THE USE OF SEDIMENT SAMPLING TO EVALUATE THE SUCCESS OF HYDROLOGIC RECLAMATION [1]

by

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Abstract Surface water monitoring efforts usually involve random, infrequent, grab sampling of the water column. This method may not detect irregular or infrequent pulses of pollutants and may be ineffective in assessing the physical and chemical quality of the benthic zone. The benthic zone can accumulate metals and often supports the aquatic insects essential to a healthy aquatic ecosystem. Sediment analysis was conducted on two mine-project sites in Kentucky and Tennessee to supplement existing chemical and biological sampling of streams and lakes. Sediments were analyzed for 15 metals and trace elements (Al, Sb, Ar, Be, Cd, Cr, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, and Zn) and fine-particle size analysis was done using air elutriation methods. Each sediment sample was analyzed using total metal extraction, EPA's Toxicity Characteristic Leachate Procedure (TCLP), and a four-step sequential extraction procedure. The four-step sequential extraction procedure provided the most meaningful indication of metals and trace elements that could be of concern. The results showed distinct sediment chemistry and particle-size distribution between mined and unmined streams. Sediment chemistry mirrored pore-water chemistry and aided interpretation of the stream water and biological data in mined and unmined streams that was not otherwise apparent by sampling the water column alone. Sequential sediment analysis and fine-particle size analysis shows promise in assessing the success of hydrologic reclamation at mined sites.

KEY WORDS: Trace Elements, Water Quality, Coal, Mining

Introduction

Hydrologic Reclamation includes, but is not limited to, the restoration of baseline water quality and sediment quality to support the aquatic ecosystem and other potential water users. Assessing hydrologic impacts and hydrologic reclamation typically includes sampling of the water-column and comparing it with ambient criteria or water-quality standards. This method alone may ignore the condition of the benthic zone that can be critical to the aquatic ecosystem. In addition, the spacial and temporal nature of water column sampling may not represent the acute or chronic water chemistry of the stream affecting aquatic life.

This report summarizes the results of stream and lake sediment sampling programs at watersheds having active and proposed coal mines. The results were used to compliment the other physical, chemical, and biologic surveys done at the sites. It was intended that the sediment sampling would reduce the time and cost of obtaining ambient water conditions over water column sampling alone and be more representative of in-field conditions. The physiochemical environment at the sediment level is generally ignored in typical coal mine stream sampling. Yet the benthic zone is host to much of the food source used by higher aquatic life such as fishes. The bottom dwelling aquatic insects rely on the sediment pore-water quality as much as the water column itself.

The effects of mining on sedimentation loads has been well documented (Walters, 1995; EPA, 1981). Stream pollutants and sediments from mining may occur in

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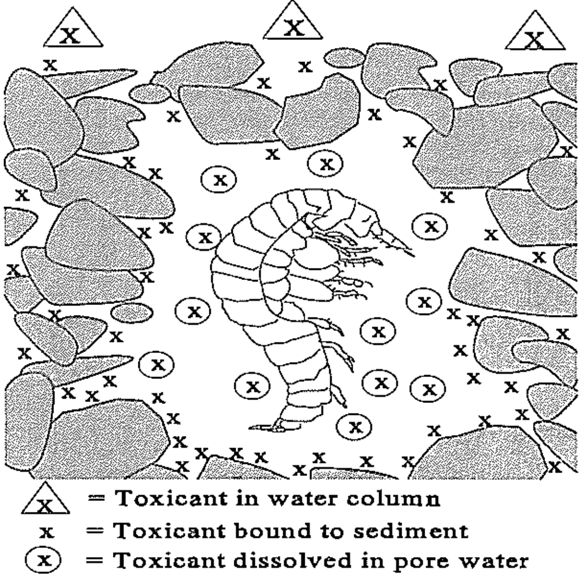
pulses due to the nature of sediment distribution and transport and also operational considerations such as the periodic opening and closing of treatment system discharge valves. Periodic random water column sampling may or may not represent the true pollutant load placed on a stream since it ignores bedload sediment (Horowitz, 1991). Frequent and composited stream water sampling is needed to characterize the stream-water-column environment fully; however, use of diffusive gradients in thin films (DGT) technology is helping fill the gap (Zhang, 1995, p. 3391). Sediment sampling aids in filling in the gaps between periodic water-column sampling and presents a more complete picture of the quality of the aquatic environment. A previous regional study in Tennessee has shown that water sampling alone only identifies 75 percent of the mine impacted drainages (O'Bara, 1993, p. 87). Another regional study in Virginia concluded benthic impacts from copper and zinc were occurring in coal mined drainages despite regulatory water column monitoring (McCann, 1993).

Several literature reviews on recent sediment research are provided by Fuller (1995, p.164) and Clement (1985, p. 236R). Sediment sampling can include both bioassay (Ingersoll, 1995A) and direct chemical analysis. Stream and overbank sediment sampling is useful in evaluating mining-related stream impacts (Ridgway, 1995; Wielinga, 1994; Prairie, 1994; Coupe, 1993).

Metal and trace element contaminants may be dissolved or settle as particulate matter. They may be adsorbed to sediments, precipitated, coprecipitated, bonded organically, undergo cation exchange, or be incorporated into the crystal lattices of sediments that coat the bottom of the stream channel. The type of sediment dictates the ability to bind with other metals. Horowitz (1991, p.41) found the relative capacity of collectors in freshwater systems were: Amorphous Iron Oxides > Total Extractable Iron > Total Organic Carbon > Reactive Iron > Clay Minerals > Total Extractable manganese > Manganese Oxides. Horowitz (1991, p. 69) also studied the relative importance of selected physical and chemical factors on sediment trace-element chemistry; he found: Amorphous Iron Oxides > Surface Area > Total Organic Matter (LOI) > total Extractable Iron > Other Organic Matter > Percent less than 63 µm > Reactive Iron > Total Organic Carbon > Percent less than 125 µm > mean grain size > percent clay minerals > percent less then 16 µm > percent less than 2 µm > Total Extractable Manganese > Manganese Oxides.

The sediment pore-water quality is a function of both the sediment and the overlying water quality (Burton, 1992). Figure 1 shows this relationship. Unless the benthic zone is restored after mining, the aquatic ecosystem will not be restored to baseline levels.

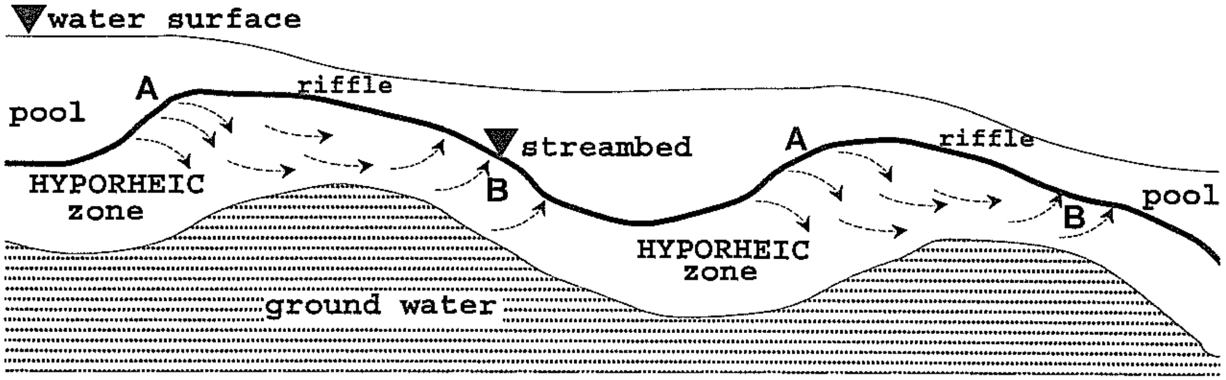
Figure 1 - X-Section of stygobite in sediment



After Burton, 1992

The sediment zone contains a reservoir of metals, trace elements, and nutrients that can be re-suspended in the water column by diagenic processes (Buffle, 1994, Horowitz, 1991, p. 49) such as floods or bioturbation, changes in physiochemical conditions (pH, eH, DO, temperature, *etc.*), and biochemical reactions (bacteria, humic substances, etc.) that increase toxicity or solubility (e.g., methylization of mercury). The sediment layer is often the location of the ground water and surface-water interaction zone, termed hyporheic zone (See Figure 2), which fluctuates seasonally and supports a diverse ground-water ecosystem (Hendricks, 1992; White, 1992, Gilbert, 1994, Dahm, 1992). Polluted ground waters recharging a stream in this zone can adversely affect the interstitial waters of the sediment without detectable change in the water quality of the water column. Therefore, the use of benthic and interstitial

Figure 2 - Conceptual Model of Hyporheic Zone



A = Zone of Down-welling B = Zone of Up-welling ---> = Direction of water

After Hendricks, 1992. (Vertical exaggeration)

invertebrates, such as stygobites, can also be used as indicators of ecosystem damage, along with sediment analysis (Plenet, 1992; Gilbert, 1994).

Heavy metals and trace elements such as Al, Cd, Cu, Se, Pb, Ni, and Zn are known to be associated with coal mine drainages (EPA, 1981; Liddle, 1994; Liddle, 1995). Often these minor elements are not monitored since it is incorrectly assumed they either do not exist in high concentrations or they are removed during the iron and manganese treatment process. For example, metal transport through the spoils to streams via fractures is unaffected by surface-water treatment ponds, yet this groundwater is seldom monitored at minesites unless it forms springs. Another example is aluminum, which is often reported in the literature as having a low (<1 mg/l) concentration at mine sites. However, it was not until August 1988 that EPA promulgated the aquatic freshwater criteria of 0.087 mg/l for aluminum (53 FR 33178). And recently the EPA is considering reducing the drinking water standard for arsenic from 0.040 mg/l to 0.006 mg/l, because of carcinogistic concerns (Eaton, 1994). Since many trace-element water-quality criteria have not been determined until recently, and EPA criteria are very low, one must guard against assuming only iron and manganese are of concern. The sediment-analysis methods presented here show techniques that can be used to determine the amount of metals available for bioaccumulation and the amount of metals easily taken back into solution in the pore water or water column. The absence of these metals in the sediments is a good indicator they are not significant in the water column.

Methods

At project site #1, sediment, biological, and water sampling was conducted in four watersheds with similar geology and topography and with little or no non-mining development: 1) 18.4 km^2 (7.1 mi^2)Little Yellow Creek in north Tennessee; 2) nearby 25.9 km^2 (10 mi^2) Little Clear Creek in southern Kentucky; and 3) Bennett Fork, and Langley Branch). Little Yellow Creek watershed is proposed for surface coal mining and the others have been mined since the late 1970's. As such, they are excellent locations to evaluate true baseline conditions with post-SMCRA mining impacts. Little Yellow Creek and Little Clear Creek historically contained a large population of the endangered Blackside Dace. However, the mined watershed has been without the Blackside Dace since 1985, according to stream surveys. Mining is suspected of causing this extirpation. Complete information on the hydrology of the sites is available from OSM (Liddle, 1995A). A second project site is Bruce Creek above Cove Lake State Park. The stream was sterilized by metal contamination in 1993 emanating from an anoxic drain in coal spoils (Sugar Ridge Mine, 200 acres) north of Knoxville, TN. While water quality has since improved due to treatment, the question of restoration of the benthic zone remains unanswered.

About 15 to 20 sediment samples less

than 4 cm deep were taken at each site and composited. Five sites were sampled on each stream at the base of a riffle zone during low streamflow (Burton, 1992, p. 89; USGS, 1995, p. 20; USGS, 1970, p. 53). These five composites were then combined to produce one sample felt to represent the stream. It was important to take many samples, because stream sediments from coal mines are spatially and seasonally variable (Gunten, 1994) and lab analysis was to be done on only a few grams of each sample. Sediments were stored at or near freezing until analyzed, which took several months. This may have produced errors; recent research has shown samples should be frozen and analyzed immediately to prevent biochemical changes (Becker, 1995). The less toxic the sediments the more susceptible they are to changes.

The sampling procedures followed recommendations of Burton (1992, p. 32), Ingersoll (1995) and the specifications of ASTM standards D3974-81 and D3976-92 (ASTM, 1993, Vol. 11.02). ASTM Standards D4822-88, D4823-88, D5074-90, and D3976-92 were also followed depending on the stream being studied (polluted vs. unpolluted). Sampling and laboratory practices generally followed the USGS procedures (USGS, 1982; USGS, 1993).

Particle size analysis was done using sieves and air elutriation methods to obtain very fine particle analysis to 0.0015 mm. Samples were analyzed in three ways: 1) total metals were extracted using hydrochloric and nitric acid digestion; 2) the EPA Toxicity Characteristic Leaching Procedure (TCLP); and 3) a 4-step sequential extraction method. The sequential extraction method is based on Tessier's (1979) work, and has been modified to fit geochemical extractions of inorganic metals and trace elements common in mining investigations (Tessier, 1979; Chao, 1983; Chao, 1984; Horowitz, 1988; Horowitz, 1990; and Horowitz, 1991a). The sequential extractions were done on samples screened to less than 0.63 micron to allow clearer comparisons based on particle size (See Horowitz, 1991a). No grinding or crushing of particles was done.

Results of Grain Size Analysis

The sediment grain-size distributions showed that the mined watershed of Little Clear Creek had more fine clays and silts than the unmined watershed of Little Clear Creek (See Figure 3). Field investigations included suspended sediment sampling during storm events to develop a sediment graph for both streams. The results revealed that during storm events the coal-mine haul roads were a significant source of sediment loads to the stream since most of the haul-road drainage entered the Little Clear Creek untreated.

The grain-size distributions for Bruce Creek revealed that stream sediments had less clays at greater distances away from the mine site. Since clays have the highest surface area per particle, and sediment surface area is directly proportional to the capacity to capture and retain metal and trace elements (Horowitz, 1991, p. 16) the grain-size distribution can shed light on the potential for metal retention.

Results of Sediment Chemistry Analysis

The total digestion of the samples with nitric and sulfuric acid did not show any meaningful trends between mined and unmined streams or downstream from the anoxic drain at Bruce Creek. This is because the amount of metals contamination was very low. In high contamination sites such as hazardous waste sites, concentrations of metals are large enough to show differences between natural and contaminated sites. The EPA TCLP extractions confirmed that none of the sediments came close to meeting EPA toxic criteria. The metals contamination at coal mines would be expected to be more subtle. The total digestion of sediments does not distinguish between metals held in the crystal lattice of the rocks, metals bound organically, metals precipitated, or metals adsorbed. Consequently the total metals results show more about the mineral content of the sediments than about the bioavailability of metals.

The total metal extraction (TME) analysis is somewhat useful as a quality check on sequential extraction methods. If a total extraction with hydrofluoric and nitric acid is conducted on ground sediments, then all metals including those in the crystal lattice should be released. (Note Hcl, HNO_3, H_2SO_4 alone will not extract all metals without HFl) One could then analyze the remaining sample after the sequential extractions to determine what metals were not released. The quality check then becomes:

$$TME = E_1 + E_2 + E_3 + E_4 + E_n \ . \ . \ . + TME_e$$

Where E_1 to ${}_nE$ is the mass of metal released from the first to last sequential extract, respectively, and TME_e is the mass of metal remaining on the extracted sediment after all sequential extracts are completed. In this study, our contract laboratory would not do the HFl extractions due to safety concerns, therefore we were unable to obtain this quality check step. Instead, splits were run on the samples to ensure reproducible results.

The sequential extractions were designed to mimic the physiochemical processes that would strip sediments of metals and trace elements from successively higher energy orders. Use of sequential extractions, while not an exact science, has been used extensively by the metal mining community for geochemical prospecting (Chao, 1983, 1984). Extraction #1 is designed to extract exchangeable, adsorbed, and carbonate metals using 1 gram residue per 8 ml 1M Sodium Acetate adjusted to pH 5 with Acetic Acid, agitated for 1 hour. Extract #2 is designed to release metals easily bound to manganese oxides and reactive iron using 1 gram of residue per 50 ml of 0.1 M Hydroxylamine Hydrochloride in 0.1 M HNO_3, shaken for 30 minutes at 25°C. Extract #3 is designed to release tightly bound metals from amorphous iron oxides and manganese using one gram residue to 250 ml solution of 0.25 M Hydroxylamine Hydrochloride in 0.25 M HCl, heated and shaken at 50°C for 30 minutes. Extract #4 should release organically bound metals using 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2, adjusted to pH 2 with HNO_3, heated and occasionally shaken at 85 °C for 2 hours. Then adding a 3 ml aliquot of 30% H_2O_2 adjusting to pH 2 with HNO_3 again and heated and agitated for 3 more hours. After cooling, add 5 ml of 3.2 M Ammonium Acetate in 20 % v/v HNO_3 , then dilute with distilled water to a 20 ml volume, shake at 25°C for 30 minutes, then analyze. Each extract was separately analyzed for Al, Sb, Ar, Be, Cd, Cr, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, and Zn.

The results of total digestion of the samples for the first project site are listed below in mg per kilogram dry weight (Figure 1). The results show the difficulty in comparing multiple sources of sediments using total sediment analysis. For some parameters such as arsenic, the unmined watershed was highest. In unmined Fern Lake the lead concentration was highest probably due to the use of lead fishing sinkers. Mining affected streams were higher in zinc, nickel, copper, and chromium. However, this method may be useful for screening out elements that are too low to consider further such as Ar, Ag, Se, Tl, Sb, Be, and Cd.

Table 1 - Total Digestion of Sediment

	L. Yello Creek	Fern Lake	Benn-ett Fork	L. Clear Creek	Lang-ley Br.
mg/kg	UNMINED		MINED		
AL	2290	14 K	2210	3410	6580
Sb	0.5	0.5	0.5	0.5	0.7
Ar	9.4	5.6	4.2	0.7	2.2
Be	0.4	1.1	0.2	1.0	0.8
Cd	0.1	0.2	0.2	0.1	0.02
Cr	5.6	8.7	8.3	8.3	9.9
Cu	5.6	20.6	15.7	10.8	15.8
Fe	12 K	40 K	9900	12 K	26 K
Pb	4.5	204	6.9	8.6	144
Mn	260	347	254	426	1220
Ni	10.4	30.3	15.7	13	32.6
Se	0.3	0.2	0.2	0.2	0.2
Ag	0.1	0.1	0.1	0.1	.001
Tl	0.1	0.2	0.2	0.1	0.1
Zn	29	107	40	49	83

The results of the first sequential extractions in mg/kg dry weight are as follows:

Table 2 - SEQUENTIAL EXTRACT #1

	Yello Cr	Fern Lake	Benne-t Cr	L. Clear	Lang-ley
mg/kg	UNMINED		MINED		
Al	263	192	34	20	87
Cu	8000	7310	1540	1010	480
Fe	331	1210	35	16	61
Pb	832	1550	29	69	47
Mn	840	304	121	509	613
Ni	12	8	4	5	10
Zn	165	1100	304	200	99

These results show concentrations in the 63μm fraction of sediment and are useful in correlation studies. The USGS has used similar procedures to find relationships between chemical and physical parameters with sediment chemistry on a regional basis. If a good correlation is found, then concentrations of the elements can be predicted for similar regions. Examples of the USGS national sediment models are:

$$Cu = 0.52\ LOI + 0.351\ Al + 0.395\ Ti + 0.875$$
and
$$Ni = 0.963\ Al + 0.248\ TOC + 0.003$$
(See Horowitz, 1991, p. 79)

To evaluate the total effects of the metals in the environment, one must consider the total metal available, not just the 63 μm fraction. Since the previous data shows mined watersheds were higher in clays, the total contribution of metals must be recalculated, based on the percentage of clays to the total sediment. One could reanalyze the total sediments, but research has shown the contribution from sands and silts to be negligible in most cases (Horowitz, 1991). The results of this comparison follow:

Table 3 - SEDIMENT TOXICITY: Extracts 1 + 2

	L. Yello	Benn-ett	L. Clear	Lang-ley
mg/kg	Un-Mined	MINED WATERSHEDS		
Al	90	57	188	266
Fe	275	192	830	551
Mn	84	46	279	405
Zn	37	99	105	71
Cu	872	1120	643	373
Pb	105	12	50	46
Clay	8.9%	28.5%	37.8%	52.2%

Assuming the sediments have similar bulk densities and assuming the first two sequential extractions represent the bioavailable fractions; the results show that the mined watersheds are higher in some metals. Lead is higher in the unmined watershed, owing to lead fishing tackle, while zinc and aluminum are generally higher in mined watersheds. Some element concentrations are not significantly different in the sediments (e.g., copper). Pore water samples taken by centrifuging sediments from Langley Branch below a strip mine revealed dissolved aluminum concentrations of 1.68 mg/l, well above the EPA chronic aquatic standard of 0.087 mg/l (53 FR 33178, 8/30/88), while the maximum concentration in the water column was only 0.02 mg/l. The dissolved iron concentration in pore water was 2.17 mg/l, which is above the 1.0 mg/l EPA threshold (EPA, 1985); the maximum iron content in the water column was 0.028 mg/l. The zinc pore water concentration was 0.053 mg/l, which is near the EPA aquatic life chronic criteria of 0.059 mg/l (52 FR 6214, 3/2/87). The water column concentration of dissolved zinc was 0.03 mg/l. The sediment analysis failed to correlate with the elevated lead concentrations of 0.006 mg/l in the pore water, which is above the EPA chronic aquatic criteria of 0.0013 mg/l (50 FR 30791, 7/29/85); the dissolved lead concentration in the water column was 0.002 mg/l.

At the second project site at Bruce Creek, sediment samples were taken at treatment ponds below an anoxic drain and in several places in the receiving stream. The purpose was to assess how far downstream the metal contamination had spread. Water from the anoxic drain flows from 0.25 to 2 cfs and contains several toxic concentrations of metals, as compared with aquatic receiving-stream standards. The following table compares concentrations from the anoxic drain with receiving-stream standards:

Table 4 - Anoxic Drain Quality

	Total Metals	Dissolved Metals	Aquatic Criteria[1]
Cu	20 μg/l	1 μg/l	6.5 μg/l
Al	1810 μg/l	940 μg/l	87 μg/l
Cd	26 μg/l	0.5 μg/l	4.6 μg/l
Fe	85 mg/l	40 mg/l	1.0 mg/l
Mn	35.4 mg/l	35 mg/l	none
Ni	470 μg/l	430 μg/l	88 μg/l
Zn	388 μg/l	190 μg/l	59 μg/l
Hg	2.3 μg/l	-	.012 μg/l

[1] EPA Freshwater Aquatic Chronic Criteria.

Although the water is now being treated under a bond forfeiture situation, the stream was already contaminated to the point where no aquatic life was found (Turner, 1995). Recent stream-water-quality sampling of the water column about 0.2 km (1/8 mile) downstream revealed aluminum, copper, iron, nickel, and zinc are still at the EPA aquatic life chronic criteria. Water samples taken about 3.2 km (2 miles) downstream showed aluminum, nickel and zinc were still at EPA freshwater aquatic life chronic criteria. The results of the sediment analysis showed decreasing metal concentrations as one sampled downstream:

Table 5 - Sediment Toxicity: Extracts 1 + 2

mg/kg	Upper pond sedimnt	Lower pond sed.	1.75 mi down stream	2 mi. Down stream
Al	575	399	242	22
Cu	584	664	466	43
Fe	4975	2223	433	74
Mn	5726	1113	725	234
Ni	104	7.5	4.5	1.5
Zn	153	221	113	10
Clay	80 %	35 %	22 %	3 %

If one looked at total metals analysis, and even TCLP data, the results would not show this trend. For example, aluminum total digestion results for the upper pond to the lower segment were 4080 mg/kg, 8460 mg/kg, 5640 mg/kg, and 3070 mg/kg respectively. Total zinc concentrations were 180, 39, 37, and 49 mg/kg respectively. Similar results were noted with Cu, Mn, and Ni. Since biological data shows aquatic life survival increases the further downstream from the anoxic drain one samples, and the water column sampling shows a similar trend in improvement, one could logically hypothesize that the availability of metals in the sediments would also increase. Pore-water sampling and biological assays would be needed to support this hypothesis.

Additional information was obtained from the sediment data. Sequential extract #11 implied that the unmined watersheds had higher available metals (i.e., easily adsorbed metals and carbonates) than the mined watersheds studied. This could be the result of the mined watersheds adding iron to the stream that resulted in higher-energy binding of metals and trace elements to the sediment. The second extractions showed much more metals in the mined watersheds. The EPA TCLP extractions did not mimic any of the sequential extractions, as might have been expected. A comparison of sequential extractions from both project sites indicates metals would likely be a problem at levels greater than 100 mg/kg total.

Evaluation of the sediment quality data currently is done using comparisons of affected and unaffected reaches. The EPA has only recently established sediment-quality criteria for several organic constituents; metal criteria are still lacking, and bioassay has been historically used in evaluating dredged sediments (EPA, 1987, Zarba, 1988, Mancini, 1992, and Iannuzzi, 1995). Some States have developed threshold criteria based on comparative sampling (Kelley, 1984) and Canada has issued Provincial Guidelines for Sediment Quality (Prairie, 1994).

CONCLUSIONS

The EPA TCLP extractions were not very useful for estimating pore-water chemistry or as indicators of affected drainages. This test was designed based on municipal waste leachate testing (Kimmell, 1988). Most coal mine drainage will not result in metal contamination that would be high enough to be classified as "toxic" according to this EPA test.

The total metals analysis was not useful in predicting either the availability of metals and trace elements or comparisons of affected verses unaffected drainages. The total metals analysis may serve as a check on the results of sequential extractions.

Sediment sequential extractions shows promise in identifying the availability of metals and some trace elements. Sequential extractions #1 and #2 were particularly useful; other extracts would be useful in other investigations such as geochemical prospecting or organic contaminants. Sequential extractions are better suited for investigating metals of elevated concentrations (>100 mg/kg) and are less valuable in looking at trace amounts of elements. The OSM is now using a five-step sequential extraction procedure to better define the speciation of metals in sediments.

Partical-size analysis of sediments is important for assessing the quality of the sediments and to evaluate the results of sediment metal extractions.

A lab experienced in sediment analysis should be used so that samples can be quickly analyzed upon collection, otherwise errors can occur. Short delays in getting a sample analyzed, even if the sample is frozen, has been shown to affect the toxicity of the sediment (Becker, 1995).

Additional research is needed in sampling and preparation of both pore-water and sediment from typical high gradient first and second-order streams. More research is needed in establishing standard sequential extraction methods that replicate bioavailable fractions typical of coal mining geochemistry (Horowitz, 1991). More comparative studies are needed of sediment quality, pore-water quality, water quality, sediment bioassay, and aquatic bioaccumulation at mine sites. Additional work is needed in establishing sediment-quality standards.

REFERENCES

ASTM, 1993. Annual Book of ASTM Standards, Section 11, Water; American Society for Testing and Materials, Philadelphia, Pa.

Becker, D.S., and Ginn, T.C., 1995. Effects of Storage Time on the Toxicity of Sediments from Puget Sound, Washington. Environmental Toxicology and Chemistry, Vol. 14, No. 5, pp. 829-835.
https://doi.org/10.1002/etc.5620140513

Buffle, J, and DeVitre, R.R., 1994. Chemical and Biological Regulation of Aquatic Sediments, Lewis Publishers, Boca Raton, Fl, 385 pp.

Burton, G.A., 1992. Sediment Toxicity Lewis Publishers, Boca Raton, Fl., 457 pp.

Chao, T., and Zhoe, L., 1983. Extraction Techniques for Selective Dissolution of Amorphous Iron Oxides from Soils and Sediments. Soil Science Society of America Journal, v. 47, p. 225.
https://doi.org/10.2136/sssaj1983.03615995004700020010x

Chao, T., 1984. Use of Partial Dissolution Techniques in Geochemical Exploration. Journal of Geochemical Exploration, v. 20, p. 101-136.
https://doi.org/10.1016/0375-6742(84)90078-5

Clement, R.E., Eicemen, G.A., and Koester, C.J.; 1995. Environmental Analysis. Analytical Chemistry, Vol. 67, June 15, 1995, p. 221R-255R.
https://doi.org/10.1021/ac00108a012

Coupe, R.H. and Macy, J.A.; 1993. Surface-Water and Streambed-Sediment Quality of Streams Draining Surface-Mined Land Reclaimed with Sewage Sludge, Fulton County, Illinois, 1972-1989. USGS Water Resources Investigations Report 93-4056, Urbana, Illinois.

Dahm, C.N., et.Al., 1992. Nutrient Cycling and Microbial Activity in the Hyporheic Zone. Proceedings of the First International Conference on Ground Water Ecology, American Water Resources Association, Bethesda, Maryland.

Eaton, A.D., February 1994. Determining the Practical Quantification Level for Arsenic. Journal of the American Water Works Association, Denver, Co., Volume 86.

EPA, 1981. Development Document for Effluent Limitations Guidelines and Standards for the Coal Mining Point Source Category. US EPA, Washington D.C., EPA 440/1-81/057-b, 429 pp.

EPA, 1986. Quality Criteria for Water 1986, "Gold Book," EPA, Washington, D.C., EPA 440/5-86-001.

EPA, 1987, Regulatory Applications of Sediment Criteria. US EPA, Washington D.C., NTIS #PB 93-174472, 44 pp.

Fuller, C.B., et. Al., 1995. Aquatic Sediments. Water Environment Research, Vol. 67, June 1995, p. 614-629.

Gilbert, J., Danielopol, D., Standord, J.A., 1994. Ground Water Ecology. Academic Press, New York, 571 pp.

Gunten, H.R., Karametaxas, G., and Keil, R., 1994. Chemical Processes in Infiltrated Riverbed Sediments. Environmental Science and Technology, Vol. 28, November 1994, pp. 2087-2093.
https://doi.org/10.1021/es00061a017

Horowitz, A.J., and Elrick, K., 1988. Interpretation of Bed Sediment Trace Metal Data: Methods for Dealing with Grain Size Effect; <u>In Chemical and Biological Characterization of Sludges, Sediments, and Drilling Muds</u>, ASTM STP #976, Philadelphia, PA. P. 114-128.

Horowitz, A.J., 1991. "The Role of Sediment-Trace Element Chemistry in Water-Quality Monitoring and the Need for Standard Analytical Methods." In Monitoring Water in the 1990's, Hall and Glysson, editors, ASTM STP 1102, p. 301-314, American Society of Testing Materials, Philadelphia, PA.

Horowitz, A.J., 1991a. A Primer on Sediment-Trace Element Chemistry, Lewis Publishers, Boca Raton, Florida, 136 pp.

Iannuzzi, T.J., et.al., 1995. Comments on the Use of Equilibrium Partitioning to Establish Sediment Quality Criteria for Non-Ionic Chemicals. Environmental Toxicology and Chemistry, Vol. 14, No.8, p 1257-1259. https://doi.org/10.1002/etc.5620140801

Hendricks, S.P., 1992. Bacterial Dynamics Near the Ground Water-Surface Water Interface (Hyporheic Zone) Beneath a Sandy-Bed, Third-Order Stream in Northern Michigan. Proceedings of the First International Conference on Ground Water Ecology, American Water Resources Association, Bethesda, Maryland. Pp. 27-35.

Ingersoll, C.G., 1995. Sediment Tests. In Fundamentals of Aquatic Toxicology, Gary Rand, editor, Taylor and Francis Publishers, Washington, D.C., p. 1125.

Ingersoll, C.G., 1995. Toxicity and Bioaccumulation of Sediment-Associated Contaminants Using Freshwater Invertebrates: A review of Methods and Applications. Environmental Toxicology and Chemistry, Vol. 14, No. 11, November 1995, pp. 1885-1894. https://doi.org/10.1002/etc.5620141110

Kelly, M., et. Al., Analysis of Surficial Sediment From 63 Illinois Lakes. In Lake and Reservoir Management; EPA, Washington, D.C., EPA 440/5/84-001, p. 248-253.

Kimmell, T.A., 1988. Development, Evaluation, and Use of the Toxicity Characteristics Leaching Procedures (TCLP). In Chemical and Biological Characterization of Sludges, Sediments, Dredge Spoils, and Drilling Muds, ASTM STP 976, American Society for Testing and Materials, Philadelphia, PA.; pp. 129-140.

Liddle, R.G., 1994. Cumulative Hydrologic Impacts From mining on Aquatic life in the Tennessee Coal Fields. Presented at the Annual meeting of the American fisheries Society - Tennessee Chapter, January 23-25, 1995. pp. 19, Available at the Office of Surface Mining, Knoxville, TN. 37902

Liddle, R.G., 1995. Hydrology of Fern Lake Watershed, Middlesboro, Kentucky, 326 pp., Available from OSM Knoxville, TN.

Mancini, J.L., and Plummer, A.H., 1992. A Review of EPA Sediment Criteria, In Proceedings: Developing Cleanup Standards for Contaminated Soil, Sediment, and Groundwater, Specialty Conference Series, January 10-13, 1992, Water Environment Federation, Alexandria, Virginia pp. 131-140.

McCann, M.T., 1993. Toxicity of Zinc, Copper, and Sediments to the Early Life Stages of Freshwater Mussels in the Powell River, Virginia. MS Thesis submitted to Virginia Polytechnic Institute, Blacksburg, Virginia.

O'Bara, C.; Adams, V.D.; and Eggleston, M.A., 1993. A Procedure to Determine the Integrity of Surface Water Quality in Streams of Coal Producing Regions. Center for the Management, Utilization, and Protection of Water Resources, Tennessee Technological University. Report submitted to OSM, Eastern Support Center, Pittsburgh, PA.

Prairie, R. And McKee, 1994, Sediment Quality Assessment Near Two Ontario Mine Sites: How Relevant are the Provincial Guidelines? In International Land Reclamation and Mine Drainage Conference and Third International Conference on the Abatement of Acidic Drainage. Vol. 1 of 4, pp. 307-316. Bureau of Mines Special Publication SP 06A-94.

Ridgeway, J., et. Al. 1995. Overbank Sediments from Central Mexico: An Evaluation of their use in Regional Geochemical Mapping and in Studies of Combination from Modern and Historical Mining. Applied Geochemistry, Vol. 10, January 1995, p. 97-109. https://doi.org/10.1016/0883-2927(94)00038-8

Sengupta, M., 1993. Environmental Impacts of Mining: Monitoring, Restoration, and Control. Lewis Publishers, Boca Raton, Florida, 494 pp.

Tessier, A., Campbell, P., and Bisson, M., 1979. Sequential Extraction Procedure for the Speciation of Particulate Trace Metals; Analytical Chemistry, v. 51, p. 844.

Turner, D., 1995. Personal Communication Tennessee Division of Water, Knoxville, TN.

USGS, 1970. Field Methods for Measurement of Fluvial Sediment. In TWRI Book 3, Chapter C2, 59 pp.

USGS, 1982. Quality Assurance Practices for the Chemical and Biological Analysis of Water and Fluvial Sediments. TWRI Book 5, Chapter A6, Lakewood, Colorado, 181 pp.

USGS, 1993. Quality Assurance Plan for the Collection and processing of Sediment Data by the US Geological Survey, Water Resources Division, Knott, JM. et.Al., USGS Open File Report 92-499, Denver, Colorado, 18 pp.

USGS, 1995. Design of the National Water-Quality Assessment Program: Occurrence and Distribution of Water-Quality Conditions. USGS Circular #1112, Lakewood, Co. 33 pp.

Waters, T.F., 1995. Sediment in Streams. American Fisheries Monograph 7, AFS, Bethesda, Maryland, 251 pp.

White, D.S., Hendricks, S., and Fortner, S.L., 1992. Grounwater-Surface Water Interactions and the Distribution of Aquatic Macrophytes. Proceedings of the First International Conference on Ground Water ecology. American Water Resources Association, Bethesda, Maryland. pp. 247-255.

Wielinga, et. Al., 1994. Geomicrobial Profile through the Hyporheic Zone of a Historic Mining Flood Plain. Proceedings of the Second International Conference on Ground Water Ecology, March 27-30, 1994; American Water Resources Association, Herndon, Va. pp. 267-276.

Zarba, C.S., 1988. Status of the US EPA's Sediment Quality Criteria Development Effort. In Chemical and Biological Characterization of Sludges, Sediments, Dredge Spoils, and Drilling Muds, ASTM STP 976, American Society for Testing and Materials, Philadelphia, PA.; pp. 13-17.

Zhang, H., and Davidson, 1995. Performance Characteristics of Diffusion Gradients in Thin Films for the In-Situ Measurement of Trace Metals in Aqueous Solution. Analytical Chemistry, Vol. 67, October 1, 1995, p. 3391-3400.

https://doi.org/10.1021/ac00115a005