Research Technical Completion Report

A CHEMICAL SPECIATION APPROACH TO EVALUATE WATER QUALITY PROBLEMS IN THE BLACKBIRD MINING AREA, IDAHO

by
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ABSTRACT

The Blackbird Mine, located at the edge of the Frank Church Primitive Area in east-central Idaho, is one of the largest potential sources of cobalt in the United States. Mining operations in the past have left many waste piles and dumps in this area. Sediments in the streams surrounding the mining area are also contaminated with arsenic, cobalt, and copper. Two streams drain the Blackbird mining area: Blackbird Creek to the south and Bucktail Creek to the north. Both streams flow into Panther Creek, which is a major tributary of the Middle Fork of the Salmon River. The effects of the contaminated sediments on the water quality of the creeks surrounding the Blackbird area are largely unknown.

Experiments were conducted in our laboratory to evaluate the leaching characteristics of arsenic species, As(III) and As(V), and other trace metals from sediments collected from Blackbird Creek and from Panther Creek. Leaching of arsenic was found to depend on the pH of the solution and on the iron content of the sediment. The amount of arsenic leached was high in acidic solutions, reached a minimum in neutral solutions, and increased again in basic solutions. The enhanced desorption of arsenic in basic solutions is probably related to the anionic properties of the arsenic species. Higher iron contents in the sediments would generally result in lower arsenic releases during leaching. The major arsenic species leached from the sediments under aerobic condition is As(V). The leaching characteristics of antimony appear to be similar to those of arsenic, except the amount of antimony leached from the sediments is much lower compared with arsenic. Leaching of cobalt, copper, and manganese generally increases with the acidity of the solution. Water samples collected from Panther Creek above the confluence of Blackbird Creek showed very low concentrations of arsenic and other metals. Below the confluence point, higher levels of arsenic, cobalt, and copper were found in creek waters. Water samples collected from Blackbird Creek usually showed lower arsenic compared to those from Panther Creek. In general, metal concentrations in the creeks were found to depend on the pH and on the flow of water. Antimony concentrations in the creek waters are low and are comparable to the natural levels found in other unpolluted rivers in Idaho. The field data are generally consistent with the results observed from the laboratory leaching experiments. The sediments from Blackbird Creek were found to contain much higher levels of arsenic and iron relative to those from Panther Creek. The high iron content in the sediment of Blackbird Creek was probably a factor responsible for the low arsenic concentration found in the creek water.

According to this study, interactions of water with the existing sediments is likely to be a major factor which controls the quality of the water in Blackbird Creek and in Panther Creek.

A solvent extraction method has been developed for the separation of arsenic and antimony species in natural waters using pyrrolidinecarbodithioate (PCDT) as a chelating agent. This analytical method for arsenic and antimony speciation study is in the process of being published by ANALYTICAL CHEMISTRY.

INTRODUCTION

The Blackbird Mine, located at the edge of the Frank Church Primitive Area in east-central Idaho, is one of the largest potential sources of cobalt in the United States (U.S.G.S., 1964). The U.S. Bureau of Mines conducted extensive geological research in the Blackbird area during World War II because of the need for a domestic cobalt source. After the war these investigations continued, and the mine was opened for the commercial production of cobalt. Production at this mine in the late sixties was decreased and finally halted because of increasing competition from foreign imports, which made the domestic production of cobalt unprofitable. The cobalt shortage in the late seventies changed this situation. Noranda Mining Company, the current owner of the Blackbird Mine, reopened the mine in 1980. However, because of a depressed metal market in the past few years, the Blackbird Mine was closed again in 1984.

Two individual streams drain the Blackbird mining area: Blackbird Creek to the south and Bucktail Creek to the north of the mine. These streams both flow into Panther Creek, a major tributary of the Salmon River (Figure 1). Mining operations from the late 40's to the late 60's left many waste piles and dumps in this area; the impact of these past mining activities on the surrounding streams is rather severe. Prior to major

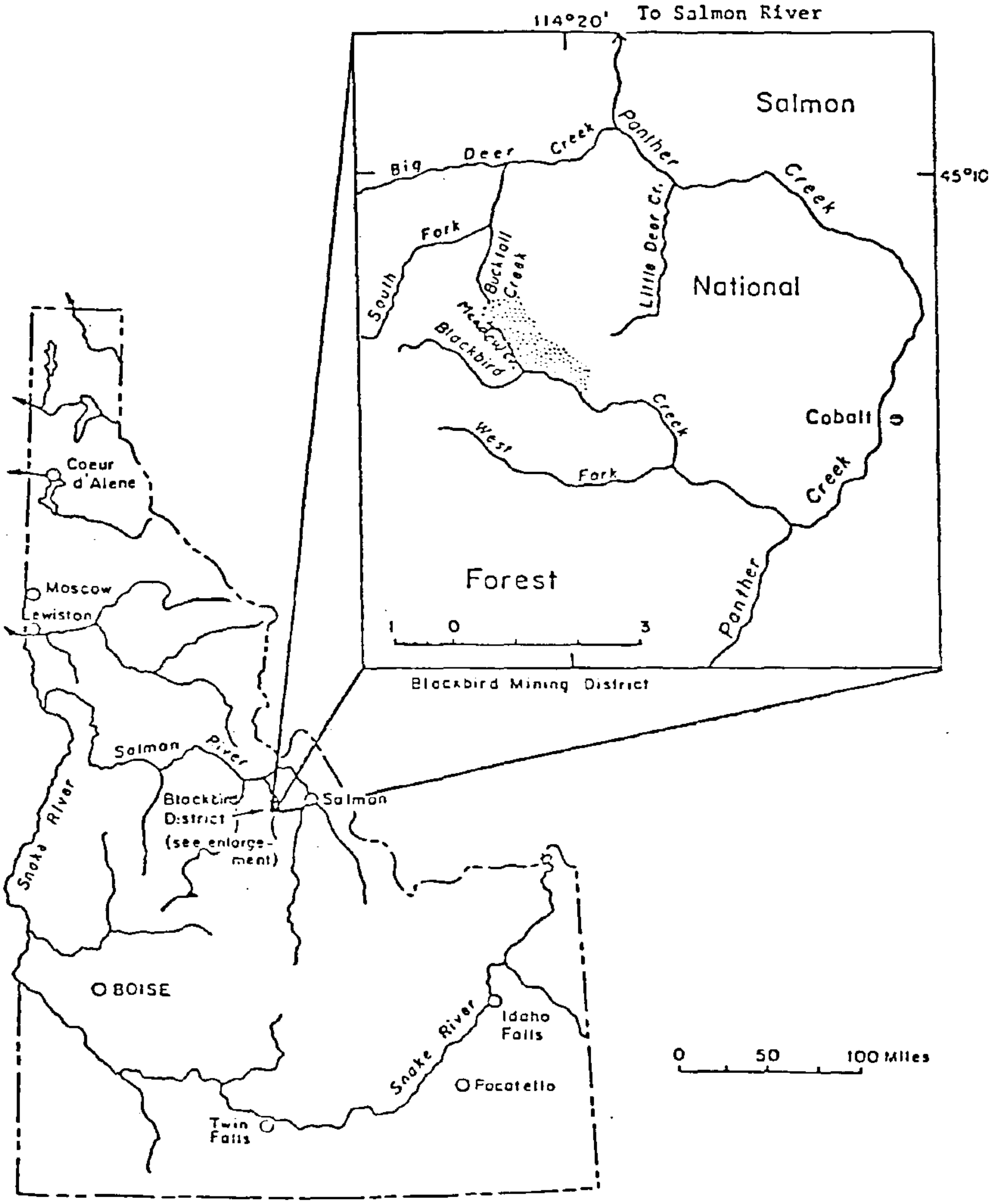

Figure 1 Map of Blackbird Mining District

development of the Blackbird Mine in 1945, no water quality problem was observed in the streams around mine. The subsequent discharge of acid and mill tailings from mining operations had a noticeable effect on the aquatic environment, prompting a number of water quality studies. Corley noted that no salmon spawning beds have been observed since 1962 and that toxic discharge from the Blackbird mining area was responsible for their disappearance (Corley, 1967). Subsequent studies by Platts continued to document the impact of the mining operation on surrounding streams (Platts, 1967; Platts et al., 1979). Baldwin in 1977 also reported a severe water quality problems in this area (Baldwin, 1977).

The major cobalt mineral found in the Blackbird area is a cobalt-arsenic sulfide called cobaltite. Chalcopyrite ($CuFeS_2$) and pyrite (FeS_2) are often present with cobaltite in the ore. It is known that mine wastes and tailings containing iron sulfides are capable of producing acid waters under oxidized conditions (Appalachian Regional Commission, 1969; Smith and Shumate, 1970). The degree of acid water formation and the subsequent leaching of metals from mine tailings containing pyrite and other sulfide minerals are strongly related to the redox status of the soil-water environment (Wai et al., 1980).

In 1980 a group of students from the University of Idaho conducted a study on the distribution of arsenic, cobalt, and copper in the Blackbird Mining District.

However, only a limited number of samples could be analyzed for arsenic by that group because of the lack of a sensitive analytical method for this element. Recently, a solvent extraction method has been developed by our research group for the measurement of nanogram levels of arsenic species in water by neutron activation analysis (NAA) (Mok et al., 1986; Mok and Wai, 1987). In natural water systems, arsenic generally exists in two oxidation states, As(III) and As(V). Biologically, As(III) is considered more toxic than As(V). Knowledge of the distribution of the As(III) and As(V) species in natural water systems is important for environmental considerations. It has also been suggested by Cherry et al. (1979) that the ratio of the two oxidation states of arsenic may be used to measure the redox potential of natural water systems.

The leaching characteristics of the various toxic metals from the mine wastes of the Blackbird area have not been thoroughly studied. The chemical behavior of arsenic in the water-sediment interface of the Blackbird area is virtually unknown. Relationship between the ratio of As(III)/As(V), pH, and other water quality parameters can be defined in laboratory controlled leaching experiments using sediments from the Blackbird mining area. Observations made in the laboratory can be used to interpret the water quality problems associated with the sediments in the Blackbird area. This laboratory approach combined with field study may provide useful information for understanding the water pollution problems associated with the existing mine wastes in this area. Since the Blackbird mine is currently inactive, field data collected at this time should not be complicated by mining activities.

This report presents the current levels of arsenic, cobalt, copper, iron, and manganese in the creek waters and the results of the leaching of these metals from representative sediments collected from the Blackbird area. The observed water quality data are then correlated with arsenic species found in the system. The factors which control the leaching and transport of trace metals from the sediments to the aqueous environment of the Blackbird Mining District are discussed.

EXPERIMENTAL METHODOLOGIES

Sampling Stations And Collection Procedures

Water and sediment samples were collected from Blackbird Creek and from Panther Creek between the fall of 1985 and the spring of 1986. Figure 2 is a map showing the locations of the sampling sites. Samples were collected from Blackbird Creek from outside the gate of the Noranda Company (#5) to the confluence point where Blackbird Creek enters Panther Creek (#12). After it leaves the mining area, Blackbird Creek flows approximately 17.5 km to its union with Panther Creek. A total of 5 sampling sites along Blackbird Creek were selected

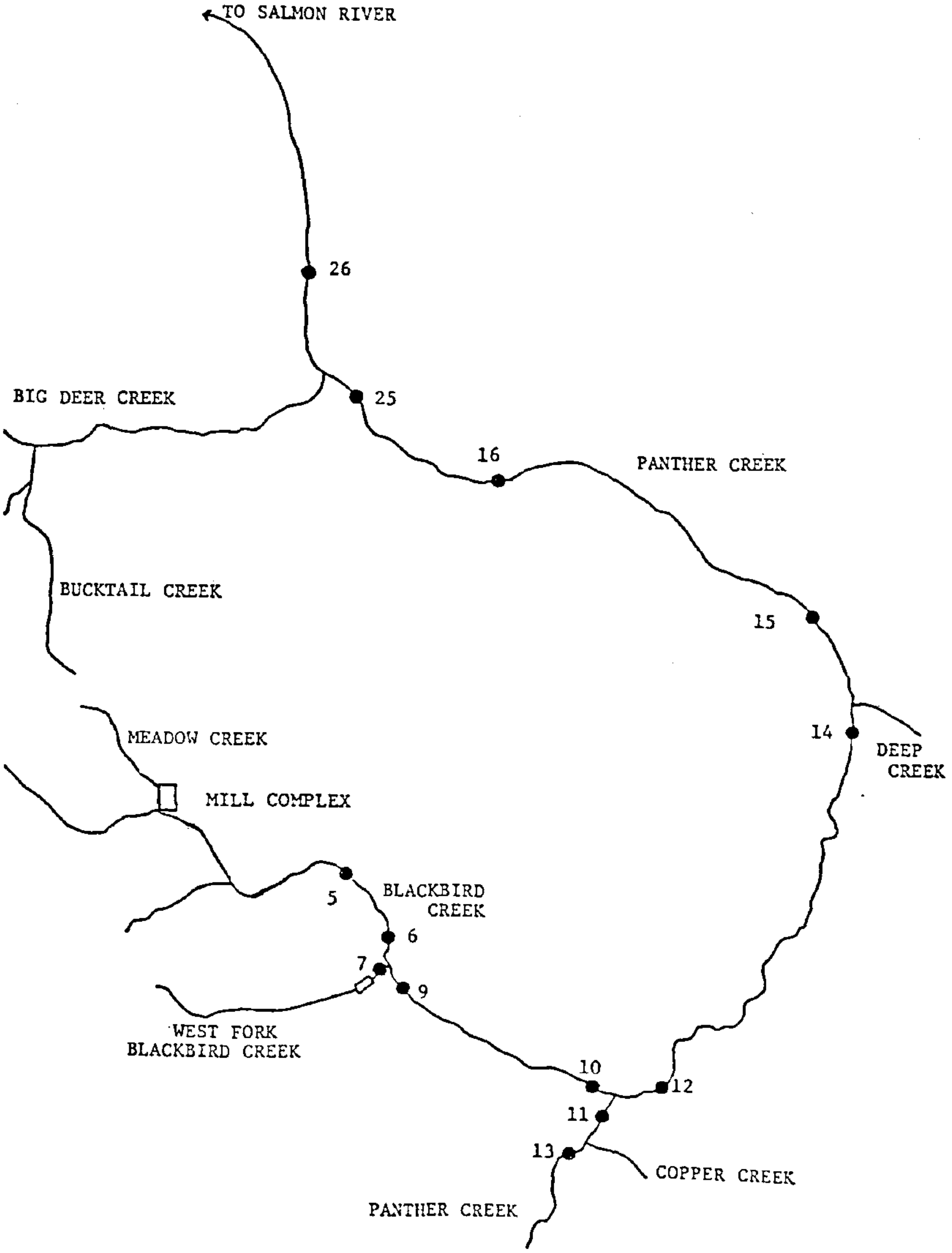

Figure 2 Locations of sampling sites in Blackbird Creek and in Panther Creek

for this study. Another 8 sampling sites were selected from Panther Creek, starting from the confluence of Blackbird Creek to the point where Panther Creek enters the Middle Fork of the Salmon River.

Water samples were collected from the creeks using one liter polyethylene bottles. All containers used were washed with nitric acid and rinsed with deionized water according to the procedures described in the literature (Mok et al., 1986). After collection, water samples were filtered using millipore filtration. A 0.45 micron membrane filter was used for the millipore filtration to remove particulate matter from the water. Sediment samples were taken at the selected sites using a plastic hand spade. After collection, samples were sealed in plastic bags and stored at 4°C in a refrigerator until used. In some locations, silt-like sediments were not available and hence no sediment samples were taken.

Analytical Procedures

A.Extraction of Arsenic(III) and Arsenic(V) from Natural Waters

The derivatives of dithiocarbamic acid are known to chelate with a large number of metal ions to form complexes which are soluble in organic solvents. One of the dithiocarbamate derivatives, pyrrolidinecarbodithioate (PCDT), is widely used for preconcentration and separation of trace elements from aqueous solutions. The exactibility of metal-PCDT complexes depends on the oxidation state of the element and the pH of the solution. For example, PCDT forms a stable complex with As(III) but

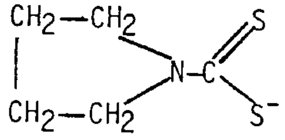

Figure 3. Structure of PCDT

not with As(V). Therefore, As(III) can be separated from As(V) by extracting the former with PCDT into an organic phase under proper conditions. The pH dependence of the extraction of As(III) and some selected divalent cations, including Cu(II), Fe(II), Mn(II), and Zn(II), with PCDT into chloroform is shown in Figure 4. One advantage of PCDT extraction is that the alkali metals, the alkaline earth metals, the halogens, aluminum, sulfate, and phosphate which do not complex with PCDT can be simultaneously removed during the extraction. The PCDT extraction method may serve three general purposes for trace analysis: (1) concentration of trace elements, (2) elimination of matrix interferences, and (3) differentiation of chemical species.

Because only As(III) can be extracted by PCDT, the reduction of As(V) to As(III) is necessary in order to determine the total arsenic in the water. Sodium thiosulfate, $Na_2S_2O_3$, is an effective reducing agent for As(V). The difference in As(III) concentrations between two aliquots of a water sample with and without reduction

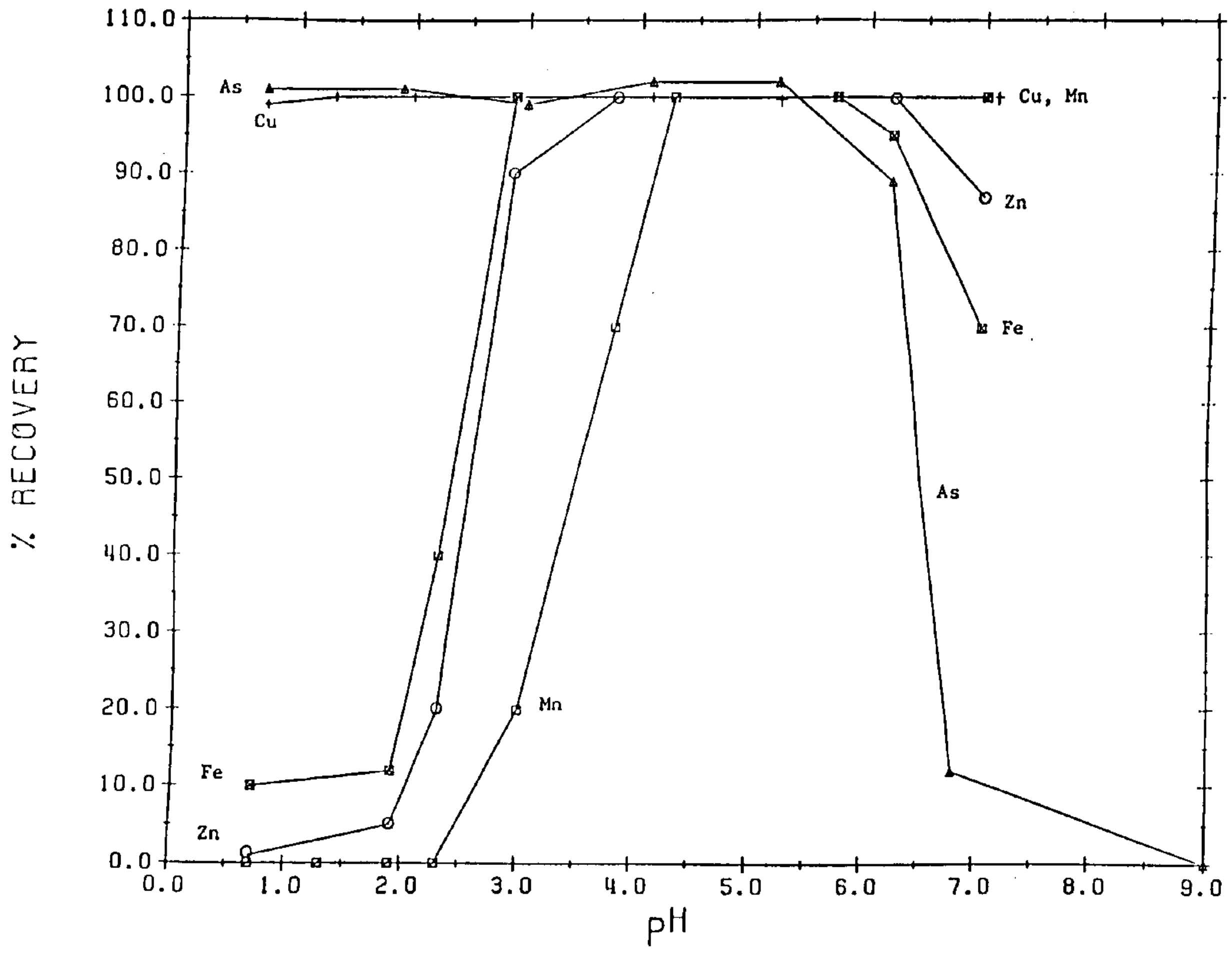

Figure 4 pH dependence of the extraction of As(III) and other metals (Cu(II), Fe(II), Mn(II), and Zn(II)) with APCDT from aqueous phase into chloroform. As(V) is not extractable at pH>1 gives the concentration of As(V) in the sample. The details of this solvent extraction method for the differentiation of arsenic species are given in the literature (Mok et al., 1986).

During the course of this study, we have modified the PCDT extraction method reported by Mok et al. (1986) so that both trivalent arsenic and antimony species, As(III) and Sb(III), in aqueous solution can be simultaneously extracted into chloroform in the pH range of 3 to 6. Extraction of As(V) and Sb(V) can be achieved by reduction with thiosulfate and potassium iodide at pH 1 followed by PCDT extraction at the same pH value. The As and Sb-PCDT complexes in the organic phase can be back-extracted into a nitric acid solution for neutron activation analysis. Detection of 10^{-2} ug/L of As and Sb can be achieved using this extraction method and NAA. The details of this new extraction method for the determination of As and Sb species in natural waters are given in the manuscript in the appendix of this report. The attached manuscript entitled "Simultaneous Extraction Of Trivalent And Pentavalent Antimony And Arsenic Species In Natural Waters For Neutron Activation Analysis" has been accepted for publication by ANALYTICAL CHEMISTRY and is scheduled to appear in that journal in January 1987.

We have included antimony speciation studies in this project because the chemical properties of antimony are similar to those of arsenic and the distribution of antimony in the Blackbird area is unknown. Antimony and its compounds are listed as priority pollutants by the U.S. Environmental Protection Agency. The antimony data obtained from this project will provide useful information for evaluating the significance of this toxic trace metal in the aquatic environment of the Blackbird area.

B. Trace Metal Analysis

Neutron activation analysis (NAA) is one of the most sensitive techniques for determining trace elements in environmental samples. This technique has been extensively used for trace analysis of various samples in our laboratory (Mok and Wai,1984; Yu and Wai, 1984). A TRIGA nuclear reactor located at the Washington State University Nuclear Radiation Center was used for sample irradiation in this study. Samples were normally irradiated with a steady neutron flux of $6X10^{12} n/cm^2 sec$ for 2 hours, followed by cooling for about 24 hours, and then counted for 2000 to 8000 seconds using an ORTEC Ge(Li) detector. The details of the irradiation and counting procedures are given in the manuscript in the appendix. Under interference free conditions, NAA is capable of detecting As and Sb at nanogram levels. However, in real samples, spectral interferences from matrix species can seriously impair the sensitivity of trace element determination by NAA. The concentrations of total As and Sb in most natural water systems are very low, in the range of 10^{-9}

to 10^{-10} g/mL. Without chemical separation and preconcentration, it is difficult to determine As and Sb directly in natural waters by NAA. The PCDT extraction method has greatly improved the sensitivity of As and Sb detection. If we start with a water sample of 100 mL and go through the PCDT extraction procedure, we can detect As and Sb at 10^{-11} g/mL level. This level of detection is generally sensitive enough to measure As and Sb species in natural waters. If necessary, the detection limits for As and Sb can be further lowered by using larger sample volumes and longer counting times.

Other trace metals including Co, Cu, Fe, and Mn were determined using direct flame aspiration with an IL-353 atomic absorption spectrophotometer which gives detection limits of about 0.001 ug/mL for Cu and Mn, 0.003 ug/mL for Fe, and 0.01 ug/mL for Co.

To determine trace metals in the sediments, an acid digestion procedure was used to extract metals from the sample. The procedure is described as follows. About 0.5 grams of dry sediment and a mixture of 3 mL of concentrated nitric acid and 9 mL of concentrated hydrochloric acid were placed in a beaker covered with a watch glass. Digestion was carried out at about 100°C on a hot plate until the acid solution was nearly dry. After cooling, 10 mL of a 50% hydrochloric solution (1:1 v/v) was added and the mixture was heated again to boiling occurred. The mixture was then cooled to room temperature and diluted with deionized water. The solution was filtered through a Whatman No. 42 filter paper and brought to a final volume of 50 mL. Atomic absorption spectrometry was used to determine Co, Cu, Fe, and Mn in the acid solution. Arsenic and Sb in the sediment digest were extracted with PCDT and determined by NAA.

Leaching Experiments

Leaching experiments were conducted on six representative sediment samples to study the rate of removal of metals from the sediments. All experiments were conducted at room temperature under atmospheric pressure. In each experiment a wet sediment sample of known weight was placed in a 1-L polyethylene bottle, and sufficient deionized water was added to each bottle to make a water-to-sediment weight ratio of approximately 15:1. The sediment-water mixture was kept in suspension by continuous stirring with a magnetic stirrer. Two hundred mL aliquots of the sample were removed from each of the systems at various time intervals and replaced by an equal volume of deionized water and the leaching continued. This volume of water was needed for analytical purposes because of the low As content in the leaching solution. Replacement of the water removed from the system was necessary to maintain a relatively constant water to sediment ratio during the leaching process. The leach solution was filtered through a 0.45 um millipore membrane filter, followed by the measurement of pH. Metal contents of the leaching solution were determined by the same procedure as described previously for creek water samples.

RESULTS AND DISCUSSION

Characteristics of the Sediments

Leaching is an important mechanism for transporting toxic metals from mine wastes and contaminated sediments to the aquatic environment of the Blackbird area. In some commonly encountered environmental situations, direct mixing of bottom sediments with water will occur as a result of sediment resuspension by propeller wash or storms. The duration of this mixing is generally short and is usually limited to days, hours, or even minutes (Wright, 1978). The study of the short-term release of toxic metals from the creek sediments of the Blackbird area during mixing is therefore of interest. Information regarding the rates of the release of trace metals from sediments during mixing can be obtained from laboratory controlled leaching experiments.

Six sediment samples collected from Blackbird Creek and Panther Creek were selected for the leaching experiments. Descriptions of the sampling sites are given in Table 1. The leaching experiments involved the measurement of pH and the analysis of leaching solutions for As(III), As(V), Sb(III), Sb(V), Co, Cu, Fe, and Mn at various time intervals for about 10 days.

The concentrations of aluminum, iron, sulfur, arsenic

Table 1. Description of the six selected sediment-sampling sites

Station No.	Site Description
#5	On Blackbird Creek, outside the gate of Noranda Co.
#9	On Blackbird Creek below the mouth of the Slippery Gulch Creek
#14	On Panther Creek below the mouth of Deep Creek
#16	On Panther Creek, halfway between the mouth of Deep Creek and the confluence of Panther Creek and Big Deer Creek
#25	On Panther Creek, 2 kilometers above the confluence of Big Deer Creek
#50	On Panther Creek, before it enters the Salmon River

and five other trace elements in the sediment samples prior to leaching were analyzed by AAS and by NAA according to the procedures described in the experimental section. The results are given in Table 2. The sediments from Blackbird Creek appear to contain much higher concentrations of arsenic, antimony, cobalt, copper, iron, and sulfur relative to the sediments from Panther Creek. The aluminum, barium, and manganese contents of the sediments from Blackbird Creek are not significantly different from those found in the Panther Creek sediments. The major minerals in the sediments appear to be quartz and aluminum silicates according to the X-ray powder diffraction patterns obtained from some selected sediments. The chemical forms of the trace metals present in the sediments could not be identified by X-ray diffraction patterns.

Leaching of Sediments

A. Release Of Arsenic Species During Leaching

The leachin of As species and other metal ions from the sediments was expressed on a mass release basis. Net mass release for a given chemical constituent is the change in the mass of that constituent in water compared to the mass originally present in the same volume of water. The movement of a chemical constituent from the sediment into water results in a positive net mass release, while a negative value is an indication of the reverse process. The formula for calculating the net

Table 2. Concentrations of some selected elements in the sediments collected from Blackbird Creek and from Panther Creek

	Conc. in ug/g							in %	
Sample	As	Sb	Co	Cu	Mn	S	Ba	Al	Fe
#5	1120.6	18.4	311.9	2330.2	183.3	3300.6	226.7	2.6	10.7
#9	2550.4	42.3	471.0	2595.4	167.2	10119.4	191.4	2.2	12.9
#14	42.1	6.0	94.1	118.5	233.3	546.3	316.1	2.5	1.9
#16	132.5	1.2	156.7	294.8	1548.0	436.3	208.9	1.9	3.2
#25	77.3	3.4	99.6	154.9	326.3	72.2	177.8	1.7	2.4
#50	135.4	1.4	543.9	1029.6	583.0	2741.2	230.1	2.7	0.8

release of a chemical constituent during leaching is given as follows:

1st sampling: y released = $V_o . X_1$

2nd sampling: y released = $V_o . X_2 - V_f . X_1$

nth sampling: y released = $V_o . X_n - V_f . (X_{n-1})$

y = species of interest X_n = concentration (ng/mL or ug/mL) corresponding to nth sampling

V_o = volume of water (mL) used in the leaching process

V_f = volume of water (mL) remaining after sampling

The summation of the net mass releases for a specific chemical constituent at a particular sampling period with all preceding net mass releases of that constituent gives the cumulative net mass release (ng/g or ug/g) for the chemical constituent at that specified sampling period, and a plot of such data as a function of sampling time gives a cumulative release curve.

Sediments were leached with deionized water under aerobic conditions with stirring. The leaching conditions were designed to simulate a situation where the whole mass of sediments was constantly exposed to the leaching solution. The variations in pH of the water in contact with sediments during the course of leaching are summarized in Figure 5. pH values of the leaching solutions from sediments collected at stations #5 and #9 were below pH 5. The low leachate pH values attained by these sediments suggest a stronger acid production capability for these sediments as indicated by their high sulfur and iron contents. Sediments from sites #14, #16,

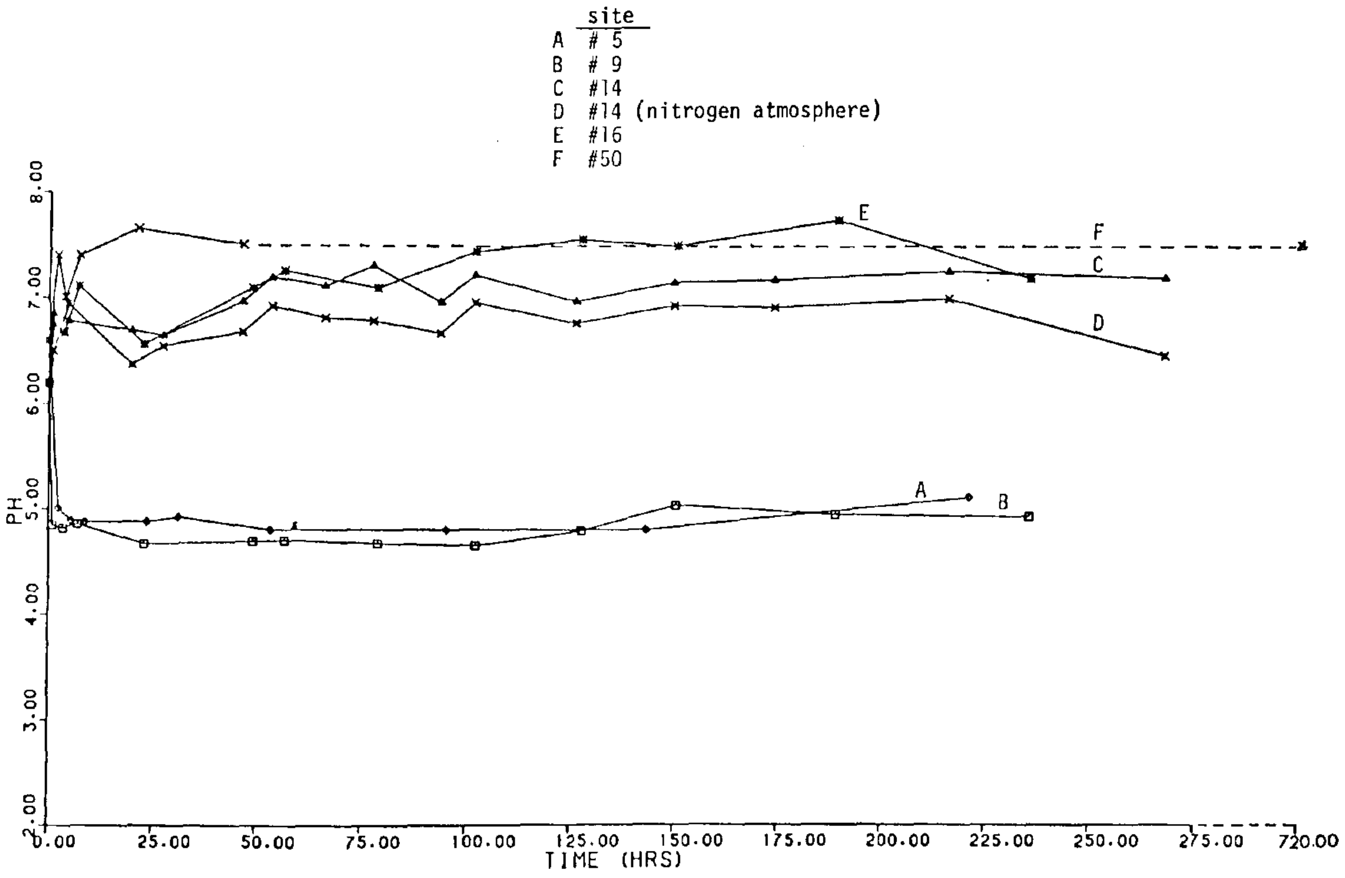

Figure 5 Variation of pH during leaching of the sediments

and #50 maintained a pH of approximately 6.8 to 7.4 in the leaching solution. These sediments from Panther Creek generally have lower iron and sulfur contents.

Cumulative net mass releases of As, Fe, Co, Cu, and Mn as a function of time for the five selected sediments during aerobic leaching are given in Figures 6-14. To evaluate the impact of the sediments on metal release during leaching, distribution coefficients (K) were calculated. The distribution coefficient (K) is defined as follows:

$$K = M_l / M_s$$

where M_s = mass of As in the sediment and M_l = mass of As in the leachate, all expressed as micrograms (ug) of the metal per gram dry weight of the sediment.

Distribution coefficients for the release of As(V) and As(III) from the sediments #5, #9, #14, #16, and #50 are presented in Table 3. The sediments were leached for about ten days, at which time the release of As and other metals (except Fe, Co, and Mn of sediment #9) tended to level off.

According to the data given in Table 3, the distribution coefficients for As were much greater in sediments #14, #16, and #50 relative to sediments #5 and #9, indicating that a relatively higher fraction of the As in the former had been released. This observation is interesting because the total concentrations of As in

Table 3. Distribution coefficients of arsenic species obtained from leaching of sediments under aerobic conditions with stirring

Sediment	As(III)	As(V)	Total As = As(III)+As(V)
#5	N.D.	$5.72X10^{-5}$	$5.72X10^{-5}$
#9	$1.21X10^{-5}$	$4.99X10^{-5}$	$6.20X10^{-5}$
#14	$1.20X10^{-3}$	$4.26X10^{-2}$	$4.38X10^{-2}$
#16	$2.08X10^{-4}$	$3.47X10^{-3}$	$3.68X10^{-3}$
#50	$6.25X10^{-5}$	$1.41X10^{-3}$	$1.47X10^{-3}$

#50 was measured after 30 days
N.D.: not detected

sediments #5 and #9 are much greater than those found in sediments #14 and #16 (Table 2). The degree of total As release from the sediments (Figure 6) apparently is not directly related to the total As content but depends on other chemical factors of the system. The Fe content of sediments #5 and #9 was at least 4 times higher than that of sediments #14 and #16 as shown in Table 2. It appears that a higher Fe content in the sediment tends to enhance the retention of As according to these data. This correlation suggests that As probably exists in the iron rich sediments as arsenical pyrite, which is very insoluble in water (Figures 6,7).

Sediment #9 has the highest Fe content. The presence of ferric hydroxide, or yellow boy, is quite visible in this sample. This brown colored precipitate was not observed in the sediments collected from Panther Creek. The leaching of sediment #9 resulted in a relatively higher As(III)/As(V) release ratio compared to the other sediments studied (Figure 10). This enhanced As(III)/As(V) ratio is probably caused by a reduced As(V) concentration in the aqueous phase due to its interaction with ferric hydroxide. Arsenic(V) may become relatively immobile if it reacts with ferric hydroxide to form the mineral scorodite as shown by the following equation:

$$Fe(OH)_3 + H_3AsO_4 = FeAsO_4.2H_2O + H_2O$$

Cumulative net mass releases of As(111) from these sediments are shown in Figure 8. Sediment #5 showed a

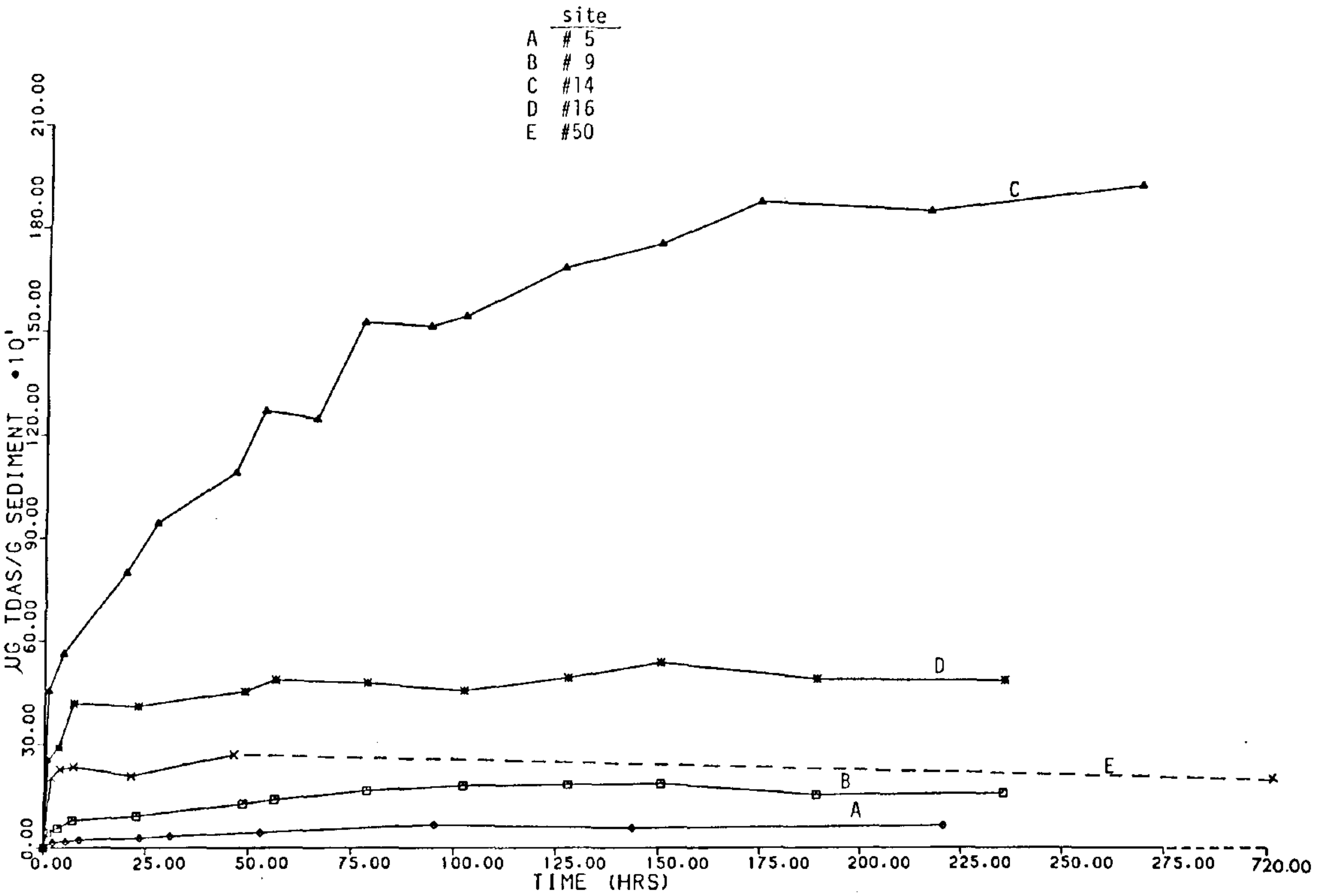

Figure 6 Cumulative total As release from sediments

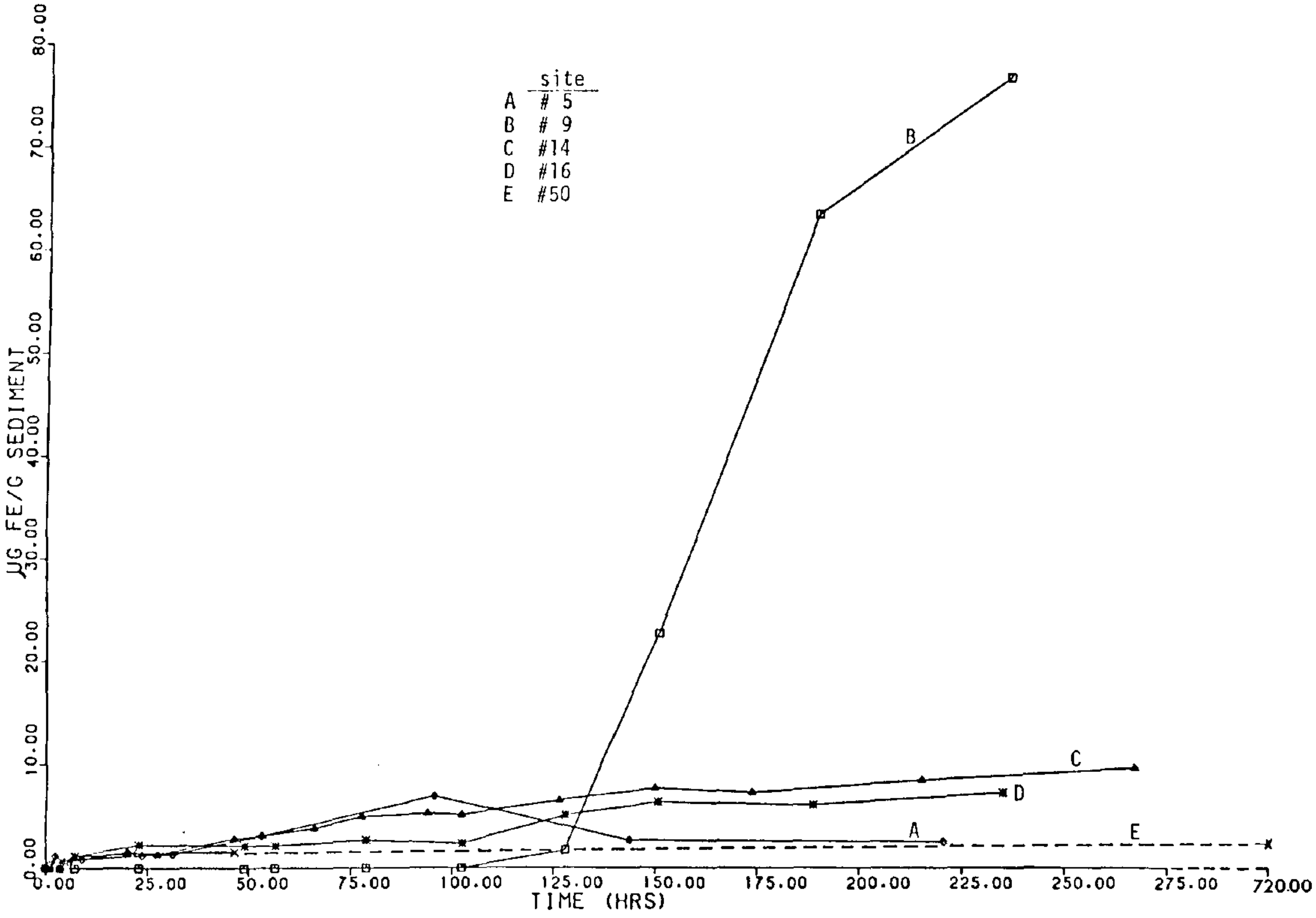

Figure 7 Cumulative Fe release from sediments

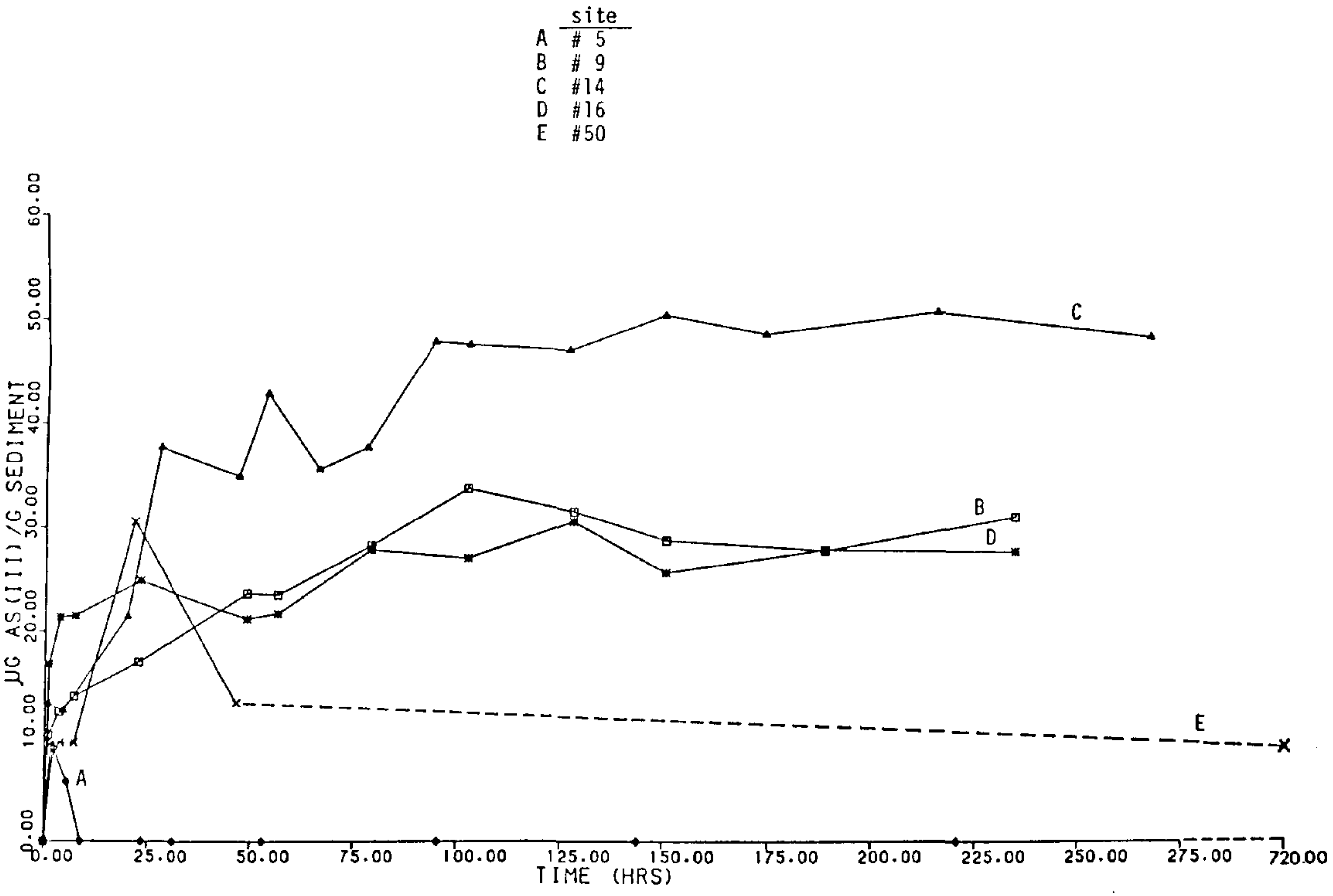

Figure 8 Cumulative As(III) release from sediments

rapid As(III) release initially. In fact, As(III) was the predominant arsenic species found in the system after 1 hour of leaching. However, the concentration of As(III) in the leaching solution was found to decrease after 1 hour although the total As release was still increasing. In general, oxidation of As(III) to As(V) in fresh water under aerobic conditions is slow in the absence of catalysts (Clement and Faust, 1973; Wagemann, 1978). This fast conversion of As(III) to As(V) suggests the possible presence of some catalysts in the sediments. While this project was in progress, Noranda Company still operated a water treatment plant at the Blackbird Mine. Station #5 is located right outside the gate of Noranda's property and is closest to the water treatment plant. It is possible that sediment from this sampling location are affected by the materials released from the water treatment plant. These sediments also showed a substantially higher initial release of Cu (Figure 14).

The sediments from Panther Creek generally exhibited a high linear release of As(V) initially followed by an asymptotic pattern during leaching. Cumulative releases of As(V) (Figure 9) from these sediments were found to be similar to the releases of total As. A plot of As(V)/As(III) ratios in leachates as a function of time during leaching of sediments is shown in Figure 10. The variation in As(V)/As(III) ratio is generally small, reflecting that the oxidation of As(III) to As(V) in these

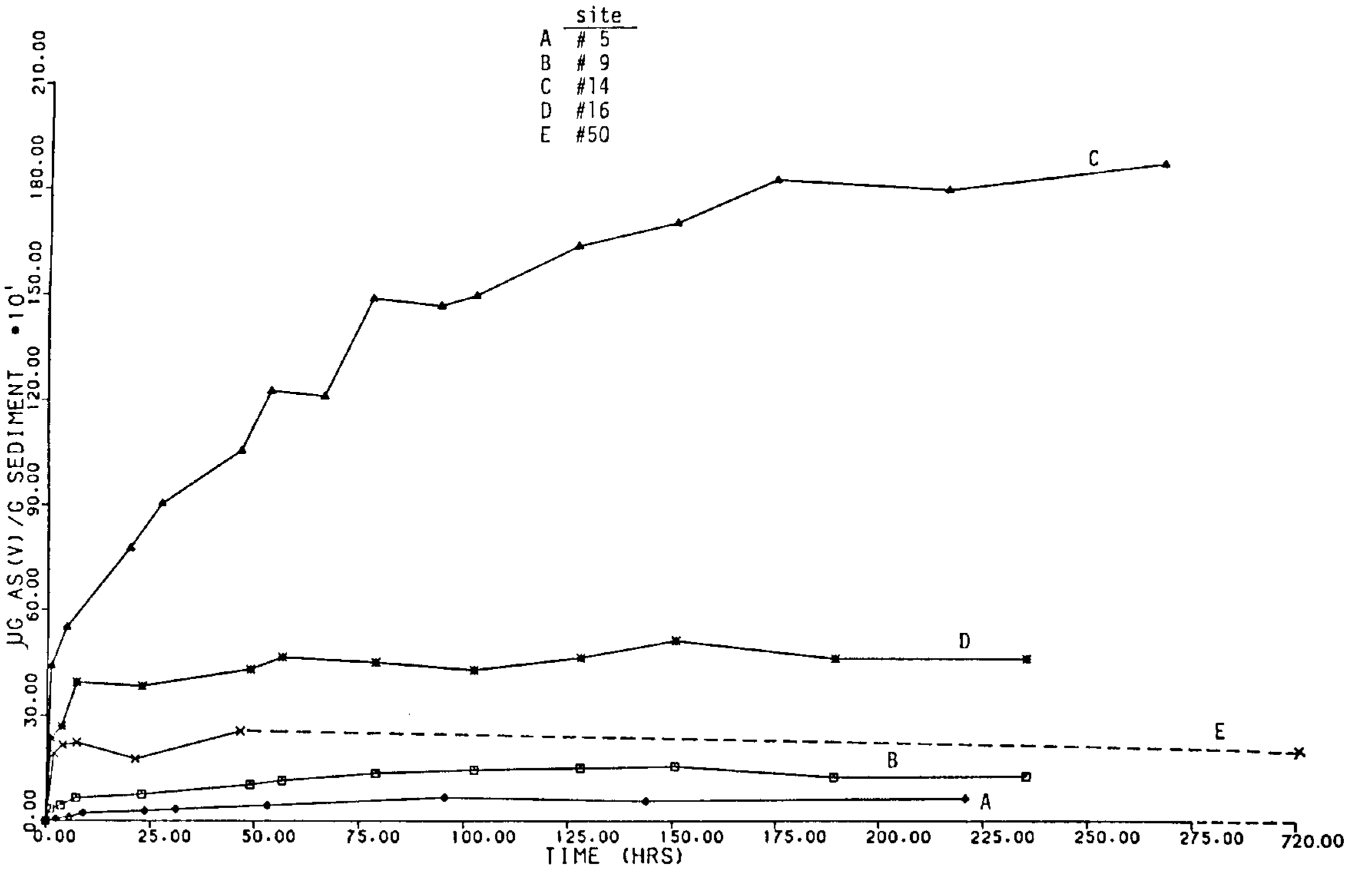

Figure 9 Cumulative As(V) release from sediments

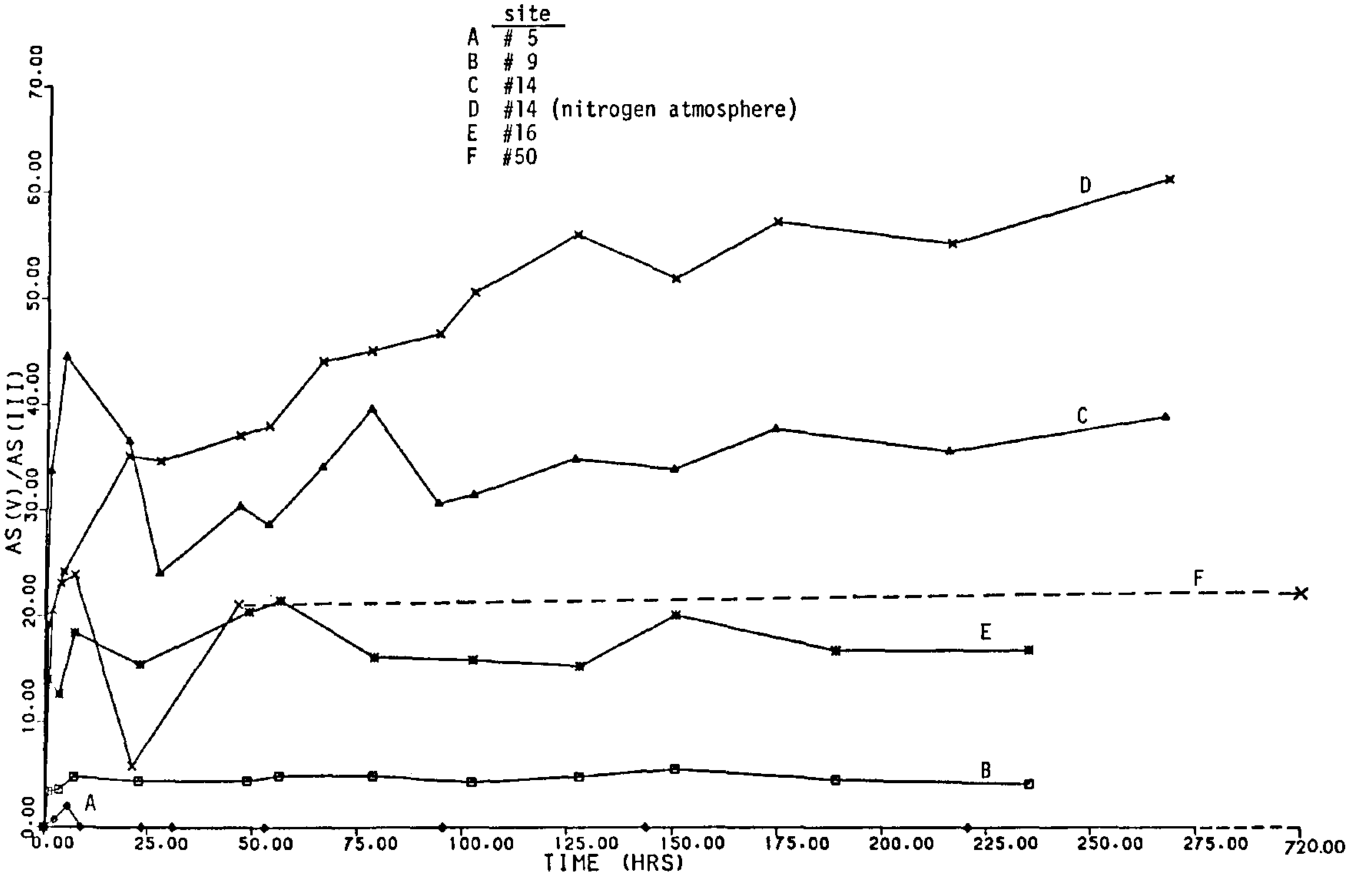

Figure 10 As(V)/As(III) as a function of leaching time

systems during leaching is slow. With the exception of sediment #5, cumulative As(III) releases from the sediments did not differ substantially from those observed for As(V). According to the literature, the oxidation of As(III) to As(V) with dissolved oxygen is very slow at neutral pH but proceeds measurably faster in strongly basic or acidic solutions and in the presence of certain catalysts (Ferguson and Gavis, 1972; Oscarson et al., 1980; Johnson and Pilson, 1975).

The results of leaching can also be presented in terms of the concentrations of arsenic species found in the leaching solution. Table 4 shows the concentrations of As(III), As(V), Fe, Cu, Co, and Mn in the leachates of sediments #5, #9, #14, and #16 after 10 days of leaching and of sediment #50 after 30 days of leaching. The concentrations of arsenic species are given in ng/mL or ppb, and the other metal ions are given in ug/mL or ppm. Leaching of the sediments from the Blackbird area generally resulted in ppb levels of the arsenic species and ppm levels of the other trace metals in the leachates after several days of stirring under aerobic conditions.

B. Release of Antimony During Leaching

The leaching of Sb species was also studied for the six sediments described in Table 1. The concentrations of Sb species in the leaching solutions were at least 3 orders of magnitude lower than the concentrations of As species found in these solutions. In fact, only sediments

Table 4. Concentrations of AS(III), As(V), Fe, Co, Cu, and Mn in the leaching solution

Sediment	Total As	As(III)	As(V)	Fe	Co	Cu	Mn
#5	4.09	<0.10	3.99	0.16	3.34	2.52	0.22
#9	11.46	2.24	9.24	5.55	12.48	2.65	0.81
#14	117.95	3.09	114.86	0.57	<0.10	0.02	<0.01
#16	30.03	1.70	28.33	0.45	0.31	0.05	0.04
#50	7.37	0.31	7.06	0.08	0.11	0.01	<0.01

As concentrations are given in ng/mL
Fe, Co, Cu, and Mn concentrations are given in ug/mL

#14 and #16 showed detectable amounts of Sb species, primarily Sb(V), during leaching. Cumulative net mass releases of Sb species from these leaching experiments are shown in Figure 11. Iron appears to fix Sb release during leaching, as seen from the leaching of sediments #5 and #9. Although these two sediments contained relatively high concentrations of Sb, releases of Sb from these sediments during leaching were virtually undetectable (<0.05 ng/mL). The Fe contents of sediments #5 and #9 and their relationship to the release of As species during leaching have been discussed in the previous section. The results indicated some similarities in the behaviors of As and Sb species during leaching.

Water soluble Sb concentrations in sediments #25 following 30 hours of leaching under controlled pH conditions are given in Table 6. The effect of pH upon leaching of Sb was again similar to As (discussed in Section D), except that there was no release of Sb(III) under basic conditions and the amount of total Sb released was much less in comparison to As (Figure 12, 16). The result reveals that higher amounts of Sb, primarily Sb(V), will be mobilized into a water soluble form under basic conditions compared with acidic conditions. For example, the disposal of lime into sediments might result in an increased desorption of Sb.

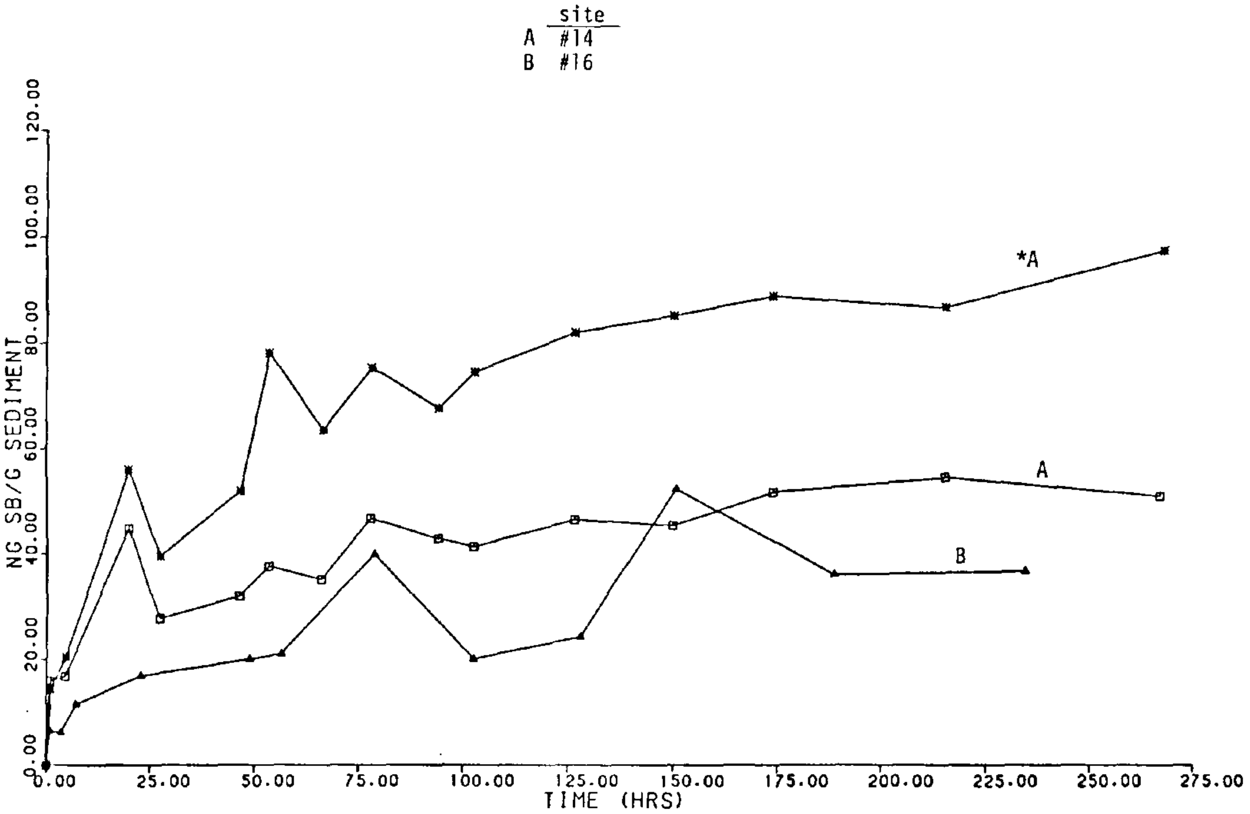

Figure 11 Cumulative Sb release from sediments #14 and #16
(* : under nitrogen atmosphere)

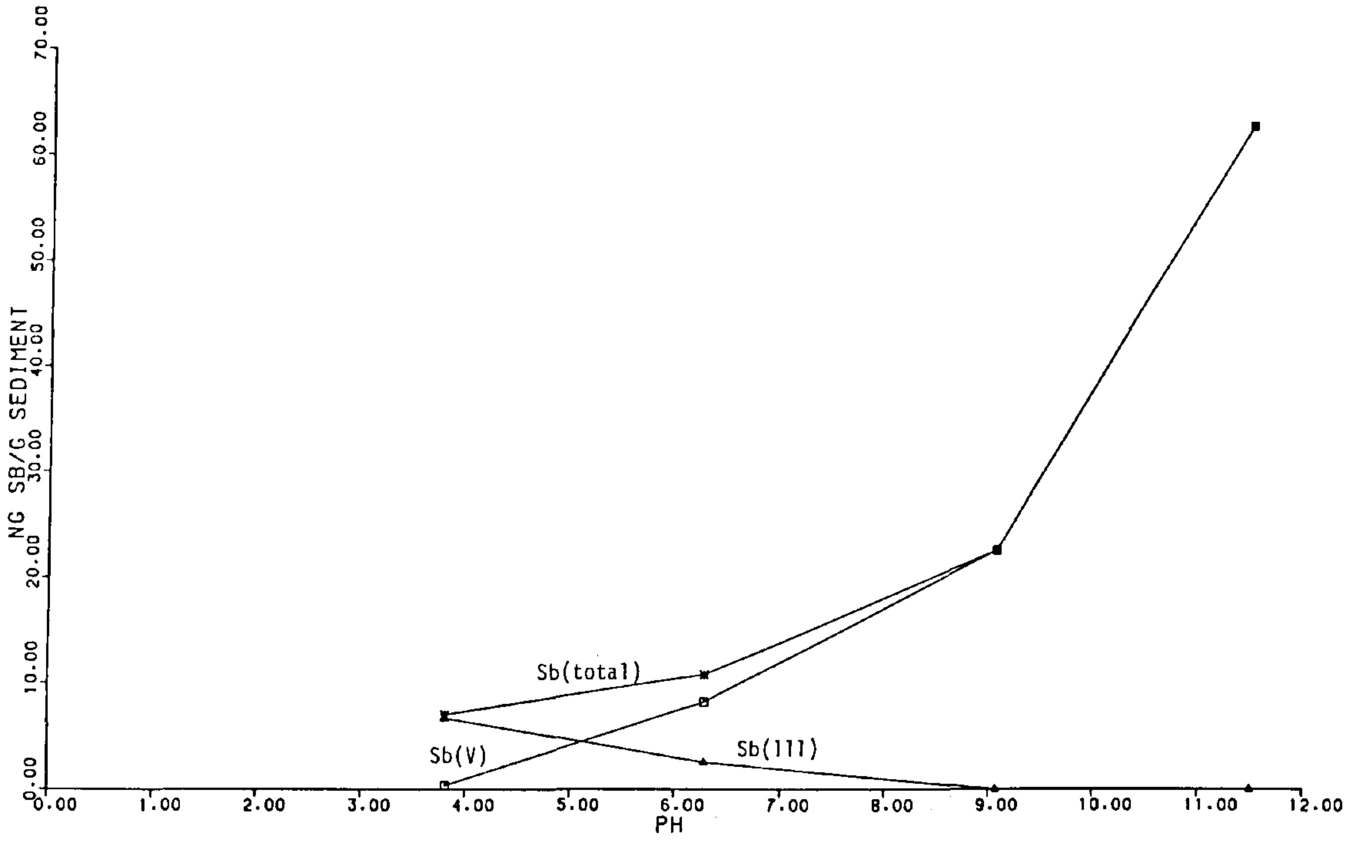

Figure 12 Release of Sb species from sediment #25 as a function of pH

Based on the analytical data obtained from the leaching of the sediments, Sb(V) appeared to be the predominant species released into the aqueous phase under aerobic conditions. The distribution of the Sb species is still less known than that of As and appears to be a subject of interest for future studies.

C. Release Of Cobalt, Copper, And Manganese During Leaching

The average pH values of the leaching solutions observed from the leaching of sediments #5 and #9 with deionized water were 4.4 and 4.8, respectively. The leaching of sediments #14 and #16 resulted in an average pH value of about 7.0, whereas value was 7.4 for the leaching of sediment #50. The leaching of the sediments from Blackbird Creek produced slightly acidic solutions, whereas the sediments from Panther Creek generally formed neutral leachates according to our experiments. This difference in the pH of the leaching solution apparently affects the dissolution of trace metals such as Co, Cu, and Mn present in the sediments (Figures 13,14,15). As shown in Table 4, the concentrations of leached Co, Cu, and Mn are much higher in the leachates of sediments #5 and #9 relative to those found in the leachates of sediments #14 and #16.

The distribution coefficients (K) of Co, Cu, and Mn observed from the leaching of different sediments are given in Table 5. The distribution coefficients were

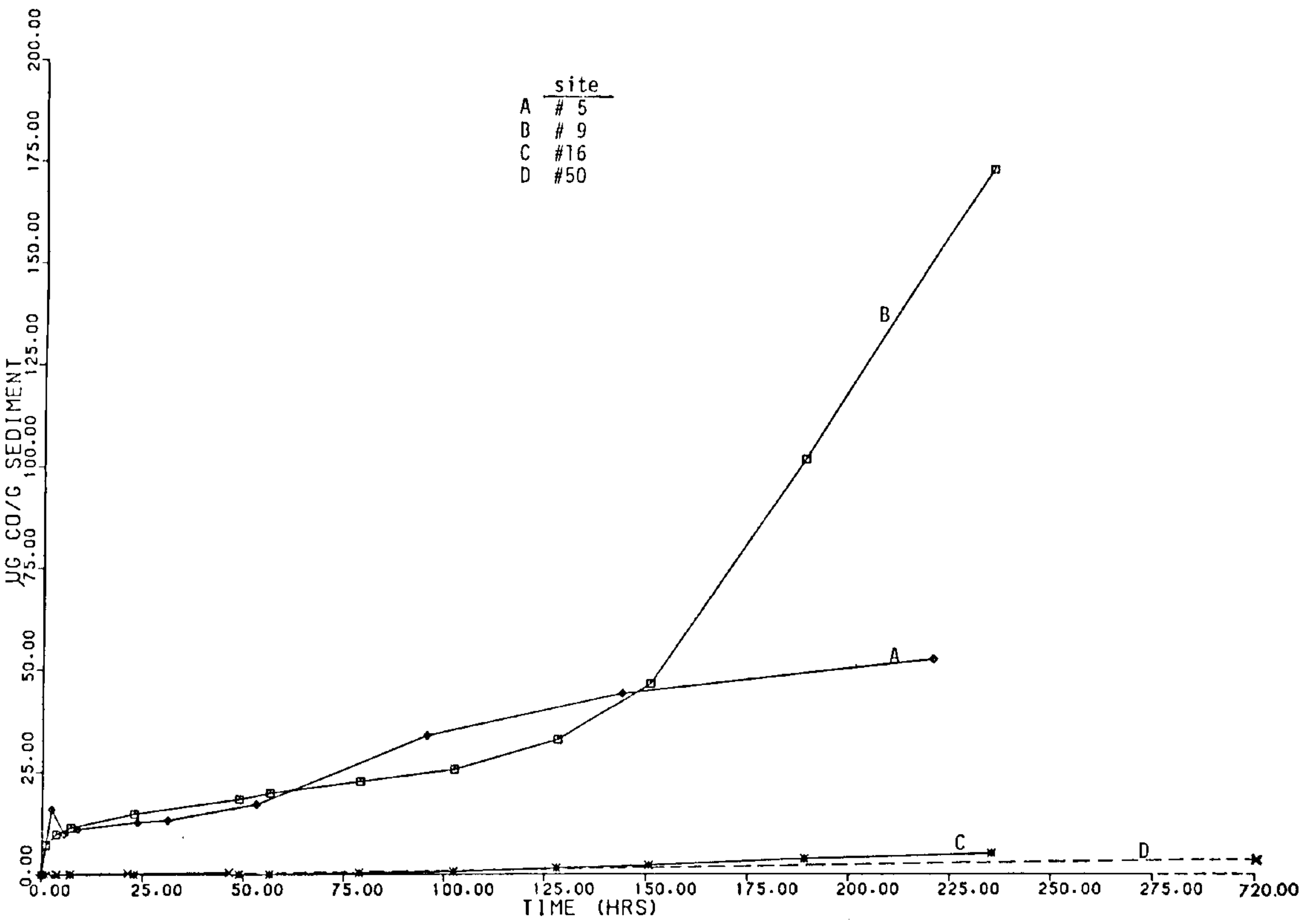

Figure 13 Cumulative Co release from sediments
(No Co release was detected in sediment from site #14)

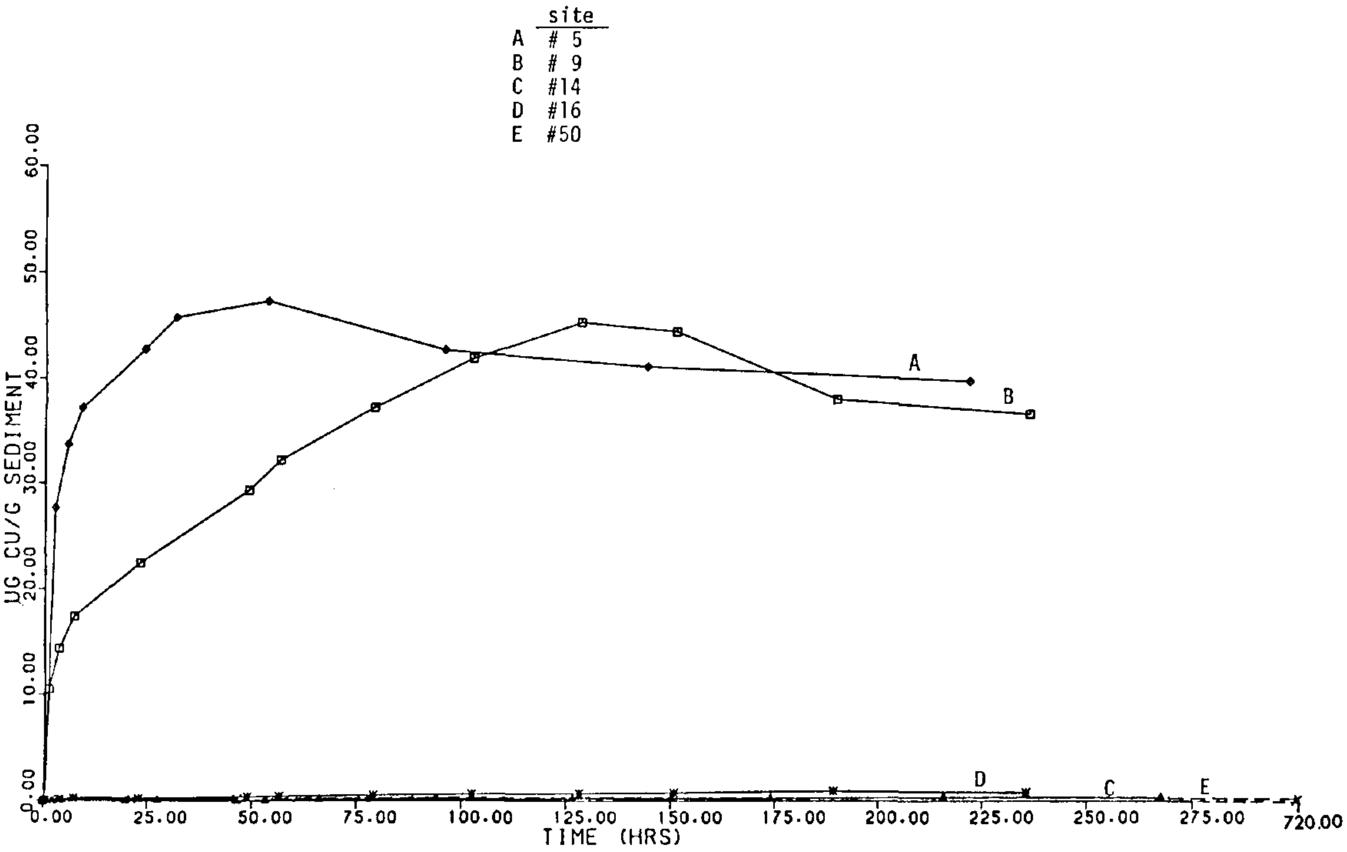

Figure 14 Cumulative Cu release from sediments

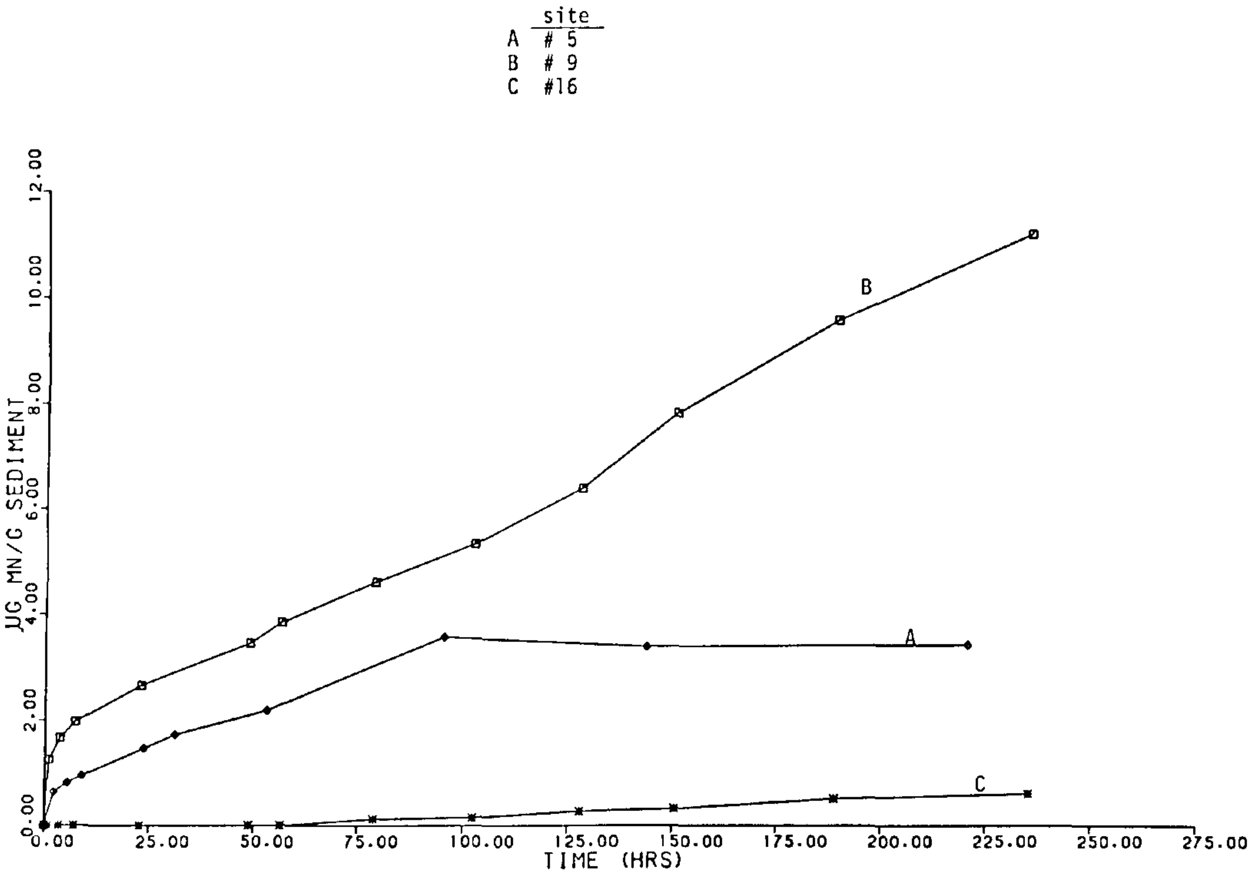

Figure 15 Cumulative Mn release from sediments
(No Mn release was detected in sediments from sites #14 and #50)

Table 5. Distribution coefficients (K) of Co, Cu, and Mn obtained from the leaching of different sediments under aerobic conditions with stirring and the Mn/Co and Mn/Cu ratios in the sediments

Sediment	Co	Cu	Mn	Mn/Co	Mn/Cu
# 5	$1.68X10^{-1}$	$1.70X10^{-2}$	$1.90X10^{-2}$	0.59	0.08
# 9	$3.66X10^{-1}$	$1.40X10^{-2}$	$6.71X10^{-2}$	0.35	0.06
#14	N.D.	$2.93X10^{-3}$	N.D.	2.48	1.97
#16	$3.22X10^{-2}$	$2.69X10^{-3}$	$3.87X10^{-4}$	9.88	5.25
#50	$5.23X10^{-3}$	$1.68X10^{-4}$	N.D.	1.07	0.57

N.D.: not detected

calculated from the experimental data obtained after about 10 days of leaching except for sample #50 which was calculated from the data collected after 30 days of leaching. In general, the cumulative mass releases of trace metals from the sediments during leaching were found to reach rather constant values after about 10 days of mixing. Therefore, the data for sediment #50 given in Table 5 should not be significantly different from the 10 day period chosen for the comparison of different samples. According to the K values given in Table 5, it is obvious that the sediments from Blackbird Creek contain much larger amounts of leachable Co, Cu, and Mn relative to the sediments from Panther Creek.

The low pH water produced from the leaching of sediments #5 and #9 is definitely one factor responsible for the higher degree of desorption of Co, Cu, and Mn from the sediments, while the high Mn content of the sediments from Panther Creek is possibly a factor responsible for the low degree of dissolution of Co and Cu from these sediments. Sediments from Panther Creek generally have much higher ratios of Mn/Co and Mn/Cu relative to those sediments from Blackbird Creek (Table 5). It is likely that Co and Cu were strongly adsorbed onto the sediment surface because of the scavenging properties of Mn which tends to retard the dissolution of these metals from the solid surface (Taylor and McKenzh, 1965).

D. Effects of pH on Leaching of Metals from the Sediments

The effects of pH upon the leaching of metals and the distribution of arsenic species were determined in leachates from a sediment sample obtained at site #25. Concentrations of total As, As(III), As(V), total Sb, Sb(III), Sb(V), Fe, Co, Cu, and Mn were measured after 30 hours of sediment-water contact time at controlled pH and under atmospheric pressure with continuous stirring. The desired pH was maintained by using dilute HCl or NaOH. The results are presented in Table 6 and Figure 16.

The concentrations of Co, Cu, and Mn were higher in acidic solutions during leaching. This is consistent with the mechanism of hydrogen ions replacing the adsorbed metal ions or causing dissolution of chemically bonded metal ions in the sediment. The behavior of arsenic species appears to be different than Co, Cu, and Mn during leaching with solutions of different pH. The total As leached was found to increase in basic solutions. The predominant arsenic species leached from the sediment was As(V), similar to the observations made in the leaching of other sediments from Panther Creek described in the previous section. The concentration of As(III) in the leaching solution was very low in the neutral solutions. This is probably related to the adsorption of arsenite on the sediment surface. Maxmium adsorption of arsenite has been reported to occur at pH 7.0 for amorphous iron hydroxides (Pierce and Moore, 1980; 1982). In alkaline

Table 6. Release of metals from sediments during leaching as a function of pH

Metal	pH=3.8	pH=6.3	pH=9.1	pH=11.5
As(total)	0.20	0.19	3.64	15.88
As(III)	7.32×10^{-2}	2.63×10^{-3}	2.80×10^{-2}	2.96×10^{-2}
As(V)	0.12	0.19	3.61	15.85
Sb(total)	7.11×10^{-3}	1.08×10^{-2}	2.26×10^{-2}	6.27×10^{-2}
Sb(III)	6.76×10^{-3}	2.55×10^{-3}	$<0.58\times10^{-3}$	$<0.57\times10^{-3}$
Sb(V)	0.35×10^{-3}	8.28×10^{-3}	2.26×10^{-2}	6.27×10^{-2}
Fe	1.78	1.86	5.15	2.17
Co	22.53	1.18	<0.1	<0.1
Cu	13.23	0.14	0.43	6.20
Mn	28.86	0.36	0.05	N.D.

Metals released are given in ug/g of dry sediment

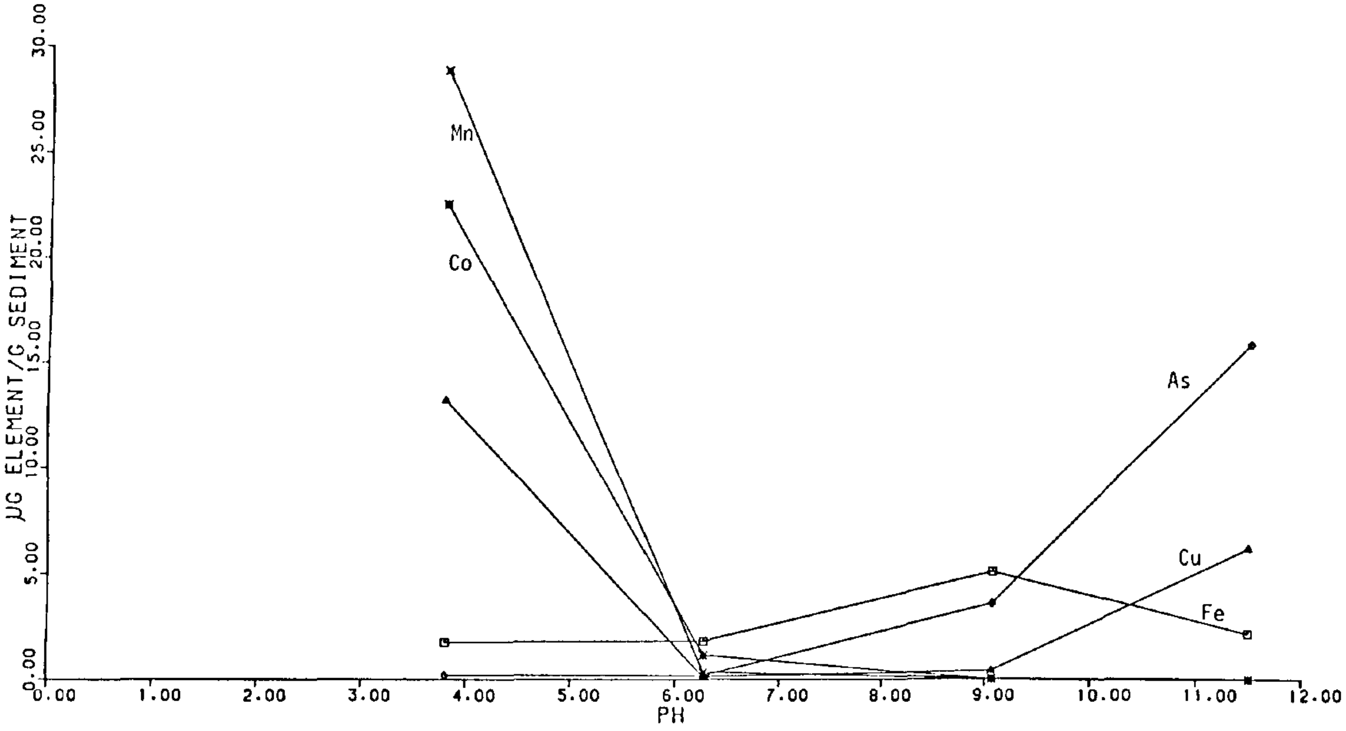

Figure 16 Release of total As, Fe, Co, Cu, and Mn from sediment #25 as a function of pH

solutions, arsenite exists as AsO_2^-, $H_2AsO_2^-$, and $As(OH)_4^-$. These anions are more mobile resulting in a higher As(III) concentration at high pH. The maximum adsorption of arsenate by amorphous iron hydroxides has been reported to be in the pH range of 3.5 to 5.3 (Pierce and Moore, 1980; 1982). Substantial increases in As(V) concentration were found in leachates at pH greater than 6.5 under our leaching conditions. In a basic solutions, arsenate can also exist in different anionic forms. Thus, the enhanced release of arsenate is probably also the consequence of its anionic property.

The observation of an enhanced arsenic solubility at high pH in our leaching experiments is significant. It suggests a case of environmental concern when alkaline solutions are discharged into the creeks with contaminated sediments. For example, discharge of lime treated waste water would increase the pH of creek water and consequently might result in a higher As release from the sediments. Lime treatment is a common method to reduce metal contents in acid mine drainages and waste waters related to mine tailings.

E. Leaching under Nitrogen Atmosphere

An experiment was performed under nitrogen atmosphere to evaluate the effects of an oxygen-free environment on the leaching of arsenic and other metals from the sediments collected from the Blackbird area. Sediment #14 was chosen for this experiment because it showed a relatively high arsenic release during leaching in open air in comparison with the other sediments from Panther Creek. The experimental conditions and sampling procedures are similar to the leaching experiments conducted under open air. The system was stirred continuously with a magnetic stirrer in a sealed flask, and nitrogen gas was flushed through the system to maintain an oxygen-free environment. The results are given in Figures 17 and 18.

Leaching under nitrogen atmosphere resulted in higher concentrations of dissolved iron and arsenic in solutions relative to leaching under open air conditions. The increase in soluble As is likely related to the reduction of ferric arsenate to ferrous arsenate, which is more soluble in water. The arsenite to arsenate ratio during leaching increased slightly indicating only a small fraction of the released As(V) was reduced to As(III). This observation is consistent with the release of arsenic from the leaching of contaminated soils reported by Deuel and Swoboda (1972). The leaching of soils in an oxygen-free environment was reported by these authors to result in higher soluble As(V) which was not reduced to As(III) under their experimental conditions. The increase in soluble As was attributed to ferric arsenate and other forms of ferric iron, which are combined with arsenate, being reduced to the relatively more soluble ferrous form (Deuel and Swoboda, 1972).

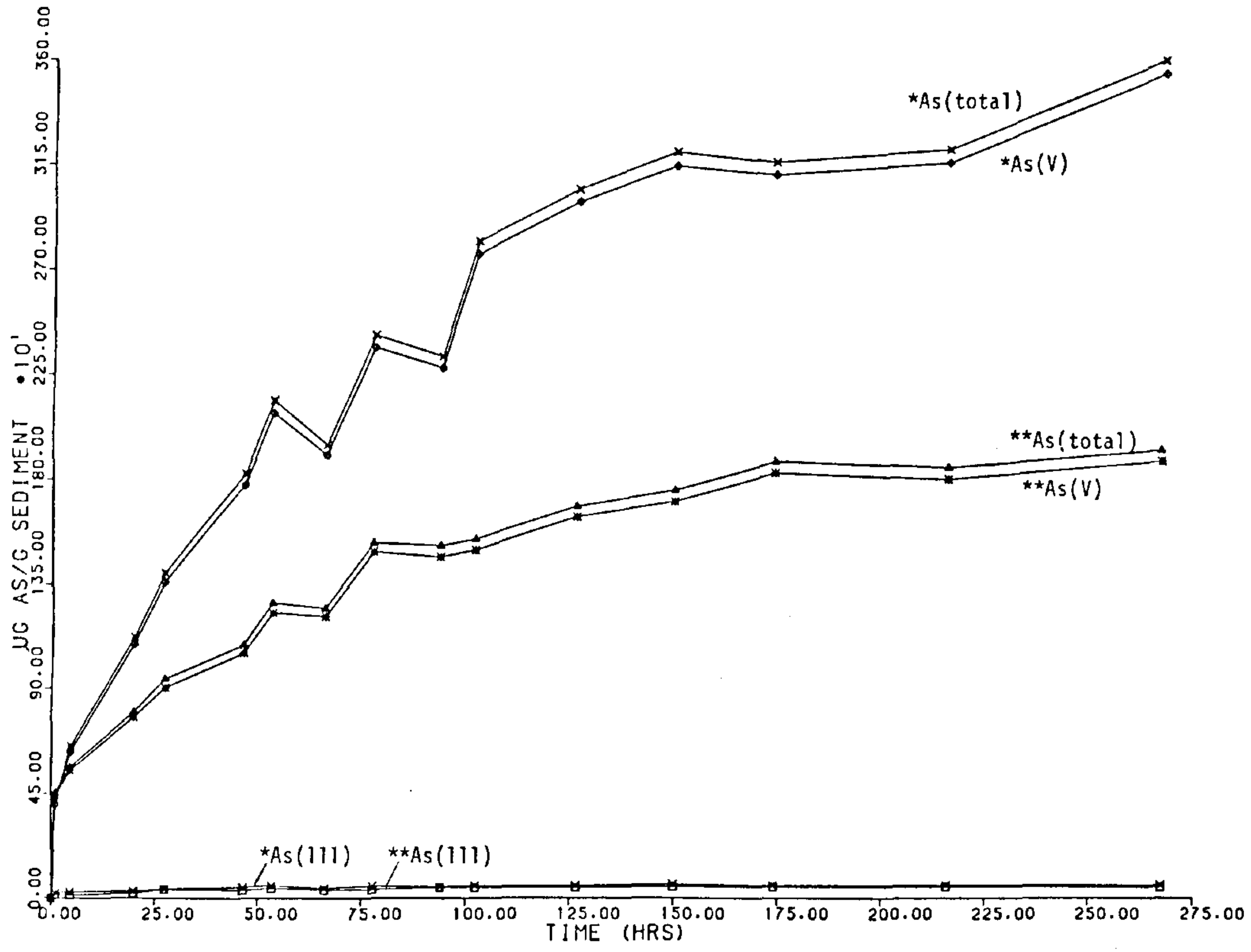

Figure 17 Cumulative release of As(III), As(V), and total As from sediments #14 under nitrogen atmosphere (*) and under aerobic condition (**)

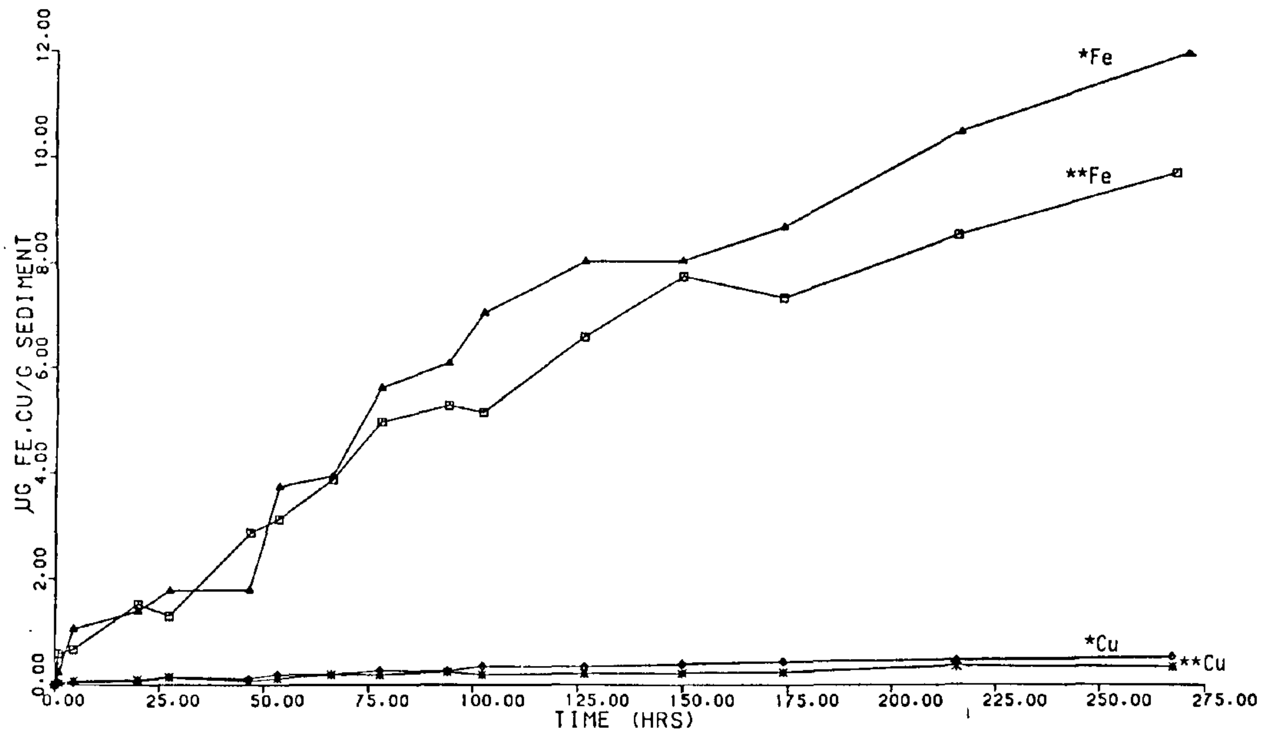

Figure 18 Cumulative Fe and Cu releases from sediment #14 under nitrogen atmosphere (*) and under aerobic condition (**)
(No Co and Mn release was detected)

The variation of the As(V)/As(III) ratio in solutions during leaching under nitrogen atmosphere was shown in Figure 10. A lower initial As(V)/As(III) ratio was observed in this system indicating that more As(III) was released under a reduced environment. The elevation of As(III) in short-term As release from anaerobic sediment-water environment suggests that caution must be utilized when evaluating the environmental impact of such releases, as As(III) is more toxic than As(V) to biological systems.

The releases of other trace metals Co, Cu, and Mn during leaching under nitrogen atmosphere did not show significant differences from the results observed from leaching under open air. The increase in Fe release came from the more soluble ferrous compounds as mentioned above.

Water Quality Data

A. Natural background levels - Panther Creek above the confluence of Blackbird Creek

Metal levels in Panther Creek above the confluence of Blackbird Creek are given in Table 7. These samples were collected on August 31 and September 29 of 1985 and on May 26 of 1986. Water samples collected from sites #11 and #13, located about 0.5 miles and 2.1 miles upstream above the confluence, respectively, are generally neutral or slightly basic with pH values in the range of 7-8. The concentrations of trace metals are very low in these water samples. The total As content was found to vary from 0.8

ng/mL to 1.1 ng/mL, generally high in As(V). This As level is comparable to the values found in unpolluted natural waters. For example, the total As in the Snake River near Lewiston, Idaho, was found to be 1.38+0.37 ng/mL with As(V) as the predominant species (Mok and Wai, 1986). The concentrations of Co, Cu, and Mn in the creek water were 0.01 ug/mL or less. The natural background levels of As, Co, Cu, and Mn in Panther Creek are probably close to the values shown in Table 7.

B. Blackbird Creek

The concentrations of As, Co, Cu, Fe, and Mn in water samples collected from five stations established along Blackbird Creek are given in Table 8. The locations of these sampling sites are shown in Figure 2. Water samples collected in August of 1985 were basically neutral. However, pH values of samples collected in September of 1985 were 3.1 and 4.7 at sites #5 and #6, respectively, while pH values of water samples at sites #7, #9, and #10 were 6.4, 5.9 and 7.1, respectively. The cause of this drop in the pH of the water is unknown. Associated with the low pH was an elevation of the concentrations of total As and the four other metals in the water sample from site #5. It appears that the quality of water at sites #5 and #6 was probably affected by the operational conditions of the water treatment plant inside the Noranda property.

Dilution by small streams along the creek resulted in lowering of the water acidity and metal concentrations in

Table 7. As, Fe, Co, Cu, and Mn concentrations in Panther Creek above the confluence of Blackbird Creek

Station		As(total)	As(III)	As(V)	Fe	Co	Cu	Mn
#11	a	1.12±0.39	0.34±0.03	0.78±0.05	0.03	<0.1	<0.01	<0.01
	b	1.01±0.11	<0.07	1.01±0.11	0.09	<0.1	0.01	<0.01
	c	0.78±0.05	0.41±0.04	0.37±0.06	0.08	<0.1	0.01	0.01
#13	a	1.00±0.08	0.30±0.07	0.70±0.11	0.06	<0.1	<0.01	<0.01
	b	0.98±0.14	<0.08	0.98±0.14	0.10	<0.1	0.01	<0.01
	c	0.80±0.07	<0.02	0.80±0.07	0.27	<0.1	0.01	<0.01

As concentrations in ng/mL, other metal concentrations in ug/mL.
a: August, 1985; b: September, 1985; c: May, 1986

sampling sites #6, #7, #9, and #10 and also counteracted the leaching of metals from the sediments. As a result, the concentrations of arsenic and other metal ions were reduced, showing an improvement in water quality.

In spring run-off, the water level of Blackbird Creek is generally high. The pH values of the water collected from Blackbird Creek was found to be near neutral, ranging from 6.6 to 7.4. The concentrations of total As, Co, Cu, Fe, and Mn were somewhat lower than those found in the fall, reflecting an improvement in water quality (Table 8). However, the As(V)/As(III) ratios were slightly higher in the late spring, indicating that the washing off of oxidized materials from the surroundings might enhance the oxidation of As species. The water quality of Blackbird Creek varies with location with respect to the source and to seasonal effects and also appears to depend on the flow, the texture of the sediments, the solution pH, and the redox conditions of the environment.

C. Panther Creek below the confluence of Blackbird Creek

Sampling sites #12, #14, #16, #25, and #26 are located in Panther Creek between Blackbird Creek and the Salmon River. The pH values of the water samples collected in the fall of 1985 and in the spring of 1986 from these sites were all near neutral, ranging from 7.3 - 7.9. The sediments of Panther Creek below the confluence are known to have arsenic and iron contents much lower than those in Blackbird Creek (Table 2). However, the total arsenic

Table 8. As, Fe, Co, Cu, and Mn concentrations in water samples collected from Blackbird Creek

Station #		As(total)	As(III)	As(V)	Fe	Co	Cu	Mn
#5	a	1.00±0.40	<0.3	1.00±0.40	0.37	2.07	1.76	0.38
	b	4.55±0.14	0.91±0.14	3.64±0.20	1.37	2.77	2.91	0.43
	c	1.11±0.07	0.18±0.04	0.93±0.08	<0.03	0.78	0.79	0.10
#6	a	0.84±0.07	0.81±0.07	<0.05	0.27	0.67	1.36	0.28
	b	0.71±0.13	0.44±0.12	0.27±0.18	0.70	2.38	2.03	0.33
	c	0.55±0.08	0.17±0.04	0.38±0.09	<0.03	0.74	0.60	0.09
#7	a	0.40±0.05	0.40±0.05	<0.05	0.14	0.38	<0.01	0.15
	b	0.78±0.10	0.51±0.12	0.27±0.16	0.32	0.69	0.02	0.20
	c	1.22±0.06	0.23±0.04	0.99±0.07	0.26	0.10	<0.01	0.02
#9	a	0.70±0.05	0.27±0.04	0.43±0.06	0.13	1.34	0.43	0.27
	c	0.48±0.08	0.32±0.05	0.16±0.09	<0.03	0.67	0.37	0.09
#10	a	2.94±0.11	0.91±0.09	2.03±0.14	0.06	0.90	0.07	0.17
	c	2.01±0.09	0.53±0.04	1.48±0.10	0.04	0.33	0.16	0.04

As concentrations in ng/mL, other metal concentrations in ug/mL.
a: August, 1985; b: September, 1985; c: May, 1986

concentrations in the creek water from these sites was found to be higher than those from Blackbird Creek. The concentrations of iron, copper, cobalt, and manganese in Panther Creek (Table 9) were lower than the values found in Blackbird Creek. Because of the small discharges of Blackbird Creek relative to Panther Creek, discharges from the former did not seem to have significant effects on the water quality of the latter. The concentration of arsenic in Panther Creek is most likely controlled by the leaching of the sediments present in the creek, and the release of arsenic appears to depend on the iron content of the sediments. This field observation again is consistent with the results observed from our laboratory leaching experiments. The predominant arsenic species found in Panther Creek is As(V).

D. Summary of Field Data

In general, the levels of Co, Cu, and Mn in creek water, measured at unpolluted locations of Panther Creek above the confluence of Blackbird Creek are very low, about 0.01 ug/mL or less. The total As in these locations is also low, about 1 ng/mL or less, with the majority of it being As(V). Elevated levels of Co, Cu, and Mn, usually in the range from 0.1 to 3.0 ug/mL, were observed in Blackbird Creek. Higher levels of these metals were found to be associated with low pH waters. The total As concentrations in Blackbird Creek waters were not

Table 9. As, Fe, Co, Cu, and Mn concentrations in Panther Creek below the confluence of Blackbird Creek

Station #		As(total)	As(III)	As(V)	Fe	Co	Cu	Mn
#12	a	1.50±0.09	0.76±0.07	0.74±0.01	0.06	0.04	0.02	0.01
	b	1.36±0.11	<0.07	1.36±0.11	0.08	0.12	0.02	0.01
	c	1.68±0.07	<0.03	1.68±0.07	0.05	0.05	0.03	<0.01
#14	a	6.20±0.10	0.90±0.10	5.30±0.10	0.03	0.07	0.02	0.01
	b	3.85±0.14	0.71±0.09	3.14±0.17	0.07	0.07	0.02	0.01
	c	1.62±0.05	0.11±0.07	1.51±0.09	<0.03	0.03	0.16	<0.01
#15	a	5.32±0.09	0.05	5.32±0.09	0.04	0.03	0.01	<0.01
	c	2.18±0.07	0.14±0.03	2.04±0.08	0.29	0.04	0.02	<0.01
#16	a	4.10±0.20	0.40±0.10	3.70±0.02	0.07	0.03	0.01	<0.01
	c	1.68±0.06	<0.03	1.68±0.06	0.14	0.01	0.02	<0.01
#25	b	3.45±0.14	0.68±0.03	2.77±0.14	0.08	0.03	0.02	<0.01
	c	1.38±0.27	0.06±0.03	1.32±0.08	0.13	0.01	0.02	<0.01
#26	a	4.41±0.11	2.11±0.08	2.30±0.14	0.03	0.02	0.04	<0.01
	b	3.16±0.12	0.58±0.08	2.58±0.14	0.05	0.04	<0.01	0.01
	c	1.87±0.07	0.07±0.04	1.80±0.08	0.20	0.03	0.06	<0.01

As concentrations in ng/ml, other metal concentrations in ug/mL
a: August, 1985; b: September, 1985; C: May, 1986

significantly different from the unpolluted background level in this area, although the sediments of Blackbird Creek contained a much higher amount of As. The As content in Panther Creek waters below the confluence of Blackbird Creek is higher than that found in Blackbird Creek. This is probably related to the high Fe content of the sediments of Blackbird Creek which tends to inhibit the release of As. Lower As(V)/As(III) ratios were generally observed in Blackbird Creek water relative to Panther Creek water. Based on the observation made from the leaching experiments, the metal concentrations in Panther Creek water are most likely controlled by leaching from the sediments.

The distribution coefficients of As in water versus As in sediments of the selected sites are given in Table 10. Because the volume of water in an unconfined system is not known, the distribution coefficient in this case is defined as

$$D = C_l / C_s$$

where C_l = As concentration (ug/mL) in the creek water and C_s = As concentration (ug/g) in the sediment. Using this definition for the distribution coefficient, we have also calculated the D values for As and other trace metals based on the data obtained from the leaching experiments. These experimental D values are given in Table 10.

The experimental D values are generally an order of magnitude higher than those found in the natural

Table 10. Distribution coefficients of As species observed in Blackbird Creek and in Panther Creek

Station	Condition	As(III)	As(V)	Total As
# 5	lab leaching	N.D.	3.65x10^{-6}	3.65x10^{-6}
	creek water - a	N.D.	8.92X10^{-7}	8.92X10^{-7}
	b	8.12x10^{-7}	3.25x10^{-6}	4.06x10^{-6}
	c	1.61X10^{-7}	7.41X10^{-7}	9.91X10^{-7}
# 9	lab leaching	8.78x10^{-7}	3.62x10^{-6}	4.49x10^{-6}
	creek water - a	1.06X10^{-7}	1.69X10^{-7}	2.75X10^{-7}
	c	1.25X10^{-7}	6.27X10^{-7}	1.88X10^{-7}
#14	lab leaching	7.34x10^{-5}	2.73x10^{-3}	2.80x10^{-3}
	creek water - a	2.13X10^{-5}	1.25X10^{-4}	1.47X10^{-4}
	b	1.68x10^{-5}	7.45x10^{-5}	9.13x10^{-5}
	c	2.61X10^{-6}	3.59X10^{-5}	3.85X10^{-5}
#16	lab leaching	1.28x10^{-5}	2.14x10^{-4}	2.27x10^{-4}
	creek water - a	3.02X10^{-6}	2.79X10^{-5}	3.09X10^{-5}
	c	2.26X10^{-7}	1.27X10^{-5}	1.27X10^{-5}
#50	lab leaching	2.29x10^{-6}	5.21x10^{-5}	5.44x10^{-5}
	creek water - b	6.72X10^{-6}	6.43X10^{-6}	1.31X10^{-5}
	c	N.D.	9.01X10^{-6}	9.01X10^{-6}

a: August, 1985; b: September, 1985; c: May, 1986; N.D.: not detected environment, indicating that the creek waters are not in equilibrium with the sediments. The D values of As in Panther Creek are higher than those in Blackbird Creek, and the values of Co, Cu, and Mn are just the opposite (Table 11). The trend is similar to the results observed in the laboratory leaching experiments. Therefore, although the creek waters are not in equilibrium with the sediments in the natural environment, the field data still show good correlation with the behavior of the various trace metals observed in the laboratory systems.

The concentrations of Sb in the creek waters of the Blackbird area were generally very low, in the order of sub-ppb levels. The Sb analytical procedure for NAA was developed near the end of this project. Therefore, only Sb concentrations in the water samples collected in May 1986, were analyzed. Total Sb in the water samples from Blackbird Creek and from Panther Creek was generally less than 0.05 ng/mL, except for sites #10, #15, and #16 where the total Sb concentrations were found to be 0.25+0.08 ng/mL, 0.16+0.03 ng/mL, and 0.23+0.04 ng/mL respectively. The Sb species detected in water from these sites was virtually all Sb(V). The Sb levels in the creeks of the Blackbird area are not very different from those found in other unpolluted rivers in Idaho. For example, the Sb level in the Snake River near Lewiston, Idaho, was found to be around 0.2 ng/mL, with Sb(V) as the predominant species (Mok and Wai, 1986). The Coeur d'Alene River in

Table 11. Distribution coefficients of Co, Cu, and Mn observed in Blackbird Creek and in Panther Creek

Station	Condition	Fe	Co	Cu	Mn
# 5	lab leaching	1.50×10^{-6}	1.07×10^{-2}	1.08×10^{-3}	1.20×10^{-3}
	creek water a	3.46×10^{-6}	6.64×10^{-3}	7.55×10^{-4}	2.07×10^{-3}
	b	1.28×10^{-5}	8.88×10^{-3}	1.25×10^{-3}	2.35×10^{-3}
	c	N.D.	2.50×10^{-3}	3.39×10^{-4}	5.46×10^{-4}
# 9	lab leaching	4.28×10^{-5}	2.65×10^{-2}	1.02×10^{-3}	4.84×10^{-3}
	creek water a	1.00×10^{-6}	2.85×10^{-3}	1.66×10^{-4}	1.67×10^{-3}
	b	6.94×10^{-7}	3.48×10^{-3}	3.08×10^{-4}	1.67×10^{-3}
	c	N.D.	1.42×10^{-3}	1.43×10^{-4}	5.38×10^{-4}
#14	lab leaching	3.08×10^{-5}	1.06×10^{-3}	1.69×10^{-4}	4.29×10^{-5}
	creek water a	1.62×10^{-6}	7.44×10^{-4}	1.69×10^{-4}	4.28×10^{-5}
	b	3.78×10^{-6}	7.44×10^{-4}	1.69×10^{-4}	4.28×10^{-5}
	c	N.D.	3.19×10^{-4}	1.35×10^{-3}	N.D.
#16	lab leaching	1.42×10^{-5}	1.98×10^{-3}	1.70×10^{-4}	2.58×10^{-5}
	creek water a	2.22×10^{-6}	1.91×10^{-4}	3.39×10^{-5}	N.D.
	c	4.43×10^{-6}	6.38×10^{-5}	6.78×10^{-5}	N.D.
#50	lab leaching	1.06×10^{-5}	2.02×10^{-4}	9.71×10^{-6}	1.72×10^{-5}
	creek water b	1.32×10^{-6}	N.D.	9.71×10^{-6}	1.72×10^{-5}
	c	2.65×10^{-6}	N.D.	N.D.	N.D.

a: August, 1985; b: September, 1985; c: May, 1986
N.D.: not detected

northern Idaho, which is known to have a heavy metal pollution problem, showed significantly higher levels of Sb (Mok and Wai, 1987). Based on these preliminary data, it appears that Sb is unlikely to be a metal of environmental concern in the drainages of the Blackbird area. Because of its low concentration in natural water, large sample volumes are needed to determine Sb accurately. The analytical technique for Sb developed from this project is currently being applied to the studies of Sb distributions in the Coeur d'Alene Mining District.

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APPENDIX

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Simultaneous Extraction of Trivalent and Pentavalent Antimony and Arsenic Species in Natural Waters for Neutron Activation Analysis

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Antimony(III) and arsenic(III) in aqueous sample can be simultaneously extracted with ammonium pyrrolidinecarbodithioate (APCDT) into chloroform from pH 3 to 6. Extraction of antimony(V) and arsenic(V) can be achieved by reduction with thiosulfate and potassium iodide at pH 1 followed by APCDT extraction at the same pH value. The Sb– and As–PCDT complexes in the organic phase can be back-extracted into a nitric acid solution for neutron activation analysis (NAA). Detection of 10^{-3} μg/L of antimony and arsenic can be achieved by using this extraction method and NAA. Applications of this method to antimony and arsenic speciation studies in natural water systems are discussed.

Arsenic and antimony are among the most interesting elements in studies of environmental pollution because of their toxic nature. Biologically, As(III) is considered more toxic than As(V) (*1, 2*). Knowledge of the distribution of As(III) and As(V) species in natural water systems is important for environmental monitoring programs. It has also been suggested that the ratio of As(III) to As(V) may be used as a chemical indicator of the redox status of groundwater systems (*3*). The distribution and toxicity of Sb(III) and Sb(V) are less known. However, antimony and its compounds are listed as priority pollutants by the U.S. Environmental Protection Agency. Thus, the toxicity and physiological behavior of As and possibly Sb are dependent on their oxidation states. These elements are found in the environment at very low concentrations. The concentrations of total As and Sb in most natural water systems are in the range of 10^{-9}–10^{-10} and 10^{-9}–10^{-11} g/mL, respectively (*4, 5*). Analytical methods capable of measuring nanogram levels of As(III), As(V), Sb(III), and Sb(V) are therefore necessary for studying the chemistry of As and Sb species in aquatic environments.

Neutron activation analysis (NAA), when coupled with specific separation procedures, is one of the most sensitive methods for the determination of trace amounts of different species of As, Sb, Se, V, etc. (*6, 7*). We have recently developed a technique for the determination of nanogram levels of As(III) and As(V) in natural waters with dithiocarbamate extraction for NAA (*8*). With some modification of the extraction procedure, the technique can be applied to determine As and Sb species simultaneously. The extraction method, which concentrates As and Sb from water and eliminates interfering elements for neutron irradiation, has greatly improved the sensitivity and accuracy for the detection of nanogram levels of As and Sb species in real samples. The details of the extraction procedure are given in the following section. In an attempt to demonstrate applicability to matrices having different chemical compositions, the following standard materials were analyzed: orchard leaves (SRM 1571), coal fly ash (SRM 1633a), and a seawater reference material (NASS-1).

EXPERIMENTAL SECTION

Reagents. A stock solution of Sb(III) (1000 mg/L) was prepared by dissolution of 0.1972 g of Sb_2O_3 (Baker) in 100 mL of 2.5 M HCl. A stock solution of Sb(V) (1000 mg/L) was prepared by dissolution of 0.2168 g of potassium antimonate in water, making up to 100 mL in 0.1% HNO_3. Stock solutions of As(III) and As(V) were prepared according to the procedures given in our previous paper (*8*).

Ammonium pyrrolidinecarbodithioate (APCDT) was obtained from the Fisher Scientific Co. Chloroform used in the extraction was Baker Analyzed reagent. The extraction solution was prepared by dissolving 5 g of APCDT in 100 mL of deionized water. The solution was always prepared fresh prior to use, filtered to remove the insoluble material, and shaken with chloroform for 1 min to remove bromine and other impurities. Deionized water was obtained by treatment of distilled water through an ion-exchange column (Barnstead Ultrapure Water Purification Cartridge) and a 0.2-μm filter assembly (Pall Corporation Utipor DFA). Ammonium citrate buffer (20%, w/v) was prepared by dissolving 200 g of ammonium citrate, dibasic (ACS grade, Fisher Scientific), in 500 mL of water, adjusting the pH to 7.2 with concentrated ammonia, and making up to 1 L with water. The containers used in this study were cleaned sequentially with a detergent wash, tap water, and distilled water rinse and soaked in 10% HNO_3 for at least 24 h. They were then rinsed with deionized water and stored in a class-100 clean hood equipped with a vertical laminar flow filter (CCI). All other reagents and solutions used were of the highest purity available. Surface seawater was collected off Bainbridge Island in Puget Sound. River waters were collected from the Snake River in Lewiston, ID, and from the Coeur d'Alene River in northern Idaho. The samples were treated as described in our previous paper (*8*).

Analytical Procedures. All water samples analyzed were saturated with chloroform before extraction. For the extraction of Sb(III) and As(III), normally a 100-mL sample was placed into a ground-glass-stoppered Erlenmeyer flask. A 10-mL aliquot of citrate buffer was added, and the pH was adjusted to a value between 3.5 and 5.5 with HCl or NH_4OH; the pH range selected for the simultaneous extraction of Sb(III) and As(III) will be explained in the next section. This was followed by the addition of 4 mL of 12.5% ethylenediaminetetraacetic acid (EDTA) solution as a masking agent (*8*). Ten milliliters of chloroform and 2 mL of 5% APCDT were then added. The mixture was extracted by shaking vigorously for 10 min on a wrist-action mechanical shaker (Burrell Model 75), and the phases were allowed to separate. After the aqueous phase was discarded, the organic phase was washed twice with 10 mL of deionized water. Exactly 8 mL of the organic phase was transferred to a 20-mL Beckman polyvial with a fast-turn cap. to back-extract Sb and As, 1.5 mL of 50% HNO_3 was added to the vial, and the mixture was shaken for 10 min. After phase separation, 1 mL of the aqueous phase was pipetted into a $^2/_5$-dram polyethylene vial and heat-sealed for neutron irradiation. A procedure blank made of an equal volume of deionized water (100 mL in this case) was run for each set of experiments.

For water samples with low As and Sb contents, the initial sample size can be increased to 300 mL or 500 mL. The amount of the buffer, the masking agent, and the chelating agent PCDT should also be increased in proportion to the sample size. About 20–30 mL of chloroform should be sufficient for effective extraction of the Sb and As complexes. After extraction, the volume of the organic phase can be reduced by evaporation at room temperature. After the volume of chloroform is reduced to less than 10 mL, back-extraction with nitric acid can be carried out according to the procedure described in the previous section. No detectable loss of Sb and As was observed during the evaporation process.

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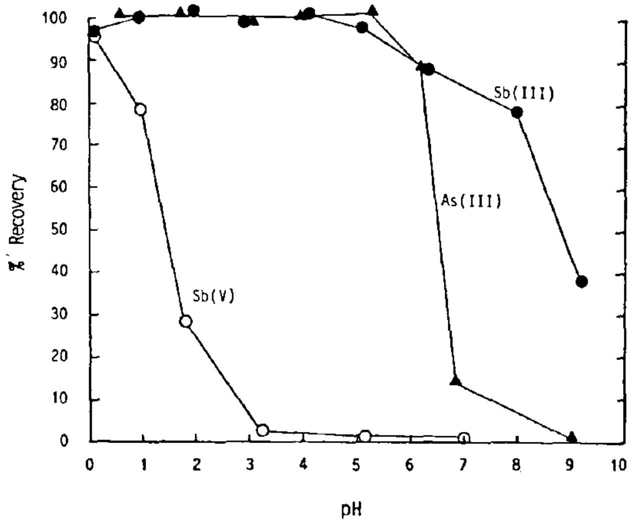

Figure 1. pH dependence of the extraction of Sb(III), Sb(V), and As(III) with APCDT from aqueous phase into chloroform.

To determine total Sb and As, a second aliquot of the water sample was placed in an Erlenmeyer flask and adjusted to a pH of about 1.0 with HCl. Reduction of Sb(V) to Sb(III) and As(V) to As(III) was carried out by using 1 mL of a 25% sodium thiosulfate solution and 1 mL of a 20% potassium iodide solution. After a waiting period of 15–30 min, 4 mL of the EDTA solution, 10 mL of chloroform, and 2 mL of 5% APCDT were added to the flask, and the complexes were extracted by the same procedure described above. The differences in Sb and As concentrations between the two aliquots represent the amount of Sb(V) and As(V) in the water sample.

NBS orchard leaves reference material was digested with a mixture of HNO_3 and H_2SO_4 in a reflux apparatus while digestion of NBS coal fly ash was carried out by using a mixture of HCl and HNO_3. The digestion procedures are given in the literature (*9*).

The details for sample irradiation and counting are given elsewhere (*8*). All irradiations were done in a 1-MW Triga reactor at a steady neutron flux of 6×10^{12} n cm^{-2} s^{-1}. Arsenic and Sb were determined as the nuclides ^{76}As ($t_{1/2}$ = 1.10 days, E_γ = 559.1 keV) and ^{122}Sb ($t_{1/2}$ = 2.74 days, E_γ = 564.0 keV) following 2–3-h irradiation and a 24-h cooling period. The nuclides were quantified by comparing net photopeak areas with those of standards. Counting times varied from 2×10^3 to 8×10^3 s depending on the concentrations of Sb and As in samples.

RESULTS AND DISCUSSION

Extraction of As(III) and As(V) using APCDT has been described in our previous paper (*8*). However, no work has been reported that combines this extraction method for the speciation of Sb with a modern analytical technique such as NAA. Both As and Sb are extremely sensitive to neutron activation. Under interference-free conditions, nanogram levels of As and Sb can be detected by NAA. However, direct measurements of As and Sb in natural waters by NAA are very difficult to carry out because of their low concentrations and matrix interferences. The advantages of using the derivatives of dithiocarbamic acid to extract trace metals from natural waters for NAA have been discussed in the literature (*8*). Briefly, the extraction may serve three purposes: (1) concentration and separation of trace metals, (2) elimination of interfering matrix species (such as Na and Br in the case of NAA), and (3) differentiation of metal species.

The effects of pH on the extraction of Sb(III) with APCDT are shown in Figure 1. The experiments were carried out in 100-mL deionized–water samples spiked with 5 ng/mL of Sb(III). Quantitative extraction of Sb(III) was observed in a pH range from 2 M HCl to pH 6. The pentavalent species, Sb(V), was quantitatively extracted from pH 1 to 2 M HCl, but there was virtually no extraction of Sb(V) at pH >3.0. It can be seen from Figure 1 that simultaneous extraction of Sb(III) and As(III) is possible only in the pH range 3.0–6.0. Since As(V) was practically unextracted over the entire range of pH and acidity studied, a pH range of 3.5–5.5 was chosen as the standard condition for the extraction of As(III) and Sb(III) with the dithiocarbamate. Ammonium citrate was the buffer used to control the pH of the solution during extraction. There is no observable interference caused by the citrate buffer for the extraction of Sb(III) and As(III) using this method.

Sodium thiosulfate is an effective reducing agent for As(V), but it took more than 30 min for complete reduction of Sb(V) to Sb(III) under the same condition. Radioisotope experiments showed that when a solution contained 0.2% KI and 0.25% $S_2O_3^{2-}$, the reduction was complete in 10 min. Subsequent studies showed that quantitative reduction could not be achieved by KI alone in 25 min. In our experiments, the reduction of Sb(V) and As(V) to their trivalent states was conducted in a 0.25% $Na_2S_2O_3$ and 0.20% KI solution at pH 1 for about 15–30 min. Our recommended procedure is to shake the solution for 5 min with thiosulfate followed by the addition of potassium iodide. This seems to give the best result for the reduction process.

For effective extraction of metal–dithiocarbamate complexes, the aqueous-to-organic-phase ratio should be kept at 20 or less. The shaking time for the extraction of Sb– and As–PCDT by chloroform had also been studied, and 2 min of shaking was found to be sufficient. In general, the required shaking time increases according to the metal concentration in solution, the sample volume used, and the sample matrix. In all our experiments, a shaking time of 10 min is used. Back-extraction with acid allows concentrating As and Sb efficiently into a small volume of aqueous phase, which can then be transferred into a polyethylene vial for neutron irradiation. With a 50% HNO_3 solution, back-extraction of both Sb and As can be achieved with 10 min of shaking. Sb can be stripped completely into a 20% HNO_3 solution, but incomplete extraction of As may result if the acid concentration is less than 30%.

By use of the two-step extraction procedures described in this paper, an overall preconcentration factor of 100 or more can be achieved. The absolute detection limit of Sb and As for 3 h of irradiation and 2×10^3 s counting was estimated to be 1.2 and 1.0 ng, respectively, on the basis of 3σ (standard deviation) of the background under the 564.0-keV peak of Sb and 559.1-keV peak of As. With a preconcentration factor of 10^2, this method should be able to detect Sb and As in natural waters at 10^{-2} $\mu g/L$ level, or about 10 parts per trillion. If a 500-mL sample and an 8×10^3 s counting time are used, the detection limit of Sb and As can be lowered to 10^{-3} $\mu g/L$, or about 1 part per trillion. This detection limit is sensitive enough to measure Sb and As species in most natural water systems.

Recovery of spikes (300 ng added to 100 mL of a seawater reference material (NASS-1) obtained from the Marine analytical Chemistry Standards Program, National Reasearch Council of Canada) into aqueous samples averaged 98.1 ± 1.7% for Sb, based on three replicate measurements and with blank correction. The total As in NASS-1 was found to be 1.49 ± 0.03 $\mu g/L$, which agrees well with the certified value of 1.65 ± 0.19 $\mu g/L$. Results for the analysis of NASS-1 are given in Table I. The accuracy of the method for Sb determination was assessed by comparison of the results with those obtained by using other independent analytical techniques. Agreement with these other values is evident from the data shown in the table.

This method has also been applied to the anaylsis of an NBS biological standard, orchard leaves (SRM 1571), whose Sb and As contents have been certified to be 2.9 ± 0.3 and

Table I. Determination of Total As and Sb in Some Reference Materials Using This Extraction Method and NAA

ref material	As		Sb	
	this work	lit.	this work	lit.
seawater (NASS-1)	1.49 ± 0.03 μg/L	1.6 ± 0.19[a] μg/L	0.28 ± 0.02 μg/L	(0.20 ± 0.02)–(0.24 ± 0.02)[d] μg/L
orchard leaves (SRM-1571)	8.84 ± 0.11 μg/g	10 ± 2[b] μg/g	3.04 ± 0.09 μg/g	2.9 ± 0.3[b] μg/g
coal fly ash (SRM-1633a)	139 ± 3 μg/g	145 ± 15[b] μg/g	7.5 ± 1.2 μg/g	7 μg/g[c]

[a] Certified value, Marine Analytical Chemistry Standards Program, National Research Council of Canada. [b] Certified value, U. S. National Bureau of Standards. [c] NBS reference value, not certified. [d] From four independent analytical techniques: APCDT-AA (*10*), electrochemical ASV-HMDE (*11*), activated charcoal-NAA (*12*), hydride generation-AA (*13*).

Table II. Recovery of Spiked Sb(III) and Sb(V)

amt added, ng		% recovery		
Sb(III)	Sb(V)	Sb(III)	Sb(V)	total Sb
200		101.3 ± 4.2		
400		109.0 ± 2.8		
800		94.6 ± 3.8		
	200		102.0 ± 4.4	
–	400		97.0 ± 2.6	
	800		101.6 ± 1.8	
70	400			100.0 ± 7.4
140	800			97.0 ± 3.9

10 ± 2 μg/g, respectively. The standard reference material was digested by using the sulfuric acid/nitric acid mixture described in the literature (*9*). On the basis of three replicate analyses, the Sb and As contents in SRM 1571 were determined to be 3.04 ± 0.09 and 8.84 ± 0.11 μg/g, respectively. These experimental values agree well with the reported values. In another case, analysis of Sb and As in digested coal fly ash samples (SRM-1633a) using this extraction method and NAA resulted in 7.54 ± 1.23 μg/g of Sb and 139.0 ± 3.4 μg/g of As in the ash. These experimental values again agree with the values 7 and 145 ± 15 μg/g for Sb and As, respectively, as reported by NBS. All these results indicate that the method for simultaneous determination of total Sb and As is reasonably accurate.

The accuracy of this extraction method for speciation of Sb(III) and Sb(V) could not be thoroughly evaluated because no standard waters containing known amounts of these two Sb species are available. Deionized water samples spiked with known amounts of Sb(III) and Sb(V) showed satisfactory recoveries of both species as given in Table II. The results of simultaneous determination of trivalent and pentavalent antimony and arsenic in 100-mL water samples spiked with known amount of the Sb and As species are presented in Table III. Satisfactory recoveries of both Sb and As species were also observed. In a previous study, spiked As(III) in a coastal seawater sample was found partially converted to As(V), presumably due to the presence of oxidating species in the natural water system (*8*). Other reports also noted that conversion of spiked arsenite to arsenate could take place at low As concentrations (*14, 15*). For this reason, relatively pure water was used in this study to test the recovery of As and Sb species by the proposed PCDT extraction method.

The method presented appears to be suitable for analysis of nanogram to picogram per milliliter levels of Sb and As species in environmental water samples. The determination of Sb and As species in surface seawater and river water samples is shown in Table IV. These values are comparable to those reported in the literature for open ocean water and for river waters (*4, 5, 16*). For surface waters, either from the sea or from the river, Sb(V) and As(V) are known to be the predominent species under the condition of thermodynamic equilibrium. The finding that very low As(III) is present in natural water samples examined agrees well with the statement of Braman and Foreback that arsenate is probably the most common environmental form of inorganic arsenic (*17*). However, under a reducing environment, As(III) was found as the major species in ground waters (*8*). As shown in Table IV, significant amounts of As(III) are also found in the waters collected from the Coeur d'Alene River in northern Idaho. The river has a serious heavy metal pollution problem caused primarily by the lead, zinc, and silver mining activities in this area (*18, 19*). The conversion of As(III) to As(V) in water exposed to air is slow in the absence of a catalyst or other oxidating agent (*3*). One possible explanation for the relatively low As(III/As(V) ratio observed in the Coeur d'Alene River may be due to the lack of biological activities which are probably needed to catalyze the conversion (*20, 21*).

The ratio of Sb(III)/Sb(V) in most natural water systems was reported to be on the order of 10^{-2} (*22*). Competing processes that modify the concentrations of the arsenic species in natural waters, as described in the literature, may also apply to antimony which enters the aquatic environment as a result of the weathering of rocks (which contain an average of 0.16 ppm Sb), from soil runoff, through effluents from mining and manufacturing, and from municipal discharge. Sensitive and

Table III. Recovery of Spiked Sb(III), Sb(V), As(III), and As(V)

ng added				% recovery			
Sb(III)	Sb(V)	As(III)	As(V)	Sb(III)	total Sb	As(III)	total As
100	100	100	100	89.7 ± 5.9	95.2 ± 3.7	107.8 ± 5.3	108.5 ± 3.2
200	200	200	200	100.2 ± 3.9	98.6 ± 2.8	111.7 ± 3.4	99.0 ± 2.3
300	300	300	300	100.8 ± 3.2	105.4 ± 2.6	104.8 ± 2.8	105.9 ± 2.1

Table IV. Sb and As Concentrations in Seawater and River Waters[a]

sample location	Sb(III)	Sb(V)	As(III)	As(V)
seawater, Bainbridge Island, WA	0.005 ± 0.003	0.24 ± 0.04	0.010 ± 0.005	1.36 ± 0.04
Snake River, Lewiston, ID	0.005 ± 0.003	0.19 ± 0.03	0.02 ± 0.01	1.36 ± 0.36
Coeur d'Alene River, Cataldo, ID	0.044 ± 0.005	1.89 ± 0.07	0.33 ± 0.04	0.34 ± 0.06
Coeur d'Alene River, Kellogg, ID	0.030 ± 0.008	7.03 ± 0.13	0.19 ± 0.04	0.48 ± 0.06

[a] Concentrations expressed in ng/mL.

reliable methods of measuring antimony species in water are needed for speciation studies. This extraction method provides a large preconcentration factor which is necessary for the determination of low levels of Sb(III) species in water. The proposed analytical method has currently been used to investigate arsenic and antimony species in some groundwater systems in the Coeur d'Alene Mining District in order to obtain a better understanding of the distribution of these species in aquatic environments. The extraction method described in this paper is not limited to NAA. It can be combined with other instrumental techniques such as graphite furnace atomic absorption spectrometry (GFAAS) for arsenic and antimony speciation studies in natural water systems.

Registry No. APCDT, 5108-96-3; H_2O, 7732-18-5; Sb, 7440-36-0; As, 7440-38-2; chloroform, 67-66-3.

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