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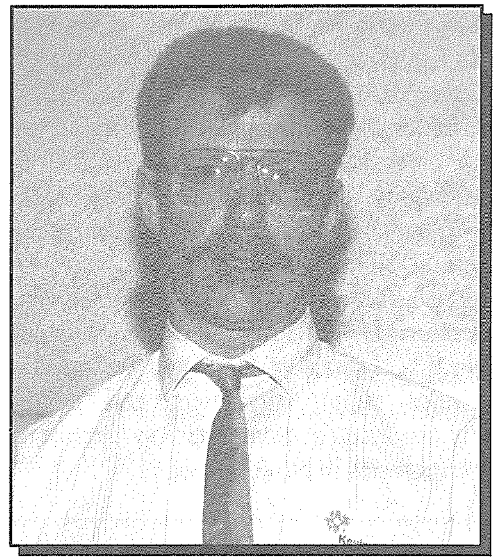

ARSENIC IN THE MIDDLE RIO GRANDE: OCCURRENCE AND REGULATORY STANDARDS

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INTRODUCTION

Arsenic is present throughout the environment, occurring both naturally and as a result of human activity. Arsenic occurs in the earth's crust at an average concentration of 1.8 micrograms per gram (μg/g) (Krauskopf 1979) and at a concentration of 2.6 micrograms per liter (μg/l) in seawater (Maidment 1993). The average concentration of arsenic in the atmosphere in areas where major emission sources are absent has been estimated at 3 nanograms per cubic meter (USEPA 1980). The average concentration of arsenic in fresh surface waters is 3 μg/l (Boyle and Jonasson 1973). A nationwide study of trace metals in waters throughout the United States found arsenic to be present at a concentration greater than 5 μg/l in 5.5 percent of the samples (Kopp and Kroner 1968). The Agency for Toxic Substances and Disease Registry (ATSDR 1990) reported on a 1970 study which found that up to 1 percent of community water supplies in the United States had concentrations of arsenic exceeding 10 μg/l. The average daily dietary intake of arsenic by adults in the United States has been estimated at 50 μg, with meat, poultry and fish accounting for 80 percent of the intake (ATSDR 1990). Natural sources of arsenic include arsenic gases and compounds formed as a result of volcanic and geothermal activity and weathering of minerals and ores containing arsenic. Major sources of human-related release include smelting of ores and use of arsenic containing pesticides. Additional sources from commercial and industrial processes include use of arsenic-containing wood preservatives and paints and pigments.

Arsenic occurs in the Middle Rio Grande Basin in central New Mexico (Figure 1) both naturally and as a result of human activity. The Middle Rio Grande is considered to be that portion of the river from Cochiti Reservoir in north-central New Mexico to Elephant Butte Reservoir in south-central New Mexico. Flow in the Rio Grande results mainly from snowmelt runoff in the San Juan, Sangre de Cristo and Jemez mountains of southern Colorado and northern New Mexico. Additional flow results from sporadic summer thunderstorms. The Rio Grande is a "controlled" river in that a series of flood and sediment control and water supply reservoirs and channelized reaches are located along the Rio Grande and its major tributaries in New Mexico.

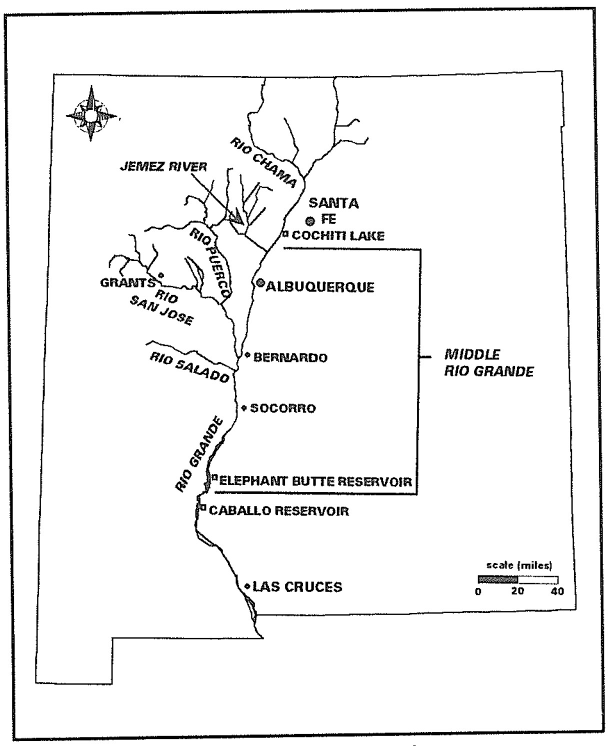

Figure 1. The Middle Rio Grande basin.

Transport of arsenic in the Middle Rio Grande occurs both in the aqueous phase and as a result of sediment transport. Much of the arsenic occurring in the Middle Rio Grande enters the river from tributaries which drain the Jemez Mountains, an area of high geothermal activity. Mining activity in the Grants Mineral Belt may mobilize arsenic into the water column with subsequent migration to the Middle Rio Grande. An additional source of arsenic to the Rio Grande is the discharge of groundwater containing arsenic, both naturally and artificially through pumping of groundwater for municipal water supply and subsequent discharge to the river via wastewater treatment plants as well as through irrigation return flow.

OCCURRENCE

Surface Water and Stream Sediments

Previous studies have looked at the presence of arsenic in surface and groundwater, stream sediments and biota (fish tissue) within the Middle Rio Grande basin. Brandvold et al. (1981) performed a study to determine the potential effect of uranium mining, milling and related activities in the Grants Mineral Belt of northwestern New Mexico on the water quality of the Rio Grande. The Grants Mineral Belt is located at the headwaters of the Rio San Jose and a major tributary of the Rio Puerco. Average concentrations of dissolved arsenic from nine separate sampling events conducted in 1979 and 1980 at ten locations along the Rio San Jose and the Rio Puerco and their tributaries ranged from 2 to 39 μg/l (Figure 2). Arsenic concentrations were highest in San Mateo Creek and in the Rio Puerco just above its confluence with the Rio Grande. Arsenic concentrations in suspended and bed load sediments were also examined. Arsenic in suspended sediments from 12 samples collected at three locations from the Rio San Jose averaged 41 μg/g of dried sediment. Arsenic in suspended sediments from 15 samples collected at three locations from the Rio Puerco averaged 16 μg/g. A previous study (Popp and Laquer 1980) found the concentration of arsenic in suspended sediments from the Rio Grande at Bernardo to be 230 μg/g.

Thomson et al. (1982) investigated the environmental impacts of uranium mining in the Grants Mineral Belt and observed an average arsenic concentration of 1,300 μg/l in 14 samples collected from acid-leach tailing raffinates from four separate uranium mills and an average of 5,000 μg/l in five samples collected from one alkalinity-leach tailing raffinate.

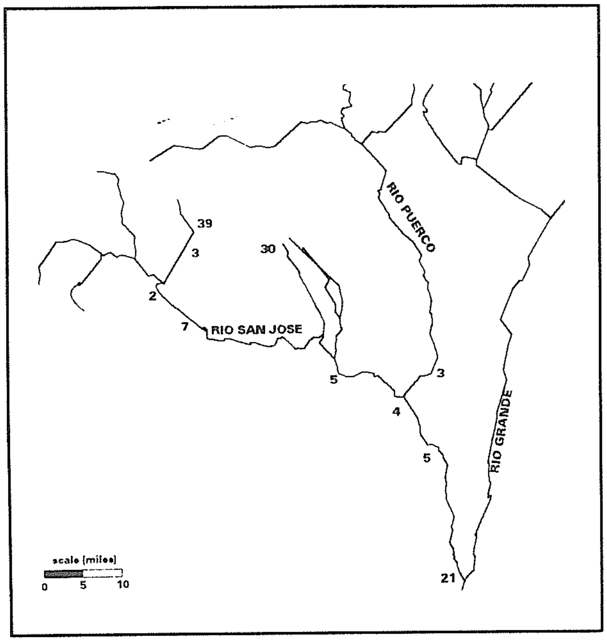

Figure 2. Mean dissolved arsenic concentrations (μg/l) during nine sampling events in 1979 and 1980 in the Rio Puerco/Rio San Jose system (Brandvold et al. 1981).

Popp et al. (1983) conducted a study that looked at the presence of toxic substances in water, sediments and fish tissue in the Middle Rio Grande. Concentrations of dissolved arsenic in four samples collected from the Rio Grande at San Marcial averaged 25 μg/l. The concentration of total arsenic averaged 14 μg/l in the Rio Grande at San Marcial and 11 μg/l in the Rio Grande at Socorro. The average concentration of dissolved arsenic in four samples collected at each of four different surface sites from Elephant Butte Reservoir ranged from 8 to 11 μg/l. The average concentration of total arsenic ranged from 2.8 to 110 μg/l. The concentration of arsenic in stream bed sediments was 5.6 μg/g in the Rio Grande at Socorro and 6.6 μg/g at San Marcial. The average concentration of arsenic in lake bed sediments collected at four sites from Elephant Butte Reservoir ranged from 3.1 to 9.1 μg/g.

Popp et al. (1984) found concentrations of arsenic in bed sediments at three sampling locations on the Rio Puerco and the Rio San Jose to range from 8.0 to 17.2 μg/g. Similar concentrations were observed in samples of older valley fill material in the region, suggesting historically long-term elevated levels.

Piatt (1987), in a statistical study of water quality in the Rio Grande basin, analyzed water quality data contained in the U.S. Environmental Protection Agency's (EPA) STORET database for the Rio Grande and some of the river's major tributaries. Concentrations of total arsenic in varying numbers of samples collected at ten sites from the Middle Rio Grande during the period from 1972 through 1986 ranged from 1 to 470 μg/l. The average concentration of total arsenic at the sampling locations ranged from 2.0 to 43.7 μg/l (Figure 3). The mean concentration of total arsenic for the Rio Grande at Cerro near the Colorado border averaged 2.0 μg/l. Arsenic concentrations generally increased downstream to the high of 43.7 μg/l at the Rio Grande floodway at San Marcial. Concentrations of total arsenic for several samples collected from the Jemez River near Jemez and from below the Jemez Canyon Dam during the period from 1974 to 1985 averaged 30.8 and 34.5 μg/l, respectively. Concentrations of total arsenic for samples collected from four locations from the Rio Puerco system during the period from 1977 to 1984 ranged from 1.0 to 820 μg/l. The average concentration of total arsenic at the sampling locations ranged from 1.0 to 111 μg/l, with San Pablo Creek near Cuba exhibiting the elevated measurements (Figure 4).

Brandvold and Brandvold (1990) compiled available data from studies completed through 1986 of trace metals in the Middle Rio Grande and the Rio Puerco/Rio San Jose system, including Brandvold et al. (1981) discussed above. This compilation did not include data available from STORET. Figures 5 and 6 show the average concentration of dissolved arsenic in samples collected at various locations along the Middle Rio Grande and the Rio San Jose/Rio Puerco system. Elevated levels of arsenic occur in the Rio Grande downstream of the Jemez River and the Rio Puerco, and also downstream of the Socorro area. Concentrations of total arsenic and of arsenic in suspended sediment samples show similar trends. The authors did comment that the concentration of arsenic at most of the sites along the Rio Grande was biased high due to interference in the laboratory analytical method used for one of the studies.

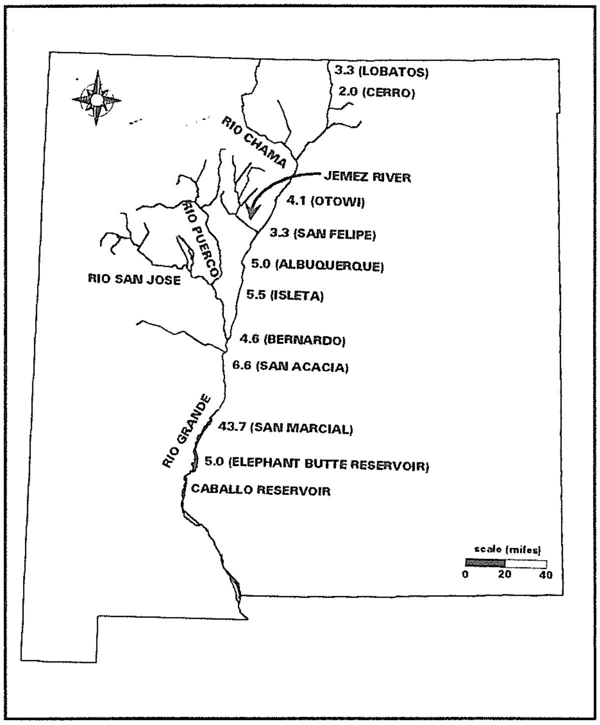

Figure 3. Mean total arsenic concentrations (μg/l) in STORET from 1972 to 1986 in the Middle Rio Grande (Piatt 1987).

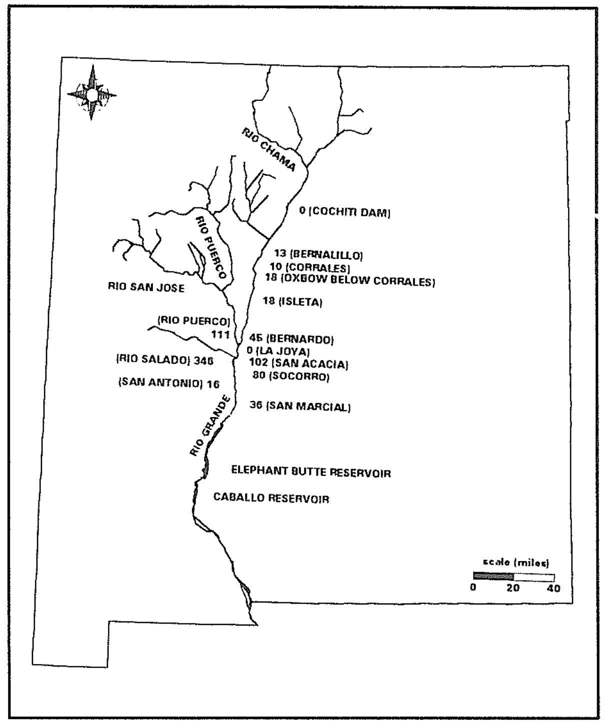

Figure 5. Mean dissolved arsenic concentrations (μg/l) in the Middle Rio Grande from 1975 to 1983 from published and unpublished sources (Brandvold and Brandvold 1990).

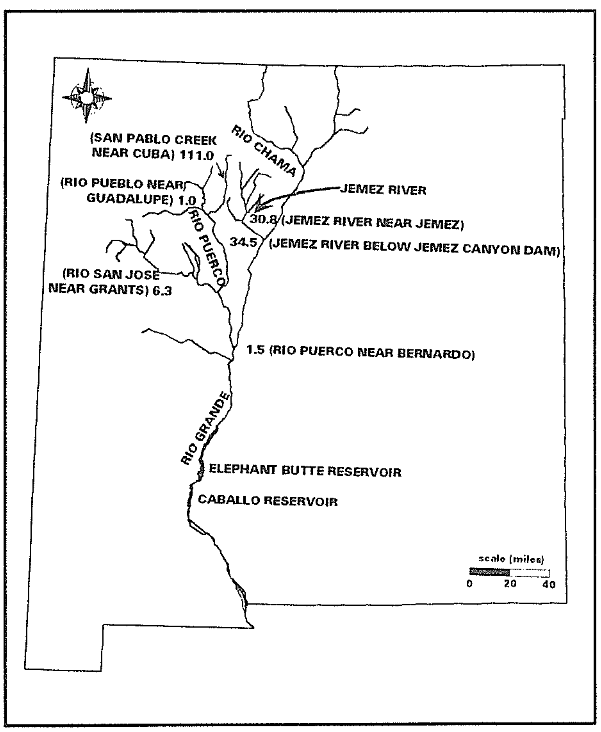

Figure 4. Mean total arsenic concentrations (μg/l) in STORET from 1972 to 1986 in major tributaries to the Middle Rio Grande (Piatt 1987).

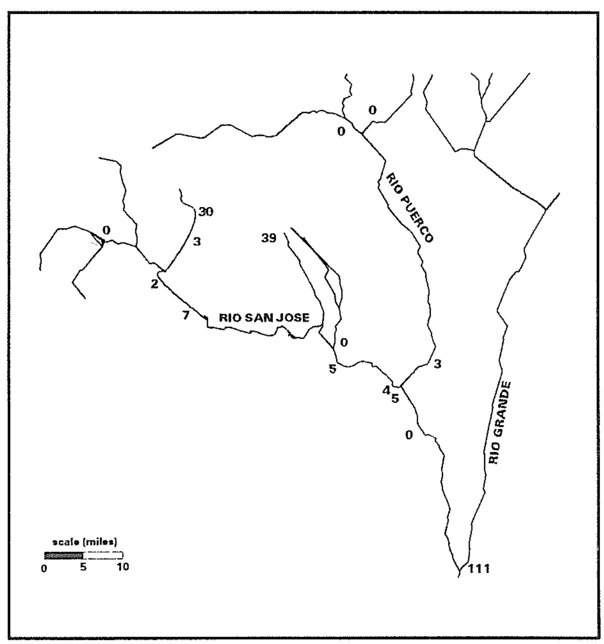

Figure 6. Mean dissolved arsenic concentrations (μg/l) in the Rio Puerco/Rio San Jose system from 1975 to 1983 from published and unpublished sources (Brandvold and Brandvold 1990).

Groundwater and Subsequent Discharge Via Wastewater Effluent

Groundwater throughout the Middle Rio Grande valley contains substantial concentrations of arsenic. This arsenic is thought primarily to be associated with poor quality deep waters and/or geothermal and volcanic activity. Purtymun (1977), studying high arsenic levels in well LA-6 of the former Los Alamos Canyon wellfield, concluded that the arsenic originated from a deep source and was circulated upward through a permeable fault zone which crossed or lay adjacent to the well. Arsenic levels in well LA-6 ranged from 50 to 225 μg/l during periodic sampling conducted from 1972 to 1975. Lesser concentrations were detected in the other wells. The Los Alamos Canyon wellfield was located near Otowi a short distance above Cochiti Dam with wells completed in the Tesuque Formation at depths up to approximately 2,000 feet deep. Trainer (1978) in a U.S. Geological Survey (USGS) study of the hydrogeology of the Jemez Mountains and vicinity compiled data on the chemical analyses of groundwater in the area. The concentration of arsenic in groundwater samples in selected wells ranged from 0 to 780 μg/l. The concentration of arsenic in selected springs ranged up to 1,300 μg/l.

The average concentration of total arsenic by wellfield in groundwater samples collected from the City of Albuquerque water supply wells for the period from 1968 to 1990 is shown in Figure 7. Averages range from a low of 3.1 μg/l at the Ridgecrest Wellfield to a high of 52.9 μg/l at the Don Wellfield (CH2M HILL 1991). The Don Wellfield was taken out of production by the City of Albuquerque due to this elevated concentration of arsenic. Other wellfields completed in the western and northeastern portions of Albuquerque also have relatively high concentrations of arsenic.

Groundwater elsewhere in New Mexico also has been found to contain arsenic. Longmire et al. (1984) observed an arsenic concentration of 87 μg/l in a groundwater sample collected from a shallow well completed in an alluvial aquifer to monitor a uranium mill tailings impoundment 18 miles north of Grants. A concentration of total arsenic of 88 μg/l was detected in shallow groundwater by the EPA (Clifford and Lin 1991) during a study of arsenic removal from drinking water in San Ysidro. A water supply well completed just prior to the study exhibited a concentration of dissolved arsenic of 230 μg/l. The concentration of arsenic in a 1980 sample from an irrigation well located in the Bosque del Apache in Socorro County was 55 μg/l (Roybal 1991).

Pumping of groundwater for municipal water supply systems results in discharge of arsenic to the Rio Grande via wastewater treatment plants (Figure 8). Data available from EPA's STORET database show that the concentration of dissolved arsenic in six samples of effluent collected in 1991 and 1992 from the Bernalillo Wastewater Treatment Plant averaged 38.3 μg/l. The concentration of dissolved arsenic in six samples of effluent collected from June to September of 1991 from the Rio Rancho Utilities Wastewater Treatment Plant #2 averaged 17.8 μg/l. Dissolved arsenic was detected at a concentration of 12 μg/l in a sample of effluent from the Los Lunas Wastewater Treatment Plant during a May 1994 sampling event conducted by the New Mexico Environment Department. The concentration of dissolved arsenic in two samples of effluent from the Rio Grande Utilities Wastewater Treatment Plant in Belen averaged 8 μg/l. The average quarterly concentration of total arsenic in treated effluent discharged from the City of Albuquerque's Southside Wastewater Reclamation Plant for the period from 1987 to 1990 ranged from 9.75 to 11.53 μg/l with a mean value of 10.3 μg/l (Hogrefe et al. 1990). More recent semi-weekly sampling for 1994 through August averaged 8.4 μg/l total arsenic.

Biota

A few studies have examined the concentration of arsenic in fish samples collected from the Middle Rio Grande and show a range of values. Concentrations of arsenic in fish muscle tissue in specimens collected from Elephant Butte Reservoir during the study conducted by Popp et al. (1983) averaged 0.42 μg/g, wet weight for gizzard shad, 2.7 μg/g, wet weight for carp and 0.27 μg/g, wet weight for white bass. Concentrations of arsenic in whole fish samples collected from Elephant Butte in 1984 as part of the National Contaminant Biomonitoring Program averaged 0.06 and 0.11 μg/g, wet weight for two composite samples of carp and

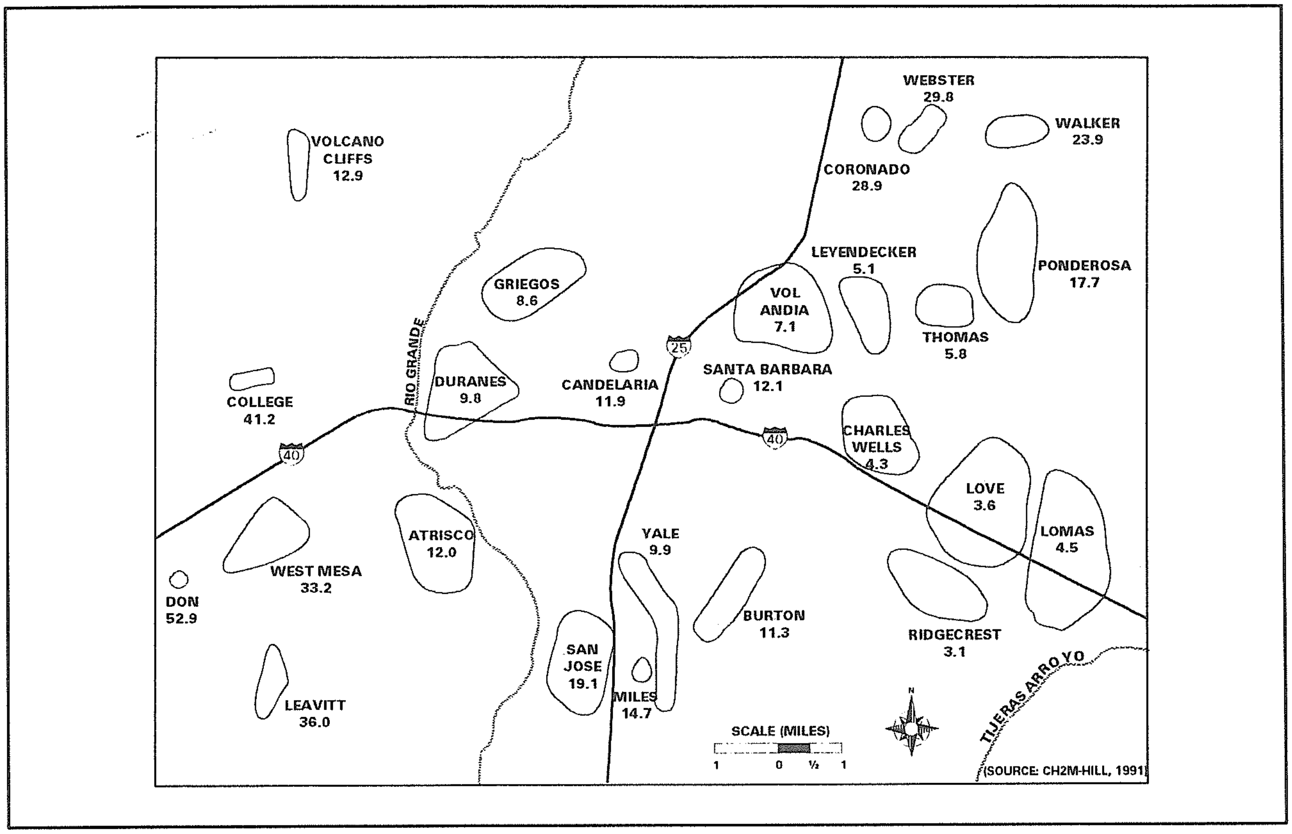

Figure 7. Mean concentration of total arsenic (μg/l) in City of Albuquerque wellfields, 1968 to 1990.

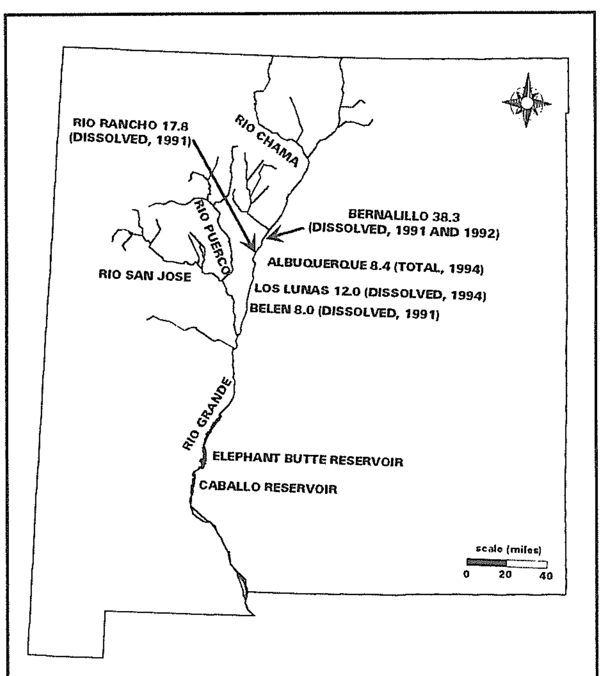

Figure 8. Average concentrations of arsenic (μg/l) in wastewater effluent discharged to the Middle Rio Grande.

0.27 μg/g, wet weight for largemouth bass (Schmitt and Brumbaugh 1990). These values are less than the muscle tissue values reported by Popp et al. (1983).

Roy et al. (1992) conducted a study of trace elements in samples of fish tissue from several different species collected from the Rio Grande in New Mexico from 1985 to 1987. The concentration of arsenic in whole-body fish samples collected from that reach of the Rio Grande from Otowi to San Marcial averaged 1.39 μg/g, wet weight, which is higher than that measured previously in samples from Elephant Butte. The maximum sample concentration was 5.0 μg/g, wet weight.

STANDARDS

Section 303 of the 1972 Federal Water Pollution Control Act (subsequently known as the Clean Water Act or CWA) established the statutory basis for the current water quality standards program regulated by EPA. States were required to adopt water quality standards which designate uses and the criteria necessary to protect those uses for surface waters under their jurisdiction. The 1987 Amendments to the CWA provided for EPA to oversee State water quality standards programs to ensure compliance with the CWA. Section 518 of the CWA authorized the recognition of Indian Tribes as States for the purpose of establishing water quality standards. EPA has summarized the relevant acute and chronic toxicity data and derived recommended criteria for parameters of concern for the protection of human health and aquatic life. The CWA mandates that State standards be equally or more restrictive than the criteria established by EPA.

The State of New Mexico, the Pueblo of Isleta, and the Pueblo of Sandia have enacted water quality standards for portions of the Middle Rio Grande which have been approved by EPA (Table 1). The Isleta Water Quality Standards (Isleta WQS) were approved by EPA on December 26, 1992. The Pueblo of Sandia Water Quality Standards (Sandia WQS) were approved by EPA on August 10, 1993. The Isleta WQS and the Sandia WQS apply to each Pueblo's jurisdictional surface waters, which include segments of the Middle Rio Grande just south and north of the City of Albuquerque, respectively.

TABLE 1. WATER QUALITY STANDARDS FOR ARSENIC FOR THE MIDDLE RIO GRANDE

	Standard (μg/l)	Designated Use/Criteria
New Mexico	20.0000	Livestock/Wildlife Watering
New Mexico	100.0000	Irrigation
Isleta Pueblo	0.0175	Human Health Criteria Based on Fish Consumption Only
Sandia Pueblo	0.0175	Human Heath Criteria Based on Fish Consumption Only
USEPA	0.0180	Human Health Criteria Based on Water /Fish Ingestion
USEPA	0.1400	Human Health Criteria Based on Fish Consumption Only

The State of New Mexico standard for dissolved arsenic in the Middle Rio Grande from Elephant Butte Reservoir to Cochiti Dam (Segments 2-105, 2-105.1, and 2-108) is 20 μg/l, to protect the designated use of Livestock and Wildlife Watering for these Segments. A less stringent New Mexico standard of 100 μg/l also is applicable to these Segments to protect the designated use of Irrigation. The Pueblo of Isleta standard for dissolved arsenic in that reach of the Middle Rio Grande which is within their jurisdiction is 0.0175 μg/l. This standard is a human health criterion based on the assumption that fish from surface waters of the Reservation are consumed, but water is not regularly ingested. The Pueblo of Sandia's standard for dissolved arsenic is the same as the Pueblo of Isleta's.

EPA criteria for arsenic are 0.018 μg/l for Water and Fish Ingestion and 0.14 μg/l for Fish Consumption Only. EPA criteria for the trivalent form of arsenic for the Protection of Aquatic Organisms and Their Uses have also been designated. The Freshwater Acute Criteria for arsenic(III) is 360 μg/l. The Freshwater Chronic Criteria is 190 μg/l. The drinking water Maximum Contaminant Level for dissolved arsenic is 50 μg/l. This standard is under review and may be lowered. Both the Isleta WQS and the Sandia WQS contain provisions for modifying their standards to match EPA criteria as new criteria documents are published.

DISCUSSION

Occurrence

Sources of arsenic to the Middle Rio Grande include tributary streams originating in areas of geothermal and mining activity and the discharge of groundwater containing arsenic. Arsenic in groundwater reaches the Middle Rio Grande both through natural discharge in areas where the river is a gaining stream and through groundwater pumping for municipal water supplies and subsequent discharge via wastewater effluent as well as pumping for irrigation with subsequent return flow. Airborne deposition of arsenic to the Middle Rio Grande has not been studied or quantified.

Relatively elevated levels of arsenic are seen in surface waters of the Jemez Mountains, portions of the Rio Puerco/Rio San Jose system, and that reach of the Rio Grande from Socorro to San Marcial. The available data indicate that the geothermally active Jemez Mountains area is a major source of arsenic to the Middle Rio Grande. The concentration of arsenic in the Jemez River is an average of one order of magnitude greater than that of the Rio Grande above their confluence. The Rio Puerco/Rio San Jose system also contributes significant amounts of arsenic to the Middle Rio Grande. Mining activity at the Grants Mineral Belt may have mobilized some of this arsenic into the environment. The elevated levels of arsenic in the Rio Grande below Socorro may be due to discharge of groundwater containing arsenic associated with known geothermally active areas in the region or the past volcanic history of the area. These elevated arsenic levels may also be due to surface enrichment of arsenic in rock in the area due to moderate and advanced potassium metasomatism of the region associated with alkaline, saline brines in a playa lake environment (Dunbar et al. 1994).

Relatively elevated levels of arsenic in groundwater are present throughout the Middle Rio Grande valley. Pumping of groundwater containing arsenic for municipal water supplies represents a significant source of arsenic to the Middle Rio Grande. This additional source results in increased concentrations of arsenic in the Rio Grande downstream of the discharge points, as illustrated by the available data for the reach of the Middle Rio Grande just above and below the City of Albuquerque's Southside Water Reclamation Plant (Figure 9). Water quality data in the USGS' WATSTORE database from the Rio Grande at Isleta (below the City of Albuquerque's treatment plant discharge) during the period from 1973 to 1990 show the concentration of dissolved arsenic ranged from 2 to 7 μg/l with a mean value of 4.0 μg/l. The concentration of dissolved arsenic in samples collected from the Rio Grande at Albuquerque (above the treatment plant discharge) during the

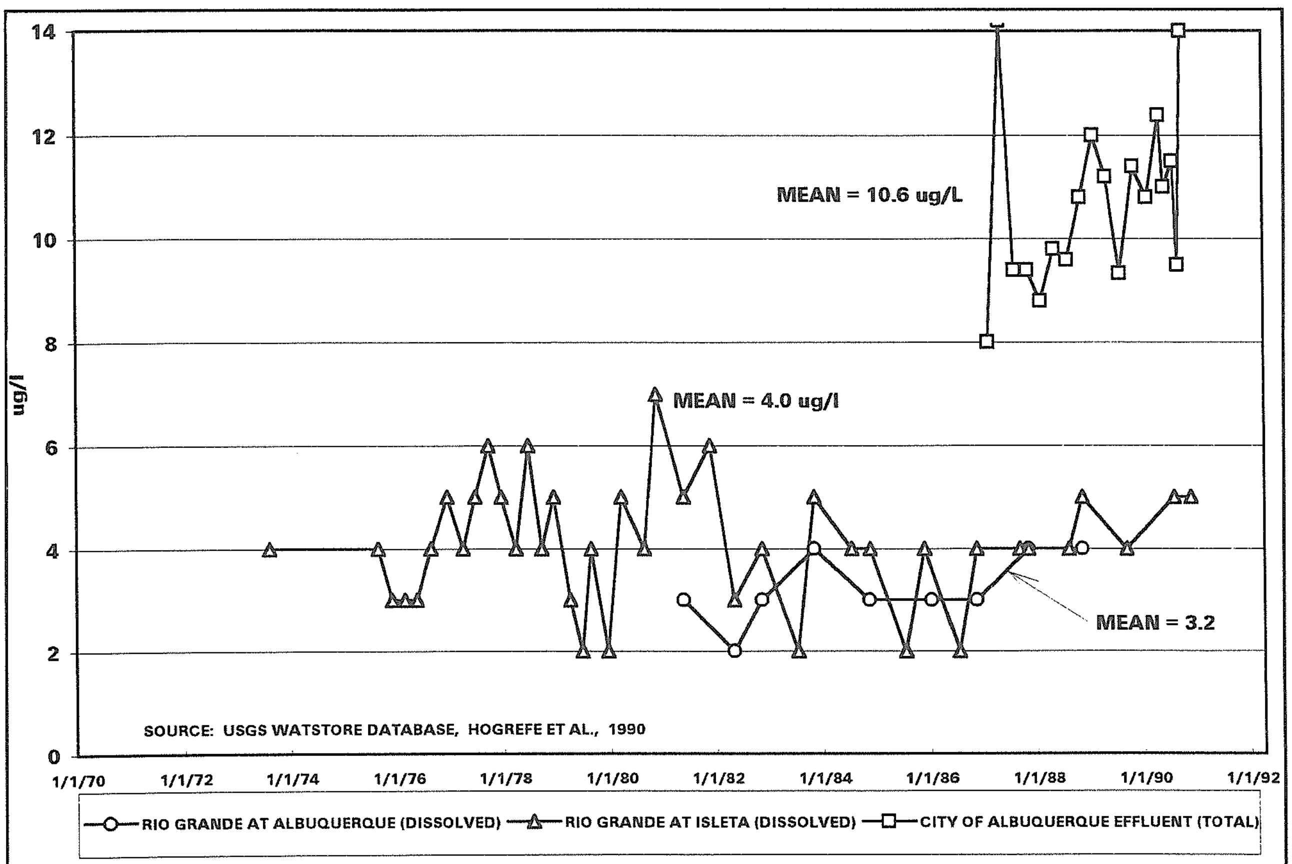

Figure 9. Increase in Rio Grande arsenic levels downstream of the City of Albuquerque's Southside Water Reclamation Plant.

period from 1981 to 1988 ranged from 2 to 4 μg/l with a mean value of 3.2 μg/l. The concentration of total arsenic (quarterly averages) in the City of Albuquerque's wastewater effluent during the period from 1987 to 1989 ranged from 8 to 14.2 μg/l, and averaged 10.3 μg/l (Hogrefe et al. 1990). Effluent from the plant appears to raise the concentration of arsenic in the Rio Grande at Isleta by 25 percent above that in the river upstream of the plant. The City of Albuquerque is the largest wastewater discharger to the Middle Rio Grande.

The available data show that arsenic is being bioconcentrated by fish in the Middle Rio Grande. The geometric mean concentration of arsenic in 315 composite samples of whole fish from 109 stations nationwide (including samples from Elephant Butte Reservoir) during 1984 and 1985 was 0.14 μg/g, wet weight (Schmitt and Brumbaugh 1990). The concentration of arsenic in whole-body fish samples collected from the Middle Rio Grande during the study by Roy et al. (1992) averaged 1.39 μg/g, wet weight, an order of magnitude above the national geometric mean.

Standards

The EPA's Human Health Criterion for Consumption of Organisms Only for dissolved arsenic is currently 0.14 μg/l. EPA amended this criterion in 1992 from the previous value of 0.0175 μg/l, which is what the Isleta WQS was and Sandia WQS are based on. This amendment resulted from a reassessment of the carcinogenic risk associated with ingestion of inorganic arsenic, which is an EPA class A carcinogen. The reassessment concluded that the most appropriate basis for an oral quantitative estimate of risk was a study which reported increased prevalence of skin cancers in humans as a consequence of arsenic exposure in drinking water (Tseng 1977). Based on that study, a unit risk factor for arsenic of 5 x 10^{-5} per μg/l was established (USEPA 1993).

EPA's Human Health Criteria for Consumption of Organisms Only are based upon the cancer slope factor and the bioconcentration factor (BCF). The unit risk factor may be converted to a cancer slope factor (SF) using an average human consumption of water of 2 l/day and an average adult male body weight of 70 kilograms (kg):

$$\left(5\text{x}10^{-5}\,\frac{l}{\mu g}\right)\left(\frac{1\,day}{2\,l}\right)(70\,kg)\left(\frac{1000\,\mu g}{mg}\right) = 1.75\,\frac{kg-day}{mg}$$

The BCF is a measure of the relationship between the concentration of a compound in fish tissue and the concentration of the compound in the ambient water. The BCF for arsenic is 44 l/kg (USEPA 1980). Based on an average adult male body weight of 70 kg and an average daily fish consumption of 6.5 g, the EPA's Human Health Criterion for Consumption of Organisms Only for dissolved arsenic may be calculated as follows:

$$\text{EPA Criterion} = \frac{(\text{RL})(70\,kg)}{(\text{SF})(\text{FC})(\text{BCF})}$$

where RL = risk level = 1 x 10^{-6}
SF = cancer slope factor = 1.75 $\frac{kg\text{-}day}{mg}$
FC = fish consumption = 6.5 g/day
BCF = bioconcentration factor = 44 l/kg

$$\text{EPA Criterion} = \frac{\left(1\text{x}10^{-6}\right)(70\,kg)\left(1000\,\frac{g}{kg}\right)\left(1000\,\frac{\mu g}{mg}\right)}{\left(1.75\,\frac{kg\text{-}day}{mg}\right)\left(6.5\,\frac{g}{day}\right)\left(44\,\frac{l}{kg}\right)} = 0.14\,\frac{\mu g}{l}$$

EPA Region 6 has recommended that tissue criteria be adopted in addition to water quality criteria for certain priority pollutants which are present in fish tissue (USEPA 1989). A tissue criterion for arsenic may be calculated as follows:

$$\text{Tissue Criterion} = \frac{(\text{RL})(70\,kg)}{(\text{SF})(\text{FC})}$$

$$= \frac{\left(1\text{x}10^{-6}\right)(70\,kg)\left(\frac{1000\,\mu g}{mg}\right)}{\left(1.75\,\frac{kg-day}{mg}\right)\left(6.5\,\frac{g}{day}\right)} = 6.15\text{x}10^{-3}\,\frac{\mu g}{g}$$

The average concentration of arsenic in fish tissue in the Middle Rio Grande reported by Roy et al. (1992) is approximately 200 times greater than this potential recommended tissue criterion for arsenic.

CONCLUSIONS

Arsenic is a naturally occurring element in the Middle Rio Grande. Sources of arsenic to the river include:

- The geothermally active Jemez Mountains area.
- The Rio Puerco/Rio San Jose system which drains the Grants Mineral Belt and a portion of the Jemez Mountains.
- The portion of the Middle Rio Grande valley below Socorro.
- Discharge of arsenic in wastewater effluent from municipalities located along the Middle Rio Grande which depend on arsenic-containing groundwater for public water supplies.
- Irrigation return flow of arsenic-containing groundwater.

The water quality standards for arsenic in the Middle Rio Grande adopted by the State of New Mexico, the Pueblo of Isleta, and the Pueblo of Sandia were established to be protective of human health and the designated uses of the river under their respective jurisdictions. The State of New Mexico's standards were adopted to protect the designated uses of Irrigation and Livestock and Wildlife Watering. The arsenic standards of the Pueblo of Isleta and the Pueblo of Sandia were adopted to be protective of human health. Both Pueblo standards will be amended to match EPA's criterion of 0.14 μg/l, which is based upon the cancer risk associated with ingestion of fish tissue contaminated with arsenic.

These standards are used in writing National Pollutant Discharge Elimination System effluent limitations for upstream dischargers. The average concentration of arsenic in the Middle Rio Grande is approximately 30 times greater than EPA's criterion of 0.14 μg/l. The average concentration of arsenic in wastewater effluent currently being discharged to the Middle Rio Grande is approximately 120 times greater than the criterion.

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