with time. A 20-year time frame was used to correspond with the period 1962 to 1982.

Inasmuch as the quantity and quality of the plant discharge during the first 20 years of operation was generally unknown, certain assumptions were made in order to begin calibration of the model. First, it was assumed that the waste products from the plant area were a saturated brine in which 30 percent of the ions were sulfate, or approximately 100,000 mg/1 sulfate. Also, since the discharge rate was estimated to range from zero to 100 gpm, it was assumed for "worst-case conditions" that the discharge was 100 gpm for 20 years.

The computer run showed that the background sulfate levels of 100 mg/1 were quickly displaced, and within a period of about 5 years the concentrations approached 100,000 mg/1 sulfate. Subsequent computer runs were made simulating concentrations of 10,500 to 10,200 mg/1 sulfate to correspond with a field measurement of 10,125 mg/l. Since the displacement of background levels occurs quite rapidly (fig. 2), it was concluded that the average concentration of discharge from the plant for the 20-year period was about 10,200 mg/1 sulfate.

Similar calibration techniques were used to determine the discharge rate of the chemical plant. Although the assumed concentration of 10,200 mg/1 sulfate data accurately matched the measured results for wells in the immediate vicinity of the plant site, simulated high concentrations were much more widespread than actually monitored. Therefore a series of calibration runs were made using a concentration of 10,200 mg/1 and discharge rates of 80, 60, and 40 gpm. The computer run using 60 gpm more nearly matched the actual sample data than the runs at 80 and 40 gpm. From this it was concluded that the average discharge from the plant was approximately 60 gpm for the first 20 years of plant operation.

Projected Plume Growth

Through the process of calibration, by varying the sulfate concentrations and the discharge rate, it was possible to achieve a good match between the available field data and the computer output. This is illustrated by the 1982 plume in fig. 3.

During the initial years of operation, the maximum

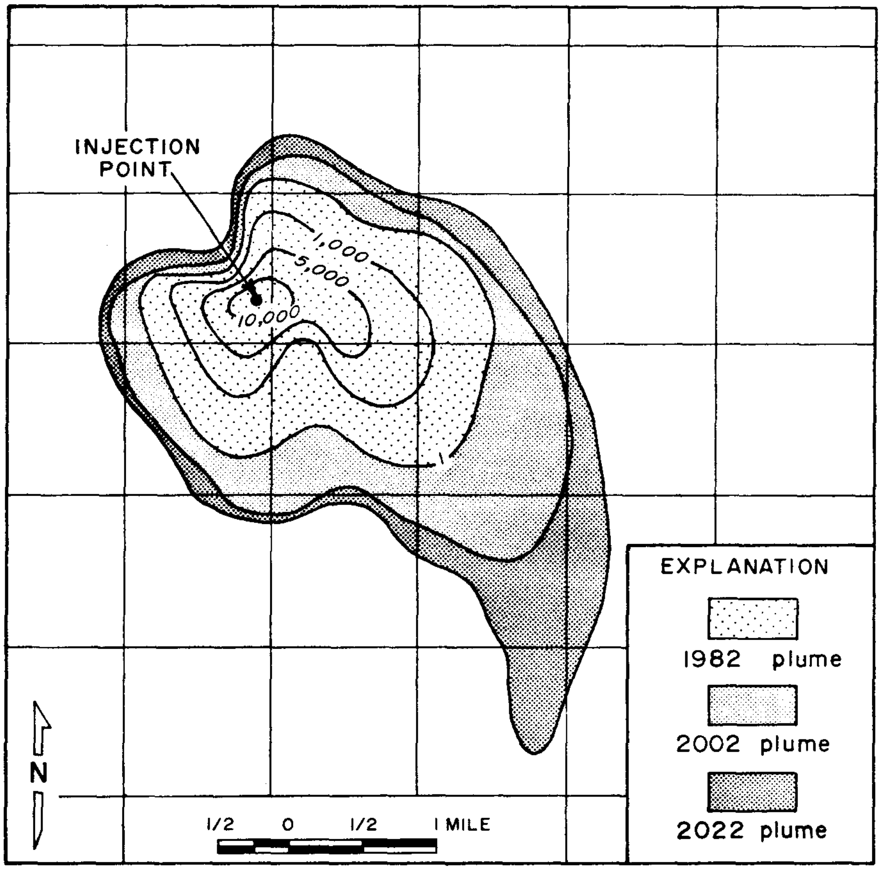


Figure 3. Diagrammatic map showing growth of contamination plume for years 1982 through 2022. Contour shows concentration of sulfate, in mg/l.

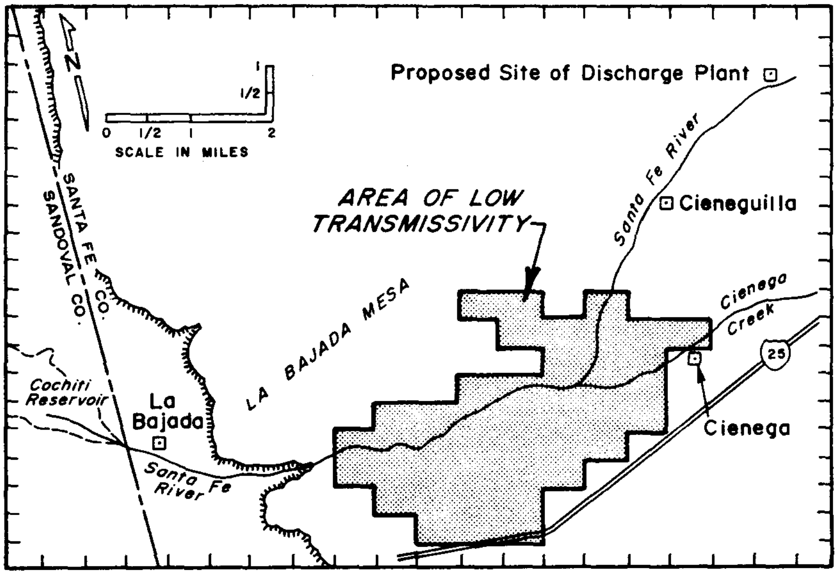


Figure 4. Location map of Santa Fe project area.

areal extent of the sulfate plume was 3.51 square miles (9.1 km^2); this was the area in which the simulation showed an increase of at least 1 mg/l. The area of 1,000 mg/1 sulfate is 1.61 square miles (4.2 km^2) and the 5,000 mg/1 sulfate levels underlie 0.79 square miles (2.0 km^2)(fig. 3). The map shows an area of 10,000 mg/1 sulfate beneath an area of about 0.10 square miles (0.26 km^2).

Following the original model application in 1982, plant modifications were made and the discharge rate was reduced 40 percent. Model simulations were then made showing the net affect of discharge by the year 2002 and 2022 (fig. 3). In general, the plume of sulfate becomes considerably more locate by the year 2022 due to the high transmissivity south and east of the disposal site; however the areas of higher concentration do not change appreciably.

STREAMBED SEEPAGE INTO COMPLEX AQUIFER

Geohydrologic Conditions

For a number of years the City of Santa Fe released effluent from waste-treatment facilities into the channel of the Santa Fe River where these waste products infiltrate into the channel alluvium and underlying Ancha Formation. In order to meet projected demands, the releases would be gradually increased from 4.5 mgd (million gallons per day) to 6.5 mgd over a period of 20 years. The level of nitrogen in the waste effluent would be 35 mg/1 as N from a conventional secondary treatment facility.

The headwaters of the Santa Fe River are impounded for municipal water use. As a result, discharge in the river is limited to the periods of high runoff during the spring when snowmelt is the principal source of water.

The headwaters are underlain by relatively impermeable rocks of the mountains, but at the edge of the city the river crosses the permeable deposits of the Rio Grande trough. The sewage treatment plant is located near the west edge of the city. From that point the river flows generally west past the community of Cieneguilla, and through a canyon that has been cut in La Bajada Mesa (fig. 4). Cienega Creek is the only important tributary in this stretch of the river. The river then enters Cochiti Reservoir which is an impoundment on the Rio Grande.

The regional water table is located in the Ancha and Tesuque Formations of the Santa Fe Group (Disbrow and Stoll, 1957; Sun and Baldwin, 1958; Spiegel and Baldwin, 1963; Geohydrology Assoc., 1978). These and other studies indicated that the transmissivity of the Ancha is about 0.01089 ft^2/ second. There are no unknown aquifer tests in the intrusive rocks which are crossed by the river between Cieneguilla and

La Bajada, but seepage runs have shown that there is a gain from ground-water inflow through this reach of the Santa Fe River. For the purposes of modeling, the bed loss was assumed to be 510 gpm (based on studies by the U. S. Geological Survey) for each mile of channel underlain by the Ancha deposits. There was neither loss nor gain assumed for the reach of river in the low transmissivity area. These assumptions are conservative yet realistic.

Although a wide range in nitrate levels was noted in the study area, the average value of 1.4 mg/1 was calculated and used from 46 laboratory analyses.

Projected Plume Development

The node array used for this particular study is shown in fig. 5. Four hundred nodes with an equidimension of 2,640 feet (1.3 km^2) were used. Each node traversed by the Santa Fe River was considered an injection well in those reaches from the proposed plant site to Cieneguilla and from La Bajada to the maximum pool level for Cochiti Reservoir. A 20-year time frame was used.

The simulation shows that after 5 years of waste discharge, the area of greatest impact is directly beneath the river channel and approximately one-half mile wide except near Cieneguilla where the plume has begun to expand to the west (fig. 5). Below the canyon near La Bajada, the concentrations are elongated along the axis of the river channel. However the direction of ground-water flow has produced a general movement of nitrates to greater distances south of the river than occurs to the north. This reflects the influence of the regional ground-water flow from north to south in the Rio Grande valley.

Twenty years of nitrate infiltration from the upper reach of the river would produce a plume that extends from the treatment facility to the vicinity of Cochiti Reservoir (fig. 5). The overall width of the plume would not significantly increase, however it would become greatly elongated. At the lower end of the plume it would nearly merge with the plume that continued to enlarge beneath the lower reach of the Santa Fe River. There would be a noticeable expansion of the 35 mg/1 contour in the upper reach of the inflow area. There would be a southward migration of nitrogen ions around the east end of the low transmissive rocks near Cienega.

CONCLUSIONS

1. The Konikow and Bredehoeft solute transport model is a useful tool in evaluating waste-pollution problems.

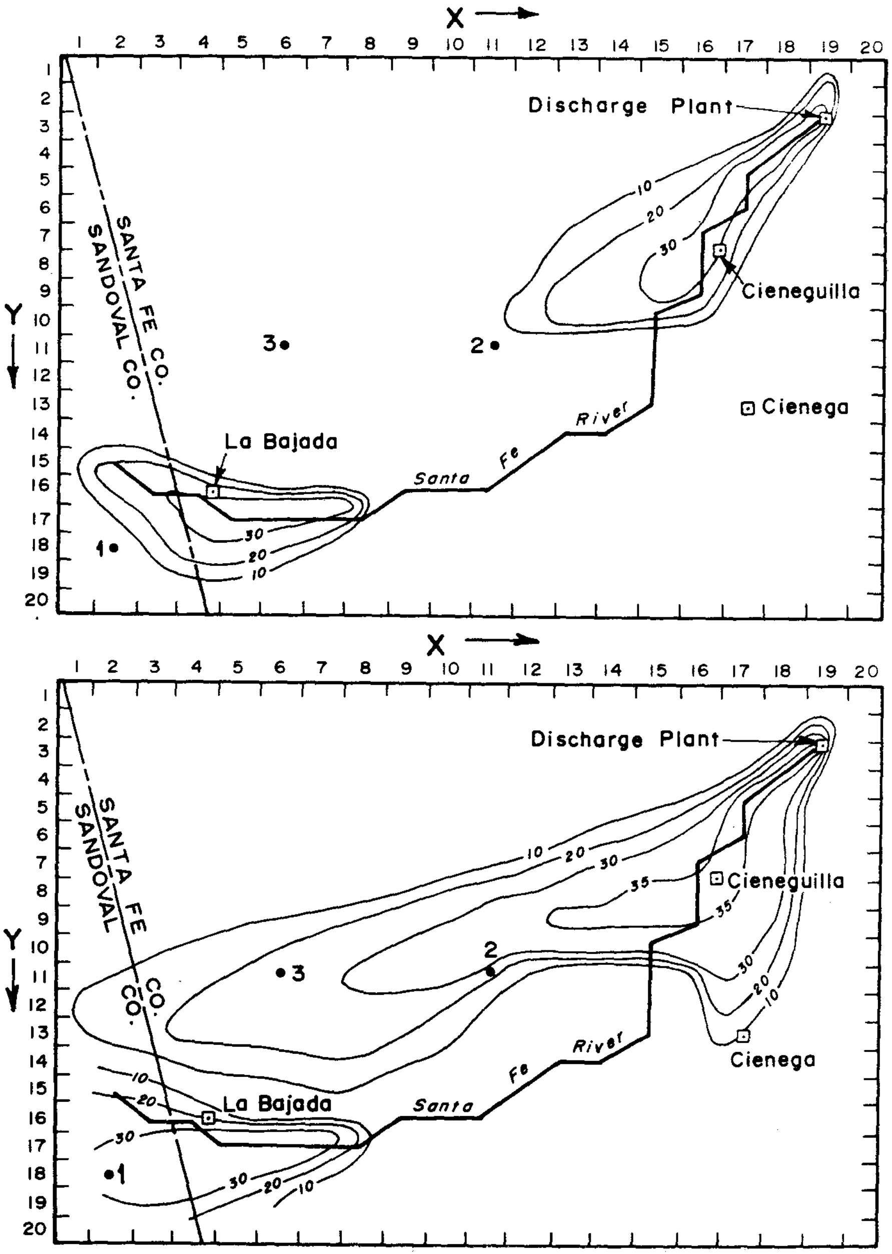


Figure 5. Maps showing distribution of nitrogen ions in aquifer systems after 5 years (above) and 20 years (below) of discharge. Contoured on concentrations of 10 mg/l nitrogen.

2. Most of the assumptions required by the model can be met, within reasonable limits, by the water-table aquifers in New Mexico.

3. The assumption that vertical variations in concentration is negligible may not be true in the immediate proximity of a disposal pit due to significantly lower vertical permeability as compared to horizontal permeability. However this assumption would be acceptable as the plume migrates away from the discharge point.

Vertical mixing may occur in the vicinity of a pumping well.

4. The model is applicable to conservative (non reacting) contaminants only. Also hydrocarbons may not meet the assumptions pertaining to fluid density, viscosity, and temperature.

REFERENCES

Bouwer, H., and Rice, R. C., 1976, A slug test for determining hydraulic conductivity of unconfined aquifers with completely or partially penetrating wells: Water Resources Research, v. 12, no. 3, pp. 423-428.

Bredehoeft, J. D., and Pinder, G. F., 1973, Mass transport in flowing groundwater: Water Resources Research, v. 9, no. 1, pp. 194-210.

Disbrow, A. E., and Stoll, W. C., 1957, Geology of the Cerrillos area, Santa Fe County, New Mexico: New Mexico Bureau of Mines and Mineral Resources Bulletin 48, 73 p.

Geohydrology Associates, Inc., 1980, Modeling of nitrogen ions in the Santa Fe River system, New Mexico: Consultant report prepared for Scanlon and Associates, Inc., Santa Fe, 31 p.

Konikow L. F., aid Grove, D. B., 1977, Derivation of equations describing solute transport in ground water: United States Geological Survey Water-Resources Investigation 77-19, 30 p.

Konikow, L. F., and Bredehoeft, J. D., 1978, Computer model of two-dimensional solute transport and dispersion in ground water : United States Geological Survey Techniques of Water-Resources Investigations, Chapter C2, Book 7, 90 p.

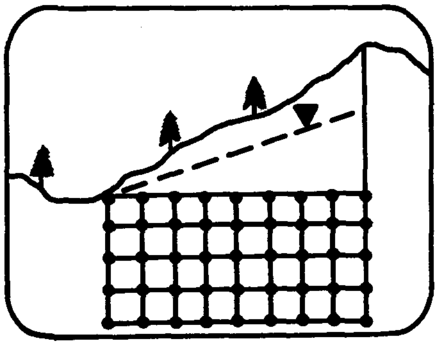
Nicholson, A., Jr., and Clebsch, A., Jr., 1961, Geology and ground-water conditions in southern Lea County, New Mexico: New Mexico Bureau of Mines and Mineral Resources Ground-Water Report 5, 123 p.

Pinder, G. F., and Bredehoeft, J. D., 1968, Application of the digital computer for aquifer evaluation: Water Resources Research, v. 4, no. 5, pp. 1069-1093.

Reddell, D. L., and Sunada, D. K., 1970, Numerical simulation of dispersion in groundwater aquifers: Colorado State University Hydrology Paper 41, 79 p.

Spiegel, Z., and Baldwin, B., 1963, Geology and water resources of the Santa Fe area, New Mexico: United States Geological Survey Water-Supply Paper 1525, 258 p.

Sun, M., and Baldwin, B., 1958, Volcanic rocks of the Cienega area, Santa Fe County, New Mexico: New Mexico Bureau of Mines and Mineral Resources Bulletin 54, 80 p.



CHARACTERIZING SOLUTE RETENTION IN NEW MEXICO SOILS

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ABSTRACT

Movement of solutes through porous materials is strongly dependent on the ability of the media to react with, and to retain the chemicals. This retention capacity is a critical factor in evaluating the suitability of porous materials as disposal media for various wastes. A study was conducted whose purpose was to characterize the retention of various inorganic solutes by soils representative of various regions in New Mexico. This report summarizes that characterization, including the general methodology used and the resulting soil reaction of several species common to wastes of concern in the state.

INTRODUCTION

In recent years concern over the movement of various chemicals (solutes) through soils and porous materials associated with waste disposal sites has intensified. The concern is national, but interest in New Mexico is particularly high because of its highly valued and limited water resources. New Mexico's soils and arid climate make it a prime candidate for expanded hazardous waste repository development. Intelligent selection of additional waste repositories will require accurate characterization of 1) solute interaction with porous materials associated with potential disposal sites, and 2) solute mobility within or beneath the site.

Movement of solutes through porous materials is strongly dependent on the ability of the media to react with, and to retain the chemicals (Fuller, 1978). This retention capacity is a critical factor in evaluating the suitability of porous materials as disposal media for various wastes (Maugh, 1979), and is especially important in the shallow burial of low—level radioactive and other hazardous chemical wastes. Integration of retention data with hydrologic data in computer models may allow predictions of solute transport.

Porous materials retain solutes by various mechanisms, including ion exchange, precipitation, and other less well—defined physical and chemical adsorption reactions such as ligand exchange, specific adsorption, etc. The retention of a particular solute may include one, or all, of the mechanisms, and is often affected by the soil to which the solute is added. Thus, although the reactions of numerous solutes with a variety of porous materials have been enumerated, few studies whose results are of general applicability have been attempted. Studies have tended to be either solute specific on soils of widely different properties (e.g. Garcia and Page, 1978; Shuman, 1977), or to be centered on the reactions of many solutes with specific porous materials (e.g. Griffin and Shrimp, 1978; Jenne, 1968). Both approaches have yielded useful information, but are difficult to apply universally or even to specific geographic regions, e.g. New Mexico.

Waste solutions vary widely in chemical composition. Therefore, there is a critical need for systematically studying reactions of solutes whose chemical properties typify a broad group of species ("type" solutes) likely to occur in waste solutions. If reactions of "type" solutes are studied in a variety of porous materials whose pertinent properties vary regularly (or within reasonable ranges for soils of a particular region), experimental results are more likely to be applicable at a wider level than most previous studies. This "chemical analog" approach was the *basis* for the results reported herein. The purpose of the study was to characterize the retention of various inorganic solutes by soils representative of various regions in New Mexico.

Details of the experimental procedures used and of the results obtained for individual solutes have been summarized elsewhere (O'Connor et al., 1983). My purpose today is to highlight significant findings and to describe the general approach we used to characterize solute reactions in soils.

MATERIALS AND METHODS

Four solutes were selected which typify important groups (chemical analogs) of inorganic species subject to waste disposal: boron, strontium, zinc, and nickel. Boron (B) is representative of weakly retained, neutral or anionic solutes that are readily mobile in many porous media (Wierenga et al., 1975; Elrashidi and O'Connor, 1982a). In recent years, borates have been used as cleaning aids and detergents. Hence, B is often present in municipal sewage and industrial wastes. Brines high in B also are discharged from various mining activities (Ping, 1976). Chemically analogous species include silicon, molybdenum, chromium, and several pesticides.

Zinc (Zn) is representative of cationic trace elements which are apparently retained by specific, high energy sorption reactions (Elrashidi and O'Connor, 1982b). Zinc has received attention as a pollutant because of its wide use in metal plating operations, and its common occurrence in industrial wastes. Chemically analogous species include cadmium, copper, manganese, and iron.

Nickel (Ni) is also representative of cationic trace elements, and was included because of its occurrence in many wastes, its chemical similarity to cobalt-60 (an important constituent of radioactive wastes), and its propensity for forming complexes with the variety of ligands possible in soils (Bowman et al., 1981).

Strontium (Sr) is representative of cationic radionuclides (and non—radionuclides) that may precipitate in basic soils, and is a common constituent in low–level radioactive waste (Keren and O'Connor, 1982). Non–radioactive strontium exhibits a low chemical toxicity to biological systems, but its isotopes (especially 90Sr) have received considerable attention because of long half–lives and a tendency to accumulate in bone tissue (Ping, 1976). Chemically analogous species include barium, radium, and calcium.

All adsorption studies were conducted using the same technique, and, wherever possible, the same initial solute concentration range (0.01 to 1000 mg/1 in 10 fold increments). Such a wide concentration range is necessary to truly characterize solute retention reactions. Most solutes exhibit vastly different retention behavior at high versus low initial concentrations. One can be misled by retention data developed from only low, or more commonly, only high initial concentrations. Even when the waste solution of interest contains high solute concentrations, reactions in the soil usually lower solute levels as solute is transported to greater soil depths.

The basic approach used was the batch equilibration technique in which soil and solute–containing solutions were shaken until the adsorption reaction reached equilibrium. The amount of solute adsorbed (retained by soil) was taken as the difference between initial and equilibrium solute masses in solution. Soil–less blanks were included to account for non–soil related solute removal. Preliminary kinetic (time) studies were conducted for each soil–solute combination to determine the shaking time necessary for equilibrium. Some soil reactions are very slow so that extensive kinetic studies are prudent.

Unless otherwise noted, adsorption studies were conducted in 0.005 M $CaC1_2$ as the background salt. This salt and concentration was chosen to simulate normal soil solution chemistries in New Mexico, to equalize ionic strengths across soils, and to aid in flocculation of the soil suspensions. Whenever possible, the background solution should simulate the expected environmental conditions as closely as possible. Inorganic and organic ligands can complex with most solutes and may dramatically alter solute retention. A one to one soil to solution ratio was used as a compromise between demands for realistic soil moisture contents (higher soil:solution) and for sufficient solution for metal analysis (lower soil:solution). Lower soil to solution ratios are more convenient, but can lead to artifically high solute loading rates and can introduce large subsampling errors associated with small quantities of soils which typically are highly heterogeneous.

Desorption isotherms involved initial preparation of a sorption isotherm as described above. Following centrifugation and index metal analysis, an aliquot (typically 5 ml) of the supernatant was removed and replaced by the same volume of solution (0.005 M $CaC1_2$) containing no index metal. In this way, the equilibrium solution metal concentration was reduced, thereby encouraging desorption of the index metal held by the soil. The soil was suspended and shaken to establish a new equilibrium between adsorbed and solution metal. The suspension was then centrifuged and an aliquot removed for metal *assay.* New adsorbed and solution values were calculated. This sequence was performed repeatedly, producing the desorption isotherms. The desorption behavior of adsorbed solute is intimately tied to solute leaching. Failure to characterize desorption characteristics is a major limitation to many adsorption studies. The tendency for a solute to desorb need not be directly correlated to adsorption tendency. Even slightly adsorbed solutes may be poorly desorbed which dramatically slows solute travel through a soil.

Following equilibration, soil suspensions were centrifuged to separate soil and solution, and an aliquot of the supernatant taken for metal analysis. The *mass* of solute retained per mass of soil (x/m) was expressed as a function of equilibrium solution concentration (C) via the

Freundlich relationship $_{x}/_{m} = KC1/n$ (1)

where K and 1/n are empirical constants. Several researchers have attempted to relate the constants to thermodynamic properties of a particular soil-solute system. Most soil scientists, however, recognize the severe limitations of applying thermodynamics to soil suspensions and choose instead to treat the values as empirical constants. Within a study, the constants may be used qualitatively to contrast solute retention among soils, or different solute retentions by a single soil. Equation (1) is usually transformed to the linear form (Eq. 2) for easy verification of whether data conform to the Freundlich relationship.

$$\log x/m - \log K + 1/n \log C \qquad (2)$$

Adsorption data plotted on log-log paper that yield a straight line are said to conform to the Freundlich relationship. The Freundlich parameters (K and 1/n) are easily obtained from the intercept and slope of the best-fit straight line for the isotherm data. Adsorption data are often found to conform to the single straight line Freundlich model over only a limited (lower) portion of the adsorption curve. Deviations of data from a single straight line at high equilibrium concentrations are common, and are often attributed to changes in sorption mechanisms, sites, or energies. In such cases, multiple Freundlich curves and associated adsorption parameters can be defined (Bohn et al., 1979).

Several other adsorption relationships (equations) are available. Most notable is the Langmuir relationship which theoretically allows calculation of an adsorptive maximum of a soil for a solute. An adsorptive maximum would be useful in predicting the maximum loading of solute that should be added to soil. Unfortunately, adsorption data often fail to conform to the Langmuir equation over the range of solute concentrations typically of interest. The Freundlich equation, however, often successfully describes solute retention over such concentration ranges. Thus, although the Freundlich equation is not as theoretically powerful as the Langmuir, Freundlich adsorption parameters are often used in simulation models of solute transport (Bohn et al., 1979). The Freundlich relationship was used to characterize all adsorption data in this study.

The soils used in this study, along with their physical and chemical properties, are presented in Table 1. The Carjo (clayey, mixed, Mollie Eutroboralf), Puye (medial, mixed, frigid, Mollic Vitrandept), and R-28, R-30, and Chem Bottom (unclassified) soils are from sites being considered for chemical waste disposal in New Mexico. Tuff is a sample of the underlying parent material from which the Carjo soil is derived.

The Glendale (fine-silty, mixed, Calcareous, thermic Typic Torrifluvent); Reagan (fine-silty, mixed, thermic Ustollic Calciorthid), Harvey (fine-loamy, mixed, mesic, Ustollic Calciorthid), and Lea (fine-loamy, mixed, thermic Petrocalcic Paleustoll) are agricultural soils of New Mexico which may be subjected to heavy metal inputs in the form of sewage sludge additions. The Doak (fine-loamy, mixed, mesic Typic Haplargid) soil occurs in an area of heavy coal mining activity in northwestern New Mexico.

The <2mm fraction of the surface horizon (0-15cm) of most soils was used in the study. The Tuff sample occurs naturally in rocklike formations and was ground to pass a 2mm sieve. Soil analyses were performed using standard methods (references given in Table 1). Electrical conductivity (EC) and pH values tabulated are for 1:1 soil to solution extracts of Tuff, Chem Bottom, R-28, and R-30, and for saturation extracts of the other materials. Soils should be characterized for as many chemical, physical and mineralogical properties as possible to aid in the delineation of retention mechanisms and to aid in the rationalization of solute retention differences or similarities.

If a regression relationship between solute retention and soil properties is desired, care must be taken to include numerous soils, and preferably, soils whose properties vary over wide ranges. Regression relationships are limited to the range of soil property values examined.

RESULTS AND DISCUSSION

Boron (B) Reactions

Boron exists in solution as boric acid (H3BO3) which can dissociate to an anionic form:

$$H_3BO_3 \quad H_2B0_3^- + \qquad pKa = 9.2$$

The relatively high acid dissociation constant (pKa) indicates that H3BO3 is a very weak acid that remains undissociated except in highly basic solutions. Silicon exists as H4SiO4 (pKa 9.7) in solution and similarly resists dissociation. Undissociated molecules such as H_3BO_3 and H4S104 are characteristically held by low-energy hydrogen bonding and van der Waals forces in soils such as those used in this study (Bohn et al., 1979). Other weak acids such as the herbicides 2,4 dichlorophenoxyacetic acid (2,4-D) and 2,4,5 trichlorophenoxy acetic acid (2,4,5-T) have lower pKa values (2,4-D, pKa = 2.8; 2,4,5-T, pKa = 3.5) and readily dissociate to anionic forms even in neutral pH solutions. Anionic species, however, are repelled by the negatively charged sites found in most soils above pH 5-6. Thus, anionic species are often very mobile in the neutral to alkaline (high pH) *soils* of New Mexico (O'Connor, van Genuchten, and Wierenga, 1976). The adsorption of neutral or anionic species is often attributed to iteractions with soil organic matter (O'Connor and Anderson, 1974) or to specific adsorption on mineral surfaces via ligand exchange (Keren and O'Connor, 1982a). In the latter case, the adsorbed

Table 1. Selected chemical and physical properties of the materials (<2 mm diameter) studied.

Soil	Particle Size[†] Analysis Sand	Silt	Clay	Texture	Clay[†] Minerals	Specific[‡] Surface	Electrical[§] Conductivity	pH[§]	$CaCO_3$[§] Equivalent	Organic[∫] Carbon	Cation[#] Exchange Capacity	Free Fe Oxides	Free[‡‡] Mn Oxides
	-------	%	-------			m^2/g	mmhos/cm		%	%	me/100g	$\%Fe_2O_3$	%Mn
Carjo	17.6	57.5	25.0	Silt Loam	m,mi,k	59.8	0.26	6.1	0.80	1.0	16.2	0.38	0.022
Puye	72.6	17.4	10.0	Sandy Loam	m,mi,k	11.4	0.20	6.5	0.35	0.45	5.5	0.27	0.020
Tuff	72.4	22.4	3.4	Loamy Sand	---	0.51	0.14	6.7	0.20	0.17	1.6	0.21	0.012
Chem Bottom	91.6	3.6	5.0	Sand	m,mi,k	11.2	0.75	8.2	8.4	0.02	6.2	0.17	0.005
R-28	90.0	2.4	7.7	Sand	m,mi,k	10.9	0.44	7.9	1.8	0.04	8.1	0.21	0.005
R-30	92.6	1.9	5.6	Sand	m,mi,k	14.6	0.47	8.4	8.0	0.04	7.8	0.10	0.003
Glendale	11.8	31.2	57.0	Clay	m,mi,k,c	177	1.67	7.6	8.8	0.97	35.2	0.42	0.032
Reagen	41.4	31.4	27.3	Clay Loam	m,mi,k	65.9	2.3	8.1	20.2	1.1	18.5	0.18	0.19
Doak	67.1	19.0	14.0	Sandy Loam	m,mi,k	46.2	0.56	7.6	0.91	0.45	10.9	0.28	0.021
Harvey	67.0	19.3	13.7	Sandy Loam	m,mi,k	64.9	1.45	7.7	0.5	0.43	14.0	-	-
Lea	66.2	19.4	14.4	Sandy Loam	m,mi,k	65.6	0.81	7.8	11.0	0.57	14.1	-	-

[†] Black (1965)
(Clay mineralogy: m = montmorillonite
k = kaolinite, mi = mica, c = chlorite)

[‡] Cihacek and Bremner (1979)

[§] U.S. Salinity Laboratory Staff (1954)

[∫] Walkley-Black Black (1965)

[#] Polemio and Rhoades (1977)

Coffin (1963)

species is assumed to displace OH^- (or H20) from the mineral surface and to form partially covalent bonds with the structural cations. Such specific adsorption can occur independently of the sign of net surface charge (Hingston et al., 1972). Nevertheless, adsorption of species such as B or 2,4,5-T is usually low in coarse textured soils of New Mexico where organic matter and clay contents are low and where the clay fraction is dominated by montmorillonitic (permanent negative charge) type clays.

In ten New Mexico soils, boron retention was correlated with soil texture. Boron was only slightly adsorbed in the coarse-textured soils, but was moderately absorbed in the finest-textured soils. Retention appeared to be via ligand exchange, competing with OH ions for exposed sites on Fe and Al oxides or the weathered edges of clay minerals. Release of absorbed boron was reversible in 4 soils, especially at low concentrations, but was irreversible in the other six soils. The reason for this irreversibility is not known, but ignoring the phenomenon will greatly overestimate predictions of boron release to leaching waters.

Zinc (Zn) Soil Interactions

Zinc is chemically analogous to cadmium, copper, manganese, and iron (Cotton and Wilkinson, 1980). Zinc exists in solution predominantly as $Zn^{2}+$ at pH <7.7 and predominantly as Zn0H+ above pH 7.7. This tendency to form hydrolysis species at normal pH values is shared by copper (Cu), manganese (Mn), and iron (Fe). Additionally, metal cations such as Zn may react with other inorganic (and organic) ligands to form complexes that can alter metal adsorption. For example, a metal ($M^{2}+$) may combine with an inorganic ligand (e.g. $S\ 01^{2-}$ to form a neutral complex;

$$M^{2}++304^{2\cdot -}\ MSO4^{\circ}$$

The complex is a true solution species (not a solid phase precipitate) so that total metal concentration is unaffected, but M^{2+} reacts to form $MS04^{\circ}$. Since metal adsorption appears in many cases to depend upon free metal ($M^{2}+$) activity (Bowman and O'Connor, 1982), the presence of $S04^{2-}$ (or other inorganic ligands, e.g. C 1, NO_3^-, etc.) can reduce metal activity and thus reduce metal adsorption. The extent of metal complex formation can be calculated (e.g. Lindsay, 1979) for a variety of inorganic and organic ligands. The only inorganic complexes of Zn of practical importance are $ZnOH^+$ and $ZnSO4^{\circ}$. The latter complex can contribute significantly to total soluble Zn when $S04^{2-}$ concentrations approach 10^{-3} to 10^{-2} M. Organic complexes are also often important and can account for >90% of soluble $Zn^{2}+$ in some soils (Lindsay, 1979). The possibility of significant $Zn^{2}+$ complication in some soil solutions led us to conduct Zn sorption studies in a variety of solutions in addition to the standard 0.005 M CaC12 systems.

Zinc retention was essentially quantitative (>99% adsorbed) by all soils studied and was largely independent of solution composition. Desorption of absorbed zinc was negligible suggesting that zinc would be essentially immobile in New Mexico soils. The only exception to this generality was in systems where synthetic (and possibly natural) chelates were present. In this case, the formation of Zn-chelate complex resulted in greatly reduced Zn sorption and greatly increased potential mobility.

Nickel (Ni) Reactions

Relatively high levels of soluble Ni may be present naturally, as in some serpentine soils, but such conditions are not common in New Mexico. The aqueous chemistry of Ni is essentially that of Ni (II), this species being stable over a wide range of pH and Eh conditions (Cotton and Wilkinson, 1980). Nickel (II) is known to complex readily with a variety of organic and inorganic ligands. Ni (II) halides and salts of oxo-acids are generally soluble in water. The least soluble common salt is nickel carbonate, but even this salt has a solubility of approximately 100 ppm at atmospheric CO2 levels at 25°C (Chemical Rubber Co., 1980). Thus, precipitation of insoluble Ni salts is not expected even in calcareous soils moderately contaminated with Ni containing waste.

Nickel was strongly retained in New Mexico soils. Nickel, however, forms a variety of complexes with inorganic and organic ligands which decreases nickel sorption. Meaningful comparisons of nickel retention in various soils systems must therefore correct for the presence of other species in the background solution via ionic strength/ion-pairing corrections. When such corrections are made, differences in Ni retention by the same soil in various background matrices can be quantified and extrapolations of results to other systems can be made.

Nickel and zinc are apparently retained by similar specific adsorption mechanisms, but each metal is retained independently of the other as long as the total metal loading does not exceed the soil's absorbing capacity (total metal concentration < 100 ppm). Nickel sorption is essentially irreversible and Ni is expected to be immobile in most situations. As with Zn, however, even small amounts of chelating agents greatly increased Ni mobility.

Strontium (Sr) Reactions

Precipitation

In addition to the normal cation retention mechanisms (e.g. cation exchange, specific adsorption), Sr is subject to inactivation in soils by precipitation as a solid phase (e.g. $SrCO_3$, strontianite).

Although precipitation of Sr as $SrCO_3$ is possible in some situations, it is not expected to be important in most soils systems of New Mexico. Strontium apparently competes with Ca and H for absorbing sites associated with Fe and Al oxides, either as discrete solid phases, or as weathered edges of clay minerals. Sorption increases with increasing soil pH as both Ca and H activity decrease. Strontium is adsorbed to a much lesser extent than Ni or Zn, and sorption is partially reversible. Thus, Sr could be expected to be mobile in high Ca, near neutral pH soils of coarse texture.

Summary and Conclusions

The movement of solutes through porous media is strongly dependent on the ability of the media to react with and retain the chemicals. Thus, knowledge of this retention capacity is critical to evaluating the suitability of porous materials as disposal media for various wastes. The purpose of this presentation was to give you an overview of our approach to evaluating solute retention capacities of New Mexico soils and to highlight our significant findings.

Industrial and municipal (sewage sludge) wastes typical ly contain a variety of constituents of potential toxicity. Heavy metals such as Zn and Ni are often of prime concern to environmental lists, but toxic organics and metals in anionic forms are also important. Our data suggest that the calcareous and/or fine-textured soils of New Mexico would greatly restrict the mobility of certain heavy metals. In the absence of significant levels of chelating agents or excessive acidity, metals like Ni and Zn (and probably Cu, Fe, Mn, Cd, Cs) would remain in the zone of soil incorporation. Boron and some metals, such as Mo and possibly Cr, on the other hand, can exist as anions and can move with leaching waters. Thus, water management at the disposal site is important. In arid or semi-arid areas where water tables are deep below the soil surface, even Uwe relatively mobile metals probably can be disposed of safely.

References

Bohn, H., McNeal, B. L., and O'Connor, G. A., 1979, Soil Chemistry: John Wiley Publisher.

Bowman, R. S., and O'Connor, G. A., 1982, Control of Ni and Sr adsorption by free metal ion activity: Soil Science Society of America Journal, v. 46, pp. 933-936.

Bowman, R.S., Essington, M. E., and O'Connor, G. A., 1981, Soil sorption of nickel:influence of solution composition: Soil Science Society of America Journal, v. 45, pp. 860-865.

Chemical Rubber Company, 1980, Handbook of chemistry and physics, 61st edition: Publishing Company, Cleveland.

Cihacek, L. J., and Brenner, J. M., 1979, A simplified ethylene glycol monethyl ether procedure for assessment of soil surface area: Soil Science Society of America Journal, v. 43, pp. 821-822.

Coffin, D. E., 1963, a method for the determination of free iron in soils and clays: Canadian Journal of Soil Science, v. 43, pp. 7-17.

Cotton, F. A., and Wilkinson, G., 1980, Advanced inorganic chemistry. 4th edition: Wiley Interscience Publishers, New York.

Elrashidi, M. A., and O'Connor, G. A., 1982a, Boron sorption and desorption in soils: Soil Science Society of America Journal, v. 46, pp. 27-31.

Elrashidi, M. A., and O'Connor, G. A., 1982b, Influence of solution composition on sorption of zinc by soils: Soil Science Society of America Journal, v. 46, pp. 1153-1158.

Fuller, W. H., 1978, Investigation of landfill leachate pollution attenuation by soils: EPA-600/2-78-158, National Technical Information Service, Springfield, Virginia.

Garcia-Miragaya, J., and Page, A. L., 1978, Sorption of trace quantities of cadmium by soils with different chemical and mineralogical composition: Water, Air, Soil Pollution, v. 8, pp. 289-299.

Griffin, R. A., and Shrimp, N. F., 1978, Attenuation of pollutants in municipal landfill leachate by clay minerals: EPA-600/2-78-157, National Technical Information Service, Springfield, Virginia.

Hingston, F. J., Posner, A. M., and Quirk, J. P., 1972, Anion adsorption by geothite and gibbsite. I. The role of the proton in determining adsorption evelopes: Journal of Soil Science, v. 23, pp. 117-192.

Jenne, E. A., 1968, Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides, in R. E. Gould (ed.), Trace inorganics in water: Advances in Chemistry, v. 73, PP. 337-387.

Keren, R., and O'Connor, G. A., 1982, Adsorption of boron by montmorillonite and illite clays--exchangeable ions and solution composition effects: Clays and Clay Minerals, v. 30, pp. 341-346.

Lindsay, W. L., 1979, Chemical equilibria in soils: John Wiley Publishers.

Maugh, T. H., 1979, Toxic waste disposal a growing problem: Science, v. 204, pp. 819-823.

O'Connor, G. A., and Andersen, J. U., 1974, Soil factors affecting the adsorption of 2,4,5-T: Soil Science Society of Americal Proceedings, v. 38, pp. 436-443.

O'Connor, G. A., Bowman, R. S., Elrashidi, M. A., and Keren, R., 1983, Solute retention and mobility in New Mexico Soils. I. Characterization of solute retention reactions: New Mexico State Agricultural Experiment Station, Bulletin 701.

O'Connor, G. A., van Genuchten, M. Th., and Wierenga, P. J., 1976, Predicting 2,4,5–T movement in soil columns: Journal of Environmental Qualtiy, v. 5, pp. 375-378.

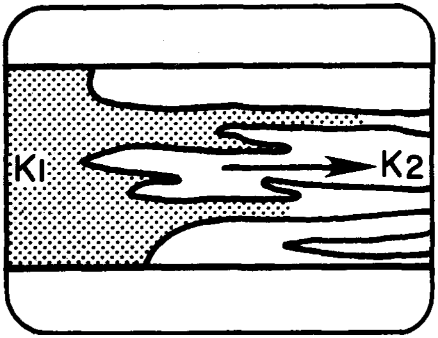
Ping, Chien–Lu, 1976, Retention of typical soluble contaminants by representative Washington Soils: Ph.D. Dissertation, Washington State University, Pullman, Washington.

Polemio, M., and Rhoades, J. D., 1977, Determining cation exchange capacity: a new procedure for calcareous and gypsiferous soils: Soil Science Society of America Journal, v. 41, pp. 524-528.

Shuman, L. M., 1977, Adsorption of Zn by Fe and Al hydrous oxides as influenced by aging and pH: Soil Science Society of America Journal, v. 41, pp. 703-706.

U. S. Salinity Laboratory Staff, 1954, Diagnosis and improvement of saline and alkali soils: Agriculture Handbook Number 60, USDA, U. S. Government Printing Office, Washington, DC.

Wierenga, P. J., van Genuchten, M. Th., and Boyle, F. W., 1975, Transfer of boron and tritited water through sandstone: Journal of Environmental Quality, v. 4, pp. 83-87.


K1
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THE BOMB -36C1 PULSE AS A TRACER FOR SOIL-WATER MOVEMENT NEAR SOCORRO, NEW MEXICO

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ABSTRACT

A pulse of 36C1 (half-life 3.01 x 10^5yrs) was released into the environment as a result of atmospheric nuclear-weapons testing in the mid-1950's. Due to the approximate square-wave shape of the pulse and the hydrophilic nature of chloride, the pulse provides an excellent tracer in the hydrologic cycle. We have tested the application of 36C1 tracing to the movement of soil water in arid climates. Chloride was leached out of soil samples from a vertical auger hole in a sandy loam near Socorro, New Mexico. The bomb-36C1 pulse was identified at approximately one meter depth, indicating a net infiltration to that depth of about 2.5 mm/yr. The 36C1 tracing method appears to have significant advantages over alternative techniques for measuring net infiltration through desert soils, especially in its ability to determine the dispersive properties of the soil.

INTRODUCTION

The net infiltration rate ("deep percolation" in agricultural terminology) has important implications both for protection of ground water from pollution and for natural ground-water quality. Areas of active recharge have long been recognized as zones which should be protected from surficial contamination in order to preserve ground-water quality. This type of protection is particularly important in arid regions such as New Mexico, where wells are frequently the only reliable water supply.

A common assumption has been that net recharge in arid regions depends chiefly on climate, rather than soil characteristics, and therefore is uniformly negligible. The fallacy of this position is clearly illustrated by a comparison of two sites near Socorro. The sites are within two kilometers of each other on the Sevilleta National Wildlife Refuge. Climate is essentially identical at both sites. One of the sites, described below in this paper and investigated by 36C1 tracing, is on a Pleistocene terrace. The other site is on Holocene alluvium and has been investigated by Daniel B. Stephens of the New Mexico Institute of Mining and Technology using soil-physics techniques. The two sites do not differ markedly in vegetation or appearance. However, the Pleistocene terrace site shows a downward pore velocity (i.e., actual solute transport rate) of less than 0.5mm/yr, while a pore velocity of over 70cm/yr was inferred in the Holocene alluvium. The danger of ground-water contamination from surface wastes is obviously drastically different at the two sites.

One direct application of the measurement of soil-water movement rates is in the siting of hazardous waste disposal facilities. Arid regions have frequently been proposed as desirable waste disposal sites due to an assumed negligible recharge (Mann, 1976; Winograd, 1981; Lavie and Barthoux, 1982). Even hazardous-waste-disposal facility siting methodologies designed for arid climates are forced to rely on indirect methods of estimating travel times, such as depth to water and proportions of sand and clay in the soil (Longmire et al., 1981). Clearly, given the range of transport rates illustrated above, direct measurements of these rates are necessary before waste-disposal sites are emplaced over potable aquifers.

Recharge rates can exert a strong influence on natural water quality as well as the potential for pollution. Meteoric fallout provides a steady source of solutes to the land surface. If recharge rates are rapid, these solutes are carried to the water table in quite dilute form. However, under arid conditions where recharge rates are very low, these meteoric solutes are concentrated by evapotranspiration.

This process can result in highly saline soil water and ground water. Chloride concentrations as high as 15,000mg/1 have been observed in the Murray Basin of South Australia (Allison et al., 1984). Rapid flushing of this saline soil water down to the water table (a result of land-use changes) has severely degraded both ground-water and surface-water quality. Although little study has been devoted to the matter, much of the saline ground water in New Mexico may derive from a similar mechanism. For example, shallow alluvial ground water in the San Juan Basin with total dissolved solids (TDS) over 50,000mg/1 has been attributed, in part, to low recharge and high evapotranspiration (Phillips et al., 1984).

BOMB-36C1 AS A SOIL-WATER TRACER

A variety of methods have traditionally been used to measure soilwater fluxes, but all of them have serious limitations in the dry natural soils of arid climates. These methods, and their limitations, will be described below. One possible alternative to the established methods is tracing of 36C1 produced by atmospheric nuclear-weapons testing.

Chlorine-36 is an unstable isotope of chlorine with a half-life of 3.01 x 10^5years. Until recently, measurement of 36C1 in natural systems was quite limited due to the difficulty of analysis. However, application of tandem accelerator mass spectrometry (TAMS) to 36C1 analysis in the last 4 years has opened a wide range of possible studies. Techniques described in Elmore et al. (1979) are capable of analytical sensitivities down to one atom of 36C1 in 10^{15} chlorine atoms, on milligram sized samples.

Small but measurable amounts of 36C1 are produced by natural atmospheric processes (Bentley et al., 1984). The natural input of 36C1 was seriously perturbed during the period 1953 to 1963 by fallout from atmospheric nuclear-weapons tests. Tests conducted close to the ocean surface in the Equatorial Pacific produced 36C1 by thermal-neutron activation of 35C1. The 36C1 produced by the surface tests was injected into the stratosphere and distributed around the globe. However, the residence time of chloride in the atmosphere is relatively short, and thus by the mid-1960's most of the 36C1 had been deposited on the land or oceans.

The 36C1 fallout was simulated by Bentley et al. (1982) using an atmospheric box model and is illustrated in Figure 1. This fallout model was tested using samples from a Greenland ice core (Elmore et al., 1982) and a shallow landfill at Borden, Ontario (Bentley et al., 1982). The temporal distribution of fallout calculated by the model matches the observed data very well. The magnitude of the fallout peak varied from 100 to 1000 times the natural fallout depending on latitude and climate, and should thus be easy to identify.

This fallout pulse constitutes an excellent hydrologic tracer. Chloride is well known as a conservative element in natural water, and 36C1 has frequently been used to "tag" water movement in unsaturated flow experiments. The relatively sharp, uncomplicated peak shape renders interpretation simple and allows determination of dispersivity.

FIELD INVESTIGATIONS

SITE

In order to test the suitability of bomb-36C1 for soil-water tracing in arid environments, a field investigation was carried out at a desert site about 25km north of Socorro, New Mexico (34°17'47"N, 106° 55'20"W). The site is located on the Sevilleta National Wildlife Refuge. The geologic unit at the site is the Piedmont unit D of Machette (1978), and is assigned an Upper Pleistocene position.

The site has a typical high-desert climate. Annual precipitation is about 20cm, while annual potential evapotranspiration is about 180cm. Precipitation is approximately evenly divided between late summer convective storms and mid-winter snow and rain from frontal storms. Seasonal variations in temperature are large, with summer daytime highs in the range of 40°C and winter lows usually below 0°C. However, winter daytime highs are usually well above 0°C. Vegetation consists of creosote and sparse bunch grass.

METHODOLOGY

Soil samples were collected from a vertical auger hole. The hole was drilled using a 30cm diameter solid-flight auger. The soil samples were take off the auger screw at preselected intervals and stored in large plastic bags. Average sample size was about 25kg. Smaller sub-samples were sealed in heavy plastic bags for moisture content and grain size analysis. The chloride was extracted by mixing the large

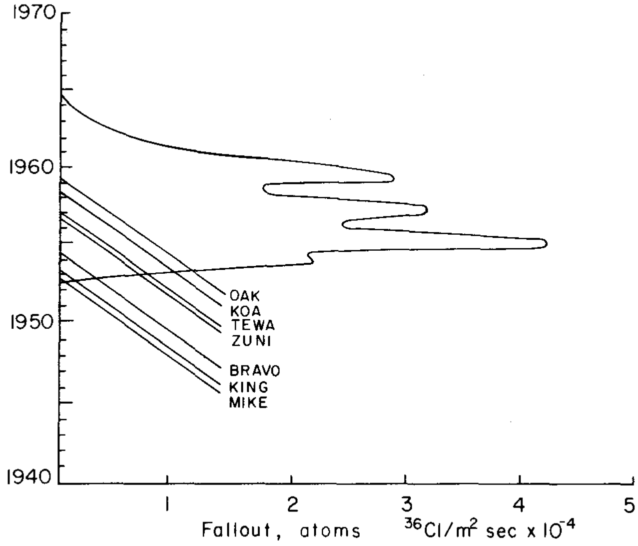

Figure 1. Modeled 36Cl fallout from nuclear weapons testing, including explosion names (adapted from Bentley et al., 1984).

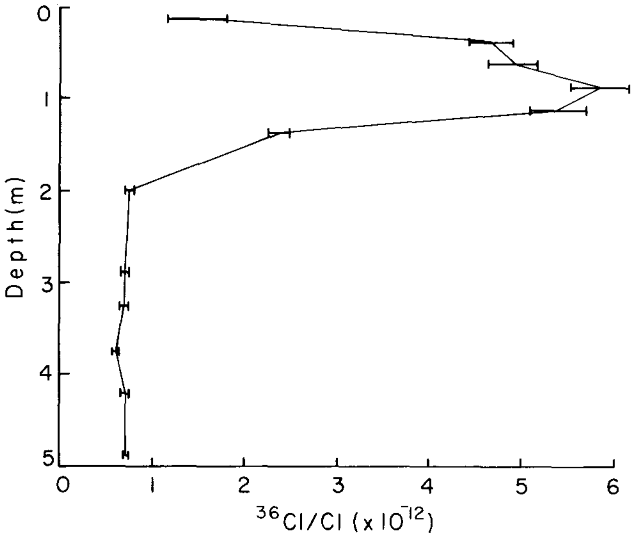

Figure 2. Variation of the 36Cl/Cl (x 10^{-12}) ratio with depth.

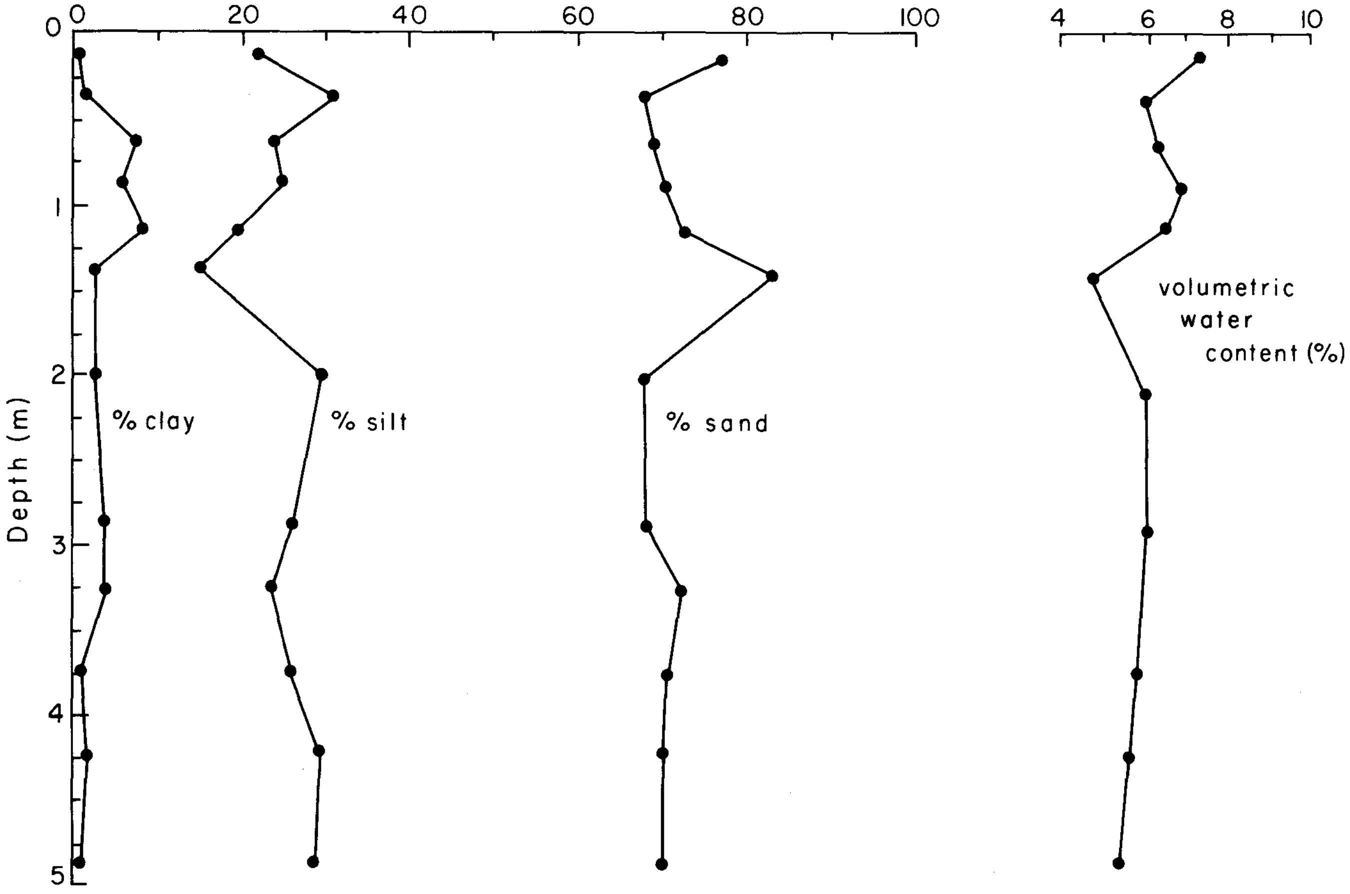

Figure 3. Grain-size percentages and volumetric water contents from Sevilleta site soil samples.

soil samples with 121 of distilled, deionized water to form a slurry, which was allowed to settle. The supernatent was decanted and filtered. The chloride concentration of the supernatent was analyzed using the mercuric nitrate method described in Standard Methods (1960). The supernatent was passed through prepared Dowex (1-x8, 20-50 mesh) anion-exchange resin to concentrate the chloride. The chloride was eluted from the columns using 1 M NaNO3. After elution, 200mg of "dead" chloride carrier was added in order to obtain sufficient chloride for TAMS analysis. The leach water from samples below 1.5m depth contained sufficient chloride that exchange-resin concentration and carrier were not necessary. The chloride was precipitated from solution as AgC1 by addition of excess AgNO3. The AgC1 was purified of sulfur (36S is an interfering isobar in the TAMS analysis) by repeated solution in NI1408 and re precipitation. The samples were analyzed on the 10 MV tandem van de Graaff accelerator at the University of Rochester Nuclear Structure Research Laboratory under the direction of David Elmore. The analytical technique has been described by Elmore et al. (1979).

Water content of the soil samples was determined gravimetrically. Particle size down to clay was measured by sieving, and the size distribution of the clay fraction by hydrometer.

RESULTS

The analytical results are presented in Table 1. The 36C1/C1 ratio of the soil water and the soil properties as a function of depth are illustrated in Figures 2 and 3. Most of the samples were sandy loamy, with a few loamy sands. All samples contained less than 10% clay. Volumetric moisture contents were low, as expected in a desert soil, ranging from about 7% to 4%. The relatively high water content at the surface is due to rainfall shortly before sample collection.

Table 1. Data from Sevilleta site auger-hole soil samples.

Depth (cm)	Volumetric Water Content (%)	Chloride (mgCl/kg soil)	36Cl/Cl x 10^{15}
0-25	7.15	0.49	1510 ± 23%
25-50	5.20	0.86	4680 ± 5.6%
50-75	5.85	2.30	4930 ± 5.5%
75-100	6.50	4.30	5890 ± 5.2%
100-125	5.85	8.30	5420 ± 6.0%
125-150	3.90	15	2400 ± 5.0%
175-225	5.20	96	789 ± 5.0%
275-300	5.85	73	723 ± 5.2%
300-350	5.52	105	718 ± 5.0%
350-400	5.20	180	620 ± 6.0%
400-450	4.81	130	722 ± 6.0%
475-500	4.55	130	737 ± 5.0%

The bomb pulse may easily be distinguished between 0 and 2m in Figure 2. The maximum is at approximately lm. Given a mean volumetric water content of 6.2% between 0 and lm and maximum 36C1 fallout in 1958 (Figure 1), the net infiltration to lm depth may be calculated to be 2.5mm/yr (1.2% of the annual precipitation).

The average 36C1/C1 ratio below 2m is 717 x 10^{-15}. This ratio compares quite favorably with the natural background ratio predicted by Bentley et al. (1984), 640 x 10.

- 15 The maximum bomb-fallout 36C1/C1 ratio measured at the site, 5890 x 10 ,is about 1 order of magnitude less than the ratio we calculated. This difference may be attributed to the effects of hydrodynamic dispersion. Solving the "pulse" advection-dispersion equation of Ogata (1970) for these boundary conditions and matching the resultant curve to that observed gave an apparent hydrodynamic dispersion coefficient of 6.0 x 107^{11}n/s. The actual flow field is neither unidirectional nor constant, as required by the equation, and thus the calculated dispersion coefficient is only an apparent value.

COMPARISON WITH CHLORIDE MASS BALANCE

A mass balance on the chloride ion may be used to determine net infiltration (Gardiner, 1967).

The mass-balance argument simply states that the difference between the chloride concentration measured at any depth in the soil and the original atmospheric input concentration (i.e., the total annual chloride input divided by the annual precipitation) may be attributed to evapotranspirative enrichment. The travel time to the bottom of the i^th^ soil depth interval is given by:

$$t = \sum_{i} \frac{\rho_B M_i d_i}{C_o P} \qquad (1)$$

where ρ_B is the dry bulk density, M the chloride concentration (in mg chloride/kg soil), d the interval length, C_0 the atmospheric input chloride concentration, and P the annual precipitation.

An average atmospheric chloride input concentration of 0.375mg/1 may be calculated from the chloride fallout and precipitation data given above. Using these values and a bulk density of 1.3g/cm, the graph of travel time versus depth shown in Figure 4 may be constructed. The bomb-36Cl fallout period was 18 to 30 years ago, and thus this time interval has been correlated to the appropriate depth interval and compared with the position of the observed 36Cl peak. The agreement is excellent, strongly validating the chloride mass balance method.

The continued increase of the chloride concentration below lm depth implies that the net infiltration below lm is less than the 2.5mm/yr calculated from the 36Cl peak. This is not unexpected, inasmuch as desert plant roots are known to penetrate many meters. The age-depth relationship is only shown down to 2m in Figure 4, in Figure 5 it is extended the full 5m. At this depth the calculated travel time is 7,000 years and the net infiltration rate 0.02mm/yr.

COMPARISON WITH NEARBY HOLOCENE ALLUVIUM SITE

In the introduction to this paper a study by Daniel Stephens at a Holocene alluvium site 2km distant was cited. Under virtually identical environmental conditions he inferred net infiltration rates (below the root zone) of about 5cm/yr. What explains the contrast between this value and the 0.02mm/yr calculated from the chloride mass balance at the Pleistocene site?

The difference is almost certainly attributable to the grain size distribution at the two sites. Figure 6 is a comparison of the grain size distributions of the two soils. Although the percentage of clay at the Pleistocene site is not large (less than 8% in all cases), it (plus the larger proportion of silt) is sufficient to decrease the ground-water recharge by over 3 orders of magnitude. The relationship between soil characteristics and net infiltration under arid conditions should prove to be a fruitful area for future research.

A GENERAL COMPARISON WITH ALTERNATIVE METHODS

Three methods of measuring soil-water movement have been widely applied:

(1) Calculation of fluxes from field measurement of water content, accompanied by laboratory determination of water content-matric potential and water content-hydraulic conductivity relationships.

(2) Weighing lysimeter studies.

(3) Tracing of the bomb-tritium pulse in the vadose zone. The bomb-36C1 tracing technique has several advantages over the first two methods in arid environments. Both of them require extensive instrumentation. The 36C1 collection and extraction are trivial in comparison.

Both the field monitoring and the lysimeter methods involve some disturbance of the natural soil. In contrast, with the 36C1 tracing technique the soil materials remain in a completely natural state until the auger hole for sample collection is dug. An even more important advantage of the 36C1 technique is the experiment duration. In arid regions precipitation events with recurrence intervals of years, or even decades, may be responsible for virtually all recharge. Thus in order to obtain representative results, measurements must be continued for many years, with a large concommitant investment of time and money. Such is not the case with tracing of the bomb-36C1 pulse. Enhanced 36C1 fallout began in 1953, and so measurement of 36C1 in a single auger hole at the present time will be the equivalent of a 30-year duration tracing test.

A final important advantage of 36C1 is the information gained on the solute distribution in the vadose zone. Although the other two methods allow calculation of the net water flux, they typically do not permit determination of the dispersive properties of the soil. Theoretical calculation of soil dispersion is greatly complicated by the oscillatory nature of flow near the soil surface, which increases the apparent dispersivity (Scotter and Raats, 1968). Also, recent research such as that of Hammermeister et al. (1982) has emphasized the role of

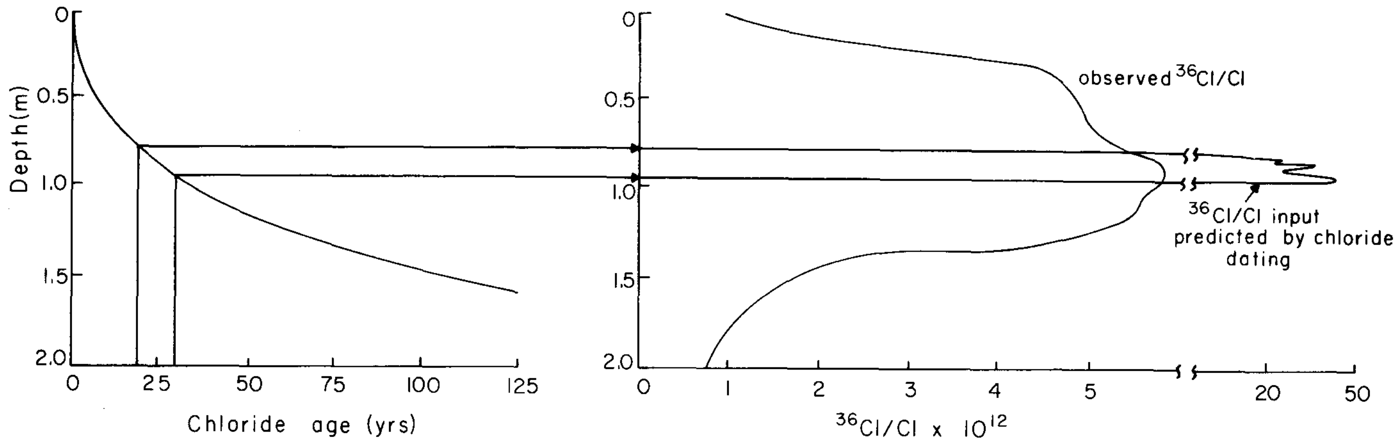

Figure 4. Soil-water infiltration times, calculated by the chloride mass-balance method, as a function of depth. Predicted position of the 36Cl peak is compared with the observed position.

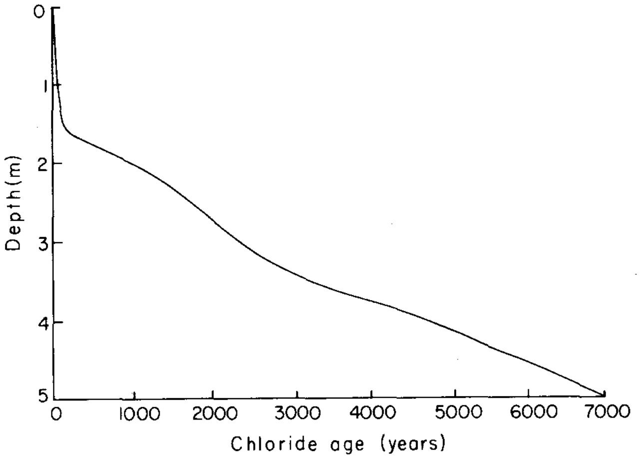

Figure 5. Chloride mass-balance infiltration time as a function of depth for entire 5 m profile.

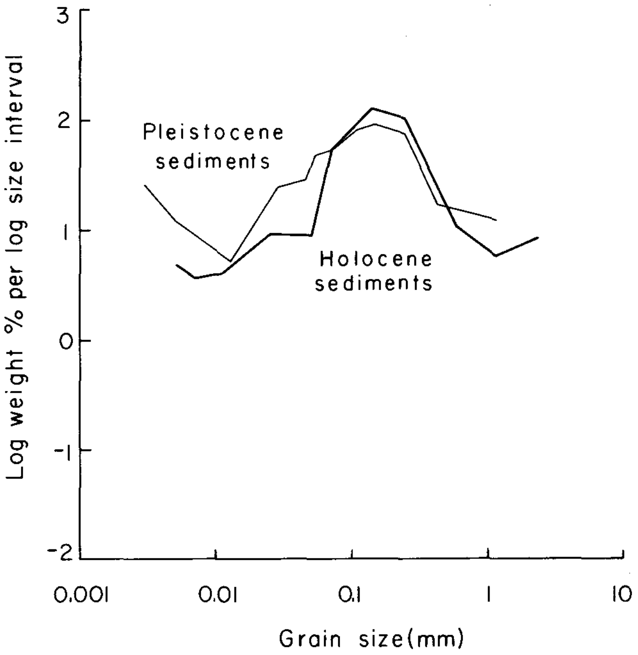

Figure 6. Comparison of grain-size distribution for Holocene and Pleistocene Sevilleta soil sites.

macropores (sometimes referred to as preferential paths) in the transport of solutes at rates far faster than would be predicted by the flow equations. These effects have been reviewed by Beven and Germann (1982). Because the bomb-36C1 input function is well known, the broadening of the peak observed in the soil will allow meaningful dispersivities to be calculated. The observed dispersion will include processes such as macropore flow which cannot be treated by classical dispersion theory.

Of the three methods, the one most similar to bomb-36C1 tracing technique is bomb-tritium tracing. The principles are virtually identical. Bomb-36C1 tracing also demonstrates significant advantages over bomb-tritium tracing. These include: 1) Sampling is much simpler. 2) Contamination problems are smaller. 3) An approximate square-wave input function simplifies interpretation and calculation of dispersion. 4) The longer half-life avoids the pulse-detection problem now beginning to affect tritium and avoids confusion of decay with dispersion.

CONCLUSIONS

The following conclusions may be drawn:

(1) The net soil-water flux is among the most important parameters in the evaluation of potential (or existing) hazardous waste sites, in assessing sources of ground-water salinity in arid regions, and in determining ground-water recharge.

(2) Blanket assumptions that the net flux is negligibly small in arid regions are not justified.

(3) Present methods are capable of measuring the net soil-water flux in arid environments only with considerable difficulty and uncertainty.

(4) Our developmental work has indicated that 36C1 soil profiles may provide a simple and reliable method of determining these fluxes in soils with small net infiltration.

ACKNOWLEDGEMENTS

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REFERENCES

Allison, G. B., Stone, W. J., and Hughes, M.W.,1984, Recharge in karst and dune elements of a semi-arid landscape as indicated by natural isotopes and chloride: submitted to Journal of Hydrology.

Bentley, H. W., Phillips, F. M., and Davis, S. N., 1984, 36C1 in the terrestrial environment: in Handbook of Environmental Isotope Geochemistry, v. 2, Fritz, P., and Fontes, J. C., (eds.), Elsevier, Amsterdam (in press).

Beven, K., and P. Germann, 1982, Macropores and water flow in soils: Water Resource Research, v. 18, pp. 1311-1325.

Elmore, D., Fulton, B. R., Clover, M. R., Mersden, J. R., Gove, H. E., Naylor, H., Purser, K. H., Kilius, L. R., Beukins, R. P., and Litherland, A. E., 1979, Analysis of 36C1 in environmental water samples using an electrostatic accelerator: Nature, v. 277, pp. 22-25.

Elmore, D., Tubbs, L. E., Newman, D., Ma, X. Z., Finkel, R., Nishiizumi, K., Beer, J., Oeschgar, H., and Andrea, M., 1982, The 36C1 bomb pulse measured in a shallow ice core from Dye 3, Greenland: Nature, v. 300, pp. 735-737.

Gardiner, W. R., 1967, Water uptake and salt distribution patterns in saline soils: in Proceedings of the Symposium on Isotope and Radiation Techniques in Soil Physics and Irrigation Studies, Istanbul Atomic Energy Agency, pp. 335-340.

Hammermeister, D. P., Kling, G. F., Vomecil, J. A., 1982 , Perched water tables on hillsides in western Oregon: II. Preferential downslope movement of water and anions: Soil Science Society of America Journal, v. 46, pp 819-826.

Lavie, J. M., and Barthoux, A., 1982, The management of low and medium level radioactive waste in France: in Waste Management '81, Post, R. G. (ed.), v. 2 Proceedings Symposium, Tucson, Arizona 8-11, March 1982, pp. 281-296.

Longmire, P. A., Gallaher, B. M., and Hawley, J. W., 1981, Geological, geochemical and hydrological criteria for disposal of hazardous wastes in New Mexico: in New Mexico Geological Society Special Publications no. 10, pp. 93-102.

Machette, M. N., 1978, Geological map of the San Acacia Quadrangle, Socorro County, New Mexico: U. S. Geological Survey Map GQ-1415.

Mann, J. F., Jr., 1976, Waste waters in the vadose zone of arid regions: Hydrologic interactions: Ground Water, v. 14, pp. 367-372.

Ogata, A., 1970, Theory of dispersion in a granular medium: U. S. Geological Professional Paper 411-I, pp. I 34.

Phillips, F. M., Kantz, K., Richardson, G. L, and Whittemore, D. 0., 1984, Isotopic and geochemical evidence for the origin of shallow ground-water salinity in northwestern New Mexico, U.S.A.: in preparation.

Scotter, D. R., and Raats, P A. C., 1968, Dispersion in porous mediums due to oscillating flow: Water Resource Research, v. 4, pp. 1201- 1206.

Standard Methods for the Analysis of Water and Wastewater, 1980, 11th Ed., American Public Health Association, New York, pp. 79-81.

Winograd, I. J., 1981, Radioactive waste disposal in thick unsaturated zones: Science, v. 212, pp. 1457-1464.

STATE LEGAL MECHANISMS FOR THE CONTROL OF GROUNDWATER POLLUTION IN NEW MEXICO

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ABSTRACT

Prior to the adoption of the New Mexico Water Quality Control Commission's ground water regulations, nuisance laws were the only legal mechanism for the control of groundwater pollution in New Mexico. State courts have demonstrated a willingness to provide relief to those aggrieved by groundwater pollution under nuisance theories.

The adoption of the ground water regulations in early 1977 established a legal mechanism which, for the first time in New Mexico, could prevent groundwater pollution through a comprehensive permit program. New Mexico courts have upheld several controversial aspects of the groundwater regulations including: placing the burden of proving compliance on the discharge plan applicant; and, the adoption of a definition of the term "toxic pollutant" which allows substantial discretion on the part of the licensing agency.

The courts have twice upheld the EID director's decisions on discharge plan applications, once on a denial and once on an approval. The director has not been overturned by the courts on a discharge plan determination. At the present time groundwater pollution may be addressed through several state legal mechanisms. Those mechanisms include common law private nuisance, common law public nuisance, statutory public nuisance, the Water Quality Act SS 74-6-1, et. _seq.,_ N.M.S.A. 1978 and the groundwater regulations of the Water Quality Control Commission adopted pursuant to the Water Quality Act.

COMMON LAW NUISANCES

One rationale for protecting groundwater against pollution is that polluted water is not available for beneficial use (domestic, agricultural, industrial) to the same extent as non-polluted water. Since New Mexico's statehood in 1912, the right to the beneficial use of water has been recognized as a property right. N.M. Const., Art. XVI. As a property right, the right to use water is subject to the protection of the common law. The common law, as distinguished from law created by the legislative enactments, consists of the principles and rules which were developed by usages, customs and court decrees dating back to the ancient unwritten law of England. BLACK'S LAW DICTIONARY 345-6 (4th ed. 1968).

Prior to 1963 only common law nuisance actions were available to a party aggrieved by pollution of groundwater. Common law nuisance claims could be made in the courts for a private nuisance or public nuisance. A private nuisance is one affecting the rights of an individual or a limited number of individuals while a public nuisance is one where the rights of the public at large are impacted. 58 Am. Jur. 2d Nuisances SS 5-10. A nuisance can be both private and public. 58 Am. Jur. 2d Nuisances § 5. Nuisances are also classified as permanent and temporary. A permanent nuisance is one in which the pollution is not remediable, removable or abatable (58 Am. Jur. 2d Nuisances §§ 117-119), while a temporary nuisance is one where the pollution or nuisance condition is subject to abatement. Aguayo v. Village of Chama, 79 N.M. 729, 440 P.2d 331 (1968). In the Aguayo v. Village of Chama case, the New Mexico Supreme court held that a sewage treatment plant which emitted offensive odors could be operated to eliminate all offensiveness and was therefore a temporary nuisance. Groundwater pollution is abatable if the ground water can be restored to a non-polluted state by a reclamation program or other remedial action. A court may order the party creating a nuisance to pay damages for loss of property value and for loss of use and enjoyment of property. A court may also issue an injunction ordering abatement of a nuisance by the responsible party.

The common law of nuisance provides an adequate means of relief for a party aggrieved by a clear and definite case of polluted groundwater such as the pollution of a well by a nearby cesspool or dumping ground. More complex types of pollution problems have come to light in recent years. These problems may involve multiple possible sources, and complicated questions of geology, hydrology, chemistry and public health which are beyond the expertise of the typical trial judge. In response to this situation new laws have been developed through the legislative process.

STATUTORY PUBLIC NUISANCE

In 1963, for the first time, the New Mexico Legislature specifically addressed water pollution. The 1963 enactment designates polluting water as public nuisance. Section 30-82, N.M.S.A 1978 states:

> Polluting water consists of knowingly and unlawfully introducing any object or substance into any body of public water causing it to be offensive or dangerous for human or animal consumption or use.

> Polluting water constitutes a public nuisance.
>
> For the purpose of this section, "body of water" means any public: river or tributary thereof, stream, lake, pond, reservoir, acequia, canal, ditch, spring, well or declared or known ground waters.
>
> Whoever commits polluting water is guilty of a misdemeanor.

A misdemeanor is punishable by up to one year imprisonment and a $1,000 fine. Section 31-19-1A, N.M.S.A. 1978. The public nuisance of polluting water is also subject to a civil action in state district court for abatement. Such an action may be brought by a private citizen as well as a public officer. Section 30-8-8B, N.M.S.A. 1978.

The general language of the water pollution nuisance statute may raise difficult legal issues if a suit is brought to enforce it. For example, does the "knowing" introduction of substances mean that the polluter has to know only that he is discharging or must he know that he is causing pollution before he is in violation of this statute? Also, is a discharge causing pollution "unlawful" if the discharger is operating in compliance with a government permit or license. Finally, in each case under this section the court must determine the level of contamination which constitutes pollution "offensive or dangerous for human or animal consumption or use." In a given case the court may choose to follow federal drinking water standards, to follow federal or state pollution standards or to hear a full range of expert testimony on which levels meet the test for pollution and decide for itself. Nothing in the public nuisance statute insures uniform application of a public nuisance "standard." A defendant might argue that the general nature of the statute renders it unconstitutionally vague. Arguably the public is not adequately put on notice of the conduct prohibited by this law. To date, the New Mexico appellate courts have not addressed the above questions in their opinions on the public nuisance statute.

The New Mexico Supreme Court, however, has addressed water pollution under another section of the public nuisance law. Under the 1963 enactment, it is also a public nuisance to knowingly create or maintain:

> anything affecting any number of citizens without lawful authority which is either:
>
> A. injurious to public health, safety, morals or welfare; or
>
> B. interferes with the exercise and enjoyment of public rights, including the right to use public property.

Section 30-8-1, N.M.S.A. 1978. This section of the public nuisance statute is also somewhat vague in defining which conduct is prohibited. It was under this section, however, that the Water Quality Control Commission (WQCC) sued the City of Hobbs for causing pollution of groundwater near its sewage treatment facility. In a 1974 opinion the New Mexico Supreme Court upheld a lower court order which required Hobbs to extend fresh water lines and provide free hook-ups to residences whose wells were polluted by the seepage of Hobbs' sewage effluent. <u>State, ex rel. N.M. Water Quality Control Commission v. City of Hobbs,</u> 86 N.M. 444, 525 P.2d 371 (1974). The City was also ordered to either move its discharge point or to "institute a program for pumping out the mound of contaminated water underneath the sewage treatment plant" and to "improve the quality of the sewage effluent", <u>supra</u> at 445. The <u>City of Hobbs</u> case established the viability of the public nuisance statute, despite its drawbacks, as a ground water quality protection tool. This tool is still available. Either section of the public nuisance statute may be enforced by a state official or a private citizen suing in the name of the state. Section 308-8B, N.M.S.A. 1978.

THE WATER QUALITY ACT

In 1967 New Mexico adopted the Water Quality Act SS 746-1, et. seg., N.M.S.A. 1978. Unlike the general provisions of the Public Nuisance Statute, the Water Quality Act established the framework for a comprehensive and detailed scheme for the prevention, abatement, and control of water pollution in New Mexico. This scheme includes the mandate to adopt "water quality standards as a guide to water pollution control" § 74-6-4C, N.M.S.A. 1978. Unlike the federal law of that time, the Water Quality Act included ground water within its scope. Section 74-6-2, N.M.S.A. 1978. The Water Quality Control Commission was created by that act and empowered to adopt regulations to prevent or abate water pollution. Sections 74-6-3 and 4, N.M.S.A. 1978. The constituent agencies of the Commission, particularly the Environmental Improvement Division of the Health and Environment Department ("EID"), were given the power to receive and expend federal funds for pollution control programs, conduct studies, inspect effluent sources, bring court enforcement actions against polluters and issue orders to abate water pollution creating emergency conditions SS 74-6-9, 10, and 11, N.M.S.A. 1978. The Commission was also authorized to require permits "for the discharge of any water contaminant either directly or indirectly into water.

Section 74-6-5, N.M.S.A. 1978. Through the permit system the State, for the first time, could require persons to notify the state of their intention to discharge and to demonstrate that their discharges would not violate criteria established by the state before the discharges could occur.

Not until the January, 1977 adoption of its groundwater regulations was the Water Quality Control Commission able to put in place a permit system for discharges onto or below the surface of the ground. WQCC Regs., Part 3. A permit under those regulations is called an approved discharge plan. The development of those regulations involved an aborted public hearing in early 1975 (the hearing was adjourned before completion to allow the witnesses time for further preparation) and a one-week public hearing in June 1976. The Commission took six months to evaluate the evidence from the 1976 hearing before finally adopting its regulations. Despite the passage of nearly ten years from the time the Water Quality Act was initially adopted until the groundwater regulations were promulgated, New Mexico was the first state to adopt such regulations and was several years ahead of parallel federal efforts to protect ground water quality.

New Mexico's 1977 groundwater regulations establish numerical standards for twenty-seven common water contaminants. WQCC Regs. 3-103. Simply stated, the regulations provide that in order to obtain permission to discharge, a person must demonstrate that his discharge will not cause in the numerical standards (or the pre-existing concentration if it is higher than the standard) to be exceeded at any place of withdrawal of groundwater for present or future use. WQCC Regs. 3-109C. If properly implemented, the regulations and their discharge plan requirement should prevent water pollution before it occurs. An industry challenge to the 1977 groundwater regulations was only partially successful. The New Mexico Supreme Court in <u>Bokum Resources v. New Mexico Water Quality Control Commission,</u> 93 N.M. 546, 603 P.2d 285 (1979) voided the 1977 generic definition of toxic pollutant as unconstitutionally vague. However, the remainder of the regulations, including the important provision placing the burden on the discharger to demonstrate compliance with the regulations were upheld by the courts.

The WQCC's new definition of toxic pollutant was upheld by the courts in 1982. <u>Kerr-McGee v. New Mexico Water Quality Control Commission,</u> 98 N.M. 240, 647 P.2d 873 (1982). That new definition, as it currently reads, establishes a list of some 76 organic compounds, the existence of which either singly or in any combination is considered toxic if a lifetime cancer risk of one cancer per 100,000 exposed persons exists. A toxic pollutant also exists under the definition if one or more of the pollutants on the list are present in concentrations which unreasonably threaten to injure human health or the health of plants or animals which benefit man. The definition specifies certain types of unacceptable injuries to health including death, clinical symptoms of disease and genetic mutations. WQCC

Regs. 1-101 U.U. The existence of a toxic pollutant or pollutants at a place of withdrawal of ground water for present or future use is forbidden by the regulations. WQCC Regs. 3-109C.

The Water Quality Control Commission's groundwater regulations removed some of the guesswork involved in enforcing common law and statutory nuisance claims. The standards for acceptable contamination are specified either by a numerical concentration or by an allowable risk of cancer. WQCC Regs. 1-101 U.U. and 3-103. The place of measurement of water quality for compliance is the place of withdrawal of groundwater. WQCC Regs. 3-109. The regulated activity is discharge of effluent or leachate which may move into groundwater. WQCC Regs. 3-104.

However, the agency responsible for approving or disapproving discharge plans is given a large degree of discretion in implementing the groundwater regulations. This discretion could be abused by either an inexperienced or overzealous regulator. For example, the regulations do not specify the degree of certainty a discharge plan must contain in demonstrating the future impact or lack of impact on groundwater. Projecting movement of contaminants through groundwater and soil involves significant scientific uncertainty. A regulator who demands one hundred percent certainty of such projections cannot, in most cases, be satisfied. The result would be disapproval of the discharge plan and no permission to discharge. The issue of which groundwater is subject to use also presents an opportunity for abuse of discretion. Theoretically, groundwater which is already highly contaminated may be capable of future use if extensive resources are expended for pre-treatment. However, as a practical matter, it is unlikely that contaminated sources will be used if other sources of water are available. Similarly very small quantities of groundwater and remotely located aquifers may be subject to protection by an overzealous regulator when, as a practical matter, they are not and will not be used as a source of water.

Discharge plan applicants may be concerned about potential abuse of administrative discretion. At the same time, others may be concerned about the limited ability of the public to participate in the administrative process or to enforce the provisions of the Water Quality Act. While the public is allowed to request and participate in public hearings on discharge plans (S 74-6-5E, N.M.S.A. 1978, WQCC Regs. 3-108) only the discharge plan applicant has a clear right to appeal the constituent agency's decision to the Water Quality Control Commission and then to the Court of Appeals. Sections 74-6-5L, M, N and 0, N.M.S.A. 1978, WQCC Regs. 3-112 and 113. Also, unlike many federal environmental statutes, the Water Quality Act has no citizen suit provision allowing members of the public to sue to enforce the Act and WQCC regulations.

Enforcement of the groundwater regulations is focused at the administrative level. Most applications for discharge plans result in approval, although additions or amendments to the plans are often required by the permitting agency. Of a handful of discharge plans which have been disapproved only one, the discharge plan for Bokum Resources' Uranium Mill, has reached the courts. The discharge plan denial by the EID in that case was upheld by the New Mexico Supreme Court without a written opinion. Bokum v. Baca, No. 12,593 (N.M. Sup. Ct. Aug. 1, 1979) EID Approval of Bokum's second discharge plan was challenged by a local citizens group and was upheld by a state district court judge. State, ex rel. SEAC v. Baca, No. SF 80-878(c) (Jan. 6, 1981).

The groundwater regulations' emphasis on administrative enforcement offers the advantage of a decisionmaker with technical expertise. While a nuisance lawsuit is tried before a court of law with little or no background in hydrology, geology, chemistry, or public health, discharge plans are reviewed by a state agency staff with such expertise. If the applicant is dissatisfied with the decision of the constituent agency, an appeal to the Water Quality Control Commission is available. Section 74-6-5L, N.M.S.A. 1978. Only after two layers of administrative review are exhausted is a discharge plan reviewed by the courts. Section 74-6-50, N.M.S.A. 1978.

THE DOCTRINE OF PRIMARY JURISDICTION

The Water Quality Act in Section 74-6-13, N.M.S.A. 1978 states:

> The Water Quality Act provides additional and cumulative remedies to prevent, abate and control water pollution, and nothing abridges or alters rights of action or remedies in equity under the common law or statutory law, criminal or civil. No provision of the Water Quality Act or any act done by virtue thereof estops the state or any political subdivision or person as owner of water rights or otherwise, in the exercise of their rights in equity or under the common law or statutory law to suppress nuisances or to abate pollution.

While that section provides that the Water Quality Act does not preempt common law nuisance or statutory public nuisance claims, the courts have the power to suspend nuisance proceedings under the Doctrine of Primary Jurisdiction. State ex rel. Norvell v. Arizona Public Service Co., 85 N.M. 165, 510 P.2d 98 (1973). The Primary Jurisdiction

Doctrine allows the court, in its discretion, to suspend judicial proceedings when enforcement of a claim in court:

> requires the resolution of issues which under a regulatory scheme, have been placed within the special competence of an administrative body. . . .

Mountain States Natural Gas Corporation v. Petroleum Corporation of Texas, 693 F.2d 1015 at 1018 (1982). In the Norvell case the New Mexico Supreme Court dismissed a statutory public nuisance action by the State Attorney General for air and water pollution. The court found that the issues raised by the lawsuit were within the jurisdiction of state regulatory agencies and should be resolved by those agencies and not by the courts. In regard to the water pollution issue the court said:

> By nothing before us is it made to appear that the trial court could solve the mercury problem either more quickly or better than the Agency. . . we are concerned lest intervention of the trial court would add little to or even hamper the solution of the overall problem.

State ex. rel., Norvelle v. Arizona Public Service Company, supra at 172. The New Mexico Supreme Court chose not to attempt to establish a water quality standard for mercury so long as the administrative agency with authority and expertise was progressing in standard development.

New Mexico appellate courts have elected not to apply the Primary Jurisdiction Doctrine in two more recent water pollution cases. In O'Hare v. Valley Utilities, 89 N.M. 105, 547 P.2d 1147 (Ct. App. 1976) modified, 89 N.M. 262, 550 P.2d 274 (1976) the New Mexico Court of Appeals stressed the language in the Water Quality Act preserving common law remedies against water pollution and found that certain legal claims of the plaintiff were beyond the expertise of the administrative agencies. In particular, the court noted that the Environmental Improvement Agency [predecessor to the EID] was powerless to grant the monetary damages requested in the lawsuit. In Gonzales v. Whitaker, 97 N.M. 710, 643 P.2d 274 (1982) the Court of Appeals again declined to apply the Primary Jurisdiction Doctrine. The court said, that in that case, the Environmental Improvement Division had already approved the proposed dairy and:

> already exercised whatever 'primary jurisdiction' it held. . .

The Court continued

> The question which still remains is: Will the dairy be a nuisance to the surrounding landowners even if applicable EIA regulations have been met. . .

97 N.M. at 713.

In any event the courts will review on a case-by-case basis the applicability of the Primary Jurisdiction Doctrine. That doctrine may serve as an obstacle to a water pollution lawsuit based on a nuisance theory.

CONCLUSION

As more complicated groundwater pollution problems have come to light the State of New Mexico has responded with a more comprehensive and detailed statutory and regulatory program to prevent and abate groundwater pollution. The regulatory trend has been in the direction of more extensive expert and technical review at the agency level and away from court enforcement, at least as the initial enforcement step. Common law nuisance claims and statutory public nuisance claims remain available to parties aggrieved by groundwater pollution, but the courts in some cases have suspended or dismissed such actions under the Doctrine of Primary Jurisdiction.

The combined legal mechanisms available to address groundwater pollution in New Mexico are capable of handling most or all cases of groundwater pollution. The effectiveness of those mechanisms depends largely on their application by the parties involved, the courts, and the responsible administrative agencies.

Acknowledgments

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References

The materials cited in the text follow the standard legal format. "N.M.S.A. 1978" is the abbreviated form for the current state statues, the New Mexico Statutes Annotated. "Am. Jur. 2d" is the abbreviated form for American Jurisprudence, Second Edition, one of the leading texts on American Law. Court decisions are cited by case name and page and volume numbers of the official reports. "N.M." is the abbreviated form for New Mexico Reports. "P.2d" is the abbreviated form for Pacific Reports, second series. "F.2d" is the abbreviated form for Federal Reports, second series.

ROOSEVELT COUNTY DISTRICT COURT RULES THAT DETERIORATION IN WATER QUALITY MAY BE CONSIDERED IMPAIRMENT TO WATER USERS

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ABSTRACT

Between 1940 and 1970, irrigated acreage in Roosevelt County increased from 11,300 acres to 103,700 acres. Increased irrigation accelerated ground-water withdrawals and water-table declines, in turn mobilizing a highly saline groundwater "wedge". Water in irrigation wells increased in chloride concentrations from less than 50 parts per million (ppm) to over 800 ppm in some areas. Decisions by the State Engineer have traditionally considered only water-level declines as a cause for impairment; changes in water quality were not considered to be factors. On April 22, 1982, the State Engineer approved a change in location of an older water right over the protest of Messers. Robert Stokes and Calvin Blevins of Portales, New Mexico. The decision was appealed to District Court on the grounds that: Deterioration in water quality may be grounds for impairment; all transient conditions must be considered in determining water-quality impairment.

INTRODUCTION

TRADITIONAL CRITERIA FOR APPROPRIATION AND USE OF GROUND WATER IN NEW MEXICO

The State Engineer in New Mexico governs the use and appropriation of all ground waters contained in declared underground water basins in the state.

At which time ground waters in a declared basin are already in existence and are being beneficially used, the owner of those ground-water rights may change the place and/or purpose of use of his appropriation with the approval of the State Engineer. As stated in Section 2, Article 2, of the Rules and Regulations Governing Drilling of Wells and Appropriation and Use of Ground Water in New Mexico (State Engineer, 1966, p. 9), rt . . .such approval will be granted only after proper application is made and the State Engineer determines that the proposed move would not impair existing rights."

Typically, impairment is considered to be one or more of the following:(1)reduction in quantity of water available to prior users for production by dewatering as a result of transferring rights to a nearby location; (2) increased costs for pumping from a lower level or deepening of the prior user's well as a result of transferring rights to a nearby location, or; (3) any deterioration in performance of the prior user's water delivery system which is determined to be a result of the transfer of rights to, and an accelerated withdrawal from, a nearby location. Any decision made by the State Engineer on this matter may be appealed to the District Court.

Normally, degradation in water quality experienced by a prior user is not considered impairment because of the rarity of the situation, and the special circumstances which must be present before it is deemed that the transfer of rights to a nearby location is causing or will cause impairment to a prior user in the form of water-quality degradation.

Oftentimes the State Engineer will model a closed basin in order to help him make appropriations and predict and analyze the behavior of the aquifer in response to withdrawals and recharge. This paper reviews the argument presented in District Court which helped to overturn a ruling by the State Engineer which allowed the transferal of water rights within the Portales Underground Water Basin. It was determined that there were two aspects of the findings of the State Engineer which can be questioned on the basis of irrigation practice, and hydrologic and hydraulic properties. They are as follows:

1. The application of conventional water-quality parameters in the vicinity of the disputed sections.
2. The failure of the State Engineer to adequately consider the transient conditions in the aquifer and the potential for long-range impacts on prior users.

PORTALES VALLEY - GEOHYDROLOGIC SETTING, PRIOR GROUND-WATER USE AND WITHDRAWALS, AND THE INDUCED MOVEMENT OF A HIGHLY SALINE GROUND-WATER "WEDGE"

Geo hydrologic Setting

The Portales Valley is a broad, shallow depression in the Staked Plains of northern Roosevelt County, New Mexico (fig. 1). The valley is characterized by gentle slopes and the absence of streams. A strip of sand dunes extends along the north side of the valley for nearly its entire length. The dunes constitute a favorable catchment area for precipitation (Conover and Akin, 1942).

The aquifer which occupies the Portales Valley is geologically an abandoned river valley filled with alluvial material derived from the Rocky Mountains (Theis, 1932). Typically, the aquifer is between 100 and 130 feet (30.5 and 39.6 meters) thick. The alluvial deposits are underlain by

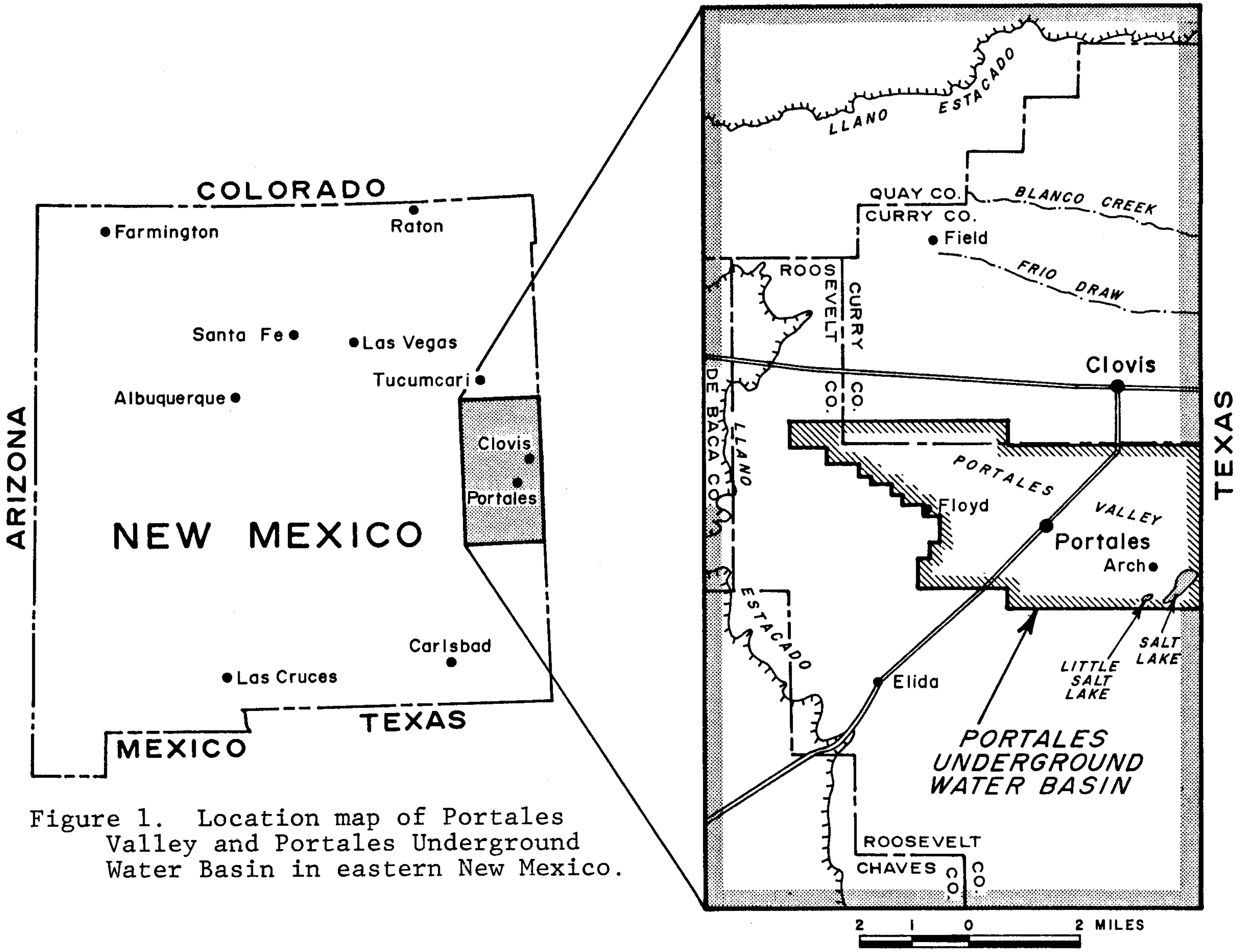

Figure 1. Location map of Portales Valley and Portales Underground Water Basin in eastern New Mexico.

the "bird-eye" clay, and a red shale known as the "red beds". These strata, Triassic in age (Theis, 1932, p. 125), are generally impermeable except where they may be fractured by impact stress due to slumping via the removal of materials from the formations beneath the alluvial material (Theis, 1932, p. 116). A number of these depressions can be seen at the surface, and some contain perennial water. For instance, Salt Lake and Little Salt Lake, located southeast of Portales (fig. 1), contain water that is highly mineralized, partly because of an increase in concentration of salts by evaporation.

Ground water exists in the red shale underlying the valley-fill alluvium. This water is also confined in interbedded sandstone by the shale and is therefore under artesian conditions. Where fractures in the shale exist, the potential exists for the upward movement of the confined ground water into the valley-fill material.

The quality of water in the Portales valley-fill alluvium is generally very good and similar to that of the Ogallala aquifer (Theis, 1932, p. 126). It is suitable for domestic use, with concentrations of chlorides generally less than 250 parts per million (ppm), and often below 50 ppm. The water contained in the underlying strata is generally much harder, and it contains a higher concentration of chlorides (Theis, 1932, p. 119). It is possible that where comingling of the two waters might exist, the quality of water in the shallow aquifer is compromised and spotty in locale.

Historic Use of Ground Water and Previous Investigations Near Portales

Particular attention was paid to the understanding of the geology and hydrology of the Portales Valley in the 1930's, 40's, and 50's. Notable investigators included C. V. Theis (1932) who is also primarily responsible for the development of the radial flow equations used in ground-water hydraulics today, C. S. Conover and P. D. Akin (1942), and S. E. Galloway (1956). These investigators were concerned about the proper development and management of the aquifers in the valley, and of particular concern was the possibility of over-stressing and eventually dewatering of the valley-fill aquifer.

In as early as 1930, Theis (1932) concluded " . . . that the State take such actions as is proper under its laws to conserve the ground-water supply of the valley and to form a ground-water district, under the supervision of the State Engineer. . ." The Portales Underground Water Basin, as declared by the State Engineer in 1950 and expanded in 1955, is shown in fig. 1.

Conover and Akin (1942) later concluded that ". . . the present irrigation development in the heavily pumped areas near Portales is probably as great as it should be for proper utilization of the ground-water supply. . ."

Finally, in the mid-1950's Galloway (1956) suggested that, ". . . the progressive water-level declines noted in the water-level records for this area (Portales Valley) are indicative that the annual ground-water withdrawal is far in excess of the annual recharge that is normally contributed to the reservoir. . ." Also notable is Galloway's observation that ". . . the top of the Triassic red beds that occurs beneath the Portales Valley is, for all practical purposes, the lower limit of water-bearing sediment from which a groundwater supply may be expected that is of suitable chemical quality and in sufficient quantities to meet the normal needs of agriculture, municipal, industrial, stock and domestic uses."

Induced Movement of a Highly Saline Ground-Water Wedge

It was noted by Galloway (1956) that excessive pumping in the vicinity of Portales resulted in a complete reversal of the generally southeastward gradient of the water table in an area south and east of Portales. Perhaps related to this phenomenon is the encroachment of a body of highly mineralized ground water southeast of Portales from the south in the vicinity of Little Salt Lake. Because such highly mineralized water is not typical of the valley-fill aquifer, its origin is very likely the underlying confined aquifer. Water contained in these sediments, as previously discussed, is generally very poor in quality and is unsuitable for any use.

Whatever its origin, the poor quality water presents a threat to farmers in that area who rely on good quality water for irrigation and domestic consumption. Increased or accelerated ground-water withdrawals north of, or down-gradient from, the migrating wedge (or interface of poor and good quality water) would only serve to accelerate its advance and worsen the situation.

STOKES AND BLEVINS VS. SANDERS AND SANDERS, JR.
STATE ENGINEER RULES IN FAVOR OF CHANGE OF PLACE OF DIVERSION

SUMMARY OF DISPUTE

Farmers owning wells and water rights in the area inundated and now occupied by the migrating saline water are no longer able to irrigate with water from their wells. Consequently, withdrawals have slowed and even ceased in these areas, and withdrawals have increased north of the wedge where good quality water can still be withdrawn from the alluvial aquifer for irrigation and domestic consumption.

Farmers unable to irrigate or even drink water from their wells destroyed by highly saline water are forced to either withdraw their allocated ground water elsewhere and transport it for use, or simply abandon their practice of irrigating. Farmers still irrigating with good quality ground water north of the wedge, and who are established prior users in that area are most concerned about protecting their valuable resource. Two such farmers, Calvin Blevins and Robert Stokes, protested the application for transferal of water rights to sections directly adjacent to their wells. David Sanders and David Sanders, Jr., were wishing to transfer their existing water rights from sections rendered useless by the invasion of saline water. As Sanders' application is a matter of public record and must be published information, the news of Sanders' intent reached Stokes and Blevins. Consequently, a protest of the application was filed by Stokes and Blevins with the State Engineer.

On March 31, 1982, the matter was heard in Portales, New Mexico. Calvin Blevins and Robert Stokes appeared pro se while Sanders' were represented by their attorney.

FINDINGS AND ORDER OF THE STATE ENGINEER

On April 22, 1982, the Findings and Order was issued by the State Engineer. The application for transferal of rights was approved providing that the move-to wells be equipped with totalizing flow meters and the amount of water diverted from the wells be monitored and recorded for the first six months of use

On April 27, 1982, the services of Geohydrology Associates, Inc. (GAI), of Albuquerque, New Mexico, were retained by the protestants and their attorney. With 30 days in which to appeal the decision made by the State Engineer, the Findings and Order were reviewed along with pertinent geo hydrologic data from the Portales vicinity. It was recommended by GAI that the following findings of the State Engineer be questioned in District Court on the basis of common irrigation practice, and hydraulic and hydrologic principles: "(1) In general, in the Portales Basin, an increase in the dissolved solids at a chloride concentration of 1,000 ppm in the water used for irrigation results in a decrease in crop yield; (2) termination of pumping at the move-from wells and commencement of pumping at the move-to wells would not accelerate the rate at which chloride concentration increases in the water at the wells (used by Stokes and Blevins); and (3) granting of application...to change place of use...and to comingle (move-to wells)...for...irrigation...of land will not impair existing rights provided that the amount taken (does not exceed the appropriated amount)."

ASSESSMENT OF FINDINGS

DEGRADATION OF WATER QUALITY

It was the position of GAI in behalf of Robert Stokes and Calvin Blevins that the State Engineer did not have sufficient water-quality data to support the findings on which the application was granted. Following is a discussion of the Portestant's position.

Sodium-Adsorption-Ratio

There was no indication that Sodium-Adsorption-Ratio (SAR) was considered by the State Engineer in granting the application.

With few exceptions, the water produced in the Portales basin is used for irrigation. Inasmuch as crop productivity is a function of many factors, including the interrelationship of water and soil, the SAR generally is used as an indicator of the suitability of water for irrigation (Hem, 1970, p. 228). The SAR is particularly critical in the Portales basin because irrigation water having a high SAR indicates the potential for sodium accumulation in the soil. This in turn ultimately reduces crop productivity.

Chloride Concentrations

In the findings it is stated that chloride concentrations of 1,000 ppm result in a decrease in crop yield. Actually the build-up of chloride and other salts may reduce crop production at lower levels. It is the position of the California State Water Quality Control Board (1963) that at a "threshold" concentration of 100 milligrams per liter (mg/l; mg/1 - ppm) the irrigator might become concerned about water quality and consider additional water for leaching. "Limiting" concentration is defined as that concentration of chlorides that might drastically reduce the yield of high-value crops, or at which value an irrigator might be forced to less valuable crops. The limiting concentration is 350 mg/l. The idea that more water would have to be applied to the soil for leaching implies a perpetual problem in the Portales area. As more water is withdrawn from the ground for irrigation and leaching (providing drainage is adequate), the movement of the saline ground-water body is accelerated even more and water quality is further destroyed.

COMPLEXITIES CREATED BY TRANSIENT CONDITIONS

Between 1962 and 1982 there was a significant change in the saturated thickness of the alluvial aquifer and the configuration of the water table in the vicinity of the proposed move-to sections (fig. 2). In those sections the water table declined as much as 30 feet (9.1 meters). The drop in water levels is a result of increased withdrawal by pumping of ground water along the axis of the ground-water trough which underlies part of the Protestant's property (fig. 3). Conversely, the water table rose as much as 10 feet (3.0 meters) in the Applicant's move-from sections. This recovery is a result of the reduction in pumping due to an increase in salinity of the available ground water.

Clearly, there is an imbalance in the geo hydrologic conditions in the Portales basin, and in particular in the vicinity of the proposed application. As shown in the cross section in fig. 4, the wedge of saline ground water has migrated a distance of over one mile since 1962 to the north toward wells owned by Robert Stokes and Calvin Blevins.

While the rates of depletion may remain constant at the move-to locations, recovery of water levels to the south in the move-from locations will serve to increase the gradient of the water table. The increased gradient will accelerate the rate of ground-water movement, and the water quality will deteriorate proportionately.

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ACTUAL IMPAIRMENT OR EXAMPLE FOR OTHERS?

Though it is clear that an imbalance in the geohydrologic system exists, will the transferal of a few hundred acre feet of water rights in themselves actually impair the Protestants, or will the Applicants simply serve as an example for other water users in the basin. If the Applicants are denied their transferal will they be the "line that had to be drawn somewhere?" Because of the nature of the protest, it had to be shown by the Protestants that the actual transferal of rights would impair their existing rights. By law, however, the burden of proof rests with the Applicants in that they must show the court that if the rights were transferred and ground water was withdrawn at the move-to locations it would <u>not</u> impair the Protestants. In actuality, the amount of water to be withdrawn by the Applicants at the move to locations is a small quantity, and that quantity in itself would not impair prior users, or in particular, Robert Stokes and Calvin Blevins. However, the argument presented by the Protestants is that any further withdrawals resulting

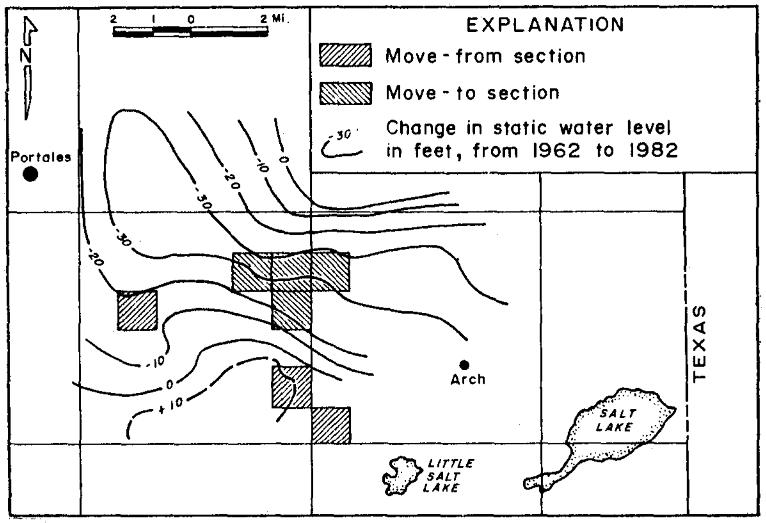

Figure 2

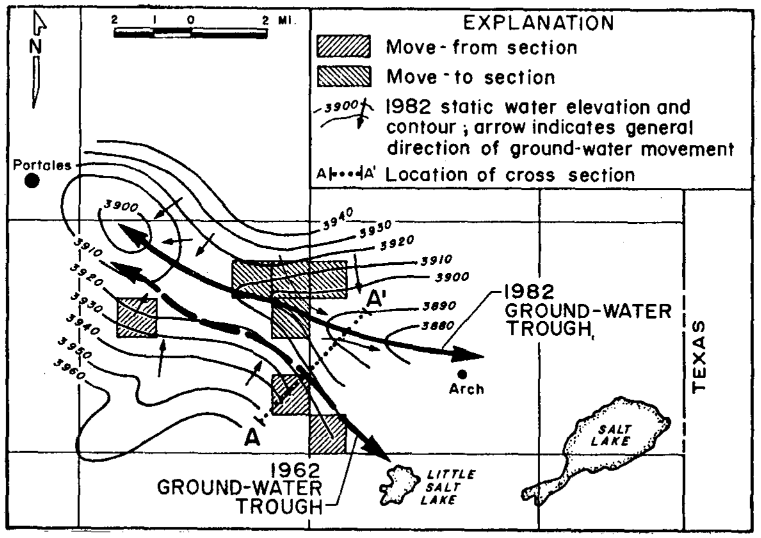

Figure 3

Figure 2. Change in static water level in the alluvial aquifer from 1962 to 1982.

Figure 3. Configuration and altitude of water table in 1982.

Figure 4. Cross section of aquifer system in Portales Valley southeast of Portales. Location of cross section is shown in fig. 3.

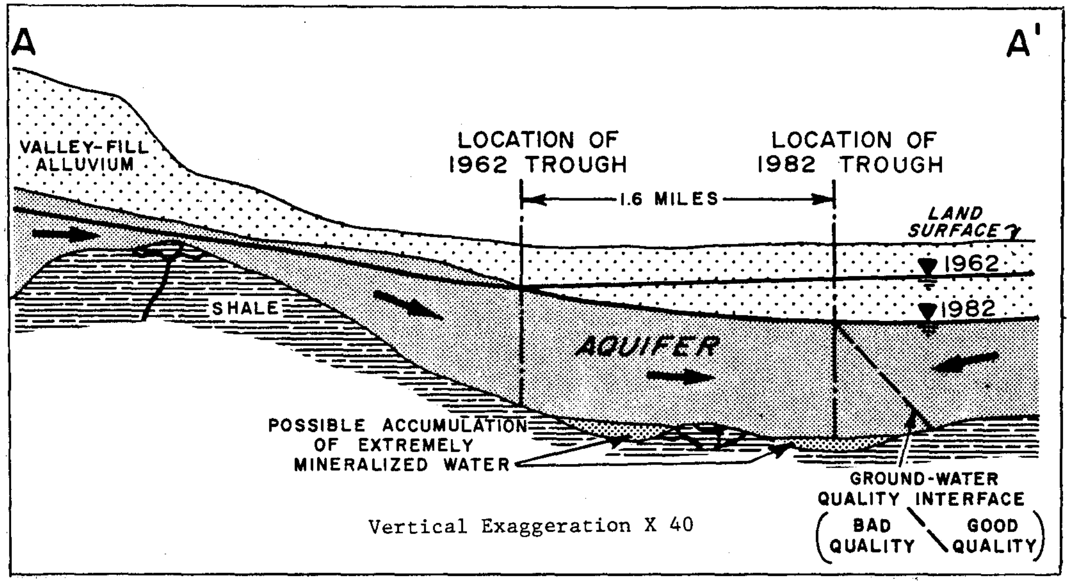

Figure 4

in water-level declines in the vicinity of the move-to locations would impair the quality of water in their wells.

SUMMARY AND RULING BY DISTRICT COURT

In April 1982 Judge Fred T. Hensley of the Roosevelt County District Court in Portales ruled against the transfer of rights. Judge Hensley concluded that the Applicants failed in their burden of proof that they would <u>not</u> impair the quality of water in the Protestant's wells. Thus, Judge Hensley ruled that the decision made by the State Engineer be overturned and the application for transferal of place and purpose of use of water rights owned by the Applicants be denied.

In April 1983 an appeal of Judge Hensley's decision was filed by the Applicants to the Supreme Court. As of February 1984 a decision is pending.

Precedence has already been set for decisions of this type in the Portales Underground Water Basin. No matter what the outcome of the decision of the Supreme Court, important points surfaced and were discussed in Portales in District Court in November 1982. Should the decision made by Judge Hensley be upheld in the Supreme Court, we can expect that water-quality degradation will be considered impairment to prior users in other closed basins in the state, and applications for new appropriations of ground water along with applications for transferals of existing rights will be considered by the State Engineer accordingly.

REFERENCES

California State Water Quality Control Board, 1963, Guides for evaluating the quality of water used for irrigation in Todd, K. T., (ed.), 1970, The water encyclopedia: Water Information Center, New York, Table 6-23.

Conover, C. S.,and Akin, P. D., 1942, Progress report on the ground-water supply of the Portales Valley, Roosevelt County, New Mexico, 33 p. in Fourteenth and Fifteenth Biennial Reports of the State Engineer of New Mexico, for the 27th, 28th, 29th, and 30th Fiscal Years, July 1, 1938, to June 30, 1942.

Galloway, S. E., 1956, Geology and ground-water resources of the Portales Valley area, Roosevelt and Curry Counties, New Mexico, 167 p., a Master's Thesis.

Hem, J. D., 1970, Study and interpretation of the chemical characteristics of natural water: United States Geological Survey Water Supply Paper 1473, 363 p.

New Mexico State Engineer, 1966, Rules and regulations governing drilling of wells and appropriation and use of ground water in New Mexico, Santa Fe, New Mexico, P. 9.

Theis, C. V., 1932, Report on the ground water in Curry and Roosevelt Counties, New Mexico, 146 p., in Tenth Biennial Report, State Engineer of New Mexico, for the 19th and 20th Fiscal Years, July 1st, 1930, to June 30th, 1932.