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TRACE METAL AND ACID-VOLATILE SULFIDE CONCENTRATIONS IN SEDIMENTS FROM THE FOREST QUEEN WETLAND NEAR SILVERTON, COLORADO: IMPLICATIONS FOR THE REMOVAL OF METALS FROM ACID DRAINAGE WATERS

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by

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ABSTRACT

The Forest Queen wetland near Silverton, Colorado, receives acidic (pH 4.7) metal-bearing drainage issuing from a collapsed mine adit. The wetland was studied for the ability of organic/clastic sediments to neutralize the acidity and remove trace metals from the influent waters.

Core samples taken from the wetland in October 1997 were leached with 6N HCl and analyzed to determine concentrations of trace metals and reduced sulfur (as acid-volatile sulfides, AVS). Results indicate that sulfate (SO_4^{2-}) reduction was active but variable with depth and location during the fall sampling period and that metals have been incorporated into AVS phases. However, the highest concentrations of trace metals are not consistently associated with black, organic-rich, AVS-bearing samples. High metal concentrations are also present in organic-rich (but generally AVS/H_2S-poor) intervals and in red Fe-oxide solids.

Metal removal is not directly related to inflow metal concentrations. Compared to the adit and upstream (surface) waters, Pb, Zn, and Al are lower in the wetland outflow, but Fe is leaving the wetland in concentrations greater than in the influent waters. Thus, other hydrological, geochemical, or biological factors are influencing the mobility of metals that enter (via the adit and streams) or exit (via outflows) the wetland, so that some of the wetland metal load reaches the E. Fork of the Animas River. This results, in part, from sulfate reduction that is discontinuous with depth and distance throughout the wetland in the fall. The inconstancy of sulfate reduction in the wetland results in variability of sediment metal and AVS concentrations.

INTRODUCTION

Site Description

The Forest Queen wetland is 10.4 km (6.5 mi) northeast of Silverton, Colorado, (San Juan County) along the East Fork of the Animas River at an altitude of approximately 2990 meters (9800 ft; Figure 1). The wetland area is approximately 1 hectare (2.5 acres), and the organic+sediment layer(s) ranges from less than 0.6m (2 ft) to at least 3m (10 ft) in thickness in sections that were cored.

As a result of geologic and anthropogenic processes, surficial material in and around the wetland is composed of differing amounts of country rock, road and railroad aggregate, mine waste rock and tailings, and river-transported tailings and rock debris from upstream locations (Figure 2). Landslides of unknown age from higher slopes above the wetland have deposited country rock rubble into the wetland area. Most country rock in the area contains pyrite (G. Desborough, pers. comm., 1997), but whether the landslide-deposited rock is mineralized with trace metals is unknown. Areas east (upslope) and north (valley of E. Fork of Animas River) of the wetland were mined from the late 1890's until the early 1950's (Bird, 1999). Abandoned grades of railroads which hauled ore from further up the valley are adjacent to the western and southern edges of the wetland (Figure 2). A 4m-high (12 ft) waste tailings mound is present in the northeast section of the wetland. The East Fork of the Animas River and the road along the river pass next to the western edge of the wetland.

Elevated aqueous concentrations of metals (primarily Fe, Al, Pb, Zn, and Cu) and acidity (imparted as sulfuric acid; $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$) derived from weathering of metal-bearing sulfides are implicated as major acid rock/acid mine drainage components in the Animas River basin (Church and others, 1997). One purpose for studying the wetland was to determine if it is capable of attenuating influent metal and SO_4^{2-} concentrations, thus improving the quality of effluent waters. Dissolved trace metals form insoluble sulfide minerals upon reaction with aqueous H_2S (total aqueous sulfide = $H_2S_{(aq)} + HS^-_{(aq)}$). Sulfide in organic-rich sediments is produced via reduction of sulfate ion.

Sulfate reduction at the temperatures and pressures present in the

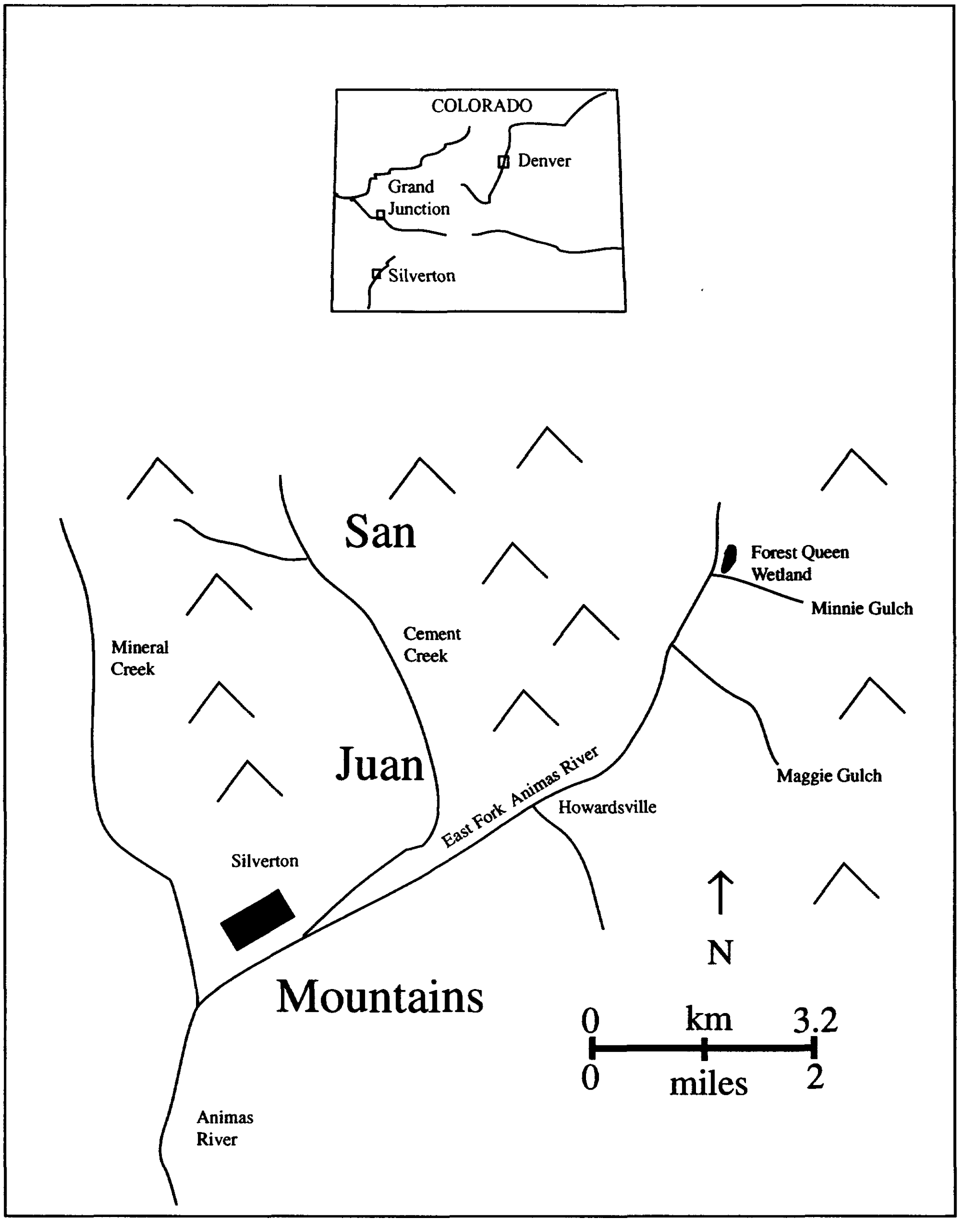


Figure 1. Location map of the Forest Queen Wetland.

Forest Queen wetland is accomplished through the action of sulfate-reducing bacteria, primarily of the genus *Desulfovibrio* (Berner, 1970). These microbes couple sulfate reduction with organic carbon oxidation to produce sulfide (S^{2-}) and ultimately H_2S; the reaction yields energy for growth of the microbes. Sulfate reduction is an anaerobic process, occurring in the absence or at very low (sub-ppm) levels of molecular oxygen [O_2]. Sulfate reduction with organic matter oxidation is summarized by the reaction $SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^-$, where CH_2O symbolizes organic matter. Active sulfate-reduction in the wetland sediments was evidenced by the odor of H_2S in many core samples and waters. Sulfate-reduction leads to an increase in the mine water pH via HCO_3^- production. Additional neutralization of acidic water occurs via ammonia and ammonium ion formation as a result of protein decomposition

($NH_3 + H_2O \rightarrow NH_4^+$ (ammonium) + OH^-). Most aqueous metals become less soluble as pH increases towards neutral and alkaline values; pH values as high as 7 (neutral) were observed in the wetland. Thus, a rise in pH may also help mitigate elevated concentrations of soluble metals.

Water enters the wetland from the Forest Queen Mine adit, which resembles a flowing spring as a result of adit collapse. At the time of the October 1997 sampling, the adit inflow contained 0.66 ppm zinc (Zn), 0.014 ppm lead (Pb), 400 ppm sulfate (SO_4^{2-}), 24 ppm iron (Fe), 1.8 ppm aluminum (Al) (T. Wildeman, Colorado School of Mines, unpub. data), and had a pH of 4.7. Water flows down from the adit on a gentle slope for about 16 m (50 ft), passes through a narrow aluminum culvert, then reaches a 5m (15 ft) diameter by 1m (3 ft) deep pool that is heavily encrusted with Fe-oxide (Figure 2). From this pool, the primary surface water flow is directly west out of the Fe-oxide pond. Water exits the wetland at several points and ultimately discharges into the E. Fork of the Animas River. These effluent waters contain dissolved Zn that ranges from 0.12-0.17 ppm and dissolved Pb from 0.001-0.008 ppm (T. Wildeman, CSM, unpub. data). Thus, Pb and Zn concentrations in outflow waters

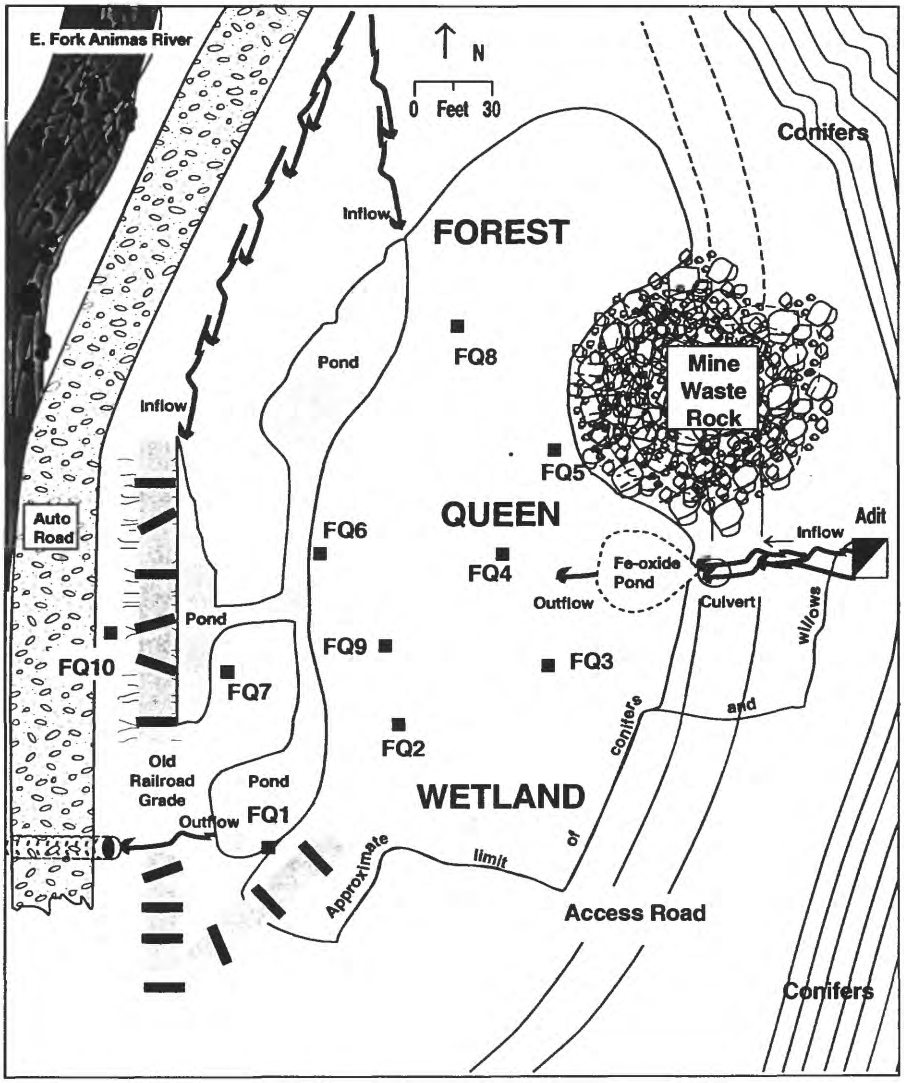


Figure 2. Detailed map of Forest Queen wetland and adjacent area. Core locations are shown by filled squares, and core numbers are prefixed by "FQ".

are only about 25% of those in the inflow waters during the sampling period. Aluminum was also lower (0.33-0.81 ppm) while Fe was higher in some outflow waters (1.9-32 ppm), a strong indication that Fe is mobile in the wetland environment.

This report describes the organic+clastic sediment stratigraphy of 6 cores from the Forest Queen wetland and focuses on trace metals potentially associated with acid-volatile sulfides. Additional core and water samples from a springtime sampling are currently being analyzed and the geochemical data is being compiled for comparison to the results presented here.

Sampling Methods

Cores were obtained by driving a 1.5 to 3 m (5-10 ft) length of 5 cm (2 in) diameter PVC pipe into the organic+clastic sediment layers. No progress could be made beyond about 3m (10 ft) by this method. Often, two or three insertions in the same location were made to ensure that the maximum thickness of sediment had been sampled. Smaller cores (1.25 cm (1/2-in) diameter) were taken at the edges of the wetland and in other locations where coring with PVC proved unworkable. The smaller-diameter cores were no deeper than approximately 1 meter. Shallow ($\leq$1m) samples were taken with an auger when PVC or 1.25-cm coring could not penetrate the root mat. Capping the top of the PVC pipe before pulling the core aided retention of cored sediments. After being pulled, cores were measured for recovery and excess PVC pipe was sawn off. The sediment was then closed off from the air by sealing the ends with PVC caps (or plastic caps for 1.25 cm cores) and cloth tape.

Recovery in each core or in an interval was variable but ranged from 50% in organic-rich layers to >90% in clay-rich layers. The midpoint (average) depth of each extracted core interval is used to identify samples in the tables or on downhole plots. For example, in Core 7, the midpoint of the 107-125 cm interval is 116 cm; this value is used to place the data points on downhole plots. Because of sediment compression, the actual recovery in a sampled interval was less than the full thickness reported for that interval. Composite samples of macroscopically-similar (color; organic and clastic content) materials were best-suited as representative of each sediment interval.

Cores were taken within approximately 2m (6 ft) of piezometers that had been installed and sampled 2 weeks earlier as part of a water-quality study directed by the Colorado School of Mines (T. Wildeman, CSM, pers. comm., 1997). While direct comparisons of sediment data to the water-quality data cannot be made, the two data sets are considered representative of geochemical conditions in the wetland and adit during comparable times of the year (in this case, fall). Each core was kept at $\leq$15 °C until transported to the lab.

On-site analyses for pH, dissolved oxygen (DO), specific conductivity (SpC), alkalinity (H_2SO_4 titration), ferrous iron (Fe^{2+}), and total iron ($Fe_{(tot)}$) were made. Ferric iron (Fe^{3+}) was determined by difference ($Fe^{3+} = Fe_{(tot)} - Fe^{2+}$). The two iron species were measured using a portable spectrophotometer (Hach Chemical Co., 1997).

Analytical Methods

The term "acid-volatile sulfide" is usually restricted to Fe-S phases that are soluble in 6N HCl (Berner, 1970): greigite (Fe_3S_4), amorphous FeS ($FeS_{(am)}$), and mackinawite (crystalline $FeS_{(c)}$). Pyrite (FeS_2) is insoluble in 6N HCl. The AVS definition is expanded here to include other HCl-soluble metal sulfides such as PbS (galena), ZnS (sphalerite), and Cu_2S (chalcocite) that may have been present in the sediment.

Cores were stored upright at 4 °C in the lab. When a core was opened, the stratigraphy was immediately described and then a composite sample over each interval was taken for use in the acid-volatile sulfide (AVS) analysis. Samples were taken under an $N_{2(g)}$ stream to prevent oxidation of AVS solids but were not dried. The type of sample taken depended on color, amount of material available, organic matter and/or clastic sediment content, presence of visible "fresh" or existing sulfides, and grain size. The amounts used ranged from 10 to 50 grams (wet weight).

The sample was placed in a round-bottom flask. After addition of 6N HCl (20 mL 6N HCl per every 10 g sample) and a 10% w/v $SnCl_2$ suspension (to prevent Fe^{3+} from oxidizing sulfide to higher oxidation states such as S°), the flask was connected to the speciation apparatus. The flask containing the sample + HCl was heated from 25°C to 90°C over 1/2-hour under an N_2 atmosphere to release the AVS (Rice and others, 1993). $H_2S_{(g)}$ released during this acid/heating step is swept by the N_2 gas into a series of 3 glass traps. Phosphate buffer (pH 4.0) in the first trap maintains sulfide as $H_2S_{(g)}$; the last two traps contain 0.1 M $AgNO_3$ that precipitates the sulfide as Ag_2S.

After AVS was recovered as Ag_2S, the organic-clastic residue + HCl solution was rinsed with deionized water (DI) through a 0.45 µm filter, air dried (25 °C), and weighed. The filtered HCl solution was analyzed for major and trace element concentrations using inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Briggs, 1990). The total amount of sulfide recovered was determined using a gravimetric conversion for Ag_2S and is reported as ppm total sulfide ($S^{2-}_{(tot)}$). The presence of recoverable AVS and trace metal(s) in a sample is not proof that the metal resides in a sulfide phase. However, in organic-rich, sulfidic sediments, trace metals are likely to be associated with organics or AVS but not an oxidized phase like Fe-oxide.

Organic content was estimated by the proportion of peat plus wood fragments (or "chips") to clastic sediment. Fragments are tan-to-dark brown macroscopic pieces of wood that generally do not exceed 2.5 cm (1 in) along any dimension. Visible high organic content was one of the major criteria used to separate samples into the different intervals.

Core Locations, Descriptions, and Results

Thirty-eight samples from six cores in the wetland were treated to recover AVS; the leachates were then analyzed for 40 major and trace elements. This data is tabulated and presented in Appendix 1. Core locations are shown on the map in Figure 1, and core stratigraphy, element abundances, and FeS recovery (yield) are described below. The variation and abundance of metals in the AVS fraction are illustrated using downhole plots of 1)major elements (Ca, Al, Fe, K, Mg, P, Si, Ba, and Mn) and 2)trace metals (Cd, Co, Cr, Cu, Ni, Pb, V, and Zn). For each core, the first plot shows major elements while the second plot shows trace metals. On both plots, total sulfide (in ppm $S^{2-}_{(tot)}$) is also shown.

The discussion that follows focuses on the major elements Fe and Al, and the trace metals Pb, Zn, and Cu, although other elements on the plots are discussed as needed. These 5 elements, as noted previously, are among the most abundant in sediment and water samples from Animas Basin watersheds (Church and others, 1997).

Core FQ3

This core was taken 9 m (30 ft) southwest of the Fe-oxide pond and contains the lowest concentrations of Al, Fe, Pb, Zn, and Cu of the 6 cores (Figure 3A). The analyzed samples cover a depth interval from 41 to 163 cm (16-64 in).

The maximum Fe value (240 ppm) is found in the 41-71 cm interval; Fe then decreases towards the bottom of the core to 28 ppm in the 132-163 cm interval. Although the uppermost interval (0-41 cm) was not analyzed, its macroscopic appearance was similar to other core intervals except that it lacked wood fragments. Aluminum values cluster in a narrow range from 27 to 34 ppm, including 30 ppm in the 41-71 cm interval. From the surface to bottom of the core, Ba decreases slightly, Ca and Mn increase slightly, and other major element concentrations vary only slightly, as illustrated by the nearly vertical lines on Figure 3A.

Pb in the 41-71 cm and 132-163 cm intervals was 0.17 and 0.13 ppm, respectively; Pb was not detected in the 2 middle layers (71-102 cm and 102-132 cm). Zn was the only metal present in detectable concentrations in the 6N HCl solution from all 4 intervals, and ranged from 1.6 to 5.9 ppm (Figure 3B). Cd, Cr, and Cu were not detected in any interval.

Thus, both Pb and Zn have their maximum abundance in the 41-71 cm interval. Similarly, other trace metals either had detectable concentrations in only the 41-71 cm interval (Ni, V) or were undetectable (Cd, Cr). Co in the 41-71 cm interval was 0.32 ppm, but in the 71-102 cm interval, Co was only 0.03 ppm, a value very close to the detection limit (0.02 ppm). Co was not

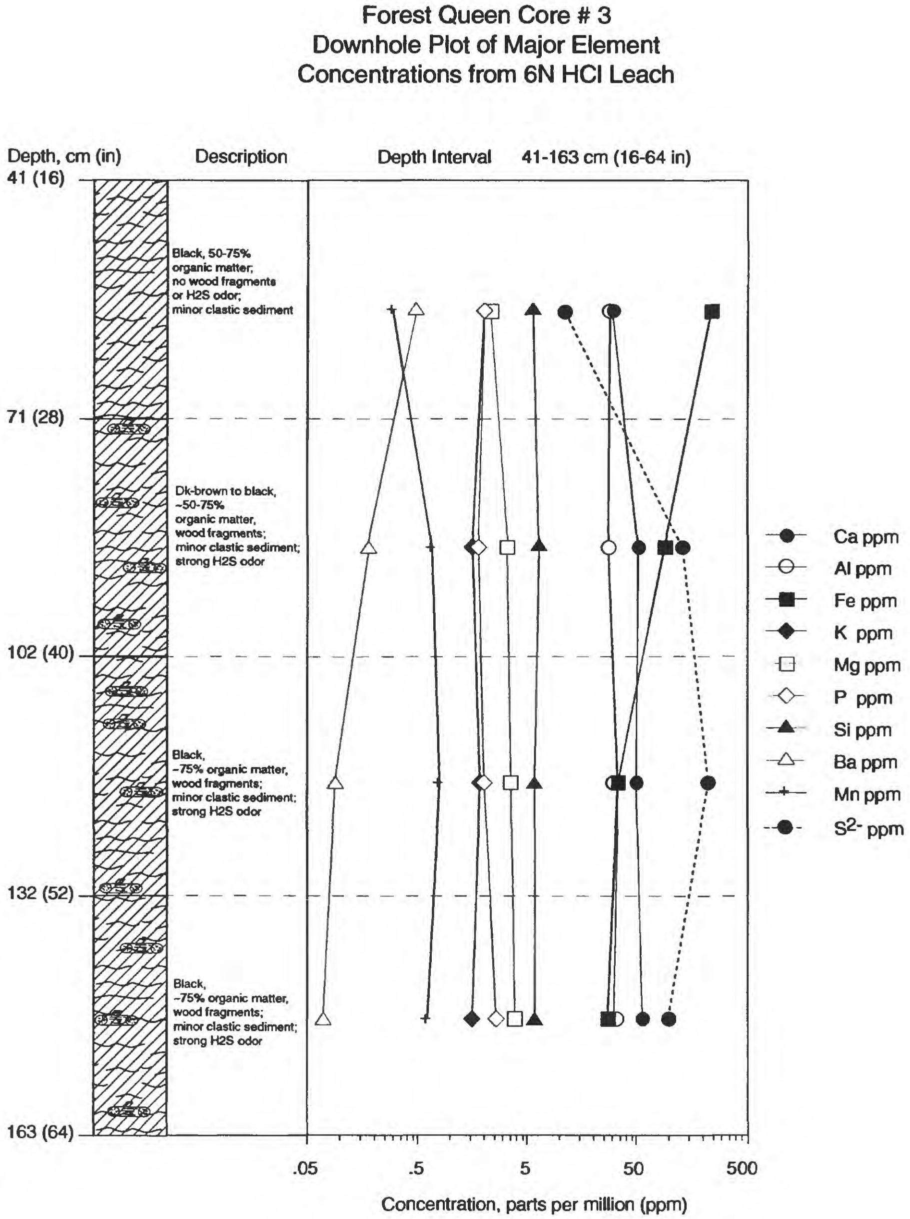
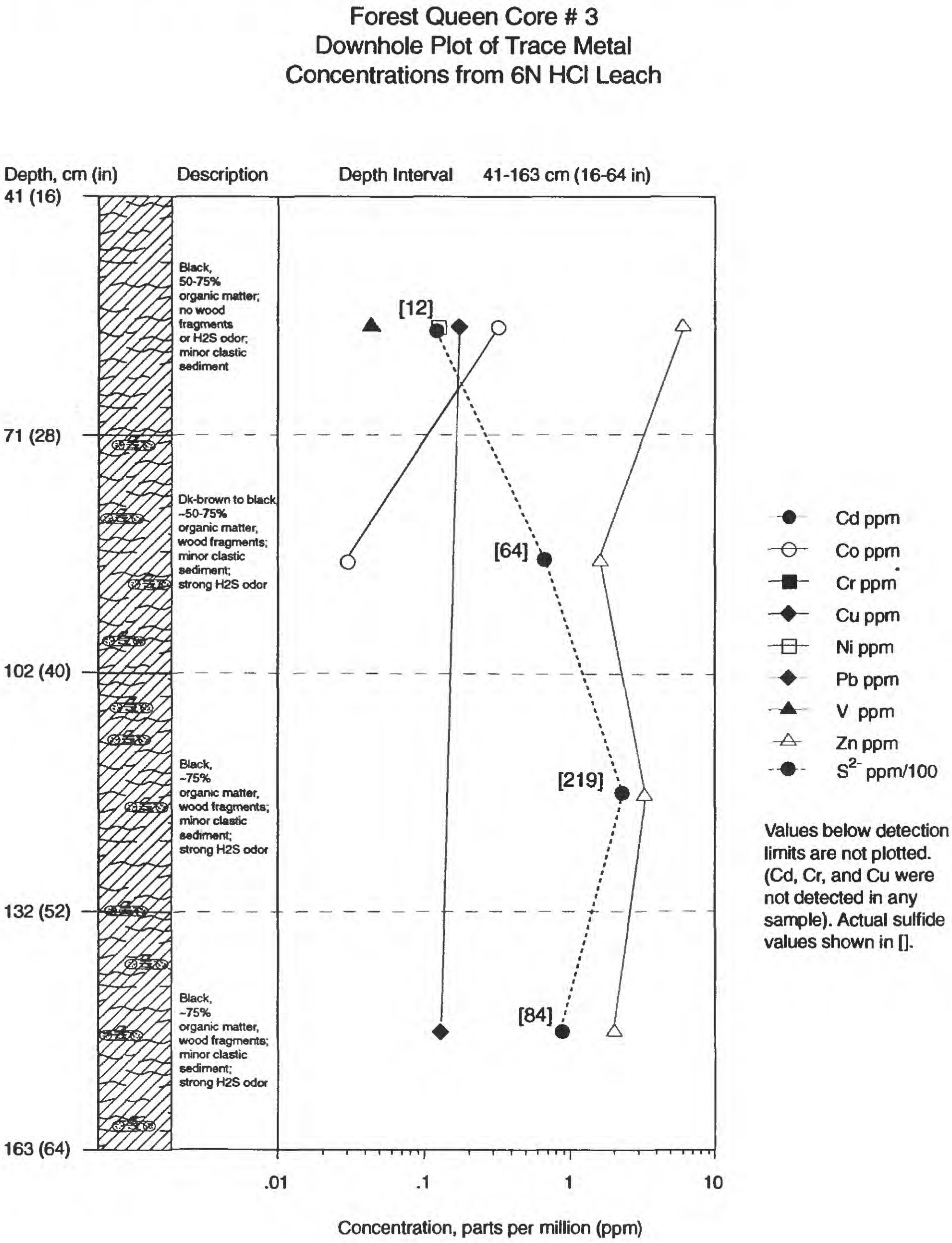


Figure 3A. Downhole plot of major element concentrations in 6N HCl leachate from Forest Queen core #3.

detected in the 2 deepest intervals. If metal sorption by the solids is actively occurring in Core #3, it appears to happen in the uppermost 71 cm (28 in) which consists almost wholly of organic matter.

The 41-71 cm sample was black but had lower organic content (50-75%, primarily peat) than deeper levels and no H_2S odor, whereas the other 3 deeper intervals were also black, had a strong H_2S odor, and equal or higher organic matter content (~75%, primarily wood fragments). The black color in all 4 intervals suggests FeS, yet trace metal abundances in the AVS-leached solution are low compared to other cores.



Values below detection limits are not plotted. (Cd, Cr, and Cu were not detected in any sample). Actual sulfide values shown in [].

Figure 3B. Downhole plot of trace metal concentrations in 6N HCl leachate from Forest Queen core #3.

The results from Core #3 are somewhat surprising because the high $S^{2-}_{(tot)}$ yields below 71 cm (28 in) indicate abundant FeS and thus potential immobilization of metals in AVS solids. However, as Figure 3A illustrates, trace metal abundances are low (compared to cores "downstream" (south) of the pond), and only Zn shows some variability in the core. The relative lack of metals in Core #3 suggests the area is not well-connected hydrologically with inflow (surface and possibly subsurface) waters at depths greater than about 71 cm. Core #3 is located SE and away from the Fe-oxide pond whose major outflow is directly to the west. Although FeS formation is active, dissolved metals from surface flow are either not reaching this area or not transported to deeper parts of the wetland; thus metals are not being sequestered within AVS. Alternatively, metals may be most strongly associated with Fe-oxide in the uppermost 41 cm. When the core was extracted, the wetland surface was damp but not flooded, and coated by large amounts of Fe-oxide, suggesting little recent flow of water into the area and oxidation of aqueous Fe.

Core FQ4

This core is 9 m (30 ft) directly west of the Fe-oxide coated pond and directly in the path of the major surface outflow from the pond. The length of analyzed core covers the interval from 20 to 152 cm (8-60 in). As before, composite samples were used for AVS work, and in addition, a "discrete" 1-cm sample at 41 cm was taken to qualify the effect that "dilution" by compositing had on the metal values.

Most major element concentrations do not vary greatly within the organic-rich layers up to the 81 cm depth (Figure 4A), although the sample at 41 cm showed higher Ba, Si, P, and Fe values. Below 81 cm, most major metal values tend to increase, especially in the 99-117 cm interval, but Fe and Si show slight decreases. The highest Fe (750 ppm) is present in the upper organic-rich interval at 41 cm and decreases with depth as in core #3. The high Fe in the upper levels is probably a result of the sediments being in the direct path of the Fe-oxide pond outflow. Periodic flushing of the pond (spring runoff?) probably results in delivery of large amounts of solid Fe-oxide to this area of the wetland.

In contrast to Fe, Al generally increases with depth and reaches its maximum abundance (210 ppm) at the bottom (142-152 cm) of the core. Most other major elements tend to follow Al in this respect. The increases may be due to a larger proportion of silicate sediment in the deeper levels of the core that provides a source of "leachable" elements (Ca and Mg, for example).

There are 2 intervals in Core #4 where trace metals (Zn, Pb, Cu) are found in relatively-higher concentration in the 6N HCl leach solution - the 41-61 cm (including the 41 cm sample) and 142-152 cm intervals (Figure 4B). Zn and Cu in the 41-61 cm interval are 6.8 and 0.30 ppm, respectively, while Pb and Zn in the 142-152 cm interval are 4.0 and 6.6 ppm, respectively. The highest Zn concentration was 13 ppm in the 41 cm sample, while Pb was highest in the 142-152 cm interval.

This result is similar to Core #3 where the greatest Zn concentration was in the organic-rich uppermost 60 cm of core, and suggests Zn is being adsorbed in the upper layers as metal-bearing water flows over and/or percolates into the upper organic-rich layers. The dominantly dark-gray color of sediment in this interval (despite some red color on outer surfaces) is indicative of FeS. As Figure 4B shows, Zn steadily decreases to less than 2 ppm at the 99-117 cm interval, then increases to 6.6 ppm in the 142-152 cm interval. Cu was present in the four upper organic-rich samples, but not in the silicate-sediment intervals below 81 cm. Pb generally mimics Zn in the upper 81 cm, but then increases in the organic-rich 99-117 cm and 142-152 cm intervals that contain black lenses.

AVS data from Core 4 indicate that sulfate reduction ceases below approximately 102 cm (40 in) in this area. No sulfide was recovered from the

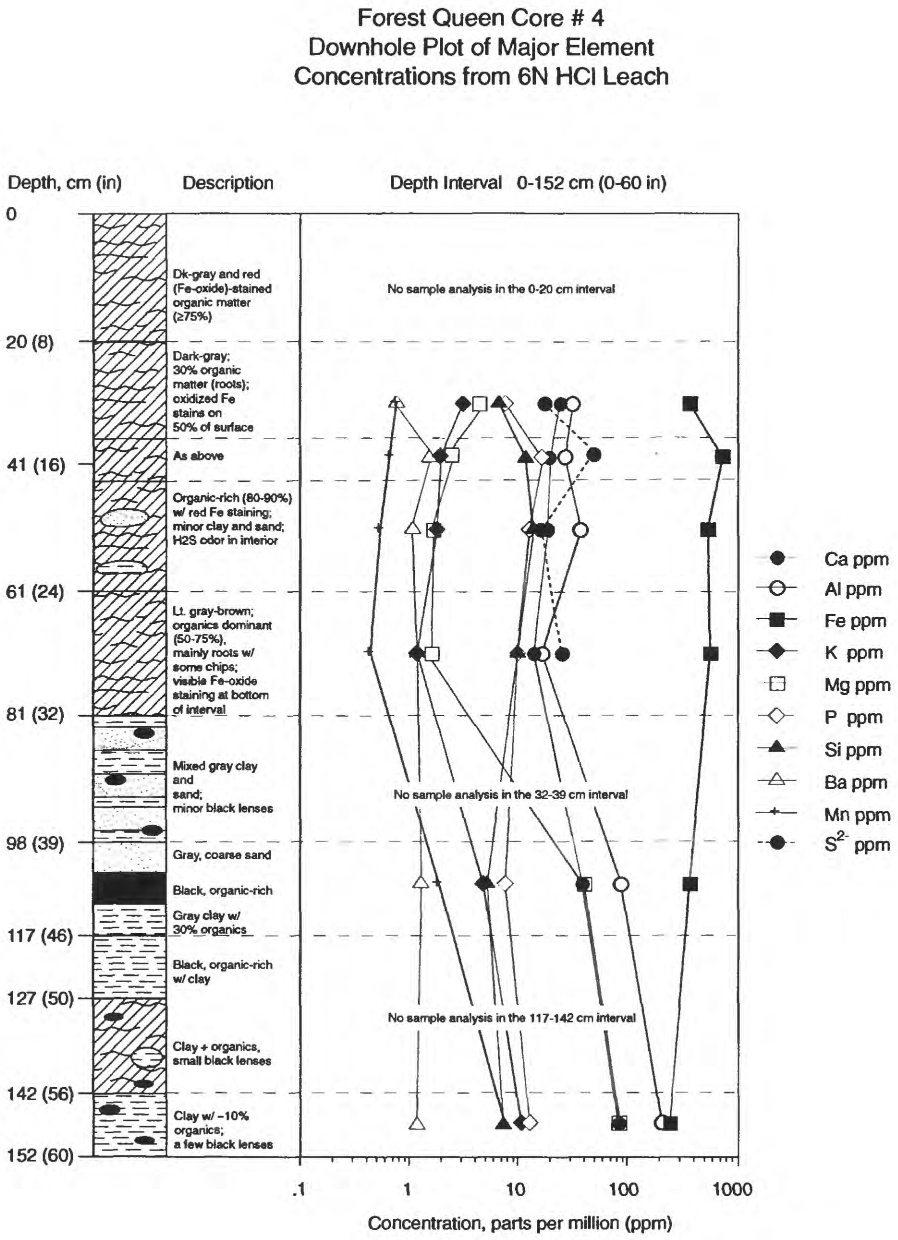


Figure 4A. Downhole plot of major element concentrations in 6N HCl leachate from Forest Queen core #4.

6N HCl leach of 2 of the deepest intervals (99-117 cm and 142-152 cm) in this core.

The high metal content in the 41-61 cm interval is probably associated with organic matter or Fe-oxides because $S^{2-}_{(tot)}$ recovered from the 6N HCl leach was relatively low (16.8 ppm). In the 142-152 cm interval, there were black lenses that indicated "fresh" FeS, but the zero yield of Ag2S (i.e, no sulfide) argues against these black lenses containing any AVS.

The only black, organic-rich layer in this core (99-117 cm) showed lower Zn but higher Pb compared to lighter-colored, organic-rich layers. Zinc

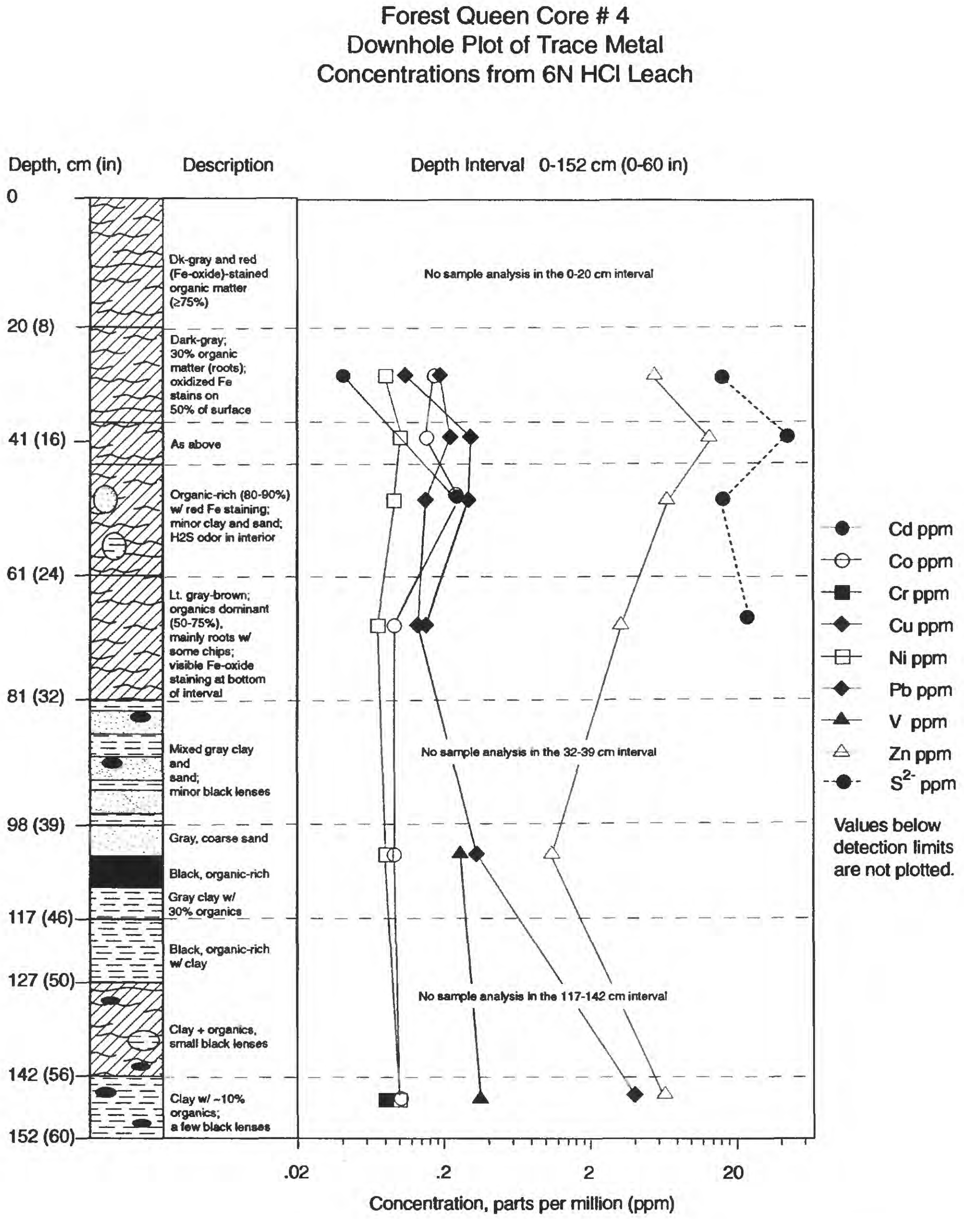


Figure 4B. Downhole plot of trace metal concentrations in 6N HCl leachate from Forest Queen core #4.

decreases from its highest concentration (6.8 ppm) at 41-61 cm to 1.1 ppm at 99-117 cm. The lack of sulfide in the 41-61 cm sample interval correlates with the lowest Zn concentration, suggesting FeS is not responsible for trapping Pb and Zn in this particular core at or below 99 cm (39 in). Zn is therefore associated with either organic matter or Fe-oxide but not FeS.

Core FQ5

Core #5 is located about 10 meters (30 ft) northwest of the Fe-oxide pond and represents an interval from 0-183 cm (0-72 in).

As in Core #4, samples from Core #5 contain relatively-high major and trace metal abundances at 2 different levels (Figures 5A and 5B). Pb and Zn are highest in the 81-102 cm interval at 5.4 and 12.0 ppm, respectively. Cu and Al are highest in the 122-145 cm interval at 1.1 and 210 ppm, respectively. Fe differs from other metals in that it remains high (290-350 ppm) over the 4 intervals (76-81 cm to 122-145 cm) where these higher metal values are present.

The two organic-rich intervals containing higher metals (81-102 cm and 122-145 cm) are separated by a gray layer of silt-clay sediment at 102-122 cm that shows evidence of Fe-oxidation, primarily rootlets whose outer surfaces are colored red (assumed to be Fe-oxide). Pb and Zn concentrations in the 102-122 cm interval (Pb=4.0 ppm; Zn=8.8 ppm) do not vary greatly from those in the organic-rich layers that encompass it, illustrating that both clastic and organic layers can contain similar trace metal concentrations.

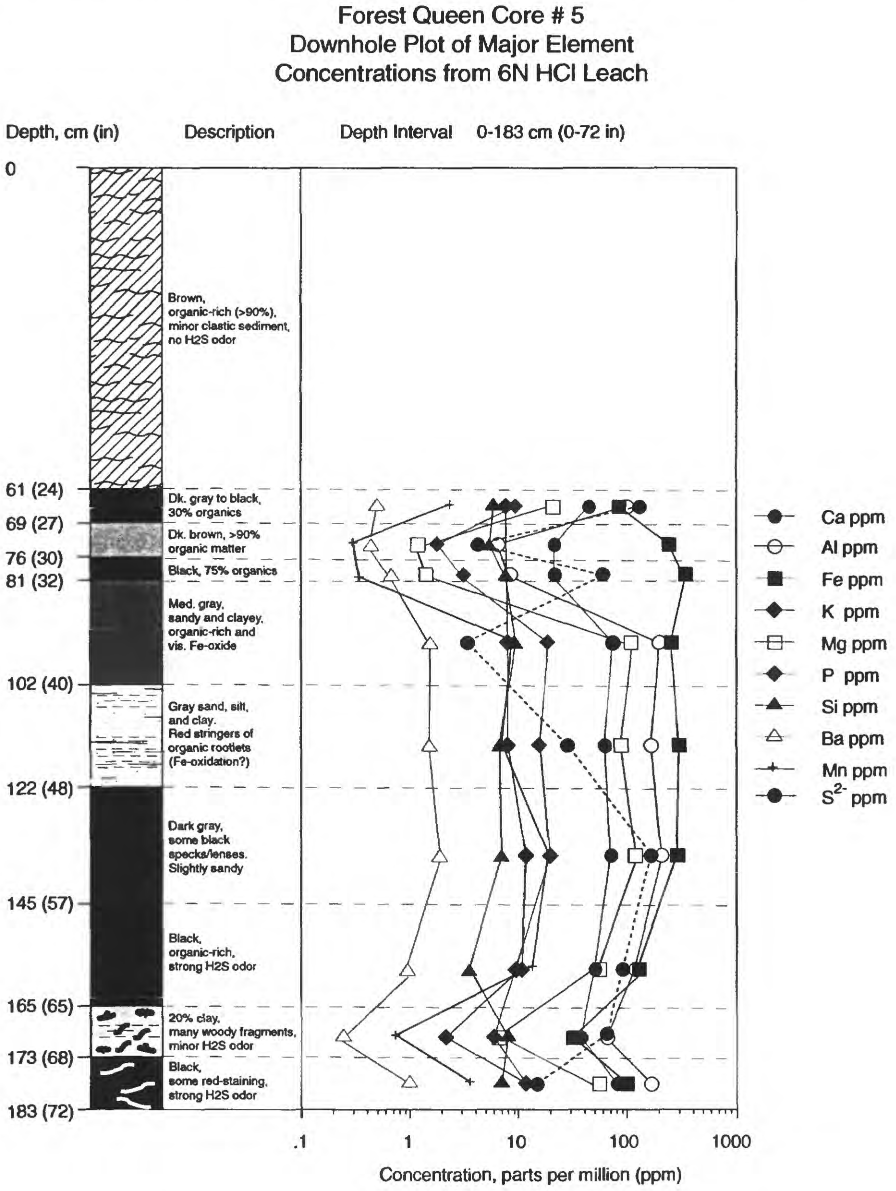

Forest Queen Core # 5
Downhole Plot of Major Element
Concentrations from 6N HCl Leach

Figure 5A. Downhole plot of major element concentrations in 6N HCl leachate from Forest Queen core #5.

The black interval with a strong H_2S odor from 145-165 cm did not show the highest metal abundances. In fact, Pb and Zn are about one-half their values in the intervals covering 81-145 cm. Furthermore, the 165-173 cm interval shows an even sharper decrease in Pb and Zn concentrations compared to the 145-165 cm interval. The 165-173 cm interval contains 20% clay, much woody material, and had only a slight H_2S odor. The 173-183 cm interval exhibits an increase in Pb and Zn concentrations, however, relative to the 165-173 cm interval.

Despite the varied types of host materials, the differences in metal concentrations in 6N HCl leachates from Core 5 samples are small over the entire interval from 81-183 cm, where Pb ranges from about 3 to 5 ppm and Zn ranges from about 5 to 12 ppm. The exception is the 165-173 cm interval where

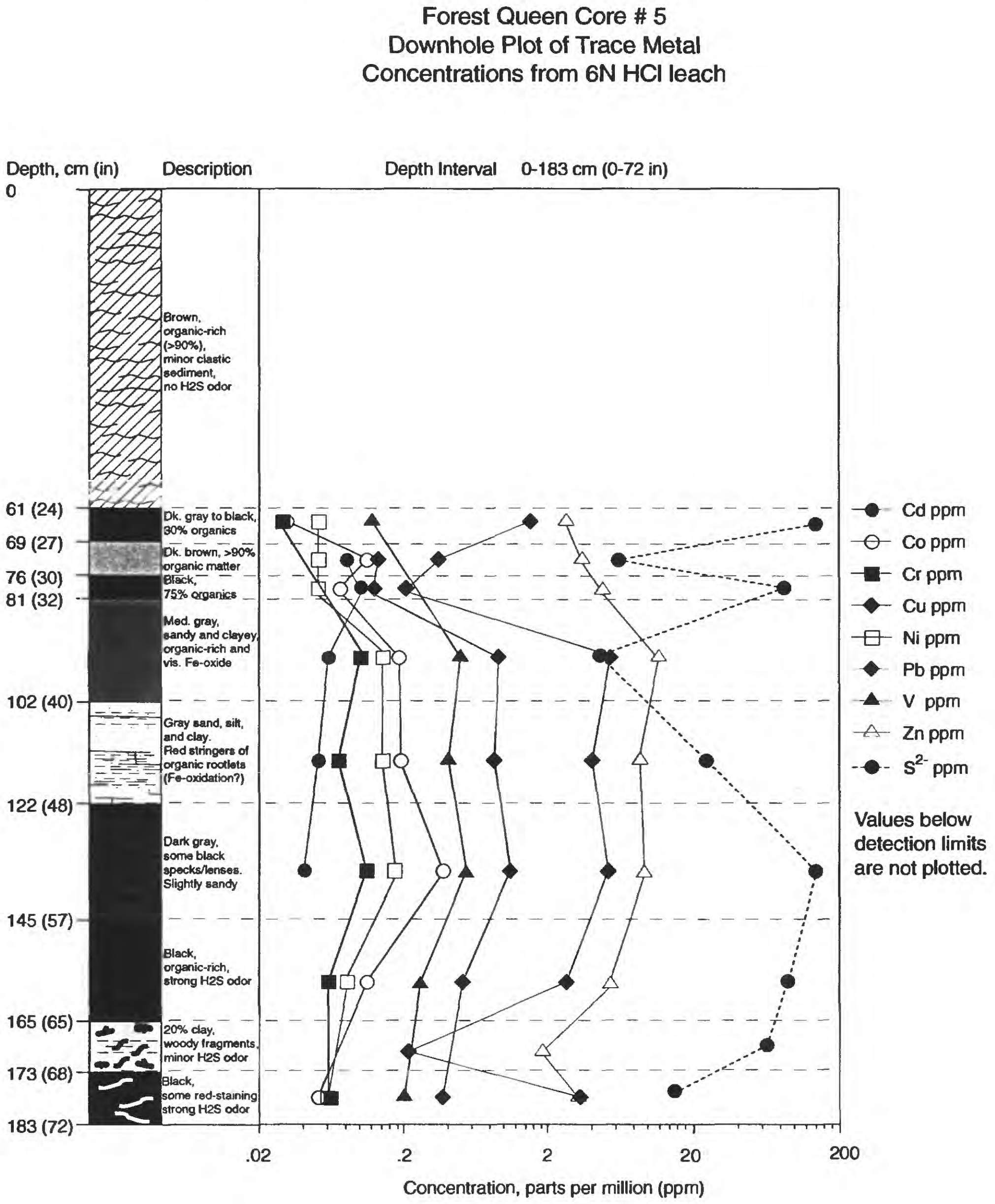


Figure 5B. Downhole plot of trace metal concentrations in 6N HCl leachate from Forest Queen core #5.

Pb and Zn both decrease. The similarity of metal contents in Core #5 suggests that clastic and organic sediment are equally capable of sorbing metals in the wetland. However, the residence of metals within specific mineral phases in the clastic sediements or specific compounds in the organic fraction is not known.

Core FQ7

Core #7, about 45 m (150 ft) west of the Fe-oxide pond on the western edge of the wetland, encompasses the 0-246 cm (0-97 in) interval and is enclosed (at the surface) on 3 sides by ponded water (see Figure 2). Core #7 is the deepest of the cores and illustrates the complexity of the wetland stratigraphy. As shown in Figures 6A (major elements) and 6B (trace metals), organic-rich upper layers are succeeded by increasingly clastic (clay, silt, and sand) sediments with depth.

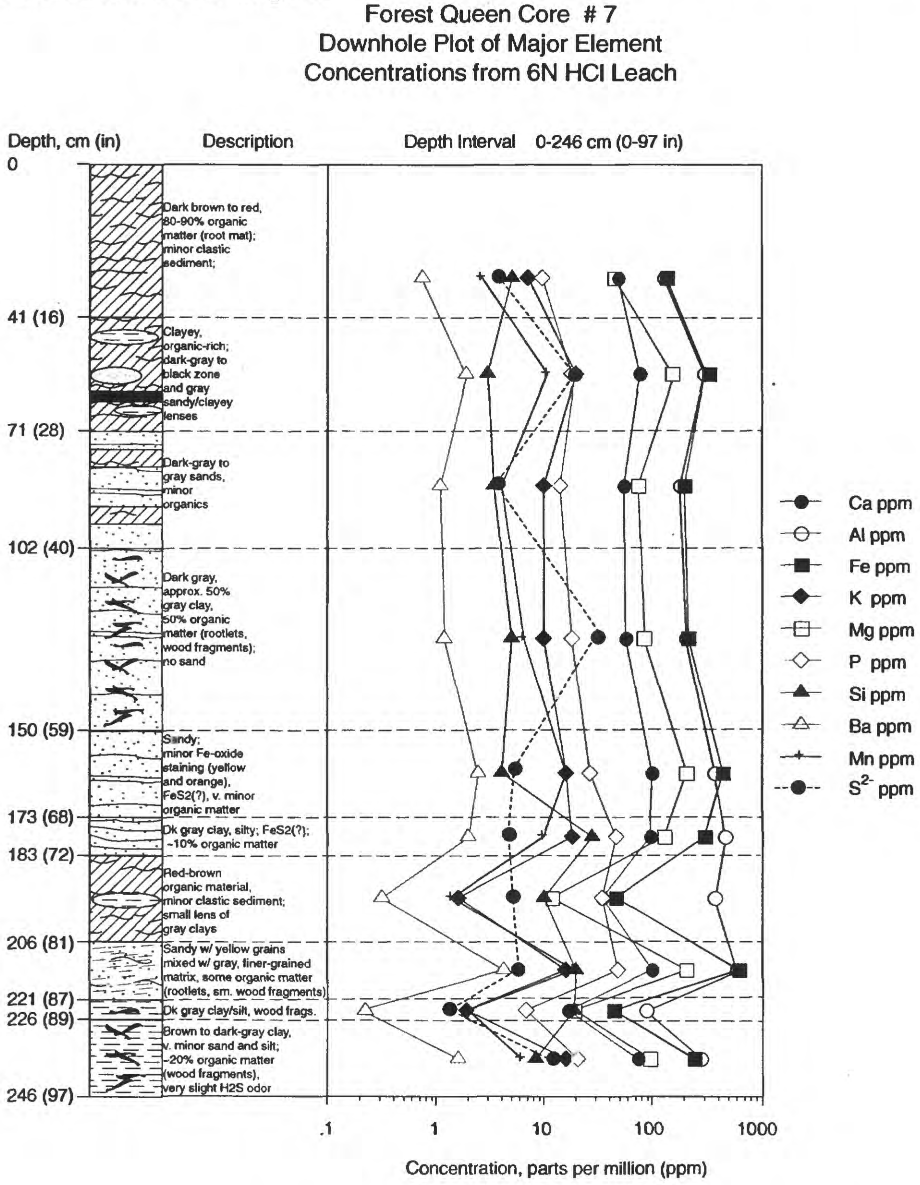


Figure 6A. Downhole plot of major element concentrations in 6N HCl leachate from Forest Queen core #7.

Al and Fe are at fairly high values (>100-400 ppm) downhole until 183-206 cm where Fe drops dramatically from 300 ppm to 45 ppm. Al, however, changes less dramatically, from 400 to 300 ppm. In the next interval, 206-221 cm, Fe and Al increase to nearly equal values of 600 ppm, then both drop below 100 ppm at 221-226 cm before increasing once more to ~250 ppm from 226-246 cm. The large variations in Al and Fe abundances, especially from approximately 183-246 cm (72-97 in), suggest significant changes in local chemistry or sediment composition. Because the sulfide content is fairly uniform over the 183-246 cm interval, the increasing clastic and decreasing organic content is likely responsible for the variable element concentrations.

Regression plots of Fe, Cu, Zn, and Pb vs $S^{2-}_{(tot)}$ (Figures 7A-D) indicate two sample populations in Core 7. This is interpreted as 2 different associations of each metal - an amount associated with monosulfide and an

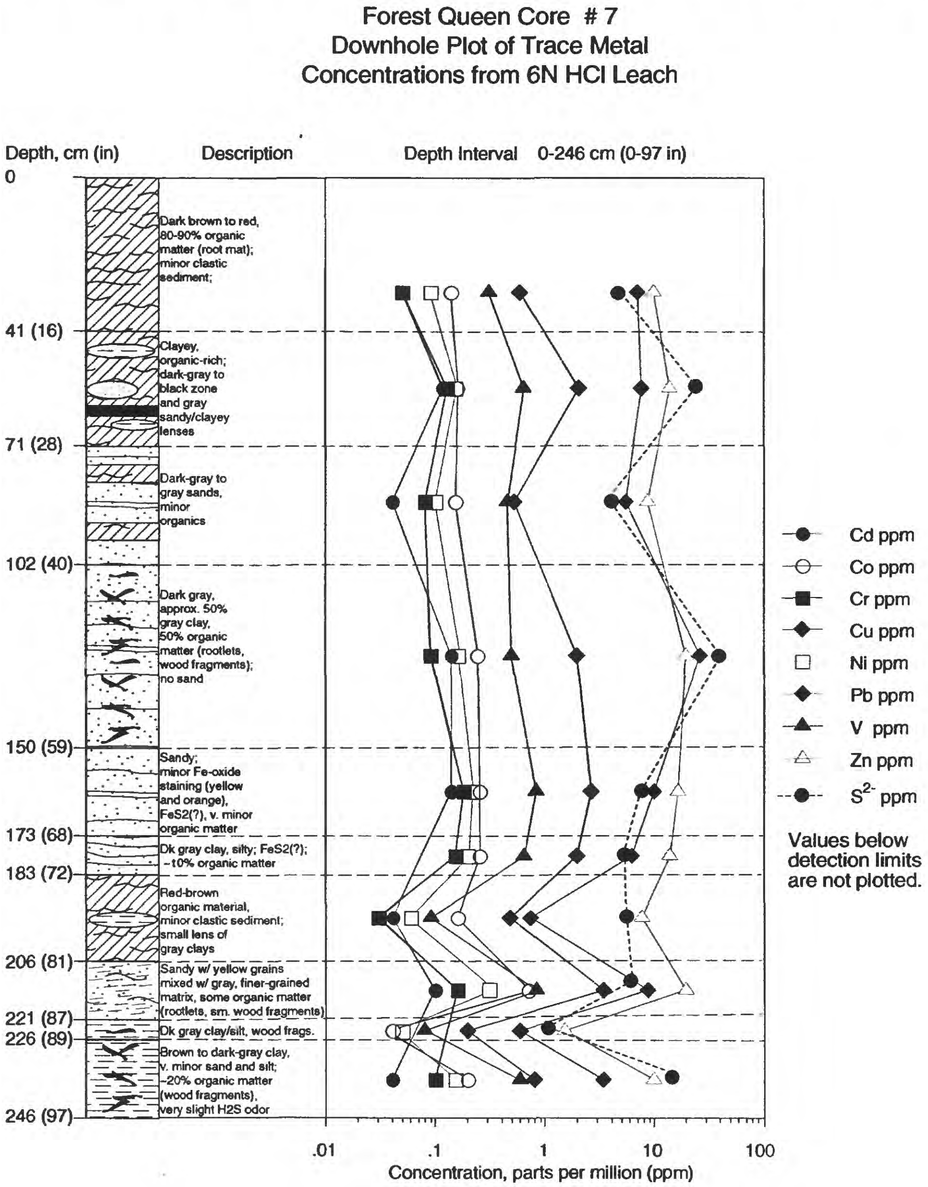
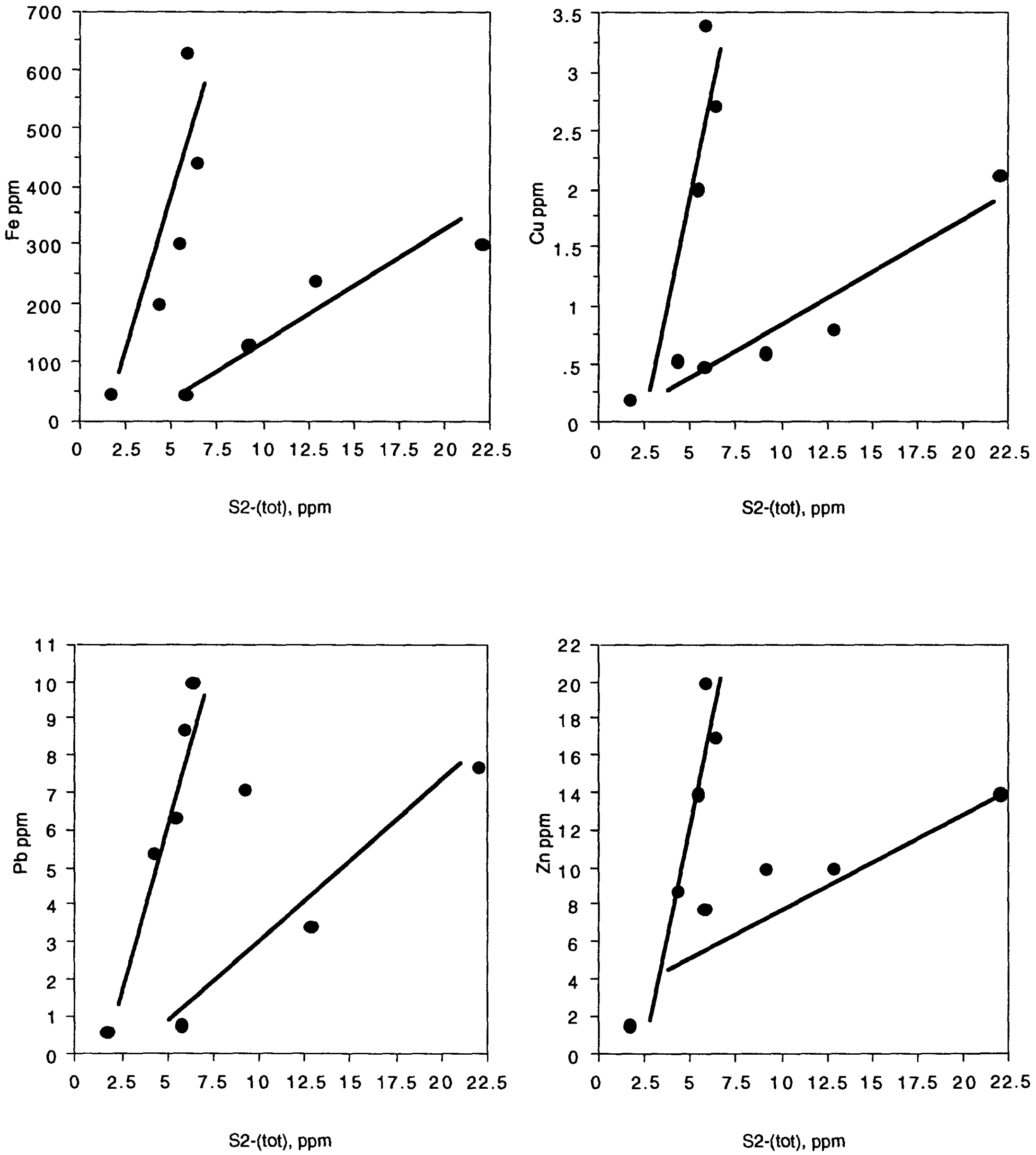


Figure 6B. Downhole plot of trace metal concentrations in 6N HCl leachate from Forest Queen core #7.

amount not associated with monosulfide. The non-monosulfide component is probably detrital sulfide-bearing material derived from sources such as mineralized country rock, or ore spilled from railroad cars or used for road ballast. This material, particularly if it consisted of larger grains or FeS_2, ZnS, or PbS, would not dissolve in 6N HCl. (The outlying sample, the 40-59 cm interval, is excluded. When included, it "forces" a strong correlation with Pb but the other 3 metals show little change in correlation with sulfide).

The gently-sloping lines on the right sides of Figures 7A-D indicate slightly-increasing metal content with large increases in monosulfide.



Figures 7A-D. Scatter diagrams of Fe, Cu, Pb, and Zn versus $S^{2-}_{(tot)}$, showing relationships of trace metal content to total sulfide in Core #7. The steep-sloping lines consist of samples dominated by clastic (clay, silt, and sand) sediment and low $S^{2-}_{(tot)}$; gentler-sloping lines are from samples dominated by organic sediment with high $S^{2-}_{(tot)}$.

Steeply-sloping lines on the left sides of Figures 7A-D, where metal content increases sharply with only slight increases in monosulfide, indicate the ore sulfide (detrital) component. The steep metal increase is probably due to metal associations with ore sulfide rather than with monosulfide.

Generally, the steeper line is made up of the samples having higher clastic (sand, silt, and clay) content, while the lower-sloping lines are primarily organic-rich intervals. However, much of the clastic material is at too great a depth to have been deposited by anthropogenic means (mining, railroad and road building). Thus, it appears that the original detritus deposited at the base the Forest Queen wetland was enriched in Pb and Zn.

In traversing the wetland from east to west (from Core 3 towards Core 7), the sediments change from having a high organic content to those that have an increasingly clastic content, particularly below about 61 cm (24 in). Although no ages for these deeper clastic sediments have been determined, they were probably present (i.e., deposited by the E. Fork of the Animas River) prior to building of the railroad and automobile road.

Vincent (USGS, pers. comm., 1999) obtained ^{14}C dates for several layers in the wetland. An accumulation rate of approximately 1 m peat (organic matter) per 1,000 years was postulated for the "growth" of the wetland. Thus, metals found in sediments below about 0.1 m (which would be have been deposited >100 years ago, before the advent of mining in the area) may have been fixed in the sediments prior to mining. However, more exact methods (e.g., Pb-210 geochronology or isotopic work) would be needed to determine the timing of metal fixation during wetland accumulation. Fe-oxide staining was present in 2 intervals in Core 7, the upper 0-16 cm and in the 59-68 cm interval. Except for the deeper clastics, the sediments were dark gray-brown to black, with several intervals exhibiting an H_2S odor.

Core FQ9

This core was taken approximately 25 m (80 ft) southeast of the Fe-oxide pond. Core #9 is a short interval 0-76 cm (0-30 in) and consists almost wholly of organic material. Because of the limited interval and consistent composition, only 3 samples were analyzed from this core. The middle interval, 20-61 cm, produced the largest sulfide yield of all samples (430 ppm).

As Figure 8A illustrates, most major element abundances down this core vary little and show similar trends. With the exceptions of Si and P, major elements increase from the 0-20 cm interval to the 61-76 cm interval. Fe and Al show systematic increases in concentrations with increasing depth.

Despite the moderate-to-high sulfide yields from all intervals (and a very high yield of 430 ppm from the middle (20-61 cm) interval), trace metals are relatively low in these core samples (Figure 8B). Zn ranges from 2.3 to 7.1 ppm, and similar to most cores, is in greatest abundance in the uppermost sample (0-20) cm rather than in deeper samples. Pb is present in low concentration in the 6N HCl leachate, ranging from 0.49 to 0.61 ppm. Other trace metals were present in varying but small abundances, and except for Co, were not detected in every sample. For example, Cu and Cd were detected in only the upper 0-20 cm while Cr was found only in the 61-76 cm interval. Vanadium was present in the 2 lower intervals, whereas Ni was found in the upper and lower, but not middle, intervals.

Organic content was at least 60% and up to 100% in the upper 61 cm, and major Fe-oxide staining was noted primarily in the upper 0-20 cm. In the lowest 61-76 cm, organic matter still comprised about 40% of the sample and Fe-oxide staining was not observed. Unidentified mineral(s) in the 61-76 cm interval resembled pyrite, but the presence of FeS_2 in the sample has not been confirmed. The moderate to high yields of sulfide in these core samples indicate that sulfate reduction activity was high. However, abundant Fe-oxide in the upper 20 cm (8 in) indicates that a strongly-reducing environment had

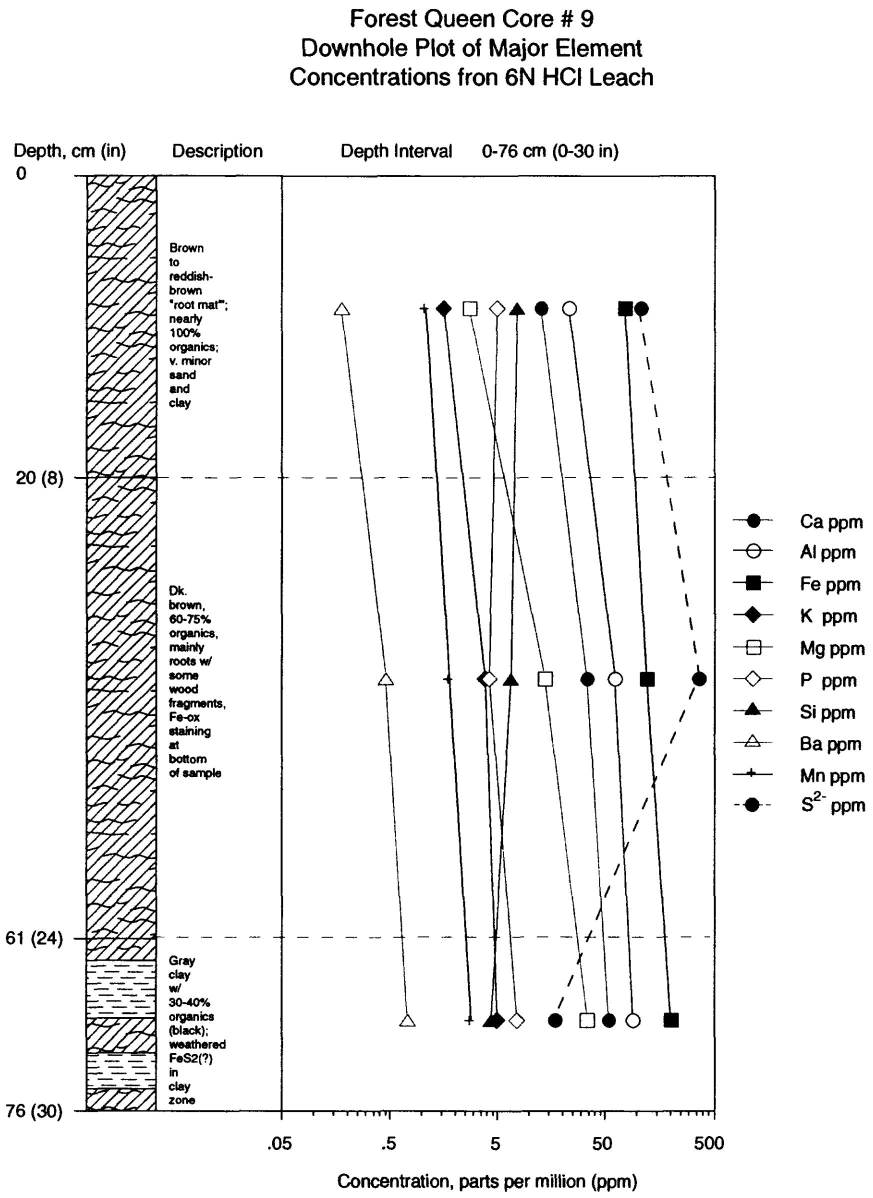


Figure 8A. Downhole plot of major element concentrations in 6N HCl leachate from Forest Queen core #9.

not been established in this level and area of the wetland at the time of sampling. At the bottom of the 20-61 cm interval (which produced the highest sulfide yield), only minor Fe-oxide was noted; this may have been an artifact of storage.

Thus, high sulfide yields in core #9 showed only relatively small concentrations of trace metals, indicating that metal trapping by monosulfide is inefficient or not occurring in this portion of the wetland.

Core FQ10

This core was taken at the greatest distance from the source of influent adit waters at approximately 55 m (180 ft) west of the Fe-oxide pond on a

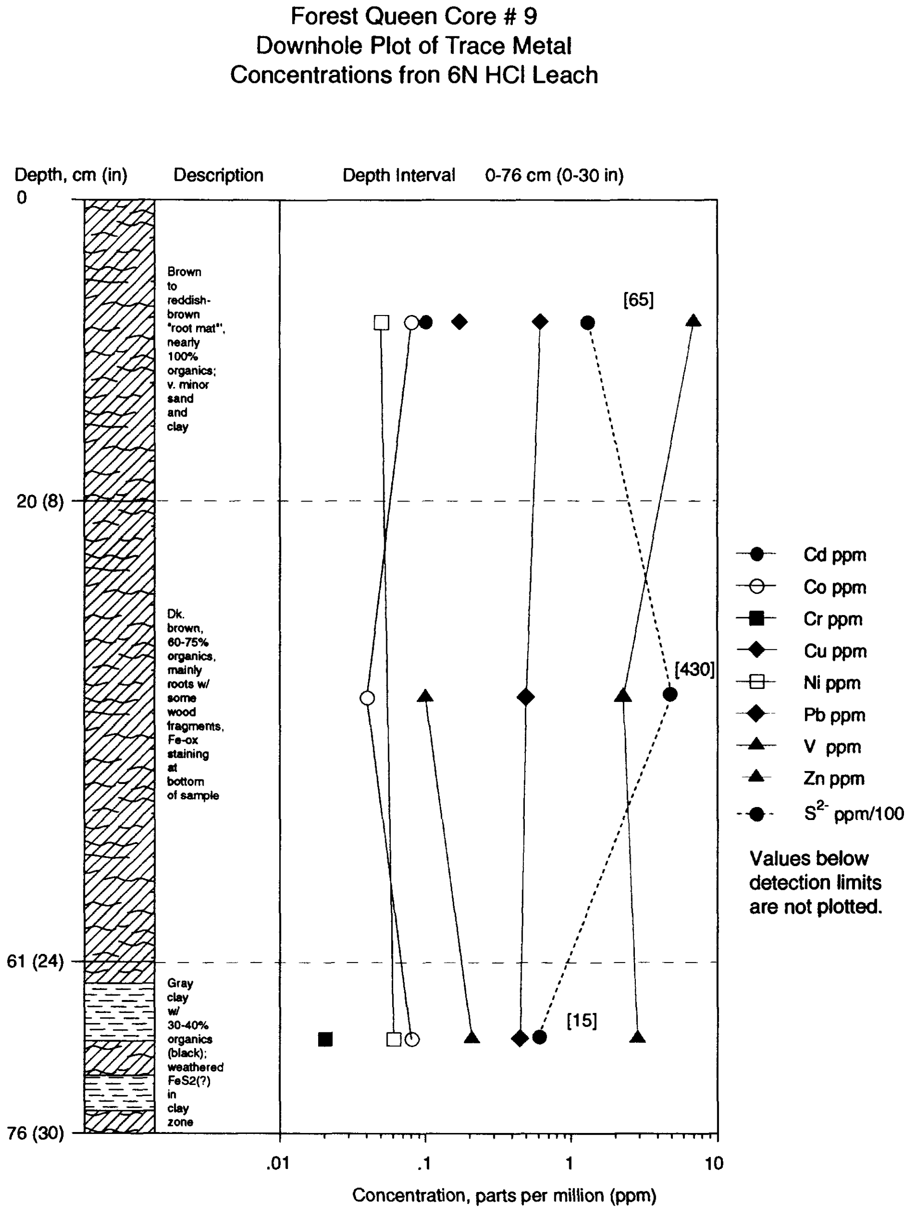


Figure 8B. Downhole plot of trace metal concentrations in 6N HCl leachate from Forest Queen core #9.

small point of dry land 2m (6 ft) higher than the wetland and 5m (15 ft) east of the automobile road. The core covers an interval from 0-58 cm (0-23 in). In contrast to all other cores examined, the uppermost 53 cm (21 in) of Core 10 is dominantly brown to light-yellow sand and clay, rather than organic matter; organic material is present only in the bottom 53-58 cm. Because of the generally similar (brown, sandy, no visible organics) character of the upper 53 cm of sediment, only samples from the lower sandy interval (33-53 cm) and the black organic interval (53-58 cm) were analyzed. The results described below concern only these two samples.

Fe concentrations in the 6N HCl leachates are 540 ppm (33-53 cm) and 95 ppm (53-58 cm) as shown in Figure 9A. The zero AVS yield and lower Fe from the black 53-58 cm layer clearly demonstrate a lack of any AVS, and especially FeS. Al exhibits a decrease similar to Fe, from 190 ppm in the upper layer to 60 ppm in the lower layer.

Pb, Zn, and Cu concentrations are at much lower concentrations (Figure 9B) than Fe or Al but show similar downhole decreases. Pb and Zn are also relatively higher in the samples from Core #10. In the 33-53 cm interval, Pb is 6.6 ppm and Zn is 20 ppm (equal to the highest Zn concentration in any 6N HCl leachate). In the 53-58 cm interval, Pb is 3.7 ppm and Zn is 12 ppm.

Core 10 contains the two samples with the highest measured Cu abundances of all cores, 6.3 ppm in the 33-53 cm interval and 5.4 ppm in the 53-58 cm interval. Interestingly, Cu in the 33-53 cm interval is associated with the

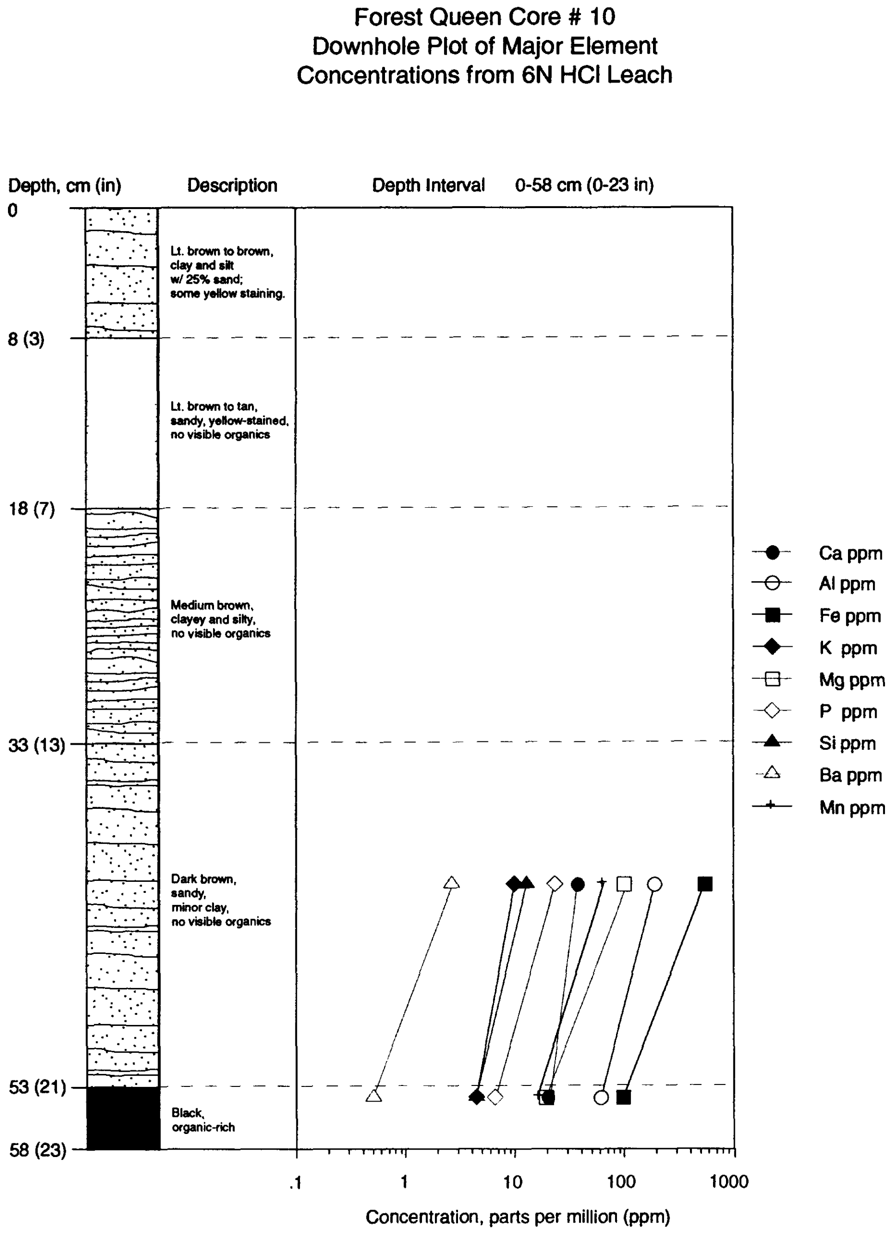


Figure 9A. Downhole plot of major element concentrations in 6N HCl leachate from Forest Queen core #10.

oxidized yellow sands and clays (clastic layers in the wetland were almost always gray or dark-gray), whereas high Cu in the 53-58 cm interval is associated with the black, organic-rich layer.

All other wetland cores contain approximately 50-100% organic matter in the upper 53 cm (24 in). The presence of the black layer of organic material at the base of Core 10 suggests this area was once part of the wetland but was isolated at some time in the past, perhaps as a result of automobile road or railroad grade construction. Based on the sediment type (sand, clay), grain size, and color, and the lack of organic matter, water, and any "fresh" (AVS) sulfides in the upper section of the core, the area where Core 10 was taken appears to be no longer sedimentologically or hydrologically connected to the wetland. And because this core is closest to the road and railroad grade, it

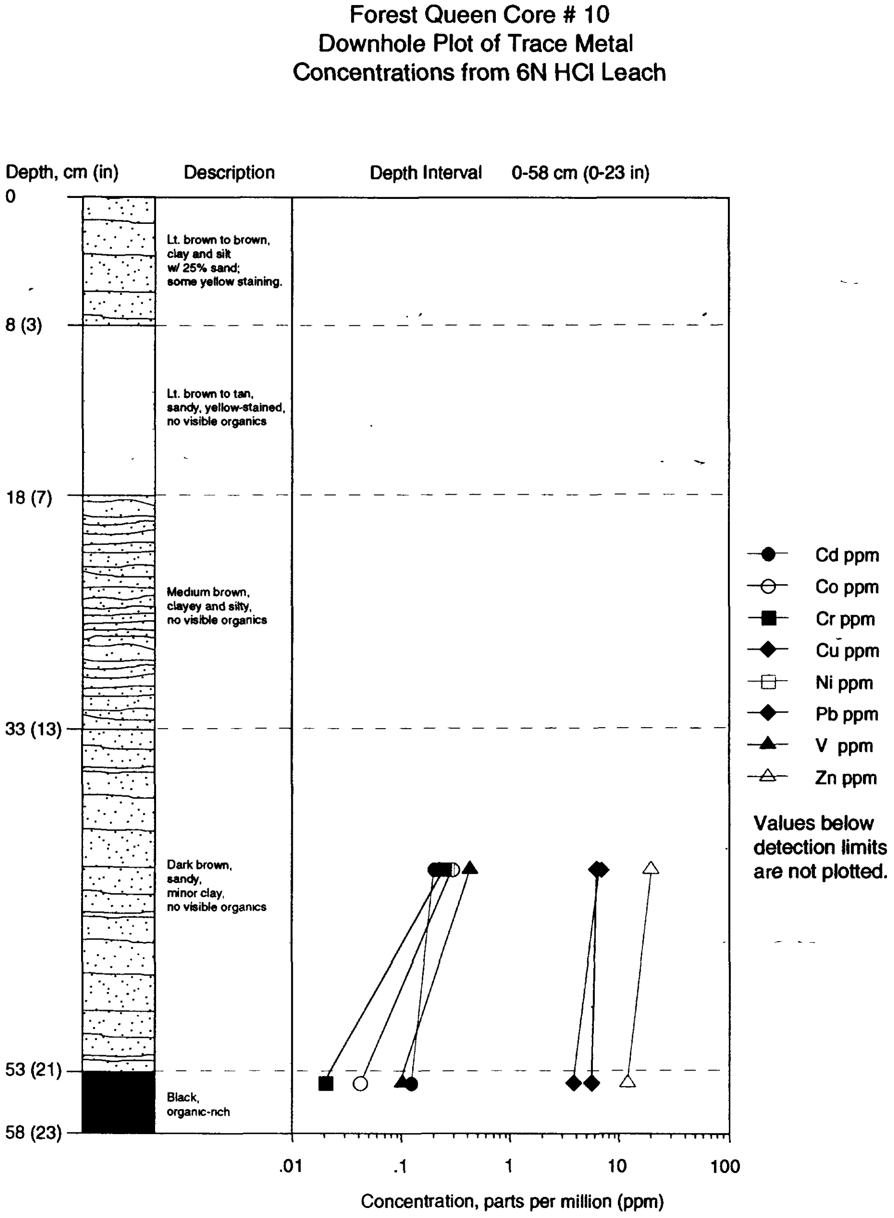

Forest Queen Core # 10
Downhole Plot of Trace Metal
Concentrations from 6N HCl Leach

Figure 9B. Downhole plot of trace metal concentrations in 6N HCl leachate from Forest Queen core #10.

is likely that clastic sediment higher in the core is windblown or anthropogenically-transported material used for road and railroad maintenance.

Fe-oxide may have been present in the 33-53 cm interval as evidenced by a dark brown color but was not visible in the black 53-58 cm layer. AVS was not recovered from the 6N HCl leach of either of these high-Cu samples. Therefore, Fe-oxide or "ore" sulfide must be responsible for the high Cu in the 33-53 cm interval, and organic matter may be the reason for high Cu in the 53-58 cm interval, but AVS could not be the residence for Cu in either sample.

The black color in the 53-58 cm interval of Core 10 is probably Mn-oxide; isolated thin layers (2-7 cm (1-3 in) thick) of Mn-oxide were observed in other areas away from the center of the wetland. Mn in the black layer is 17 ppm; among all cores, this is the 4th-highest Mn concentration. Mn in the 33-53 cm interval is the highest of all samples (64 ppm), however, no black color is imparted to the sediment. The dark brown color of the 33-53 cm interval may represent a mixed Mn/Fe-oxide, but the mineralogy of the layer has not been determined.

DISCUSSION

AVS Content

Yields of sulfide (as ppm $S^{2-}_{(tot)}$) varied widely from sample to sample in each core. The largest yields (≥200 ppm) came from dark (black, brown), organic-rich layers. The smallest yields (0-10 ppm) came from lighter-colored or red (Fe-oxide-stained) organic or silicate sediment layers. Intermediate FeS yields (≥10-200 ppm) were from dark-gray to brown organic layers and from silicate sediment with small black lenses which appeared to be "fresh" FeS forming in place.

The highest yields of AVS do not consistently coincide with the highest major or trace metal abundances (Al, Fe, Pb, Zn, Cu), and high metal abundances are present in samples that produced little or no AVS. While high metal concentrations in the 6N HCl leachate were often observed when FeS yields were large, this was not always the case. For example, the highest Pb (27 ppm) and Zn (20 ppm) in Core 7 come from a layer that contains about 50% gray clay and 50% organic matter, and produced an intermediate yield of 36 ppm $S^{2-}_{(tot)}$. Yet, the second-highest Pb and Zn values (10 and 17 ppm, respectively) in Core 7 are from a yellow-sand, gray-clay layer immediately below the high Pb/Zn layer which has minor organic matter content and produced only 6 ppm $S^{2-}_{(tot)}$. In contrast, Pb and Zn are quite low (0.49 ppm and 2.3 ppm, respectively) in the sample from Core 9 that produced the highest AVS yield (430 ppm $S^{2-}_{(tot)}$) of all samples.

Metals Concentrations

Major and trace metals present in high concentrations in the 6N HCl leachates were Fe, Al, Pb, Zn, and Cu. However, concentrations of these metals associated with the AVS fraction are not always elevated, even though they are all present in water that drains into the wetland from the adit. Pb and Zn were detected in nearly all samples from each core; in contrast, Cu was detected in far fewer samples from each core. Among all core samples, the maximum value of Pb is 27 ppm (Core 7); Zn is 20 ppm (Cores 7 and 10); and Cu is 6.3 ppm (Core 10); see Figure 10. The variable trace metal concentrations associated with the AVS indicate that metal removal by sulfide is sporadic, perhaps slow, and subject to oxidation that may release AVS-metals. These results also indicate that metals are associated with non-AVS phases, such asorganic matter, clastic (silicate or sulfide) sediment, and Fe-oxide. Because the samples were not dried prior to AVS treatment, an unknown concentration of metal in each sample is also associated with the aqueous phase (residual water). Based on aqueous analyses (T. Wildeman, written comm., 1998) which show Pb and Zn present in water at an order of magnitude less than in the solids, the total amount of metal associated with residual

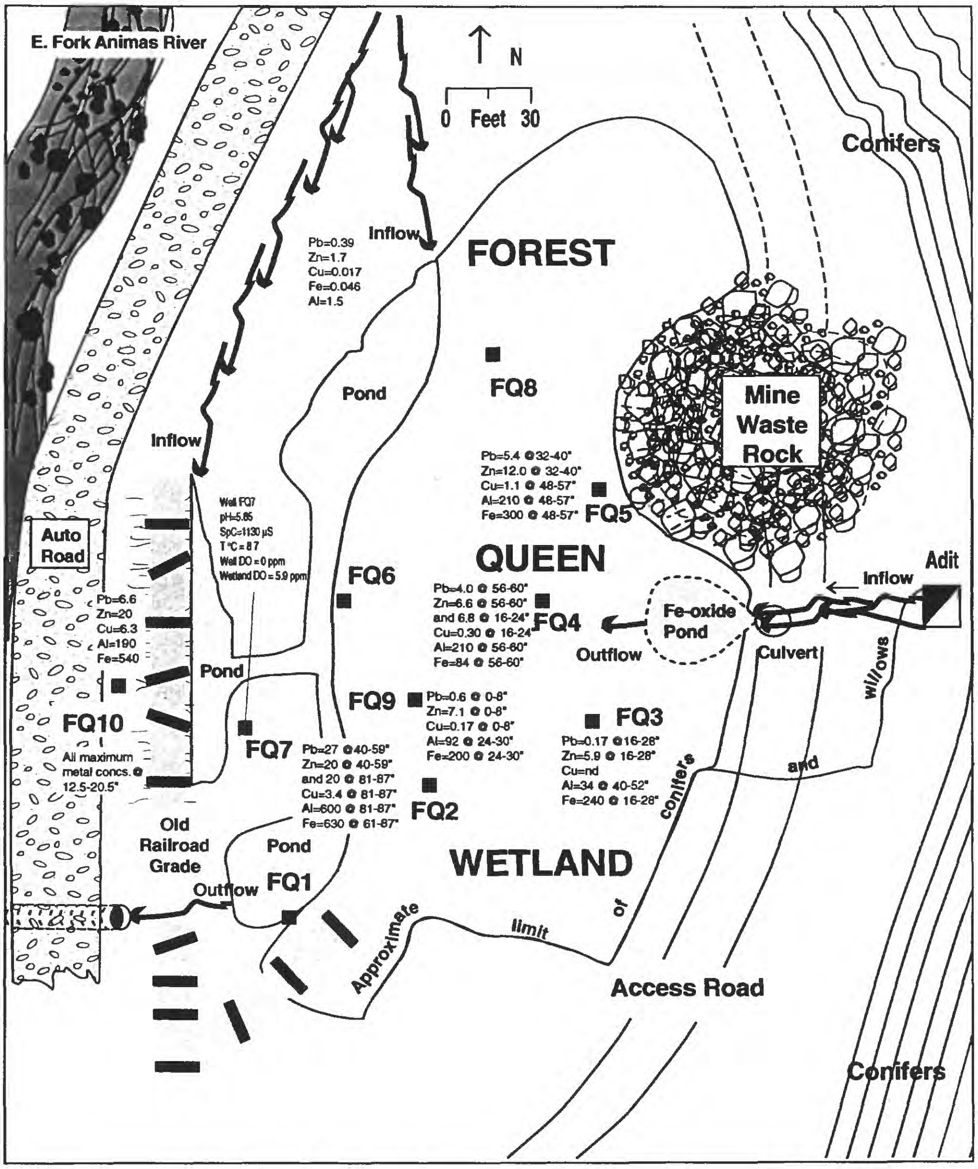


Figure 10. Map showing depths at which maximum concentrations of Pb, Zn, Cu, Al, and Fe are present in solid phases in Forest Queen wetland.

water in the core samples is likely to be small relative to that in the solid phases.

Fe and Al exceed several hundred ppm in many samples; this is not unexpected because of the large input of Al and Fe into the wetland. The large pond located a few feet above and east of the wetland (Figure 2) is coated with several mm of Fe-oxide, and Al substitutes for Fe to a great extent in Fe-oxides such as goethite (Fortin et al., 1993).

Al and Fe concentrations in AVS leachates are relatively consistent downhole (100-500 ppm) in most cores. Increases in Fe are usually seen when a red or brown zone (indicative of oxidized Fe) is encountered; Al concentrations generally increase when a clastic sediment layer is present.

Figures 11 and 12 show Pb and Zn concentrations from several cores

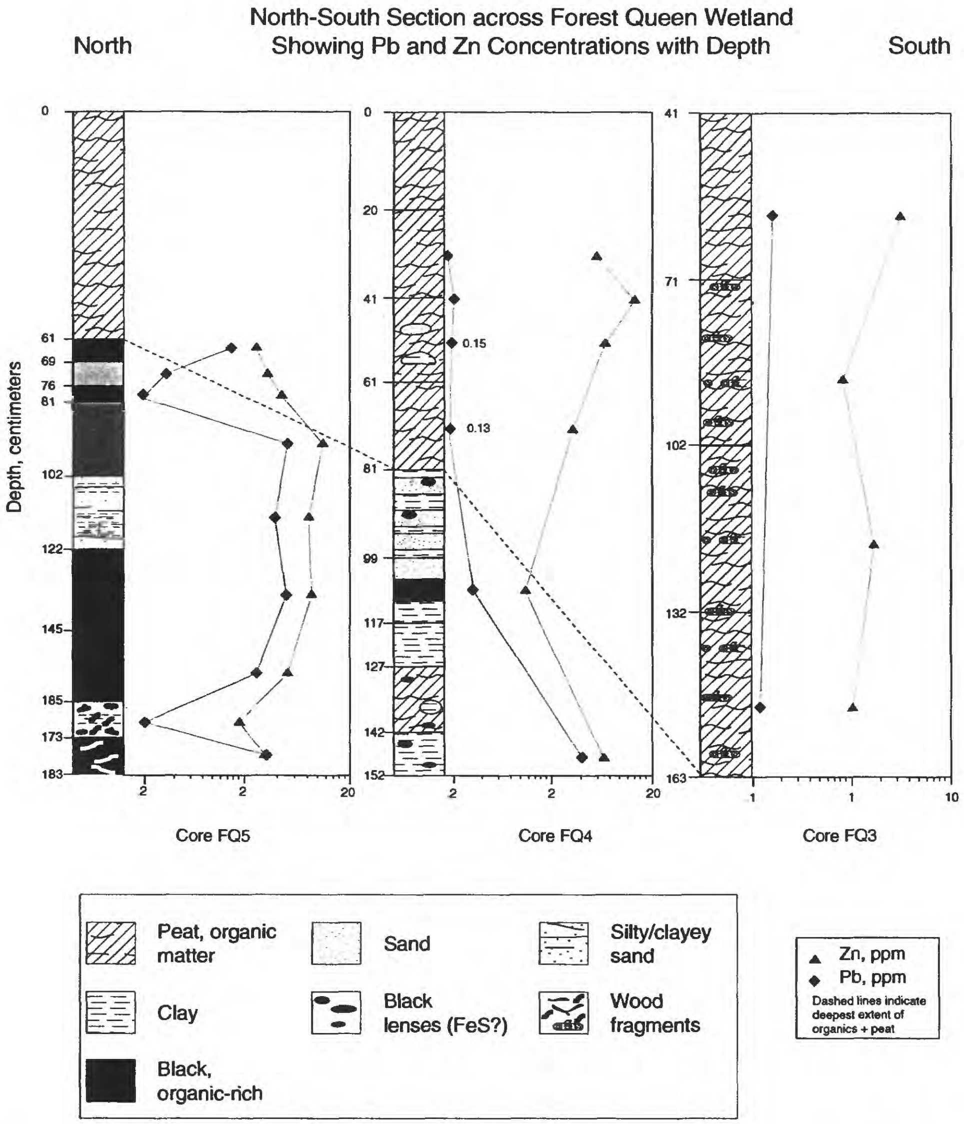


Figure 11. Lead and Zn concentrations in solids along N-S profile.

aligned N-S (cores 5, 4, and 3) and E-W (cores 4, 9, 7, and 10). Pb and Zn concentrations are generally higher in the upper portions of cores, and decrease from N to S and from E to W. This suggests that Pb and Zn fixation happens closest to the adit (source) waters, that Pb and Zn fixed in the (upper) core solids originated from the adit source waters, and that fixation is strongest in the upper, usually organic-rich, layers. However, some high Pb and Zn is found in the deeper parts of cores 4 and 7 (see Figure 10). Those values suggest that another deeper source of metal-bearing water or solid may be present.

CONCLUSIONS

Trace metal contents associated with AVS are not greatly elevated in solid samples, and high or maximum metal concentrations are not always associated with black intervals or those with H_2S (for example, core 3). Often, intervals that exhibited some red staining also had high metal values. The highest abundances of Pb, Zn, Cu, Al, and Fe are often but not consistently found in black, organic-rich layers, with equal or lesser concentrations in red or brown organic layers, and the smallest concentrations generally in clastic sediments. Core 10 is an exception in having high metals in clastic sediments; those sediments probably originated in part from ore that fell from railroad cars or was used in road building.

The variable red-to-brown staining indicative of iron oxide may have resulted from oxidation during short-term core storage. However, even during sampling, Fe oxide was observed in samples up to 1m (3 ft) deep. Sulfate reduction was not occurring in all core locations or at similar depths in the wetland, and at this time of year the wetland appeared to be drying out, as evidenced by low water level. In contrast, during the spring sampling, 3-4 cm of water covered about 70% of the wetland surface, and H_2S was measured in every core and water sample taken. Drying and lowered water levels allow air diffusion and Fe-oxidation to take place at greater depths in the wetland

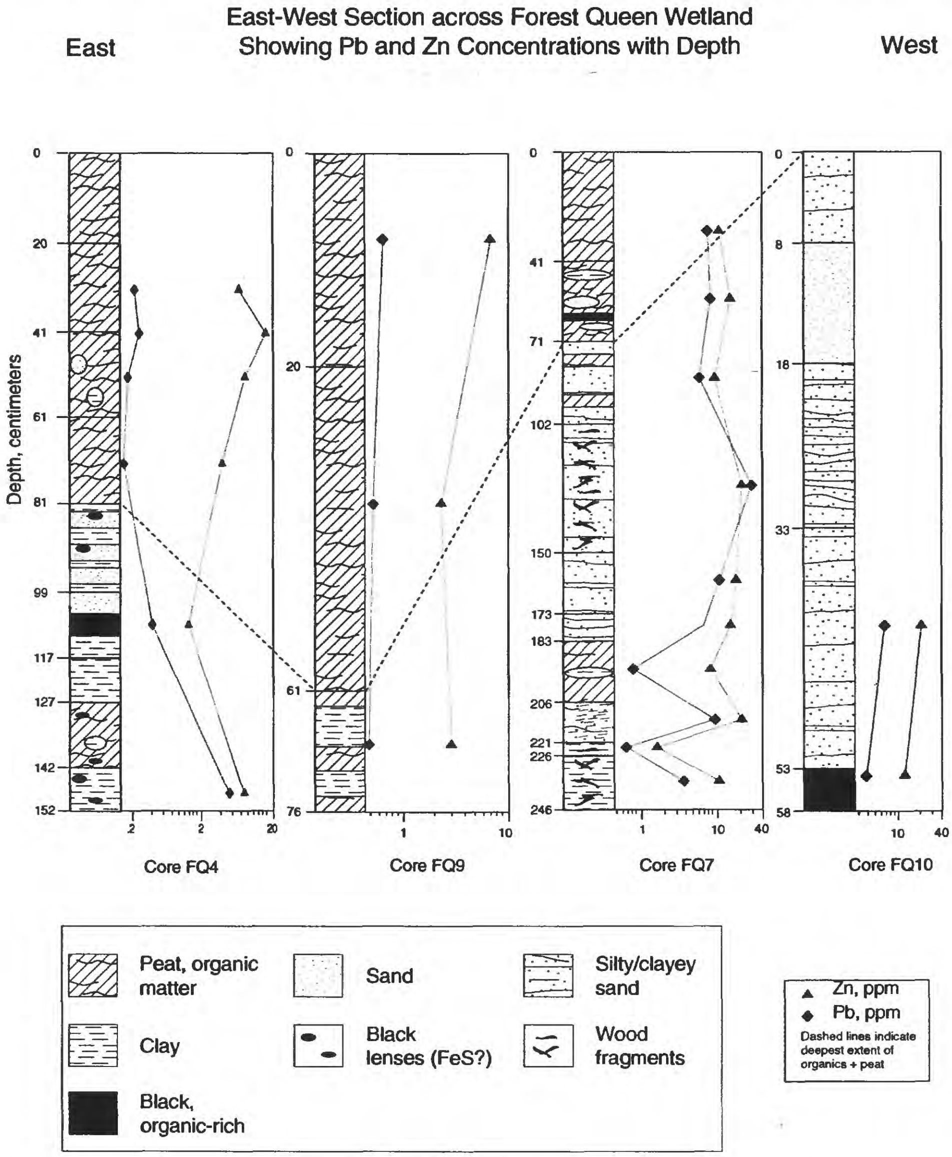


Figure 12. Lead and Zn concentrations in solids along E-W profile.

sediments. Thus, sulfate reduction, metal immobilization by AVS formation, or metal release by AVS oxidation, are all subject to variability as a result of seasonal changes.

While no single explanation for the variability in metal concentrations in the solid phases is evident, it appears that the hydrologic flowpath in the wetland is changeable and leads to fluctuations in the delivery of aqueous phase metals to isolated pockets of sulfate reduction or Fe-oxidation within the sediment column. The presence of 2 zones of relatively-enriched trace metal (Pb and Zn) concentrations implies that aqueous metals may be moving along 2 different paths in the wetland sediments. The most obvious path is metal-bearing surface (adit) water percolating downward into the sediments. Another potential path is (metal-rich? acidic?) regional groundwater moving downgradient from higher slopes which then upwells beneath the wetland (Pavlik and others, 1999). Upon encountering the sulfate-reducing zones, metals could become entrapped by reaction or co-precipitation with sulfide phases.

The Forest Queen wetland will likely continue to provide scattered removal of metals by sequestration within AVS, Fe-oxide, and organic solid phases. However, storage of metals in these solid phases is probably short-lived as a result of seasonal fluctuations of sulfate-reduction. In the absence of sulfate-reduction to buffer pH, metals could be resolubilized by newly-introduced acidic water that would aid Fe-oxide dissolution. Acidic pH would also tend to desorb metals from organics. And, lowered water levels in the fall season would allow AVS oxidation and release of sorbed or co-precipitated metals to occur. Thus, the combination of seasonal variations and variable flowpaths leads to intermittent, scattered removal and storage of metals in the wetland.

The efficiency of the FQ wetland in trapping metals from influent waters is also variable and intermittent. Improvement in the wetland's "cleansing" ability might be improved if aqueous flowpaths could be directed to areas where sulfate reduction appears to be maximum. The wetland area around cores 3, 4, 5, and 9 shows the highest sulfide yields and sulfate reduction activities. Artificial methods that enhance sulfate reduction, such as addition of specific nutrients or maintenance of anaerobic conditions by keeping the wetland flooded, might also improve the metal-removal capability (by AVS) in the sediments. These methods could be instituted as part of an engineering program aimed at controlling direction and flowrate of influent waters into the wetland, similar to constructed wetlands that have produced some success in applications to mine drainage remediation.

ACKNOWLEDGMENTS

Ken Leib and John Evans of the USGS-WRD District Office in Durango provided invaluable assistance with collection of sediment cores and on-site analysis of water samples during the fall and spring sampling. Tom Wildeman of the Colorado School of Mines provided access to the wells and additional water data. Funding for this work was provided through Rob Robinson of the Bureau of Land Management (BLM).

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APPENDIX

Appendix. Geochemical data for Forest Queen wetland cores, numbers 3, 4, 5, 7, 9, and 10. All units are ppm (parts per million). "<" signifies values below the detection limit. Ctr Dpth, cm = center depth of sampled interval, in centimeters.

Geochemical data, Forest Queen Cores 3 and 4.

Field No/Depth Interval	Ctr Dpth,cm	Al ppm	Ca ppm	Fe ppm	K ppm	Mg ppm	Na ppm	P ppm	Si ppm	Ti ppm
FQ3 C-5 41-71	56	30	30	240	2	2.3	< 1	2	5.8	< 1
FQ3 C-5 71-102	86	27	53	89	1.6	3.2	< 1	1.8	6.5	< 1
FQ3 C-5 102-132	117	34	49	34	1.9	3.6	< 1	2	5.9	< 1
FQ3 C-5 132-163	147	31	58	28	1.6	3.8	< 1	2.6	6	< 1
FQ4 C-1 20-41	30	32	25	380	3.1	4.5	< 1	7.9	6.8	< 1
FQ4 C-1 @ 41	41	27	19	750	2	2.5	< 1	17	12	< 1
FQ4 C-1 41-61	51	37	19	540	1.8	1.7	< 1	13	14	< 1
FQ4 C-1 61-81	71	17	14	580	1.2	1.6	< 1	10	9.8	< 1
FQ4 C-2 99-117	108	88	39	370	4.8	41	< 1	7.8	5.2	< 1
FQ4 C-2 142-152	147	210	84	240	11	86	1	13	7.4	< 1

Field No/Depth Interval	Ctr Dpth,cm	Ag ppm	As ppm	B ppm	Ba ppm	Be ppm	Bi ppm	Cd ppm	Ce ppm	Co ppm
FQ3 C-5 41-71	56	< 0.04	< 0.2	< 0.1	0.47	< 0.02	< 0.2	< 0.4	0.13	0.32
FQ3 C-5 71-102	86	< 0.04	< 0.2	< 0.1	0.18	0.04	< 0.2	< 0.4	< 0.8	0.03
FQ3 C-5 102-132	117	< 0.04	< 0.2	< 0.1	0.09	0.05	< 0.2	< 0.4	< 0.8	< 0.2
FQ3 C-5 132-163	147	< 0.04	< 0.2	< 0.1	0.07	0.1	< 0.2	< 0.4	< 0.8	< 0.2
FQ4 C-1 20-41	30	< 0.04	< 0.2	< 0.1	0.78	< 0.02	< 0.2	0.04	0.09	0.17
FQ4 C-1 @ 41	41	< 0.04	< 0.2	< 0.1	1.6	< 0.02	< 0.2	< 0.4	< 0.8	0.15
FQ4 C-1 41-61	51	< 0.04	< 0.2	< 0.1	1.1	< 0.02	< 0.2	0.24	< 0.8	0.25
FQ4 C-1 61-81	71	< 0.04	< 0.2	< 0.1	1.2	< 0.02	< 0.2	< 0.4	< 0.8	0.09
FQ4 C-2 99-117	108	< 0.04	< 0.2	< 0.1	1.3	< 0.02	< 0.2	< 0.4	0.38	0.09
FQ4 C-2 142-152	147	< 0.04	< 0.2	< 0.1	1.2	3E-2	< 0.2	< 0.4	0.71	0.1

Field No/Depth Interval	Ctr Dpth,cm	Cr ppm	Cu ppm	La ppm	Li ppm	Mn ppm	Mo ppm	Ni ppm	Pb ppm	Sb ppm
FQ3 C-5 41-71	56	< 0.2	< 0.2	0.04	< 0.4	0.3	< 0.04	0.13	0.17	< 0.1
FQ3 C-5 71-102	86	< 0.2	< 0.2	< 0.4	< 0.4	0.66	< 0.04	< 0.4	< 0.8	< 0.1
FQ3 C-5 102-132	117	< 0.2	< 0.2	< 0.4	< 0.4	0.81	< 0.04	< 0.4	< 0.8	< 0.1
FQ3 C-5 132-163	147	< 0.2	< 0.2	< 0.4	< 0.4	0.63	< 0.04	< 0.4	0.13	< 0.1
FQ4 C-1 20-41	30	< 0.2	0.11	< 0.4	0.04	0.76	< 0.04	0.08	0.19	< 0.1
FQ4 C-1 @ 41	41	< 0.2	0.3	< 0.4	< 0.4	0.67	< 0.04	0.1	0.22	< 0.1
FQ4 C-1 41-61	51	< 0.2	0.29	< 0.4	< 0.4	0.54	< 0.04	0.09	0.15	< 0.1
FQ4 C-1 61-81	71	< 0.2	0.15	< 0.4	< 0.4	0.44	< 0.04	0.07	0.13	< 0.1
FQ4 C-2 99-117	108	< 0.2	< 0.2	0.2	0.15	1.9	< 0.04	0.08	0.33	< 0.1
FQ4 C-2 142-152	147	0.08	< 0.2	0.44	0.48	7.8	< 0.04	0.1	4	< 0.1

Field No/Depth Interval	Ctr Dpth,cm	Sn ppm	Sr ppm	Th ppm	V ppm	W ppm	Y ppm	Zn ppm	Zr ppm	S2- ppm
FQ3 C-5 41-71	56	80	0.41	< 0.08	0.04	< 0.1	0.52	5.9	< 0.04	12
FQ3 C-5 71-102	86	88	0.68	< 0.08	< 0.4	< 0.1	0.17	1.6	< 0.04	64
FQ3 C-5 102-132	117	81	0.71	< 0.08	< 0.4	< 0.1	0.06	3.3	< 0.04	219
FQ3 C-5 132-163	147	76	0.8	< 0.08	< 0.4	< 0.1	0.04	2	< 0.04	84
FQ4 C-1 20-41	30	61	0.39	< 0.08	< 0.4	< 0.1	0.11	5.5	< 0.04	18
FQ4 C-1 @ 41	41	97	0.35	< 0.08	< 0.4	< 0.1	0.09	13	< 0.04	52
FQ4 C-1 41-61	51	74	0.32	< 0.08	< 0.4	< 0.1	0.14	6.8	< 0.04	17
FQ4 C-1 61-81	71	65	0.23	< 0.08	< 0.4	< 0.1	0.06	3.2	< 0.04	28
FQ4 C-2 99-117	108	74	0.58	< 0.08	0.26	< 0.1	0.15	1.1	< 0.04	0
FQ4 C-2 142-152	147	89	1.4	< 0.08	0.36	< 0.1	0.34	6.6	< 0.04	0

Geochemical data, Forest Queen Core 5.

Field No/Depth Interval	Ctr Dpth,cm	Al ppm	Ca ppm	Fe ppm	K ppm	Mg ppm	Na ppm	P ppm	Si ppm	Ti ppm
FQ5 C-2A 61-69	65	100	44	86	7.8	21	< 1	9.6	6	< 1
FQ5 C-2B 69-76	72	6.5	22	240	< 1	1.2	< 1	1.8	5.5	< 1
FQ5 C-2C 76-81	79	8.5	22	350	< 1	1.4	< 1	3.1	7.8	< 1
FQ5 C-2 81-102	91	200	74	260	8.2	110	< 1	19	9.5	< 1
FQ5 C-2E 102-122	112	170	62	300	8.2	87	< 1	16	6.7	< 1
FQ5 C-2D 122-145	133	210	72	290	12	120	< 1	20	7	< 1
FQ5 C-2C 145-165	155	120	50	120	11	54	< 1	9.7	3.6	< 1
FQ5 C-2B 165-173	169	64	37	31	2.2	6.4	< 1	6	8.1	< 1
FQ5 C-2A 173-183	178	170	80	100	12	54	< 1	12	7.1	< 1

Field No/Depth Interval	Ctr Dpth,cm	Ag ppm	As ppm	B ppm	Ba ppm	Be ppm	Bi ppm	Cd ppm	Ce ppm	Co ppm
FQ5 C-2A 61-69	65	< 0.04	< 0.2	< 0.1	0.51	< 0.02	< 0.2	< 0.4	0.29	0.03
FQ5 C-2B 69-76	72	< 0.04	< 0.2	< 0.1	0.45	< 0.02	< 0.2	0.08	< 0.8	0.11
FQ5 C-2C 76-81	79	< 0.04	< 0.2	< 0.1	0.68	< 0.02	< 0.2	0.1	< 0.8	0.07
FQ5 C-2 81-102	91	< 0.04	< 0.2	< 0.1	1.6	0.03	< 0.2	0.06	0.89	0.18
FQ5 C-2E 102-122	112	< 0.04	< 0.2	< 0.1	1.5	0.02	< 0.2	0.05	0.73	0.19
FQ5 C-2D 122-145	133	< 0.04	< 0.2	< 0.1	1.9	0.02	< 0.2	0.04	0.96	0.37
FQ5 C-2C 145-165	155	< 0.04	< 0.2	< 0.1	0.95	< 0.02	< 0.2	< 0.4	0.6	0.11
FQ5 C-2B 165-173	169	< 0.04	< 0.2	< 0.1	0.23	< 0.02	< 0.2	< 0.4	0.14	< 0.2
FQ5 C-2A 173-183	178	< 0.04	< 0.2	< 0.1	1	< 0.02	< 0.2	< 0.4	0.63	0.05

Field No/Depth Interval	Ctr Dpth,cm	Cr ppm	Cu ppm	La ppm	Li ppm	Mn ppm	Mo ppm	Ni ppm	Pb ppm	Sb ppm
FQ5 C-2A 61-69	65	0.03	< 0.2	0.16	0.26	2.5	< 0.04	0.05	1.5	< 0.1
FQ5 C-2B 69-76	72	< 0.2	0.13	< 0.4	< 0.4	0.32	< 0.04	0.05	0.35	< 0.1
FQ5 C-2C 76-81	79	< 0.2	0.12	< 0.4	< 0.4	0.36	< 0.04	0.05	0.2	< 0.1
FQ5 C-2 81-102	91	0.1	0.89	0.52	0.42	9.5	< 0.04	0.14	5.4	< 0.1
FQ5 C-2E 102-122	112	0.07	0.84	0.42	0.32	7.3	< 0.04	0.14	4	< 0.1
FQ5 C-2D 122-145	133	0.11	1.1	0.54	0.36	20	0.06	0.17	5.3	< 0.1
FQ5 C-2C 145-165	155	0.06	0.5	0.38	0.19	14	< 0.04	0.08	2.7	< 0.1
FQ5 C-2B 165-173	169	< 0.2	< 0.2	0.08	0.04	0.76	< 0.04	< 0.4	0.21	< 0.1
FQ5 C-2A 173-183	178	0.06	0.37	0.35	0.38	3.7	< 0.04	0.06	3.3	< 0.1

Field No/Depth Interval	Ctr Dpth,cm	Sn ppm	Sr ppm	Th ppm	V ppm	W ppm	Y ppm	Zn ppm	Zr ppm	S2- ppm
FQ5 C-2A 61-69	65	63	0.78	< 0.08	0.12	< 0.1	0.15	2.7	< 0.04	138
FQ5 C-2B 69-76	72	67	0.24	< 0.08	< 0.4	< 0.1	0.06	3.4	< 0.04	5
FQ5 C-2C 76-81	79	50	0.27	< 0.08	< 0.4	< 0.1	0.07	4.9	< 0.04	71
FQ5 C-2 81-102	91	< 0.1	1.1	< 0.08	0.49	< 0.1	0.23	12	< 0.04	4
FQ5 C-2E 102-122	112	< 0.1	0.94	< 0.08	0.4	< 0.1	0.19	8.8	< 0.04	23
FQ5 C-2D 122-145	133	< 0.1	1.2	< 0.08	0.54	< 0.1	0.2	9.4	< 0.04	144
FQ5 C-2C 145-165	155	< 0.1	0.78	< 0.08	0.26	< 0.1	0.16	5.4	< 0.04	97
FQ5 C-2B 165-173	169	0.1	0.54	< 0.08	< 0.4	< 0.1	0.12	1.8	< 0.04	77
FQ5 C-2A 173-183	178	0.4	1.5	< 0.08	0.2	< 0.1	0.26	3.2	< 0.04	15

Geochemical data, Forest Queen Core 7.

Field No/Depth Interval	Ctr Dpth,cm	Al ppm	Ca ppm	Fe ppm	K ppm	Mg ppm	Na ppm	P ppm	Si ppm	Ti ppm
FQ7 C-3 20-41	30	130	48	130	7.1	44	< 1	9.5	5	< 1
FQ7 C-3 41-71	56	300	77	300	20	150	1	18	3	< 1
FQ7 C-3 71-99	85	180	56	200	9.8	74	< 1	14	3.5	1
FQ7 C-3 102-150	126	210	57	220	9.8	84	1	18	5.1	< 1
FQ7 C-3 150-173	161	380	98	440	16	210	1	27	4.1	< 1
FQ7 C-3 173-183	178	460	95	300	18	130	1	47	28	< 1
FQ7 C-3 183-206	194	370	35	46	1.6	12	< 1	34	10	< 1
FQ7 C-3 206-221	213	600	100	630	16	210	1	49	20	< 1
FQ7 C-3 221-226	224	88	17	44	1.9	19	< 1	6.7	19	< 1
FQ7 C-3 226-246	236	280	74	240	16	97	1	21	8.6	< 1

Field No/Depth Interval	Ctr Dpth,cm	Ag ppm	As ppm	B ppm	Ba ppm	Be ppm	Bi ppm	Cd ppm	Ce ppm	Co ppm
FQ7 C-3 20-41	30	< 0.04	< 0.2	< 0.1	0.73	< 0.02	< 0.2	0.05	0.54	0.14
FQ7 C-3 41-71	56	< 0.04	0.3	< 0.1	1.9	0.03	< 0.2	0.12	1.3	0.16
FQ7 C-3 71-99	85	< 0.04	< 0.2	< 0.1	1.1	< 0.02	< 0.2	0.04	0.69	0.15
FQ7 C-3 102-150	126	0.1	< 0.2	< 0.1	1.2	< 0.02	< 0.2	0.14	0.84	0.25
FQ7 C-3 150-173	161	0.05	0.2	< 0.1	2.5	0.03	< 0.2	0.14	1.6	0.26
FQ7 C-3 173-183	178	0.04	0.3	< 0.1	2	0.09	< 0.2	< 0.4	1.7	0.26
FQ7 C-3 183-206	194	< 0.04	0.2	< 0.1	0.32	0.06	< 0.2	0.04	0.56	0.16
FQ7 C-3 206-221	213	0.05	0.4	< 0.1	4.3	0.09	< 0.2	0.1	2	0.71
FQ7 C-3 221-226	224	0.08	< 0.2	< 0.1	0.21	< 0.02	< 0.2	< 0.4	0.18	0.04
FQ7 C-3 226-246	236	< 0.04	< 0.2	< 0.1	1.6	0.03	< 0.2	0.04	1.2	0.2

Field No/Depth Interval	Ctr Dpth,cm	Cr ppm	Cu ppm	La ppm	Li ppm	Mn ppm	Mo ppm	Ni ppm	Pb ppm	Sb ppm
FQ7 C-3 20-41	30	0.05	0.6	0.29	0.27	2.7	< 0.04	0.09	7.1	< 0.1
FQ7 C-3 41-71	56	0.13	2.1	0.78	0.77	11	0.04	0.15	7.7	< 0.1
FQ7 C-3 71-99	85	0.08	0.53	0.38	0.42	4	< 0.04	0.1	5.4	< 0.1
FQ7 C-3 102-150	126	0.09	2	0.44	0.47	6.5	< 0.04	0.16	27	< 0.1
FQ7 C-3 150-173	161	0.18	2.7	0.87	1	16	0.05	0.22	10	< 0.1
FQ7 C-3 173-183	178	0.15	2	0.95	0.86	10	0.08	0.2	6.3	< 0.1
FQ7 C-3 183-206	194	0.03	0.48	0.17	0.11	1.4	< 0.04	0.06	0.74	< 0.1
FQ7 C-3 206-221	213	0.16	3.4	0.74	1.7	19	0.2	0.34	8.7	< 0.1
FQ7 C-3 221-226	224	<0.02	0.2	0.09	0.12	2	< 0.04	0.05	0.6	< 0.1
FQ7 C-3 226-246	236	0.1	0.8	0.61	0.58	6.3	< 0.04	0.15	3.4	< 0.1

Field No/Depth Interval	Ctr Dpth,cm	Sn ppm	Sr ppm	Th ppm	V ppm	W ppm	Y ppm	Zn ppm	Zr ppm	S2- ppm
FQ7 C-3 20-41	30	< 0.1	0.82	< 0.08	0.32	< 0.1	0.32	10	< 0.04	9
FQ7 C-3 41-71	56	< 0.1	1.3	< 0.08	0.65	< 0.1	0.37	14	< 0.04	22
FQ7 C-3 71-99	85	< 0.1	0.99	< 0.08	0.47	< 0.1	0.25	8.8	< 0.04	4
FQ7 C-3 102-150	126	< 0.1	0.92	< 0.08	0.5	< 0.1	0.46	20	< 0.04	36
FQ7 C-3 150-173	161	< 0.1	1.5	< 0.08	0.86	< 0.1	0.44	17	< 0.04	6
FQ7 C-3 173-183	178	< 0.1	1.5	< 0.08	0.65	< 0.1	0.57	14	< 0.04	5
FQ7 C-3 183-206	194	< 0.1	0.54	< 0.08	0.09	< 0.1	0.35	7.8	< 0.04	6
FQ7 C-3 206-221	213	< 0.1	1.9	< 0.08	0.84	< 0.1	0.72	20	< 0.04	6
FQ7 C-3 221-226	224	0.29	0.25	< 0.08	0.08	< 0.1	0.14	1.5	< 0.04	2
FQ7 C-3 226-246	236	< 0.1	1.3	< 0.08	0.6	< 0.1	0.47	10	< 0.04	13

Geochemical data, Forest Queen Cores 9 and 10.

Field No/Depth Interval	Ctr Dpth,cm	Al ppm	Ca ppm	Fe ppm	K ppm	Mg ppm	Na ppm	P ppm	Si ppm	Ti ppm
FQ9 0-20	10	23	13	78	1.6	2.9	< 1	4.9	7.6	< 1
FQ9 20-61	41	62	34	120	3.8	14	< 1	4.2	6.6	< 1
FQ9 61-76	69	92	55	200	5	34	< 1	7.6	4.4	< 1
FQ10B 32-52	42	190	38	540	9.9	99	< 1	23	13	< 1
FQ10A 52-56	54	60	20	95	4.4	19	< 1	6.4	4.5	< 1

Field No/Depth Interval	Ctr Dpth,cm	Ag ppm	As ppm	B ppm	Ba ppm	Be ppm	Bi ppm	Cd ppm	Ce ppm	Co ppm
FQ9 0-20	10	< 0.04	< 0.2	< 0.1	0.18	< 0.02	< 0.2	0.1	< 0.8	0.08
FQ9 20-61	41	< 0.04	< 0.2	< 0.1	0.45	< 0.02	< 0.2	< 0.4	0.2	0.04
FQ9 61-76	69	< 0.04	< 0.2	< 0.1	0.74	< 0.02	< 0.2	< 0.4	0.38	0.08
FQ10B 32-52	42	0.05	1	< 0.1	2.7	0.02	< 0.2	0.2	0.92	0.29
FQ10A 52-56	54	< 0.04	< 0.2	< 0.1	0.51	< 0.02	< 0.2	0.12	0.33	0.04

Field No/Depth Interval	Ctr Dpth,cm	Cr ppm	Cu ppm	La ppm	Li ppm	Mn ppm	Mo ppm	Ni ppm	Pb ppm	Sb ppm
FQ9 0-20	10	< 0.2	0.17	< 0.4	< 0.4	1.1	< 0.04	0.05	0.61	< 0.1
FQ9 20-61	41	< 0.2	< 0.2	0.11	0.08	1.8	< 0.04	< 0.4	0.49	< 0.1
FQ9 61-76	69	0.02	< 0.2	0.2	0.15	2.9	< 0.04	0.06	0.45	< 0.1
FQ10B 32-52	42	0.25	6.3	0.55	0.34	64	0.1	0.24	6.6	< 0.1
FQ10A 52-56	54	0.02	5.4	0.35	0.06	17	< 0.04	< 0.4	3.7	< 0.1

Field No/Depth Interval	Ctr Dpth,cm	Sn ppm	Sr ppm	Th ppm	V ppm	W ppm	Y ppm	Zn ppm	Zr ppm	S2- ppm
FQ9 0-20	10	65	0.19	< 0.08	< 0.4	< 0.1	0.09	7.1	< 0.04	65
FQ9 20-61	41	200	0.46	< 0.08	0.1	< 0.1	0.2	2.3	< 0.04	430
FQ9 61-76	69	62	0.77	< 0.08	0.21	< 0.1	0.2	2.9	< 0.04	15
FQ10B 32-52	42	< 0.1	0.44	< 0.08	0.42	< 0.1	0.22	20	< 0.04	0
FQ10A 52-56	54	0.38	0.23	< 0.08	0.1	< 0.1	0.16	12	< 0.04	0