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Effects of uranium mining discharges on water quality in the Puerco River basin, Arizona and New Mexico

PETER C. VAN METRE* & JOHN R. GRAY

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Abstract From 1967 until 1986, uranium mine dewatering increased dissolved gross alpha, gross beta, uranium and radium activities and dissolved selenium and molybdenum concentrations in the Puerco River as indicated by time trends, areal patterns involving distance from the mines and stream discharge. Additionally, increased dissolved uranium concentrations were identified in groundwater under the Puerco River from where mine discharges entered the river to approximately the Arizona-New Mexico State line about 65 km downstream. Total mass of uranium and gross alpha activity released to the Puerco River by mine dewatering were estimated as 560 Mg (560×10^6 g) and 260 Ci, respectively. In comparison, a uranium mill tailings pond spill on 16 July 1979, released an estimated 1.5 Mg of uranium and 46 Ci of gross alpha activity. Mass balance calculations for alluvial ground water indicate that most of the uranium released did not remain in solution. Sorption of uranium on sediments and uptake of uranium by plants probably removed the uranium from solution.

Effets des rejets provenant de l'exploitation des mines d'uranium sur la qualité des eaux du bassin du fleuve Puerco, en Arizona et au Nouveau-Mexique

Résumé De 1967 à 1986, les opérations d'essorage des mines d'uranium ont eu pour effet d'augmenter les radioactivités alpha (valeur approchée), beta (valeur approchée), uranium et radium en solution, ainsi que les concentrations en sélénium et molybdène dissous, dans le fleuve Puerco, comme l'ont mis en évidence les relations liant ces valeurs aux facteurs de temps, distance aux mine et débit. En outre, des concentrations accrues d'uranium dissous ont été identifiées dans le réseau de nappes aquifères sous le fleuve Puerco, dans un secteur s'étendant du point où les effluents miniers débouchent dans le fleuve jusqu'au voisinage approximatif de la ligne de démarcation entre l'Arizona et le Nouveau-Mexique, à une distance d'environ 65 km en aval. Au total, la masse d'uranium et l'activité alpha (valeur approchée) déversées dans le fleuve Puerco par le procédé d'essorage minier ont été estimées, respectivement, à 560 Mg (560×10^6 g) et 260 Ci. Par comparaison, le débordement du bassin à résidus de l'usine d'uranium, survenu le 16 juillet 1979, a rejeté dans le fleuve des quantités évaluées à 1.5 Mg d'uranium et 46 Ci d'activité alpha (valeur approchée). Les calculs d'équilibre des masses pour les eaux souterraines alluviales indiquent que la plus grande partie de l'uranium rejeté n'est pas restée en solution. L'absorption de l'uranium par les dépôts sédimentaire et par les végétaux ont probablement éliminé l'uranium de la solution.

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INTRODUCTION

The Puerco River, in the southeastern part of the Colorado Plateau (Fig. 1), is an ephemeral stream that drains about 7800 km² along its 230 km length. The headwaters are in the uranium-rich Grants Mineral Belt of northwestern New Mexico. Uranium mine dewatering from 1967 until 1986 and a tailings pond dike failure in July 1979 resulted in releases of radionuclides and other trace constituents to the Puerco River (Weimer *et al.*, 1981; Gallaher & Cary, 1986).

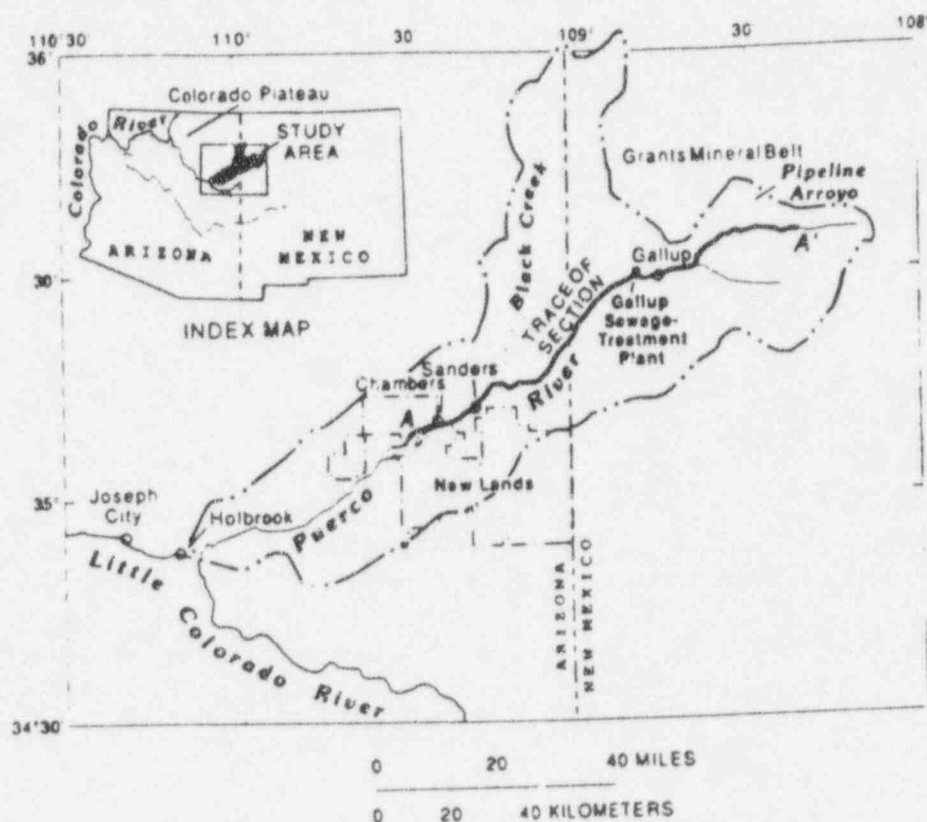


Fig. 1 Puerco River basin in Arizona and New Mexico.

Previous studies of the effects of uranium mining discharges on water quality in the Puerco River basin have documented greater selenium, molybdenum and uranium concentrations and gross alpha activities in mine-related discharges than in runoff. Greater concentrations of those constituents also were found in some shallow wells near the Puerco River between the mines and Gallup, New Mexico (Gallaher & Cary, 1986), and increased concentrations of selected radionuclides were found in downstream stream bed sediments after the 1979 tailings pond failure (Weimer *et al.*, 1981).

In this report, results of a study that expanded on an earlier evaluation by Gallaher & Cary (1986) are presented. The study included analyses of additional chemical constituents, incorporated data collected after mine dewatering

ceased in February 1986, and evaluated the relationships of chemical constituents to stream discharge and to distance downstream from the mines. Total releases of uranium and gross alpha activity by dewatering and by the tailings pond spill were estimated. The likely fate of uranium released by the mines in alluvial ground water was evaluated using mass balance calculations.

Data used for these analyses were primarily from four sources: the US Geological Survey (USGS), the New Mexico Environmental Improvement Division (NMEID), the US Environmental Protection Agency (EPA, data reported to EPA by United Nuclear Corporation and Kerr-McGee Corporation), and the Arizona Department of Health Services. Data collected prior to October 1988 were compiled by Wirt *et al.* (1991). Mine dewatering discharge data were from Perkins & Goad (1980), Gallaher & Cary (1986) and in written summaries of discharges provided to the EPA by United Nuclear Corporation and Kerr-McGee Corporation.

The amount of radionuclide in a give volume of water can be measured and reported either as mass concentration or as activity. The relationship between the concentration of the radionuclide, in $\mu\text{g l}^{-1}$, and the activity, in pCi l^{-1} , is calculated from:

$$C = 10^{19.05} W T D \quad (1)$$

where: C = concentration ($\mu\text{g l}^{-1}$); W = atomic weight; T = half life (s); and D = activity (pCi l^{-1}).

Equation (1) indicates that the activity of an element is inversely proportional to the half life, and therefore radionuclides with short half lives produce larger amounts of activity for the same concentration than radionuclides with long half lives.

History of mining

Beginning in 1960, uranium was mined near Pipeline Arroyo (Fig. 1), a small tributary to the Puerco River about 35 km northeast of Gallup, New Mexico. From 1960 to 1961 and from 1967 to 1986, dewatering of as many as three uranium mines near Pipeline Arroyo maintained continuous stream flow in the Puerco River from the mouth of pipeline Arroyo to as far as a few kilometres downstream from Chambers, Arizona (Shuey, 1986). Effluent from the sewage treatment plant in Gallup, about 37 km downstream from the mines, also contributed to this continuous flow.

Uranium mine shafts near Pipeline Arroyo averaged 500 m in depth. Because the ore bodies being mined are below the regional water table, water seeping into shafts was pumped to prevent mine shaft flooding (Gallaher & Cary, 1986). From 1967 until 1986, daily discharge rates from mine dewatering averaged about $0.23 \text{ m}^3 \text{ s}^{-1}$ (Perkins & Goad, 1980; US EPA records on mine dewatering, 1979-1985).

Before the mid-1970s, untreated mine discharges from dewatering operations discharged directly into Pipeline Arroyo (Gallaher & Cary, 1986). Beginning in the mid-1970s, measures were taken to improve the quality of mine waters discharged to watercourses to comply with limitations specified by permits of the Federal National Pollution Discharge Elimination System (NPDES). The mine discharges were treated in ponds using a flocculant and barium chloride to reduce suspended solids concentrations and to coprecipitate radium. Dissolved uranium concentrations were reduced by a separate ion exchange treatment (Perkins & Goad, 1980) which reduced average concentration and activity of these constituents by about 85% from 1975 to 1982 (Table 1).

Implementation of mine discharge treatment for each of the three mines near Pipeline Arroyo occurred over several years during the mid-1970s. Uranium mining ceased in February 1985, and mine dewatering ceased in February 1986.

On 16 June 1979, a tailings pond dike failed at the United Nuclear Corporation uranium mill near Pipeline Arroyo. An estimated 360 000 m³ of uranium mine tailings liquid and 1000 Mg of tailings were discharged to the Puerco River through Pipeline Arroyo (Weimer *et al.* 1981). The pH of the tailings liquid was about 1.6, and the total gross alpha activity was estimated as 130 000 pCi l⁻¹ (US EPA, 1982).

Table 1 Comparison of uranium concentrations and radium-226 activities from unfiltered samples of mine effluent in 1975 and 1981-1982

Constituent	Flow-weighted means		1981-1982	Number of samples
	1975	Number of samples		
Total radium ²²⁶ (pCi l ⁻¹)	71.2	23	10.5	15
Total uranium (natural) (mg l ⁻¹)	7.25	23	1.0	14

from Gallaher & Cary (1986, p. 82).

EFFECT OF MINE DEWATERING ON WATER QUALITY OF STREAM FLOW

An assessment of mine-dewatering effects on water quality in the Puerco River was made by comparing the occurrence of selected water quality constituents with three factors: time, distance downstream from the mines and discharge. Constituent concentrations in stream flow at a given location were expected to decrease with time from the early 1970s until after 1986 as mine discharge treatment systems were implemented and as mine discharges finally ceased. Constituent concentrations were also expected to decrease with distance downstream from the mines because of chemical reactions such as sorption on

stream channel sediments and precipitation and because of dilution by runoff and treated waste water effluent discharge from the city of Gallup. Additionally, constituent concentrations were expected to vary inversely with discharge at a given location because of dilution.

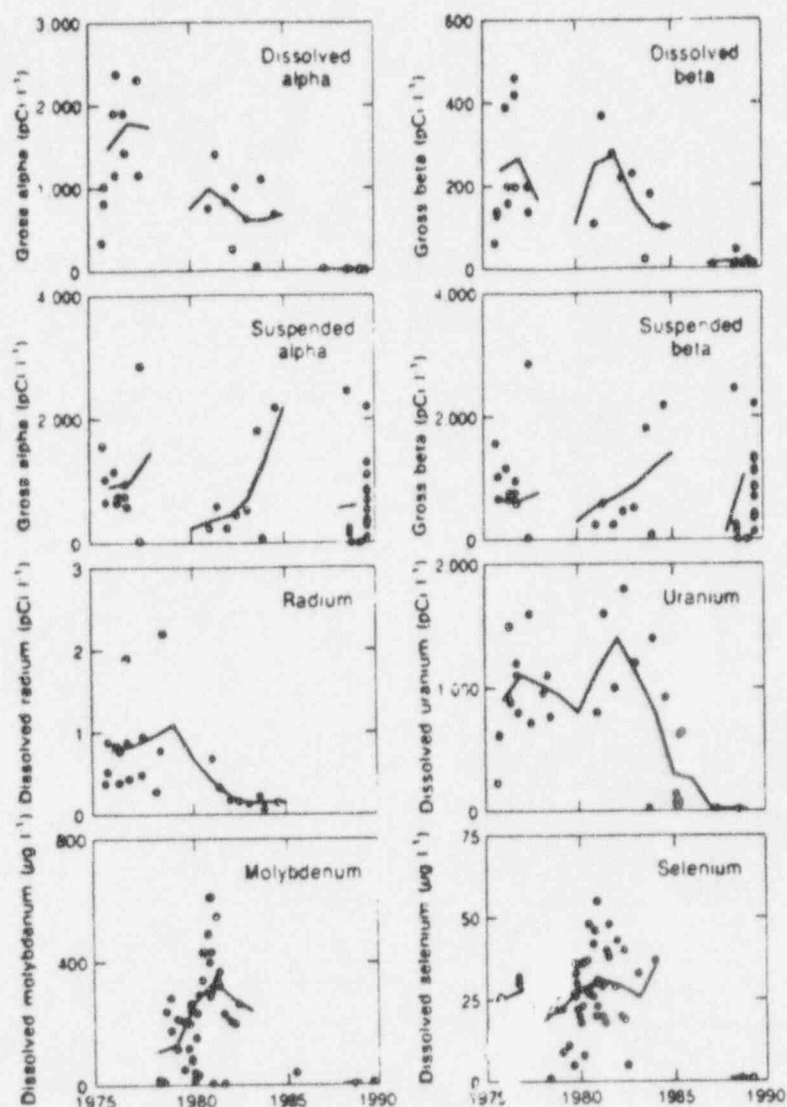
Selected water quality constituents analysed for this assessment included uranium, radium, molybdenum and selenium, which commonly occur in uranium deposits (Hem, 1985; Gallaher & Cary, 1986; Brandvold *et al.*, 1981). Additionally, dissolved and suspended gross alpha and gross beta activities were analysed to assess the overall radiological effect of mine dewatering on stream water quality and the relative effect of dewatering on dissolved and suspended activities. Because this analysis focused on evaluation of effects of mine dewatering on water quality, samples collected on the day of the tailings pond spill and for 1 month thereafter were excluded. The 1 month period was based on a review of gross alpha activities in the Puerco River at Gallup (Fig. 1), which returned to pre-spill levels within about 3 weeks after the spill at that location (Wirt *et al.*, 1991).

Almost no sediment was discharged to the Puerco River in mine dewatering discharges because these discharges were impounded in settling ponds before being released to the stream. The predominant effect of mine discharges on water quality, therefore, was expected to be on the dissolved phase and not on the suspended phase of the chemical constituent of concern. If that hypothesis were correct, the dissolved activities would show distinct inverse relationships to time, distance downstream and discharge, whereas the suspended activities would not necessarily exhibit these time trends or areal patterns.

Relationship of constituent concentrations with time

The time series for samples collected near Gallup for each of the eight water quality constituents included in this analysis are shown on Fig. 2. Only samples collected in the 6 km reach upstream from the Gallup waste water treatment plant outfall were used in this analysis to minimize the variance caused by distance from the mines and dilution by mixing. Correlations (r) and Spearman's rank correlations (r_s ; Iman & Conover, 1983) were computed between time and each constituent as a measure of the linear relationships between the variables and the ranks of variables (Fig. 2). In this case, the hypothesis tested was that the population correlation coefficient was equal to 0 ($H_0: r = 0$) at a confidence level of 95%. If the magnitude of the test statistic (t) was greater than t at the 95% confidence level (t_{95}), the hypothesis was rejected (Haan, 1977; p. 223). Rejection of the hypothesis implies that the correlation coefficient is not zero, and a statistically significant relationship exists between that constituent and time for the period of available data.

A statistically significant decrease in activities of dissolved uranium, radium, gross alpha and gross beta occurred over time, but no significant changes in suspended gross alpha and gross beta activities or in dissolved



Explanation: — moving average for samples

Fig. 2 Time series of selected water quality constituents for a 5 km reach near Gallup, New Mexico; three to six sampling sites depending on constituent.

molybdenum and dissolved selenium concentrations occurred with time (Table 2 and Fig. 2). A 2-year moving average of each constituent (shown as a bold line on Fig. 2) was calculated by taking the mean of all samples within 2-year ranges centred on 1-year intervals; the moving average suggests a decrease in dissolved concentrations of molybdenum and selenium since the time that mine dewatering ceased. Suspended gross alpha and gross beta activities do not show a statistically significant change from the mining phase

to post-mining phase. This conclusion supports the hypothesis that mine discharges increased dissolved activities in stream flow but did not increase suspended activities. The moving averages of dissolved gross alpha activities and uranium concentrations in the late 1970s were approximately 200 times and 100 times the moving averages in the late 1980s, respectively (Fig. 2).

Table 2 Correlation coefficients and test statistics for water quality constituents in relation to time in a 5 km reach near Gallup, New Mexico

Constituent	Correlation		Test statistic			Conclusion ($H_0: r=0$)	Significant time trend
	r	r_s	t	t_s	t_{95}		
Dissolved gross alpha	-0.86	-0.86	13.0	13.1	2.00	Reject	Yes
Dissolved gross beta	-0.78	-0.83	8.04	9.61	2.02	Reject	Yes
Suspended gross alpha	-0.18	-0.14	1.21	0.88	2.04	Do not reject	No
Suspended gross beta	0.25	0.24	1.57	1.49	2.04	Do not reject	No
Dissolved uranium	-0.55	-0.57	3.99	4.20	2.04	Reject	Yes
Dissolved radium	-0.48	-0.60	2.51	3.41	2.08	Reject	Yes
Dissolved molybdenum	-0.16	0.22	1.15	1.64	2.01	Do not reject	No
Dissolved selenium	-0.19	0.14	1.54	1.10	2.00	Do not reject	No

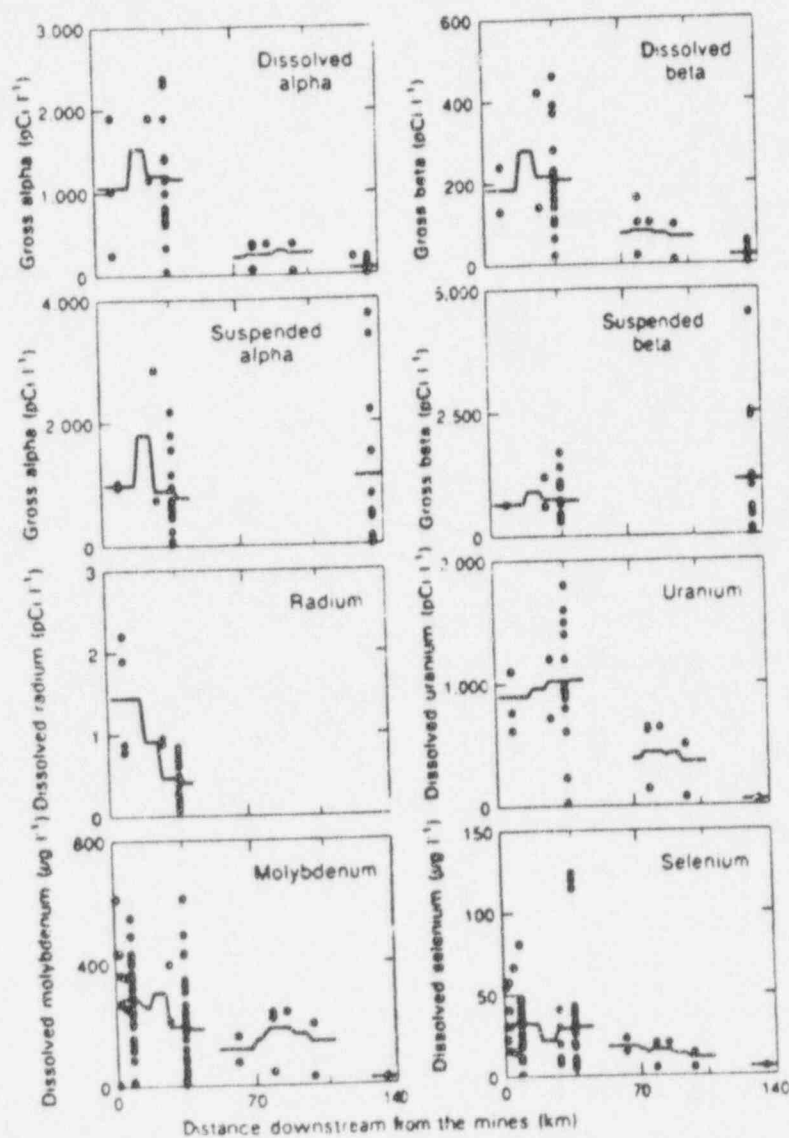
r : correlation coefficient; r_s : Spearman's rank correlation coefficient; t : test statistic based on r ; t_s : test statistic based on r_s ; t_{95} : test statistic at the 95% confidence level; and $H_0: r=0$ a statement of the hypothesis that correlation coefficients are equal to zero being tested by the comparison of t values to t_{95} .

Relationship of constituent concentrations with distance downstream from the mines

Relationships between the concentrations of the eight water quality constituents and distance downstream from the mines for samples collected from 1975 until 1984 are shown on Fig. 3. The bold line on Fig. 3 represents a moving average of the data calculated as the mean of all samples falling within 20 km reaches centred on 5 km intervals. Much of the variance about the mean probably can be attributed to effects of changes in mine discharge treatment practices over time and to dilution caused by variations in stream discharge. Concentrations and activities of dissolved constituents decreased with distance downstream. The reduction in concentration downstream from the Gallup waste water treatment plant, about 40 km downstream from the mines, was caused by mixing with waste water containing smaller concentrations of those constituents. A significant trend was not observed between suspended radionuclide activities and distance, even in the reach downstream from the waste water treatment plant in Gallup.

Correlation coefficients, r and r_s , and test statistics, t and t_s and t_{95} , were determined for each constituent (Table 3). Correlation coefficients that were

significantly different from zero were observed for all dissolved constituents and activities. Decreases in constituent concentrations and activities with distance downstream from the mines can be attributed to dilution by a combination of runoff and treated waste water and possibly to chemical reactions and sorption on stream channel sediments. Such inverse relations prove that mine effluents contained larger concentrations or activities of those constituents compared with runoff and sewage effluent. Mine dewatering increased



Explanation: — moving average for samples collected from 1975 until 1984

Fig. 3 Relationships between distance downstream from the mines and selected water quality constituents, Puerco River, Arizona and New Mexico.

dissolved concentrations of all constituents except radium in the Puerco River for a distance of 100 km or more downstream from the mines (Fig. 3).

Increased dissolved gross alpha activities, when compared with activities in runoff, persisted for more than 200 km downstream, possibly to the mouth of the Puerco River at the Little Colorado River (Fig. 4). The mean dissolved gross alpha activity of the Puerco River at Chambers, 135 km downstream from the mines, during dewatering years until early 1986 was 74 pCi l⁻¹ compared with 5.9 pCi l⁻¹ after dewatering ceased.

Table 3 Correlation coefficients and test statistics for water quality constituents in relation to distance from the mines, 1975-1984

Constituent	Correlation		Test statistic			Conclusion	
	<i>r</i>	<i>r_s</i>	<i>t</i>	<i>t_s</i>	<i>t₉₅</i>	(<i>H</i> : <i>r</i> = 0)	Significant trend
Dissolved gross alpha	-0.71	-0.82	7.42	10.5	2.00	Reject	Yes
Dissolved gross beta	-0.71	-0.84	7.29	10.9	2.00	Reject	Yes
Suspended gross alpha	0.10	-0.19	0.52	1.06	2.04	Do not reject	No
Suspended gross beta	0.22	-0.13	1.21	0.73	2.04	Do not reject	No
Dissolved uranium	-0.70	-0.70	5.99	6.06	2.04	Reject	Yes
Dissolved radium	-0.76	-0.66	5.31	4.07	2.07	Reject	Yes
Dissolved molybdenum	-0.44	-0.47	4.53	4.92	1.99	Reject	Yes
Dissolved selenium	-0.38	-0.49	4.21	5.78	1.98	Reject	Yes

r, correlation coefficient; *r_s*, Spearman's rank correlation coefficient; *t*, test statistic based on *r*; *t_s*, test statistic based on *r_s*; *t₉₅*, test statistic at the 95% confidence level, and *H*: *r* = 0, a statement of the hypothesis that correlation coefficients are equal to zero being tested by the comparison of *t* values to *t₉₅*.

Relationships of constituent concentrations with stream discharge

A few samples of constituent concentrations were analysed concurrent with measured discharge. Fourteen of those samples were collected for analyses of five of the six dissolved constituents. The samples were collected at three sites in the Puerco River between the mines and Gallup from 1975 until 1984 (Fig. 5). Molybdenum was excluded from this analysis because discharge was known for only four samples from 1975 until 1984. Twenty-three measurements of suspended gross alpha and gross beta activity of the Puerco River at four sites were made prior to 1986 concurrent with discharge between the mines and Chambers (Fig. 5). Suspended-phase samples collected between Gallup and Chambers were included here because, unlike the dissolved-phase constituents, suspended activities did not appear to be significantly affected by the addition of waste water treatment plant effluent downstream from Gallup (Fig. 3).

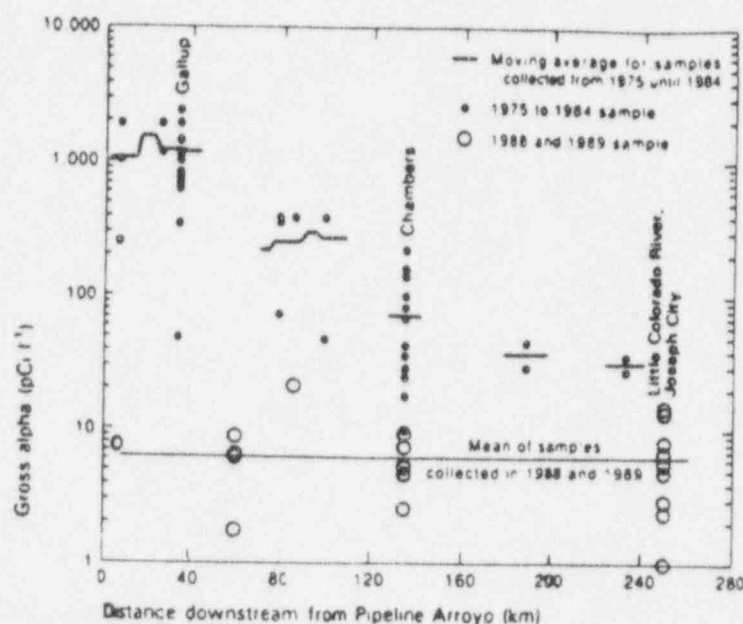


Fig. 4 Relationship between distance downstream from the mines and dissolved gross alpha activity during and after mining, Puerco River, Arizona and New Mexico.

Correlation coefficients, r , and test statistics, t and t_{95} , relating concentration to the logarithm (base 10) of discharge (Table 4) were computed. The correlation was significant for dissolved gross alpha and uranium activities and for suspended gross alpha and gross beta activities. In the case of the suspended activities, a positive correlation is expected because suspended sediment concentrations tend to increase with discharge (Fig. 5). The remaining dissolved constituents showed weak inverse correlations to discharge, and the hypothesis that the population correlations were significantly different from zero was not rejected.

ESTIMATION OF TOTAL MASS OF URANIUM AND GROSS ALPHA ACTIVITY RELEASED BY MINE DEWATERING AND THE TAILINGS POND SPILL

The total mass of uranium and total gross alpha activity released by mine dewatering were estimated as 560 Mg and 260 Ci, respectively. Estimates were made using historical water quality and mine discharge data (Table 5). Because those data were from a variety of sources and, in some cases, were collected by undetermined methods (for example, mine discharge flow rates), the accuracy of the estimates is difficult to assess.

The mass of uranium and gross alpha activity released by the tailings

pond spill on 16 July 1979 were also estimated. The volume of tailings solution released was estimated as 360 000 m³ (Weimer *et al.*, 1981). The concentration of uranium in the tailings solution was measured on 5 February 1979 as 4.1 mg l⁻¹ (Weimer *et al.*, 1981; sample collected by R.W. Miller, United Nuclear Corporation). A representative sample of the tailings solution contained 130 000 pCi l⁻¹ (US EPA, 1982). Multiplying those concentrations by the volume of tailings solution released in the spill yields 1.5 Mg of uranium and

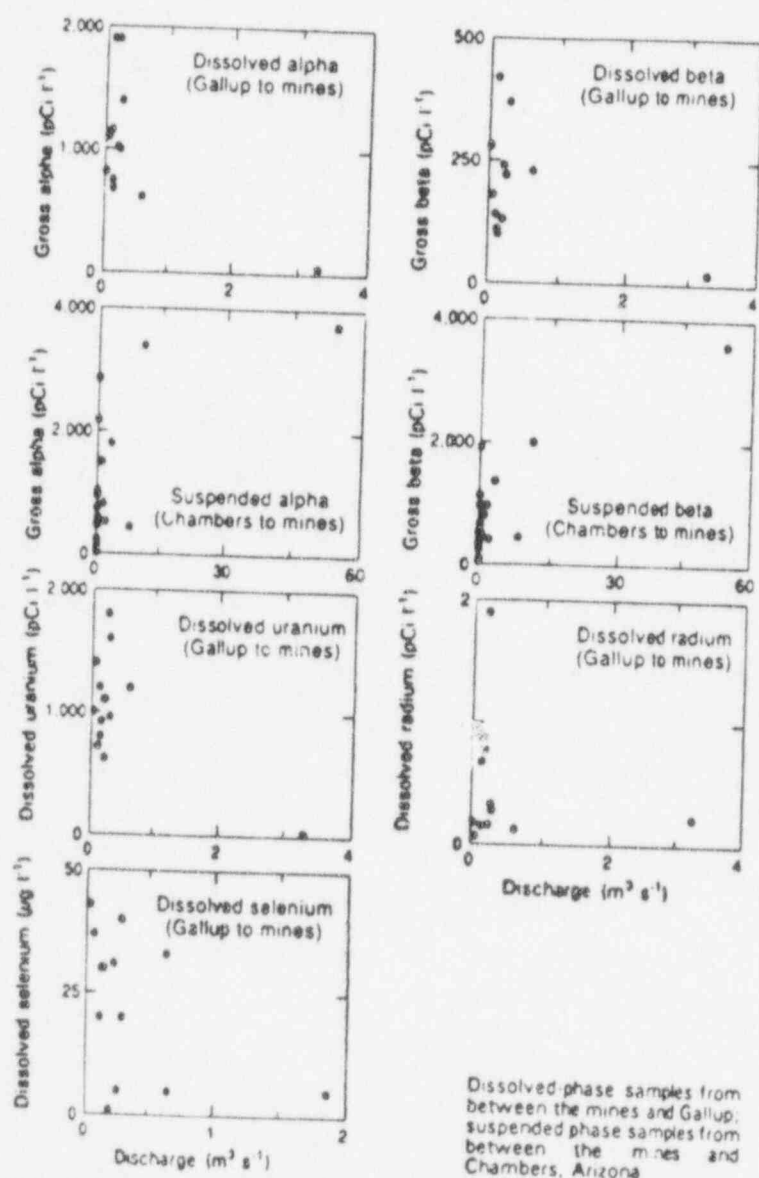


Fig. 5 Relationships between discharge and selected water quality constituents, Puerco River, Arizona and New Mexico, 1975-1984.

Table 4 Correlation coefficients and test statistics for water quality constituents in the Puerco River in relation to the logarithm of discharge, 1975-1984

Constituent	Correlation	Test statistic		Conclusion ($H_0: r = 0$)	Significant trend
	r	t	t_{95}		
Dissolved gross alpha	-0.61	2.43	2.23	Reject	Yes
Dissolved gross beta	-0.48	1.72	2.23	Do not reject	No
Suspended gross alpha	0.60	3.53	2.07	Reject	Yes
Suspended gross beta	0.81	6.43	2.07	Reject	Yes
Dissolved uranium	-0.63	2.80	2.18	Reject	Yes
Dissolved radium	-0.20	0.73	2.18	Do not reject	No
Dissolved selenium	-0.46	1.70	2.20	Do not reject	No

r : correlation coefficient; t : test statistic based on r ; t_{95} : test statistic at the 95% confidence level; and $H_0: r = 0$ a statement of the hypothesis that correlation coefficients are equal to zero being tested by the comparison of t values to t_{95} .

46 Ci of gross alpha radioactivity. Comparing those amounts with the 560 Mg of uranium and 260 Ci of gross alpha activity released by dewatering indicates that an estimated 380 times more uranium and an estimated 6 times more gross alpha activity were released by dewatering than by the spill. The ratios of uranium and of gross alpha released by dewatering and by the spill were 2.1 Mg Ci^{-1} and 0.032 Mg Ci^{-1} , respectively.

Dewatering released much larger amounts of uranium and gross alpha

Table 5 Estimated releases of water, uranium and gross alpha radioactivity by mine dewatering, 1960-1986

Year	Discharge		Concentration		Total release	
	$\text{m}^3 \text{ s}^{-1}$	Mg year^{-1}	Uranium mg l^{-1}	Gross alpha pCi l^{-1}	Uranium Mg	Gross alpha Ci
1960	10.025	746	27.25	33200	5.77	2.55
1961	10.025	746	27.25	33200	5.77	2.55
1967	10.15	4770	27.25	33200	34.6	15.3
1968	10.15	4580	27.25	33200	33.1	14.6
1969	10.13	4000	27.25	33200	28.9	12.7
1970	10.23	6960	27.25	33200	50.4	22.3
1971	10.23	7160	27.25	33200	51.9	22.9
1972	10.24	7960	27.25	33200	57.7	25.5
1973	10.24	7960	27.25	33200	57.7	25.5
1974	10.24	7470	27.25	33200	57.7	25.5
1975	10.27	8450	27.25	33200	61.3	27.1
1976	10.27	8450	27.25	33200	33.8	16.9
1977	10.28	8950	42.0	4000	17.9	8.95
1978	10.34	10700	42.0	4000	10.7	6.45
1979	10.32	10000	21.0	2600	10.0	6.03
1980	10.32	10000	21.0	2600	10.0	6.03
1981	10.24	7700	21.0	2600	7.70	4.62
1982	10.22	7040	21.0	2600	7.04	4.22
1983	10.17	5370	21.0	2600	5.37	3.22
1984	10.19	5970	21.0	2600	5.97	3.58
1985	10.19	5970	21.0	2600	5.97	3.58
Summary		141500			559.3	260.1

1: Perkins & Goad, 1980, Table III, p. 22; 2: Gallaher & Cary, 1986, Table 7.2, p. 82; 3: Gallaher & Cary, 1986, Table 7.1, p. 81; 4: Estimated on assumption of gradual implementation of treatment; 5: Gallaher & Cary, 1986, Table 7.3, p. 83, and 6: summarized from US Environmental Protection Agency records on mine dewatering, 1979-1985.

activity than did the spill; however, concentrations of alpha emitters other than uranium, including radium and thorium, were smaller in dewatering discharges. Concentration of thorium-230 in the tailings solution was 12 000 pCi l⁻¹, compared with 0 to 210 pCi l⁻¹ in untreated dewatering effluent (Gallaher & Cary, 1986). Landa (1980; p. 5) noted that, although 90-95% of uranium in ore is extracted in the milling process, most of the uranium decay products, which composed about 85% of the total radioactivity in the ore, remain with the tailings. The smaller concentration of uranium in the tailings compared to gross alpha activity results in a smaller ratio of uranium to gross alpha activity in the tailings solution than in dewatering effluent. Most of the gross alpha activity in the dewatering effluent was caused by uranium, and most of the gross alpha activity in the tailings solution was caused by alpha emitters other than uranium.

At near neutral pH in oxidized water, uranium is more mobile than radium and thorium (Landa, 1980, pp. 11, 16, 17). Thorium is subject to extensive sorption by clay minerals and humic acid at near neutral pH (Ames & Rai, 1978). The median percents by weight of suspended sediments finer than 0.062 mm (silt sized) and 0.002 mm (clay sized) were 93% and 58% respectively for 21 samples collected from the Puerco River during 1988 and 1989. The median suspended sediment concentration for those 21 samples was 80 000 mg l⁻¹ indicating that large amounts of silt- and clay-sized sediments are available for sorption in the Puerco River. The maximum gross alpha activity measured by the US Geological Survey at Gallup on the day of the tailings pond spill was 38 000 pCi l⁻¹, and of the amount only 5200 pCi l⁻¹ was dissolved. For those reasons, it was expected that the radionuclides released by the tailings pond spill would be more likely than radionuclides released by dewatering to sorb onto sediments and be transported out of the basin or deposited in aggrading zones of the channel. The much larger amount of uranium released by dewatering discharges would be more likely to remain in solution, and, therefore, be more likely to infiltrate the alluvial aquifer underlying the Puerco River.

AN EVALUATION OF THE FATE OF MINE-RELEASED URANIUM IN ALLUVIAL GROUNDWATER

Mass balance calculations were used to investigate the possible effect of mine-released uranium on alluvial groundwater quality and to evaluate the possible fate of the uranium. The calculations did not account for spatial variations in parameters and assumed a homogenous, well-mixed system. Although such an approach has many limitations and requires many assumptions, it can provide information on the potential magnitude of the contaminant problem and, in some cases, can indicate processes affecting the contaminant of interest.

The mass balance calculations assessed whether uranium released by

mining is accounted for by the uranium in alluvial groundwater underlying the reach of the Puerco River that was subject to mine dewatering and flow from the tailings pond spill. This part of the aquifer, referred to as the modelled system, consists of groundwater in the alluvial aquifer under the Puerco River from the mouth of Pipeline Arroyo to Chambers. If observed uranium in groundwater does not account for mine-released uranium, then the conclusion is that some uranium is no longer in solution or has migrated away from the modelled system. The following assumptions were made:

- (a) the initial or background concentration of uranium in alluvial groundwater was zero;
- (b) mine dewatering and the tailings pond spill were the only sources of uranium to the modelled system;
- (c) removal of uranium by entrainment of mine effluent in runoff out of the modelled system could be estimated by the percentage of time that discharge exceeded the average mine dewatering discharge of $0.23 \text{ m}^3 \text{ s}^{-1}$ at Gallup, or 23%;
- (d) removal of uranium by transport in groundwater to underlying aquifers was negligible;
- (e) uptake of uranium by plants was negligible;
- (f) removal of uranium by groundwater pumping was negligible;
- (g) removal of uranium by chemical reactions and sorption was negligible; and
- (h) the alluvial aquifer is a well-mixed system.

Assumptions (a) and (b) are conservative because if they are not met and some uranium in alluvial groundwater occurs naturally, then it is more likely that observed concentrations will approximate or even exceed modelled concentrations and no conclusion regarding processes or pathways removing uranium is possible. Assumptions (c) to (g) represent possible processes or pathways for the removal of uranium from the system. If modelled uranium concentration significantly exceeds observed concentrations, then uranium is leaving the modelled system by one or more of those pathways. Assumption (h) is necessary to the mass balance calculations and leads to a predicted average concentration instead of spatially varying concentrations.

Gallaher & Cary (1986) reported that continuous flow from mine dewatering, mixed with sewage effluent downstream from Gallup, extended more than 80 km downstream from the mines beyond the Arizona-New Mexico State line before all the water from these sources had either infiltrated or evaporated. Shuey (1986) reported that continuous flow from these sources extended 135 km downstream from the mines. Weimer *et al.* (1981) reported that flow from the spill extended 30 to 40 km downstream from the Arizona-New Mexico State line. During February 1990, perennial flow caused only by sewage effluent discharge was observed to extend from Gallup to downstream from Chambers. During warmer, drier conditions in May 1990, perennial flow evaporated or infiltrated the aquifer within about 20 km downstream from Gallup and did not reach the Arizona-New Mexico State line. On the basis of

these observations, the assumption was made that most of the uranium in mine effluents and the spill infiltrated the alluvial aquifer within the 135 km reach between the mines and Chambers.

Estimating the volume of water in storage in the alluvial aquifer between the mines and Chambers required estimates of the areal extent, saturated thickness, and porosity of the alluvial aquifer. The areal extent of the aquifer between the mines and Chambers was estimated as 210 km² from aerial photographs and US Geological Survey quadrangle maps at 1:24 000 scale. Thickness of the aquifer was estimated using the average saturated thickness of 10 monitor wells that reached bedrock, drilled in the reach from Manuelito, New Mexico, to Chambers, Arizona. The average saturated thickness was thus estimated as 21 m. Porosity of the predominantly medium-fine sand aquifer was estimated as 30% (Freeze & Cherry, 1979, p. 37). Using those values, the volume of water in storage in the alluvial aquifer was estimated as 1.3×10^{12} l.

Stream flow was monitored at Gallup from 1940 until 1946 and from 1977 until 1982. Before mine dewatering began, stream flow in the Puerco River at Gallup exceeded $0.028 \text{ m}^3 \text{ s}^{-1}$ only 20% of the time. During the period stream flow was monitored coincident with mine dewatering (1977 until 1982), stream flow at Gallup exceeded the average mine dewatering discharge rate of $0.23 \text{ m}^3 \text{ s}^{-1}$ for 23% of the time. Assuming that all the mine-released uranium was transported out of the modelled system whenever stream flow at Gallup exceeded the average mine dewatering discharge rate (assumption (c)) reduces the estimated mass of uranium used in the mass balance calculations by 23%. The estimated mass of uranium released by dewatering and the spill, 560 Mg, was thus reduced to 430 Mg. That mass of uranium was then divided by 1.3×10^{12} l to yield a concentration of $330 \text{ } \mu\text{g l}^{-1}$, equivalent to about 230 pCi l⁻¹.

Calculated uranium concentration was then compared with measured concentrations. Monitoring wells were sampled in 1988 and 1989 upstream from the confluence of the Puerco River and Pipeline Arroyo to downstream from Chambers. Dissolved uranium concentrations in groundwater are shown for a cross section of the alluvial aquifer under the Puerco River for the monitored reach on the basis of the 1988 and 1989 samples (Fig. 6; A to A' on Fig. 1). A zone of increased uranium concentrations in the alluvial aquifer, in relation to concentrations upstream from Pipeline Arroyo, is approximately delineated by the $100 \text{ } \mu\text{g l}^{-1}$ contour; however, uranium concentrations greater than about $10 \text{ } \mu\text{g l}^{-1}$ may indicate mine effects. The zone delineated by the $100 \text{ } \mu\text{g l}^{-1}$ contour extends from where mine effluent entered the Puerco River to approximately the Arizona-New Mexico State line. The zone generally is shallow, especially downstream from Gallup, where it extends less than a few metres below the stream bed, and generally does not extend laterally more than a few tens of metres from the stream bed. Dissolved uranium concentrations exceeded $330 \text{ } \mu\text{g l}^{-1}$ in only two samples that were collected 0.7 m and 2.4 m below the stream bed and 2 km downstream from the mines. Actual uranium concentrations approximated the calculated concentration of $330 \text{ } \mu\text{g l}^{-1}$ in only

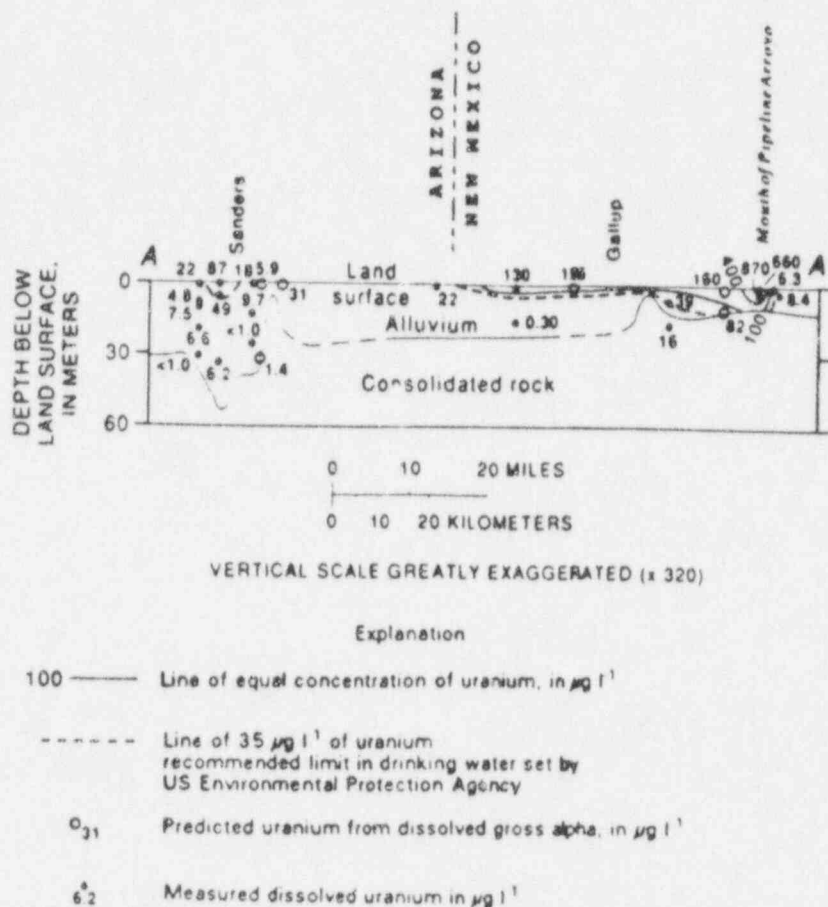


Fig. 6 Occurrence of dissolved uranium in the alluvial aquifer that underlies the Puerco River, Arizona and New Mexico; samples collected between December 1988 and November 1989.

a small fraction of the alluvial aquifer from the mines to Chambers as represented by the area encompassed by the $100 \mu\text{g l}^{-1}$ contour line (Fig. 6).

The comparison between measured dissolved uranium concentrations and calculated concentrations indicates that some of the mine-released uranium left the system represented by the mass balance calculations. Assumptions (d) to (g) listed above represent possible processes or pathways for the removal of uranium from the system that were not accounted for by the calculations. The only part of the alluvial aquifer where increased uranium (greater than $100 \mu\text{g l}^{-1}$) was observed in 1988 and 1989 was near the channel (Fig. 6). The occurrence of uranium suggests that assumptions (d) and (f) are relatively more valid and that significant amounts of uranium have not migrated to deeper aquifers or wells. Uptake of uranium by plants (assumption (e)) was investigated by Wehh *et al.* (1987) who sampled grasses for uranium on the flood plain of the Puerco River and on higher terraces in five locations in December

1986 and found concentrations of uranium in samples from the flood plain that averaged twice the concentrations of samples from the terrace. The relative significance of uptake of uranium by plants is not known.

Another reasonable explanation for the difference between calculated uranium concentrations and measured concentrations is the removal of uranium from solution by chemical reactions and sorption (assumption (g)). One chemical reaction that could remove uranium from solution is the precipitation of a mineral containing uranium as a result of supersaturation (Stumm & Morgan, 1981). Sorption involves many processes, including ion exchange of charged uranium complexes with cations on clays (Beard *et al.*, 1980), adsorption on the surfaces of particles, and reactions with organic compounds that cause adsorption, ion exchange or uptake by plants (Landa, 1980). Uranium is strongly sorbed into organic compounds or clays (Ames & Rai, 1978). Uranium also can be adsorbed onto particles with amorphous iron oxyhydroxide coatings, and the amount of adsorption is greatest between pH levels of 5.5 and 8.5 (Langmuir, 1978; Hsi & Langmuir, 1985). The pH levels in samples shown on Fig. 6 were from 7.5 to 8.0.

Removal of uranium from solution by chemical reactions or sorption, and possibly by plant uptake, is strongly suggested by the mass balance calculations presented herein. Some of that uranium attached to stream sediments probably has been transported to the Little Colorado River that discharges to the Colorado River (Fig. 1). Some may still be on deeper sediments below the stream bed, on sediments in the alluvial aquifer and on sediments in channel deposits. Investigations of uranium concentrations in stream bed and near-channel alluvial sediments could provide evidence to support or refute this hypothesis.

REFERENCES

- Ames, L. L. & Rai, D. (1978) Radionuclide interactions with soil and rock media. Vol. 1, Processes influencing radionuclide mobility and retention, element chemistry and geochemistry, and conclusions and evaluation. US Environmental Protection Agency Report EPA 520/6-78-007-A, Las Vegas, Nevada, USA.
- Beard, H. R., Salisbury, H. B. & Shirts, M. B. (1980) Absorption of radium and thorium from New Mexico uranium mill-tailings solutions. US Bureau of Reclamation Report 8463.
- Brandvold, D. K., Papp, C. J. & 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 Report 132.
- Freeze, R. A. & Cherry, J. A. (1979) *Groundwater*. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, USA.
- Gallagher, B. M. & Cary, S. J. (1986) Impacts of uranium mining on surface and shallow ground waters, Grant, Mineral Belt, New Mexico. New Mexico Environmental Improvement Division Report EID/GWH-86/2, Santa Fe, New Mexico, USA.
- Haan, C. T. (1977) *Statistical Methods in Hydrology*. Iowa State University Press, Ames, Iowa, USA.
- Hem, J. D. (1985) Study and interpretation of the chemical characteristics of natural water. USGS Water Supply Paper 2254.
- Hsi, C. D. & Langmuir, D. (1985) Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model. *Geochimica* 49, 1931-1941.
- Iman, R. L. & Conover, W. J. (1983) *A Modern Approach to Statistics*. John Wiley, New York, USA.
- Landa, E. (1980) Isolation of uranium mill tailings and their component radionuclides from the biosphere. Some earth science perspectives. USGS Circular 814.
- Langmuir, D. (1978) Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochimica* 42, 547-569.

- Perkins, B. L. & Goad, M. S. (1980) Water quality data for discharge from New Mexico uranium mines and mills. New Mexico Environmental Improvement Division report, New Mexico Health and Environment Department, Santa Fe, New Mexico, USA.
- Shuey, C. (1986) The Puerco River: Where did the water go? In: *The Workbook* 11(1), 1-10. Southwest Research and Information Center, Albuquerque, New Mexico.
- Stumm, W. & Morgan, J. J. (1981) *Aquatic Chemistry*. John Wiley, New York, USA.
- US EPA (1982) Rio Puerco monitoring program. US Environmental Protection Agency report, San Francisco, California, USA.
- Webb, R. H., Rink, G. R. & Favor, B. O. (1987) Distribution of radionuclide and trace elements in ground water, grasses and surficial sediments associated with the alluvial aquifer along the Puerco River, northeastern Arizona. A reconnaissance sampling program. USGS Open-File Report 87-206.
- Weimer, W. C., Kinnison, R. R. & Reeves, J. H. (1981) Survey of radionuclide distributions from the Church Rock, New Mexico, uranium mill tailings pond dam failure. US Nuclear Regulatory Commission Report NUREG CR-2449, Washington, DC, US.
- Wirt, Laurie, Van Metre, P. C. & Favor, B. O. (1991) Historical water-quality data, Puerco River basin, Arizona and New Mexico. USGS Open-File Report 91-196.

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