



Selenium geochemistry at Bosque del Apache Wildlife Refuge

John L. Persico and Douglas G. Brookins

1988, pp. 211-216. <https://doi.org/10.56577/FFC-39.211>

in:

Cretaceous and Laramide Tectonic Evolution of Southwestern New Mexico, Mack, G. H.; Lawton, T. F.; Lucas, S. G.; [eds.], New Mexico Geological Society 39th Annual Fall Field Conference Guidebook, 216 p.

<https://doi.org/10.56577/FFC-39>

This is one of many related papers that were included in the 1988 NMGS Fall Field Conference Guidebook.

Annual NMGS Fall Field Conference Guidebooks

Every fall since 1950, the New Mexico Geological Society (NMGS) has held an annual [Fall Field Conference](#) that explores some region of New Mexico (or surrounding states). Always well attended, these conferences provide a guidebook to participants. Besides detailed road logs, the guidebooks contain many well written, edited, and peer-reviewed geoscience papers. These books have set the national standard for geologic guidebooks and are an essential geologic reference for anyone working in or around New Mexico.

Free Downloads

NMGS has decided to make peer-reviewed papers from our Fall Field Conference guidebooks available for free download. This is in keeping with our mission of promoting interest, research, and cooperation regarding geology in New Mexico. However, guidebook sales represent a significant proportion of our operating budget. Therefore, only *research papers* are available for download. *Road logs*, *mini-papers*, and other selected content are available only in print for recent guidebooks.

Copyright Information

Publications of the New Mexico Geological Society, printed and electronic, are protected by the copyright laws of the United States. No material from the NMGS website, or printed and electronic publications, may be reprinted or redistributed without NMGS permission. Contact us for permission to reprint portions of any of our publications.

One printed copy of any materials from the NMGS website or our print and electronic publications may be made for individual use without our permission. Teachers and students may make unlimited copies for educational use. Any other use of these materials requires explicit permission.

This page is intentionally left blank to maintain order of facing pages.

SELENIUM GEOCHEMISTRY AT BOSQUE DEL APACHE NATIONAL WILDLIFE REFUGE

JOHN L. PERSICO and DOUGLAS G. BROOKINS

Department of Geology, University of New Mexico, Albuquerque, New Mexico 87131

Abstract—Selenium is recognized in many areas as a contaminant of surface water, ground waters and soils. In New Mexico the Bosque del Apache National Wildlife Refuge has been identified by the U.S. Department of the Interior as a potentially contaminated site. Accordingly, we have investigated the behavior, speciation and environmental impact of selenium at this site.

Selenium contents in sediments at Bosque del Apache range from 0.17 to 0.37 ppm, values well below what personnel of the U.S. Fish and Wildlife Service consider dangerous to wildlife and waterfowl. The selenium present does not correlate with ferric iron, pH, clay mineralogy or organic carbon content. More than 50% of the selenium is present in the sediments as Se(VI). Irrigation and impounded waters at the site contain less than 1.5 ug/L selenium, and the dissolved selenium appears to be due to the original sediment. Again, the selenium content of the waters is well below the safety level of 10 ug/L advocated by the U.S. Environmental Protection Agency.

These studies show that selenium is not of major concern for water and sediment contamination at the Bosque del Apache National Wildlife Refuge at the present time. We recommend continued monitoring, however, using the results of this study as comparative background.

INTRODUCTION

Environmental concern over high abundances of selenium as responsible for adverse health effects in humans dates back at least to Marco Polo (see discussion in Persico, 1987). Selenium is an element for which hormesis is well known; Se deficiency can lead to muscular problems and stunted growth, while Se excess has been linked to numerous adverse health effects, including possibly cancer (Cannon and Hopps, 1971). While there is debate over the exact nature of cause and effect, the consensus is that Se excess is detrimental to animal life, with documented cases for severe nervous system disorders. In the early 1980s attention was drawn to the Kesterson NWR in the San Joaquin Valley, California, where excess Se in impounded areas and in irrigation ditches resulted in the death of numerous waterfowl (Deverel, 1984).

In 1985, the Department of the Interior, in response to the concern over Se poisoning of the environment, published a list of sites where such contamination might be possible. Included on this list were the Bosque del Apache NWR (National Wildlife Refuge) and the Poison Canyon area of New Mexico. We have chosen to investigate these two sites to assess and evaluate the environmental impact of possible Se contamination, but only the Bosque del Apache site will be reported on here. Specifically, the goals are to (1) measure the concentration of total and hexavalent selenium in geologic materials, (2) assess the role of the relevant geochemical parameters in controlling the speciation and mobility of selenium and (3) estimate the importance of selenium added by irrigation waters at Bosque del Apache to the environmental quality of this area.

BACKGROUND GEOCHEMISTRY

Selenium is somewhat similar to sulfur in its geochemical behavior. Both possess -II, 0, +IV and +VI valences in the Eh-pH range of natural waters. Both have large ionic radii for the -II valence (Se: 1.98 Å, S: 1.84 Å), and both have similar electronegativities (Se: 2.4, S: 2.5). Thus, in natural materials Se is often camouflaged by S in materials such as seleniferous pyrite ($\text{Fe}(\text{S},\text{Se})_2$), etc. However, once oxidized, both selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}) ions may form along with SO_4^{2-} and SO_3^{2-} and be very mobile in the surface and near-surface environments. The speciation of Se is important to the health consequences of contamination, as SeO_3^{2-} is considered to be more toxic than SeO_4^{2-} or Se(0) and Se(-II). Speciation is also important in Se mobility. The concentration of selenium in soil, sediment or water is a function of the availability of a source as well as the geochemical reactions that control selenium speciation and mobility. High concentrations of selenium in soil do not necessarily lead to high concentrations in plants (and therefore animals) because under certain conditions selenium is fixed in the soil (Lakin, 1972; Lakin and Davidson, 1967). An accurate

evaluation of the potential threat of selenium poisoning at any location will require an understanding of both the geochemistry of selenium and the specific geochemical environment in which it occurs.

The principal controls on trace element distribution in a soil system have been identified by Mattigod et al. (1981) as: (1) acid-base reactions, (2) redox reactions, (3) complexation with organic inorganic ligands, (4) precipitation and dissolution of solids and (5) ion exchange and adsorption. All of these processes are known to influence the behavior of selenium in soils. In particular, oxidation state, reactions with organic matter, adsorption on iron hydroxides and adsorption on clays are important factors in selenium speciation and mobility (Lakin, 1972; Sharma and Singh, 1983; Adriano, 1986).

Because of its environmental significance, association with uranium and sulfide ores and industrial uses, the geochemistry and geochemical cycling of selenium have been the subject of many summaries. Most notable among these are Lakin and Davidson (1967), Lakin (1972), Sharma and Singh (1983), Kabata-Pendias and Pendias (1984) and Adriano (1986).

The stability fields of selenium species are shown on an Eh-pH diagram (Fig. 1). In contrast to sulfur, native and tetravalent selenium occupy the majority of the stability field of water, and Se^{6+} exists only at high Eh values. In humid areas selenite is the predominant form of Se in soils (Geering et al., 1969; Lakin, 1972; Adriano, 1986). Sharma and Singh (1983) and Adriano (1986) state that Se should be present as selenate in alkaline soils of semiarid regions based on Eh-pH considerations. Selenate has been observed in soils in Ireland and South Dakota (Peterson et al., 1981). Selenium in surface waters near Kesterson National Wildlife Refuge is predominantly in the higher oxidation state; this is approximately in equilibrium with atmospheric conditions (Weres et al., 1986).

Although Eh-pH conditions may favor the conversion of Se^{4+} to Se^{6+} , enough selenite can persist into the selenate field that the Se^{4+} to Se^{6+} ratio is greater than that calculated for a given Eh-pH condition. This may be due to the slow rate of oxidation of Se^{4+} (Geering et al., 1969; Adriano, 1986).

Early study suggested an association of Se with iron (Williams and Byers, 1936). Geering et al. (1969) and Howard (1977) have demonstrated that the association of Se with iron hydroxides is a result of adsorption and not coprecipitation. The affinity of Se^{4+} for the iron hydroxide surface is so strong that 99% of the selenium in this oxidation state can be removed from solution at pH between three and eight.

The presence of iron hydroxides is one of the most important controls on selenium speciation and mobility in soils. Seleniferous soils in Puerto Rico and Hawaii, containing up to 15 ppm Se, show a positive correlation of Se content with Fe content. Vegetation grown on these soils

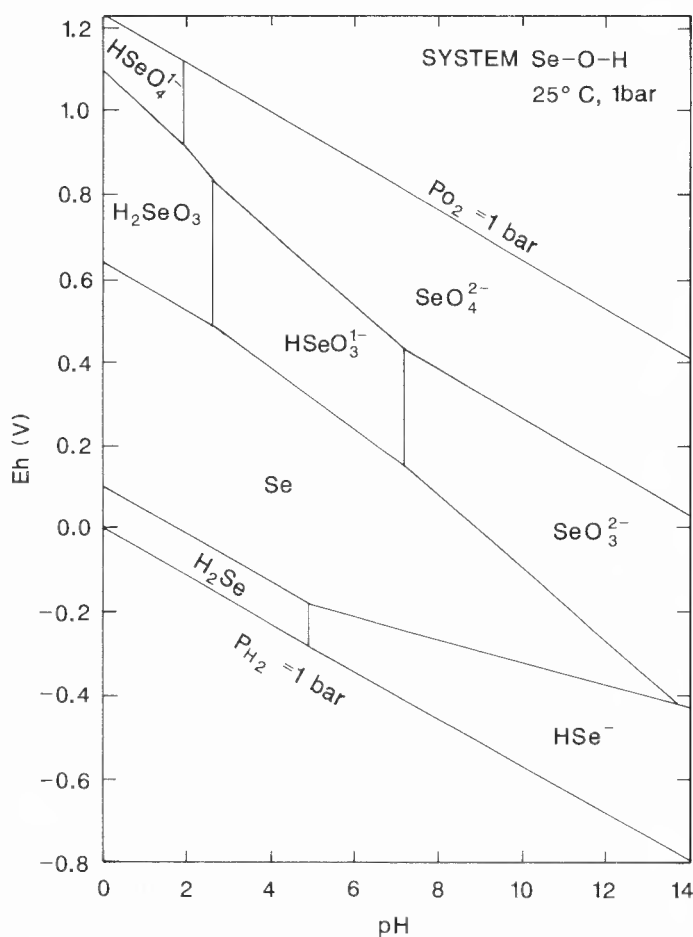


FIGURE 1. Eh-pH diagram for part of the system Se-O-H at 25°C, 1 bar pressure. Activity of dissolved Se = 10^{-6} .

does not contain excessive selenium because the soil selenium is tetravalent and strongly adsorbed by the iron hydroxides (Lakin and Davidson, 1967).

Studies of selenium adsorption by clay minerals are not as extensive as research on the association of selenium with iron in soils (Olson and Lewis, 1983). As with iron hydroxides, immobilization of Se is pH dependent. At low pH values, negatively charged sites on clay surfaces are activated by protons, allowing sorption of Se^{4+} oxyanions. Adsorption is greatest in the pH range three to five and decreases significantly above or below this interval (Frost and Griffin, 1977; Sharma and Singh, 1983). Olson and Lewis (1983) found illite to be a more effective sorbent than bentonite or kaolinite, but attributed this to an iron coating on the illite used in their measurements. The amount of selenium removed from solution by clay minerals is substantially less than that removed by iron hydroxides in the pH range normally found in soils.

The affinity of both selenite and selenate for soils with relatively high organic carbon contents was demonstrated by Singh et al. (1981). The higher solubility of selenium in calciferous media may be due to the buffering capacity of $CaCO_3$ rather than the presence of calcium itself. Higher pH values typically allow oxidation to selenate at a lower Eh (Fig. 1).

The discovery of selenium poisoning at Kesterson National Wildlife Refuge in 1983 (Deverel, 1984) led to intensive research into the geochemical behavior of Se in that region. The source of the selenium appears to be sedimentary rocks in the California Coast Range and valley fill in the San Joaquin Valley. Restricted downward drainage in the valley concentrates the Se. This may be exacerbated by irrigation of nearby farm land and attempts to collect and remove agricultural drainage water via the new San Luis Drain. Presser and Barnes (1984,

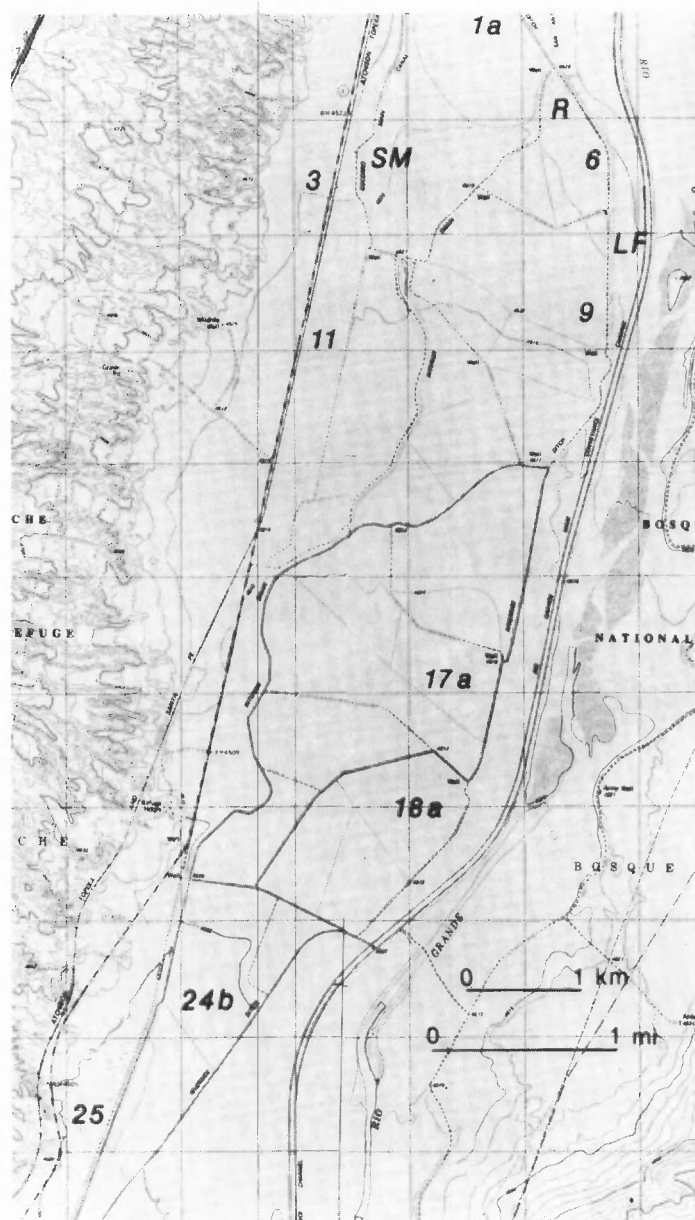


FIGURE 2. Sampling sites (numbered) at the Bosque del Apache National Wildlife Refuge, New Mexico (see text for exact location coordinates).

1985), Deverel et al. (1984) and Weres et al. (1986) present results of selenium studies in this area.

SAMPLING SITES

The location of the Bosque del Apache NWR area is shown in Figure 2. Bosque del Apache NWR is located in Socorro County, N.M. ($106^{\circ} 45'$ to $106^{\circ} 58'$ longitude, $33^{\circ} 32' 30''$ to $33^{\circ} 52' 30''$ latitude; T5 and 6S, R1E, R1W). The study area is a system of impoundments separated by earth dams up to two meters in height constructed in the alluvial deposits west of the Rio Grande. It is maintained by the Fish and Wildlife Service as a wintering ground for migratory waterfowl, including sandhill cranes, Canada and snow geese and ducks. Several whooping cranes also winter at the Bosque.

Rainfall averages only 22 cm/yr, but the areas used by the birds are flooded by irrigation water from upstream farms each year from September to April or May. After the water is released, grass, alfalfa or other forage is grown in the impoundments. Brandvold et al. (1973) reported that evaporation of the impoundment waters led to a 122 percent increase in salinity in some cases.

Sampling methods used at Bosque del Apache NWR

All sampling at Bosque del Apache NWR was conducted on June 25, 1986, after a night of fairly hard and consistent rain. Sediment was collected at nine impoundments. In each case, 400 to 800 g of sediment were taken from the surface, and a similar amount was collected at 30 to 40 cm depth with a soil auger. Two impoundments were flooded when sampled: impoundment 18a was submerged below approximately 80 cm of water, and impoundment 25 was below approximately 200 cm of water. Sample locations are shown in Figure 2.

Water samples were taken at five locations (Fig. 2). The temperature and pH of these waters were measured in the field.

Sample locations at the Bosque were chosen by the Fish and Wildlife Service. Concerns about the possible sources of selenium and the impact of selenium on wildlife use areas, as well as disturbances caused by sampling near wildlife use areas, were considered in the selection of these sites. The water samples were associated with specific impoundments in order to allow correlations between source and sediment to be examined.

ANALYTICAL METHODS

Standard analytical methods were used in this study for the determination of pH, organic carbon, ferric oxyhydroxides, CaCO_3 and clay mineralogy (see detail in Husler, 1984; and Persico, 1987). For selenium, however, the analytical methods were found to be inappropriate for much of the material, and a new method was developed. Details of this method are given in Persico (1987); it allows determination of total Se, Se(IV and lower valence), and thus the amount of SeO_4^{2-} can be calculated.

After drying, the samples were weighed, and the less than two-mm fraction was separated by sieving. This fraction was weighed in order to determine the amount of gravel (greater than two mm in diameter). All subsequent measurements were performed on the less than two-mm fraction.

Two aliquots weighing approximately ten grams were taken for measurement of pH. Fifteen to thirty grams of soil, sediment and some tailings samples were set aside for particle size distribution analysis. Carbonate was removed from these splits with an acetic acid-sodium acetate solution (pH approximately 5) before particle size distribution was determined.

The selenium analytical methods developed for use in this study have the following advantages: (1) applicability to both graphite furnace and flame AA, allowing measurement of selenium concentrations as low as 0.10 ppm and higher than one percent without using dilutions; (2) little or no interference from dissolved solids; (3) use of methyl isobutyl ketone (MIBK) as an extractant, which is relatively non-toxic and suitable for use in the flame or furnace and (4) ability to determine the concentrations of both total Se and Se in the 4+ or lower oxidation states, allowing calculation of the concentration of and percent Se^{6+} .

In nine samples, an aliquot of the clay fraction was used for qualitative assessment of mineralogy by x-ray diffraction. Two sediment samples from Bosque del Apache (1aB and 24bB) were chosen because their high clay contents would result in better resolution. The samples were analyzed on a Scintag automated x-ray diffractometer utilizing $\text{Cu}_{K\alpha}$ radiation. For each sample, an air dried, glycolated and heated (400°C) slide was run.

Fifteen to twenty grams were split from each sample and crushed to pass through a one hundred mesh sieve. This crushed sample was used for the remainder of the measurements. Organic carbon content and dithionite extractable iron were determined in all sediment samples.

Two sites at Bosque del Apache were chosen for determination of calcium carbonate content. Site 17a seemed to have CaCO_3 content similar to most of the other impoundments, while site 25 appeared to have a relatively high calcium carbonate content when reacted with 10% HCl.

RESULTS

In the remainder of this paper, the term "HNO₃-extractable Se" will be used to indicate all selenium in the 4+ or lower oxidation state.

TABLE 1. Temperature, pH and Se content of waters at Bosque del Apache NWR.

Sample Location	Temp. (C)	pH	Se (ug/l)
Low Flow	19	7.6	< 1.5
Riverside	19	7.6	< 1.5
Socorro Main	19	7.7	< 1.5
Impoundment 18b	25	8.4	< 1.5
Impoundment 25	23	8.2	< 1.5

The term "HBr Se" will be used synonymously with "total Se." The concentration of Se^{6+} is calculated by subtracting the HNO₃ extractable from the total selenium. The iron concentrations referred to in the text are only the dithionite extractable fraction. The standard deviations included in the data tables are population standard deviations.

Waters

The temperature, pH and selenium content of waters collected at the Bosque are given in Table 1. The irrigation streams are both colder and less alkaline than the impoundment waters. All of the waters contained less than 1.5 ug/L Se.

Sediments

The results of the chemical analyses of sediments at the Bosque are reported in Table 2. All of the sediments are alkaline. pH values are between 7.7 and 8.1 with the exception of the subsurface sample at impoundments 3, 11 and 18. These have pH values of about nine. The average pH value is 8.0 ± 0.25 , if these three samples are disregarded.

TABLE 2. Chemical characteristics of sediments at Bosque del Apache NWR. A = sample collected at surface. B = sample collected 30-40 cm below the surface. (-) = not measured.

Sample	pH	Dithionite Fe (ppm)	Organic C (%)	Clay (%)	CaCO_3 (%)	HNO ₃ Se (ppm)	HBr Se (ppm)	Se 6+ (ppm)	Se 6+ (%)
1aA	7.7	1060	0.60	45.1	-	0.064	0.22	0.16	71
1aB	7.8	1100	0.56	50.4	-	0.067	0.33	0.26	80
3A	8.1	1040	0.29	39.8	-	0.12	0.28	0.16	57
3B	9.1	775	0.74	39.5	-	0.073	0.25	0.18	71
6A	8.0	941	0.74	25.7	-	0.079	0.23	0.15	66
6B	8.1	964	0.77	23.6	-	0.11	0.32	0.21	66
9A	8.1	1160	0.54	15.5	-	0.070	0.20	0.13	65
9B	7.9	1190	0.40	18.2	-	0.094	0.24	0.15	61
11A	8.1	714	0.56	29.5	-	0.080	0.20	0.12	60
11B	8.9	637	0.59	37.3	-	0.13	0.34	0.21	62
17aA	8.0	978	0.70	23.2	5.96	0.090	0.18	0.09	50
17aB	7.8	1110	0.62	20.3	7.15	0.11	0.26	0.15	58
18aA	7.9	1760	0.35	26.3	-	0.079	0.13	0.10	56
18aB	9.0	1210	0.52	31.1	-	0.18	0.28	0.10	56
24bA	7.8	1810	0.52	43.4	-	0.062	0.25	0.19	75
24bB	8.1	1850	0.93	48.7	-	0.068	0.18	0.11	62
25A	7.7	2060	2.35	32.3	18.5	0.13	0.37	0.24	65
25B	7.7	1500	2.99	23.8	11.7	0.10	0.17	0.07	41
Averages:	8.1	1210	0.82	31.9	10.8	0.095	0.28	0.18	61
Std.Dev:	0.43	402	0.68	10.4	4.9	0.030	0.039	0.05	11
High:	9.1	2060	2.99	50.4	18.5	0.18	0.37	0.26	50
Low:	7.7	637	0.29	15.5	5.96	0.062	0.17	0.07	36
Range:	1.4	1420	2.70	34.9	12.5	0.12	0.20	0.19	44

The average value for calcium carbonate content in samples 17A, 17B, 25A and 25B is probably not representative of the Bosque sediments. Although only four determinations might accurately characterize the sediments if chosen randomly, samples 25A and B were analyzed specifically because they had a stronger reaction with hydrochloric acid than other samples. The true average should be lower than that reported in Table 2.

Sixteen of the samples have organic carbon contents below one percent. Samples at impoundment 25 contained 2.35% and 2.99% organic carbon. Excluding these samples, the mean organic carbon content of the sediments is 0.59% with a standard deviation of 0.16%.

X-ray diffraction indicated a relatively simple mineralogy in these sediments. The clay fraction of both samples was composed predominantly of smectite, with smaller amounts of kaolinite and quartz.

The maximum selenium content in these samples is 0.37 ppm. In sixteen of the sediment samples, Se^{6+} is from 50 to 80% of the total Se. At both of the locations where sediment was sampled below water (impoundments 18a and 25), the selenium in the deeper sample (30–40 cm below the sediment-water interface) is predominantly in the lower oxidation states. These two locations also show the greatest difference in percent Se^{6+} between the upper and lower samples. Where CaCO_3 contents were measured, the higher percent Se^{6+} occurs in the same sample as the higher CaCO_3 content.

Impoundment 11 has not been irrigated by the Fish and Wildlife Service (J. Taylor, pers. commun.) and can be used to represent background selenium concentrations at the Bosque. The total Se and fraction of hexavalent selenium do not appear to be appreciably different from the other samples.

Both parametric and non-parametric methods were used to examine relationships between total selenium and percent selenate and the geochemical parameters that control Se geochemistry. Explanations of linear regression and its non-parametric counterpart, rank correlation, are given in Walpole and Myers (1985, p. 315–352 and 553–558). The correlation coefficient (r) and the Spearman rank correlation coefficient (r_s) for each correlation are given in Table 3. There are no significant linear relationships, and only Se^{6+} and clay have a significant rank correlation at $\alpha = 0.05$. With this exception, selenium content is not correlated with the geochemical parameters measured in this study.

DISCUSSION

Correlation of selenium with other geochemical characteristics of the sediments

As the data in Table 3 indicate, there are no significant linear correlations and only one significant rank correlation between total selenium or percent selenate and the geochemical controls measured in this study. At least three explanations might account for this lack of relationship: (1) the behavior of Se is controlled by one or more geochemical parameters not measured in this study; (2) the variations in pH or the

amounts of iron, organic carbon or clay in these sediments are not large enough to result in a noticeable relationship with total selenium or percent selenate or (3) the distribution of Se is not primarily a function of *in situ* geochemistry, but rather is dependent on the original selenium concentrations in the sediments or waters that flow into the impoundments.

The first case seems unlikely since almost all the geochemical controls on Se behavior that are reported in the literature were measured, with the exception of Eh. However, the amount of selenium in the 6+ state was measured. This is a more direct approach to assessing the importance of the various oxidation states of Se than determining oxidation potentials in the sediments.

The lack of significant variation in the concentrations of the geochemical parameters can be seen by trying to treat these data with the non-parametric sign test using $n = \text{nine}$ and $p = 0.5$ (Walpole and Myers, 1985, p. 530). At each impoundment, the occurrence of the higher selenium content in the same sample as the higher iron, organic carbon, clay content or pH would be considered a "success." This approach assumes that Se is locally mobile and has the opportunity to accumulate in the sample (either surface or subsurface) with the more geochemically favorable environment.

If a "success" occurs more or less frequently than expected based on chance, a relationship might be inferred. However, at many of the impoundments there is no significant difference within experimental error in the amount of one or more of the geochemical parameters between the surface and subsurface samples. These impoundments cannot be included in the test. The result is that the data set becomes too small for even a non-parametric method. Therefore, there might be a relationship between Se and the geochemical controls on its behavior that is not recognizable because of limitations in the methods of analysis.

The Se contents of the waters are uniform and low (Table 1). None of the irrigation streams appear to be an important source of Se at present. The selenium content of the sediments is within the range reported for "typical" sediments and soils (Persico, 1987). It is likely that all of the selenium is an original component of the sediments. In this case, the amounts of organic carbon or the other controls might bear no relationship to selenium concentrations. If the selenium was not mobile in these sediments it would not have had the opportunity to become redistributed in areas that favored its retention, even on a local scale (provided these areas exist).

Adsorption on ferric hydroxides is a reasonable mechanism for immobilizing at least part of the Se^{4+} . However, it seems unlikely that selenate would not be mobile in these sediments. Alrichs and Hossner (1987) have demonstrated the extreme mobility of Se^{6+} in surface environments. Numerous other authors have commented on the lack of mechanisms for selenate retention (Lakin, 1973; Howard, 1977; Kabata-Pendias and Pendias, 1983; Adriano, 1986).

The correlation between percent selenate and clay content in these sediments is insufficient evidence to conclude that the clay minerals are efficiently retaining the selenate, although some adsorption could be taking place. Selenate might also be very weakly adsorbed on organic matter or precipitated as an extremely soluble salt such as CaSeO_4 or $\text{Ca}(\text{S,Se})\text{O}_4$ (or gypsiferous equivalents) when the sediments dry. When the sediments are wetted by precipitation or irrigation, the selenate is remobilized. It never accumulates because it does not have a chemical affinity for any of the other compounds in the system.

Oxidation state of selenium

The majority of the selenium in sediments at Bosque del Apache NWR is in the most oxidized form (Table 2). Although neither total nor hexavalent Se has a significant linear or rank correlation with pH (Table 3), the importance of Se^{6+} is probably related to the alkalinity of the sediments. Selenate is stable relative to selenite at lower oxidation potentials as pH increases (Fig. 1). At the average pH of sediments at the Bosque, Se^{6+} is the predominant dissolved selenium species at Eh values as low as 0.4 volts, providing the conditions assumed in Figure 1 apply.

The fraction of Se^{6+} is also affected by iron oxides and hydroxides. Howard (1977) states that iron can prevent the oxidation of Se^{4+} because

TABLE 3. Correlation coefficient (r ; left column) and Spearman rank correlation coefficient (r_s ; right column) for the association of total and hexavalent Se with iron, organic carbon and clay at Bosque del Apache NWR.

Total Se vs.		
pH:	.204	.138
Fe:	.0805	-.165
Org. C:	.0153	-.0733
Clay:	.252	.269
Hexavalent Se vs.		
pH:	.210	-.115
Fe:	-.110	-.147
Org. C:	.283	.148
Clay:	.464	.441

the stability field of selenite is expanded into both higher and lower Eh values by adsorption onto ferric hydroxides. Adsorption decreases above pH eight. Considering the relative amounts of selenite and selenate, iron does not appear to be controlling the oxidation state of Se in this environment. This might be due to either the amount or form (e.g., crystallinity) of the iron compounds, or to the high pH of the sediments. Iron may absorb some or even most of the selenite at these pH values (Fig. 1) but will not exert a significant influence on the overall mobility of Se at the Bosque since it does not retain selenate (Adriano, 1986; Plotnikov, 1960).

The selenate content of sediment below flooded impoundments shows a marked decrease with depth. Sediment samples in contact with water (18aA and 25A) have more Se^{6+} than the deeper samples (18aB and 25B). In fact, the deep (30–40 cm below the sediment-water interface) sediments at these impoundments are the only samples with less than 50% selenium as selenate. The predominance of selenite over selenate in samples 18aB and 25B cannot be explained by either low pH values or high iron contents relative to the other sediments. The low percent Se^{6+} might be due to a deficiency of dissolved oxygen, if diffusion or advection of oxygen to these sediments is restricted. High organic carbon content at impoundment 25 might also result in an oxygen deficiency, but organic matter is probably not necessary to cause reducing or less oxidizing conditions since impoundment 18a exhibits the same trend in Se oxidation states without having a high organic carbon content.

Considering the amount of selenate relative to selenite, and the alkalinity of the sediments, it appears that selenate is the more stable form. Without data on the original oxidation state of Se in the sediments, it is difficult to predict the direction of the transformation. In the case of the deeper sediments at the flooded impoundments, Se^{4+} might be stable or oxidizing more slowly. The oxygen content of the pore waters probably fluctuates as the impoundment is drained or flooded.

Environmental impact

The most important potential source of selenium at Bosque del Apache is incoming irrigation waters. Selenium could later be concentrated to more dangerous levels in the impoundment waters by evaporation, as discussed in Brandvold et al. (1973). However, the selenium content of both irrigation and impoundment waters at the Bosque (Table 1) is well below the Environmental Protection Agency drinking water limit of ten $\mu\text{g}/\text{L}$ (U.S. E.P.A., 1980). The heavy rains that preceded sampling may have had an effect on the concentrations, but even if the waters had been diluted by a factor of five, the concentrations before the rain would still be within the E.P.A. limit.

A concentration of 0.56 ppm Se in sediments is the lowest level believed to damage wildlife (J. Taylor, pers. commun.). Assuming this is correct, the Se concentrations found at the refuge should not be a concern. The selenium content in an unirrigated field within the Bosque (Impoundment 11) is not significantly less than the other impoundments, suggesting that irrigation waters have not contributed a significant amount of selenium to the Bosque. Field inspections have revealed no evidence of problems in either numbers or health of birds or other wildlife (J. Taylor, pers. commun.). In short, there is no reason to suspect any threat to wildlife at the Bosque due to selenium in water or sediment.

The situation could change if irrigation streams begin to deliver higher concentrations of Se to the impoundments. The oxidized selenium in the sediment is easily available to plants (Van Dorst and Peterson, 1982). Selenium would rapidly work its way into the food chain in an amount proportional to that carried by the streams.

CONCLUSIONS

Selenium is distributed quite uniformly in sediments throughout the Bosque with respect to both impoundment location and variations in sediment chemistry. This might be due to a uniform Se distribution in the sediments when they were deposited. Selenite could be immobilized by adsorption on ferric hydroxides. Highly mobile selenate remains in the Bosque sediments but never accumulates in any particular area.

The original percent Se^{6+} in the sediments is unknown. Selenate appears to be the more stable form of selenium because of the high pH

values and the apparent inability of ferric hydroxide compounds to strongly influence the ratio of Se^{6+} to Se^{4+} .

The Se content of sediments and waters are both low. None of the data suggest that selenium poses a threat at present to the continued use of the Bosque as a wildlife refuge. It would be worthwhile, however, to initiate a program of water monitoring to guard against any possible future problems due to selenium poisoning.

REFERENCES

- Adriano, D. C., 1986, Trace elements in the terrestrial environment: New York, Springer-Verlag, 533 p.
- Alrichsto, J. S. and Hossner, L. R., 1987, Selenate and selenite mobility in overburden by saturated flow: *Journal of Environmental Quality*, v. 16, p. 95–98.
- Brandvold, D. K., Brierty, J. A. and Popp, C. J., 1973, Chemical and biological character of Rio Grande water in the Bosque del Apache Wildlife Refuge: New Mexico Water Resources Research Institute, Report 30, 50 p.
- Cannon, H. L. and Hopps, H. C., 1971, Environmental geochemistry in health and disease: Geological Society of America, Memoir 123, 230 p.
- Deverel, S. J., 1984, Selenium in the San Joaquin Valley of California: U.S. Geological Survey, Water Supply Paper 2275.
- Deverel, S. J., Gilliam, R. J., Fujii, R., Izbicki, J. A. and Fields, J. C., 1984, Areal distribution of selenium and other inorganic constituents in shallow groundwater of the San Luis Drain service area, San Joaquin Valley, California: A preliminary study: U.S. Geological Survey, Water Resource Investigations Report 84-4319.
- Frost, R. R. and Griffin, R. A., 1977, Effect of pH on adsorption of arsenic and selenium from landfill leachate by clay minerals: *Soil Science Society of America Proceedings*, v. 41, p. 53–57.
- Geering, H. R., Cary, E. E., Jones, L. and Allaway, W. H., 1969, Solubility and redox criteria for the possible forms of selenium in soils: *Soil Science Society of America Proceedings*, v. 32, p. 35–40.
- Howard, J. H., III, 1977, Geochemistry of selenium: formation of ferroselite and selenium behavior in the vicinity of oxidizing sulfide and uranium deposits: *Geochimica et Cosmochimica Acta*, v. 41, p. 1665–1678.
- Husler, J., 1984, Methods for the analysis of rocks, ores, and minerals: Departmental Procedures, University of New Mexico, Department of Geology, unpublished report.
- Jackson, M. L., 1969, Soil chemical analysis, advanced course: Madison, Wisconsin, published by the author (2nd ed.), p. 44–51.
- Kabata-Pendias, A. and Pendias, H., 1984, Trace elements in soils and plants: Boca Raton, Florida, Chemical Rubber Company Press, 315 p.
- Lakin, H. W., 1972, Selenium accumulation in soils and its absorption by plants and animals: *Geological Society of America Bulletin*, v. 83, p. 181–190.
- Lakin, H. W., 1973, Selenium in our environment; in Kothny, E. L., ed., Trace elements in the environment: Washington, D.C., American Chemical Society, p. 96–111.
- Lakin, H. W. and Davidson, D. F., 1967, The relation of the geochemistry of selenium to its occurrences in soils; in Muth, O. H., ed., Selenium in Biomedicine, Procedures First International Symposium, Oregon State University: Westport, Connecticut, Avi Publishing Company, p. 27–56.
- Mattigod, S. V., Sposito, G. and Page, A. L., 1981, Factors affecting the solubilities of trace metals in soils; in *Chemistry in the Soil Environment*: American Society of Agronomy, Special Publication 40, p. 302–321.
- Olson, T. M. and Lewis, B. G., 1983, Selenite ion adsorption on clays and other mechanisms for selenium removal from uranium mill tailings: *Transactions of Society of Mining Engineering, American Institute of Mining and Metallurgical Engineers*, v. 274, p. 2040–2045.
- Persico, J. L., 1987, Behavior, speciation and environmental impact of selenium at Bosque del Apache National Wildlife Refuge and Poison Canyon, New Mexico [M.S. thesis]: Albuquerque, University of New Mexico, 113 p.
- Peterson, P. J., Benson, L. M. and Zieve, R., 1981, Metalloids; in Lepp, N. W., ed., Effect of Heavy Metal Pollution on Plants: v. 1, Effects of Trace Metals on Plant Functions: New Jersey, Applied Science Publishers, p. 279–343.
- Plotnikov, V. I., 1960, Coprecipitation of selenium and tellurium with metal hydroxides: *Russian Journal of Inorganic Chemistry*, v. 5, p. 351–354.
- Presser, T. S. and Barnes, I., 1984, Selenium concentrations in the waters tributary to and in the vicinity of the Kesterson National Wildlife Refuge, Fresno and Merced Counties, California: U.S. Geological Survey, Water Resources Investigations Report 84-4122.
- Presser, T. S. and Barnes, I., 1985, Dissolved constituents including selenium in waters in the vicinity of Kesterson Wildlife Refuge and the West Grassland, Fresno and Merced Counties, California: U.S. Geological Survey, Water Resource Investigations Report 85-4220.

- Singh, M., Singh, N. and Relan, P. S., 1981, Adsorption and desorption of selenite and selenate selenium on different soils: *Soil Science*, v. 132, p. 134–141.
- Sharma, S. and Shingh, R., 1983, Selenium in soil, plant, and animal systems: *Chemical Rubber Company Reviews in Environmental Control*, v. 13, p. 23–50.
- United States Environmental Protection Agency, 1980, Ambient water quality criteria for selenium: Environmental Protection Agency, Document 440/5-80-0070.
- Van Dorst, S. H. and Peterson, P. J., 1982, Selenium speciation in solution and its relevance to plant uptake; *in* Scaife, A., ed., Ninth International Plant Nutrition Colloquium: Bucksport, England, Commonwealth Agricultural Bureau, v. 1, p. 134.
- Walpole, R. E. and Myers, R. H., 1985, Probability and statistics for scientists and engineers: New York, Macmillan Publishing Company, 639 p.
- Wares, O., White, A. F., Wollenberg, H. and Yee, A. W., 1986, Geochemistry of selenium at Kesterson Reservoir and possible remedial measures: Lawrence Berkeley Laboratory, Earth Sciences Division Annual Report, p. 159–162.
- Williams, K. T. and Byers, H. G., 1936, Selenium compounds in soil: *Industrial and Engineering Chemistry*, v. 28, p. 912–914.