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The Impact of Black Shale Weathering on Sediment Quality

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Abstract

Weathering of black shales leads to elevated metal concentrations in both surface water and stream sediments. In spite of the recent focus on black shales, few data exist on the ecological impacts of this process particularly on aquatic organisms. The key objective of this study was to determine the impact of trace metal concentrations in sediments upon aquatic organisms. To achieve the above objective, stream sediment samples were collected from streams draining black shale and limestone (used as a reference stream) lithologies located in central Arkansas between June 2003 and January 2004. Trace metal concentrations were measured by the dynamic reaction cell inductively coupled plasma mass spectrometry (ICPMS; Perkin Elmer DRC II) following EPA 6020 methodology. Sediment samples were tested for toxicity using standard EPA protocols. The trace metal concentrations in sediments and acute toxicity test findings using midge larvae, *Chironomus tentans* with endpoints measured as growth and survival is presented. Our results showed that there are significant differences in survival of the midge larvae among the study sites and also among the different sampling occasions. Percent survival of the midge larvae in the sediments derived from black shales was lower than that observed in the limestone-derived stream sediments. Significant differences in growth of the midge larvae were also observed among the sites with the control and reference stream sediments having higher growth than the black shale stream sediments. Though our measured metal concentrations in the black shale-derived sediments were below the Effects Range-Low, there is a great potential of metal accumulation in the fine sediment fraction particularly during baseflow regimes. At the time, metals can be concentrated in the fine sediment fraction due to the low discharge and less dilution. The study thus far has shown that the black shale metal-enriched stream sediments have both lethal and sublethal effects on aquatic organisms and higher organisms through food chain transfer.

Introduction

Chemical weathering of rocks is one of the principal processes governing the cycling of elements at the Earth's surface. Chemical weathering of fine-grained, organic- and metal-rich sediments under pH 7 causes mineral dissolution thus releasing metals from mineral surfaces into the surface waters (Garrels and Mackenzie, 1971; Aiuppa et al., 2000). Black shales contain abundant organic matter, pyrite, and sometimes carbonate nodules and are enriched in trace metals such as copper, nickel, uranium, and vanadium (Kim and Thornton, 1993; Loukola-Ruskeeniemi 1994). The black shales can be mechanically, chemically and biologically broken-down with authigenic processes (mineral transformation within the system; Kennedy et al., 2002) and biogenic processes (microbial activity; Nordstrom and Alpers, 1999). Chemical weathering is enhanced by mechanical weathering due to the increased surface area for chemical reactions to take place (Di-Giovanni et al., 2002). Numerous studies have demonstrated that chemical weathering of black shales may lead to reduced water and sediment quality due to elevated metal concentrations (Loukola-Ruskeeniemi 1994; Loukola-Ruskeeniemi et al., 1998; Kim and Thornton, 1993; Piispanen and Nykyri, 1997; Tuttle et al., 2001). Metal concentrations above threshold levels in streams may be lethal or cause impairments to aquatic organisms which include fish kills (Pasava et al., 1995), lower total abundance of aquatic organisms and decreased taxa richness and Ephemeroptera-Plecoptera-Trichoptera (EPT) richness of benthic macroinvertebrates (Cain et al., 1992; Mize and Deacon, 2002).

The increased metal loads in stream water and sediments are also a human health concern due to biomagnification of metals along the aquatic and terrestrial food chains and food webs. Overall, human health risks are primarily due to the release of metals such as Hg, Pb, Cd, As, and Se from black shales into potable groundwater supplies. Since sediments provide habitat for many aquatic organisms and are considered major repositories for many contaminants introduced into the surface waters, they may be potential sources or sinks of metals in black shale drainage systems. The objectives of this study were two-fold: (1) to quantify the metal concentrations in stream sediments derived from black shales; and (2) to assess the toxicity of these sediments to the midge larvae, *Chironomus tentans.* These objectives were achieved by examining the relationship between measured trace metal concentrations in stream sediments and the observed toxicity of these sediments to the test organisms. The working hypothesis of this study is that trace metal release from the black shales in this area reduced the habitat quality for the threatened or endangered speckeled pocketbook mussel (*Lampsilis streckeri*) and the yellowcheek darter (*Etheostoma moorei*). In this paper, we present the measured total-extractable trace metals in rock and stream sediment samples and the observed sediment toxicity using *Chironomus tentans* (Fabricius) with endpoints being measured as survival and growth.

Materials and Methods

Geologic Setting.--The study site is located in an extensive black shale outcrop (Mississippian Fayetteville Shale) in the Little Red River (LRR) watershed of central Arkansas (Fig. 1). The LRR watershed includes 4883 total river km contained within an area of 2902 km^2. More than 75% of the entire watershed area is forest riparian habitat, and less than 20% is agricultural/urban riparian habitat with the southern portion of the watershed (Greers Ferry Lake and south) characterized by row-crop production and logging. The first site is the Devil's Backbone catchment located to the south of Marshall (92° 38' 00 W, 35° 91' 25 N) in Searcy County. Surface waters in this area drain the Mississippian Fayetteville Shale and flow to the south into Trace Creek and then mix with Cove Creek before entering the Middle Fork of the Little Red River, which drains into Greers Ferry Lake. Black shales are in intimate contact with surface and ground water throughout the length of Trace and Cove creeks. The second site is the Blue Mountain catchment in Searcy County (92° 51' 67 W, 35° 84' 17 N) that lies northeast of city of Leslie. Surface waters in this region are also in contact with the Fayetteville Shale and drain into Begley Creek and then enter Trace Creek approximately 0.5 km downstream from the confluence of Trace Creek and Cove Creek. The third site is the South Mountain catchment (92° 63' 33 W, 35° 84' 17 N) where Cove Creek water travels to the southwest to mix with Trace Creek. The fourth study site, the Middle Fork rises from Reves Knob catchment (92° 45' 00 W, 35° 42' 00 N) draining the younger Mississippian Pitkin Limestone and flows to the east to Greers Ferry Lake.

Sediment Sample Collection, Processing, and Analyses.--Sediment collection followed methods described by Mudroch and MacKnight (1994) and Shelton and Capel (1994). Sediment from the Black River, Arkansas, (Moore et al., 1996) was used as a "control" sediment in toxicity tests to provide a measure of test acceptability, evidence of organism health, and as a basis for interpreting data obtained from the test sediments. The samples were analyzed for total extractable metals using the multi-acid digestion method as described by Briggs and Meier (1999). USGS SDO-1 (Devonian Ohio Shale) was also measured as an unknown to assess accuracy and reproducibility of measurements. The trace metals analyzed included Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn, Se, and As. Metal concentrations were measured by dynamic reaction cell inductively coupled plasma mass spectrometry (ICP-MS; Perkin Elmer DRCII) following EPA 6020 methodology. Concentrations were calculated by external calibration with internal standardization. Based on comparisons between literature and measured SDO-1, values the error on the reported concentrations is less than 3% for all analytes. Sediment particle size separation was done according to methods described by Forth et al. (1982) and Kemble et al. (1994). In addition to assessing particle size composition and total extractable metals, we also measured cation exchange capacity, total organic carbon, total solids, and volatile solids as described by Plumb (1981). Finally, whole sediment toxicity was evaluated by conducting 10-day acute toxicity tests using *C. tentans* as described in USEPA (2000) with endpoints being measured as survival and growth.

Table 1. Particle size composition, organic carbon and ph of study site sediments. TRC-A and B, BGC-A and B, CVC-A and B, MFR-A and B, represent sediment samples collected from Trace Creek, Begley Creek, Cove Creek, and Middle Fork, respectively.

Site name	Sand %	Clay %	Silt %	Organic carbon (%)	pH
TRC-A	65.8	3.1	31.1	5.9	5.5
TRC-B	65.4	2.9	31.8	6.0	6.3
BGC-A	59.6	2.9	37.5	5.5	5.9
BGC-B	57.5	2.9	39.6	6.6	5.7
CVC-A	69.6	3.8	26.5	4.6	6.1
CVC-B	67.4	2.5	30.1	4.5	6.3
MFR-A	66.5	0.3	33.2	2.0	7.5
MFR-B	68.2	0.5	31.3	2.5	7.7

Results

Particle Size Analysis and Trace Metals.--Particle size analysis for the black shale and limestone stream sediments showed a similar distribution with sand having the highest percentage of the three size fractions (Table 1). Both the

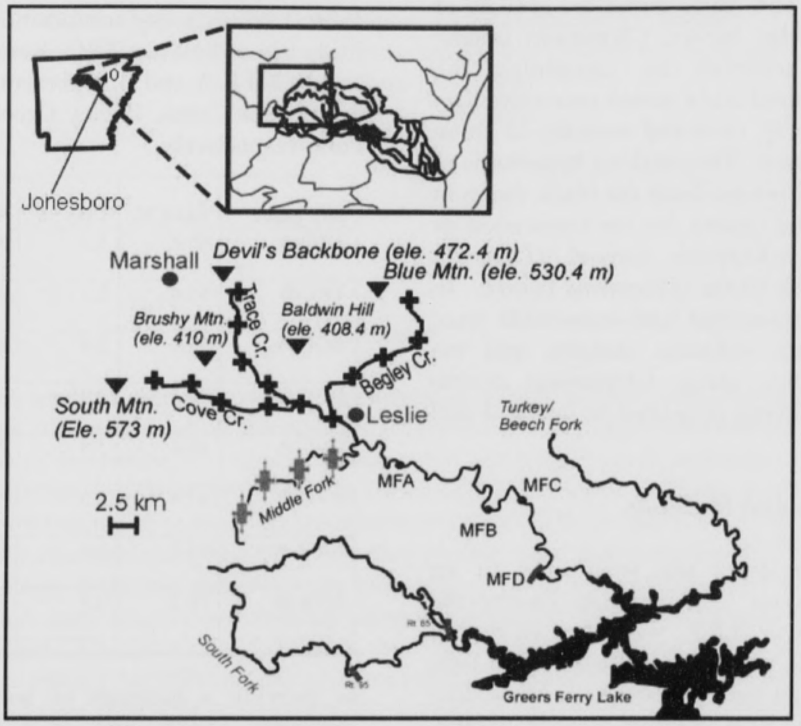

Fig. 1. Schematic map showing the location of the Little Red River watershed (HUC 11010014). The study area includes the black shale-draining streams: Trace Creek, Begley Creek, Cove Creek, and the limestone-draining stream, Middle Fork. The solid pluses (+) represent sampling sites on the black shale-draining streams while the arrowed solid pluses represent Middle Fork sampling sites.

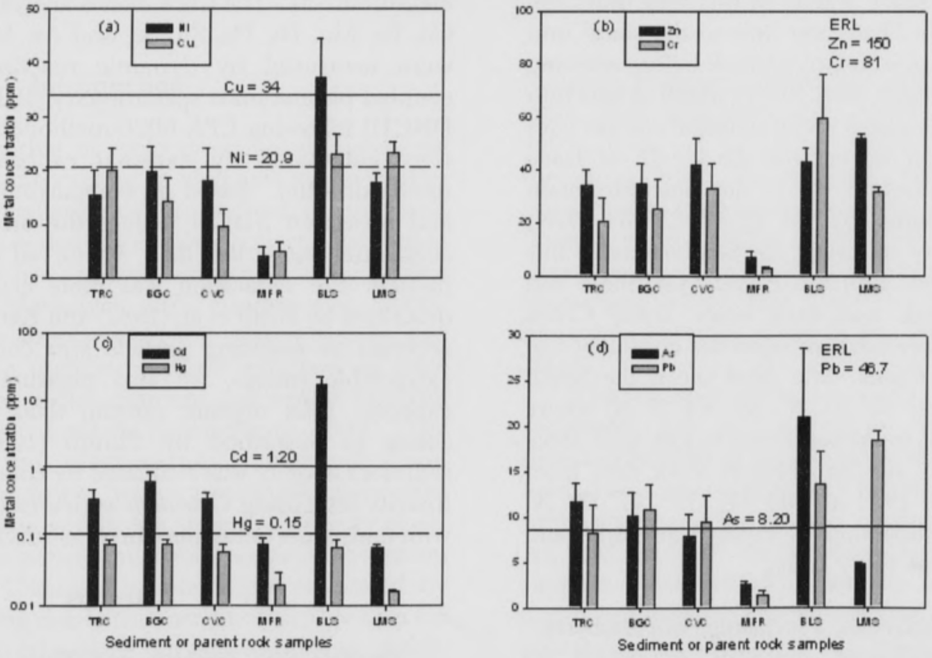

Fig. 2 a - d. Trace metal concentrations in study site unweathered rock (black shale and limestone) and stream sediment samples. BLS: black shales, LMS: limestone, TRC: Trace Creek, BGC: Begley Creek, CVC: Cove Creek, MFR: Middle Fork. Solid and dashed lines represent Effect-Range-Low (ERL) levels for the respective metals according to NOAA (1999).

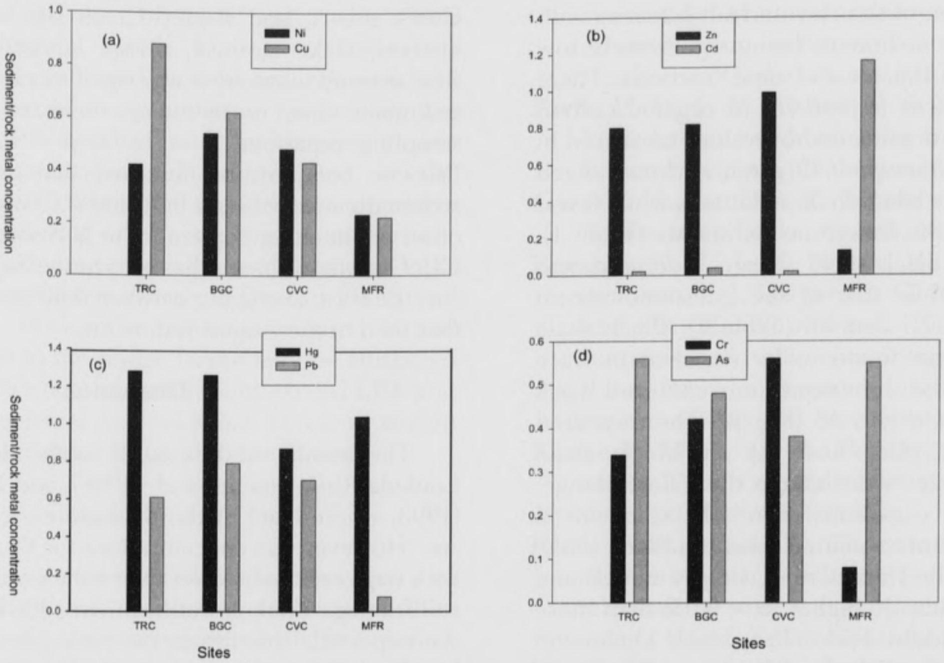

Fig. 3 a - d. Stream sediment/rock ratios for different trace metals. Sediment metal concentrations from TRC, BGC, and CVC were normalized to the corresponding unweathered black shales while sediments from MFR were normalized to the unweathered limestone.

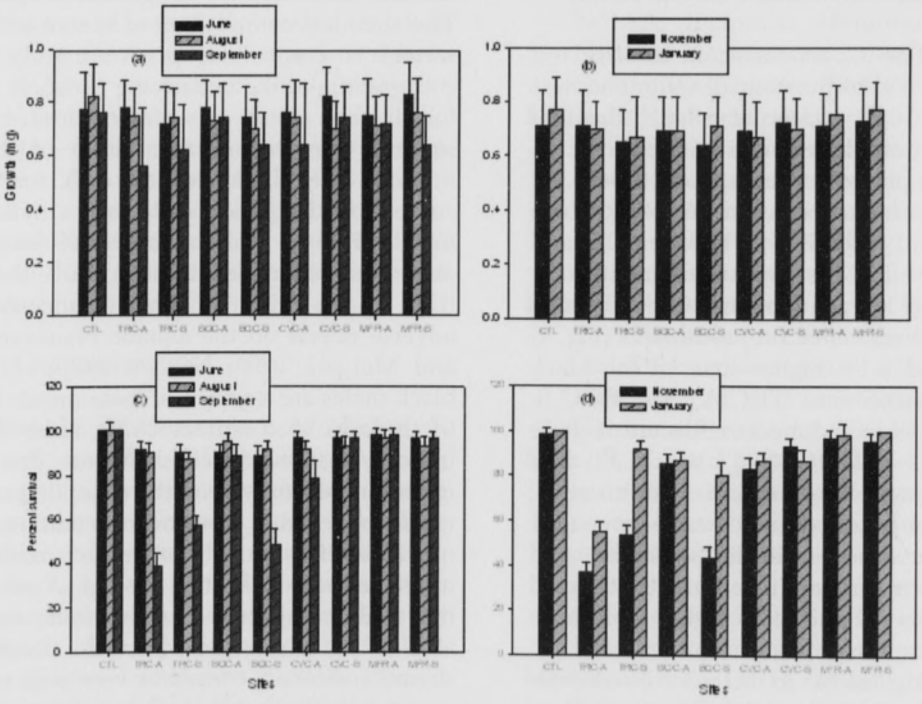

Fig. 4 a -d. Growth (a – b) and percent survival (c – d) of *Chironomus tentans* in the study sites and control sediments. TRC: Trace Creek, BGC: Begley Creek, CVC: Cove Creek, MFR: Middle Fork, CTL: control sediment.

black shale and limestone sediments also showed a similar pattern in the distribution of the clay and silt fractions with percent clay in all these sediments being significantly low ($\alpha = 0.05$) compared to the silt and sand fractions. There were significant differences ($\alpha = 0.05$) in organic carbon among sites with higher organic carbon values measured in black shale stream sediments. Organic carbon ranged between 5 and 7% for the black shale sediments while it was between 2 and 3% for the limestone sediments (Table 1). The pH range for the black shale stream sediments was between 5.5 and 6.3 while that of the limestone stream sediments was between 7.5 and 7.7 (Table 1). Black shale parent rock samples were found to be enriched in trace metals compared to the limestone unweathered rock particularly for Ni, Cr, Cd and As (Fig. 2). The measured concentrations for Ni, Cd, and As in black shale unweathered rock samples were above the Effect Range-Low (ERL) for aquatic organisms. Similarly, trace metal concentrations in sediments obtained from the black shale-draining streams, namely Trace Creek, Begley Creek and Cove Creek were significantly higher ($\alpha = 0.05$) than those collected from the Middle Fork. The black shale and limestone parent rocks were found to be the sources of trace metals in sediment samples except for Cd and Hg (Fig. 3). The ratio sediment / NASC ratio for Hg was greater than one for the sediments collected from Trace Creek and Begley Creek (Fig. 3). The sediment – GSR-6 normalization for Hg and Cd showed ratios of 1.1 and 1.2, respectively.

Sediment Toxicity.--The *C. tentans* acute toxicity test findings showed that survival in the control sediments was significantly higher ($F = 6.56$; $P = 0.001$; $df = 8, 32$) than that observed in the black shale and limestone sediments (Fig. 4). A follow-up with Tukey's pairwise comparisons ($\alpha = 0.05$) revealed that the midge larvae survival in black shale draining sites TRC-A, and BGC-B was between 0.5 and 6.1% less than that observed in the control sediments ($\alpha = 0.05$). Survival of the midge larvae in the limestone-draining Middle Fork (i.e., the field reference site) sediments (Fig. 4) was also between 0.2 and 5.1% higher than of the black shale stream sediments from sites TRC-A, and BGC-B. Survival of these organisms in sediments collected in June was significantly higher ($F = 4.95$; $P = 0.003$; $df = 4, 32$) than that of sediments of other sampling occasions. For instance, survival of *C. tentans* in the June sediments was between 0.1 and 3.4% higher than that observed in the September and November sediments. Their survival in sediments collected in August was also between 0.2 and 3.3% higher than those grown in sediments collected in September ($\alpha = 0.05$).

Growth of the midge larvae in the control sediment was significantly higher ($F = 3.03$; $P = 0.012$; $df = 8, 32$) than that observed in both the black shale and limestone stream sediments (Fig. 4). The *C. tentans* from the control sediment were between 0.01 and 0.16 mg heavier than those of Trace Creek site A, and Begley Creek site B (95% confidence interval). Like survival, midge larvae growth showed a similar trend whereby it was significantly higher in the June sediments than in sediments collected during the other sampling occasions ($F = 11.71$; $p = 0.001$; $df = 4, 32$). Pairwise comparisons indicated that growth in the June sediments was between 0.01 and 0.15 mg heavier than that observed in either September or November sediments (95% CI). Growth of these organisms in the September sediments was the least, averaging between 0.02 and 0.15 mg less than that seen in the August sediments.

Discussion

The results of this study were similar to those of Loukola-Ruskeeniemi et al. (1998), and Kim and Thornton (1993) where black shale rocks are enriched in Ni, Cd and As. However, the concentrations for Cr, Hg, and Zn in the rock were relatively lower than values obtained from related studies (e.g., Loukola-Ruskeeniemi, 1994; Lee et al., 1998). As expected, the limestone rock contained significantly lower concentrations of these metals with a negligible probability of being a potential source for these toxic metals. All the study sites depicted a similar particle size distribution with sand being the dominant size fraction. Even though constituting the lowest percentage composition, the clay fraction accounted for the greater proportion of the metals. The chemical composition of stream sediments and surface waters is controlled, predominantly by the chemical composition of the underlying bedrock. The concentrations for all trace metals in sediments from black shale-draining streams were higher than those of the limestone rock-draining stream, the Middle Fork further supporting our contention that black shales are a natural source of toxic metals (Fig. 2). The concentrations of Cd, As and Pb are above the with concentrations above the Effect Range-Low (ERL: that is indicative of metal concentrations above which adverse effects on the aquatic organisms will occur; Long and Morgan, 1990; NOAA, 1999). The suggestion that black shales are a source of these metals is further supported by the calculated sediment/rock ratios (Fig. 3). These ratios indicate that the black shales are the primary source of metals under study, with the exception of Zn and Hg whose ratios suggest that there may be additional sources of these metals such as run off and/or accumulation/concentration in the sediments through biological activity. The results of this study compare well with similar studies (e.g., Tuttle et al., 2001) that have shown that the distribution of metal-rich stream sediments correlates very well with outcrops of the metal-rich black shales. Often the metals of concern are found in the sulfide fraction of the black shales. Exposure of black shale sulfides (i.e., iron sulfide pyrite, FeS_2) to xidative chemical weathering at the bedrock-soil interface an lead to the formation of metal salts which can emporarily complex the metals. During rainfall events hese salts are dissolved and metals are released and ransported into the receiving streams. The metals are adsorbed to oxyhydroxides and consequently are precipitated from solution and accumulated in the sediments. Our results attest to the significant contribution of black shale weathering in the cycling of many trace metals, many of which are potentially toxic to stream biota including macroinvertebrates (Mize and Deacon, 2002), and fish (Pasava et al., 1995). The reduction in survival and growth impairments in the midge larvae may be attributed to Cd, As, and/or Pb whose concentrations exceed ERL and therefore can cause lethal and sublethal effects to stream organisms particularly those living in the sediments.

Conclusions

Environmental and public health authorities require an understanding of black shale weathering processes and the consequent release of potentially toxic metals into surface water and sediments. Thus these findings will facilitate formulation of realistic pollution guidelines and targets and provide for effective environmental monitoring by taking into account the non-point sources of metal pollution through natural weathering of these metal-enriched rocks. Finally, there is need to stress that the sporadic and isolated unusually high enrichments of potentially harmful metals in otherwise pristine areas are likely to present serious risks to human health due to biotic transfer of metals along the aquatic and terrestrial food chains.

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Literature Cited

Aiuppa A., P. Allard, W. D'Alessandro, A. Michel, F. Parello, M. Treuil, and M. Valenza. 2000. Mobility and fluxes of major, minor and trace elements during basalt weathering and groundwater transport at Mt. Etna volcano (Sicily). Geochim. Cosmochim. Acta 64: 1827-1841.

Briggs, P. H., and A. L. Meier. 1999. The determination of forty-two elements in geological materials by Inductively Coupled Plasma-Mass Spectrometry: U.S. Geological Survey Open–File Report 99-0166, 15pp.

Cain, D. J., S. N. Luoma, and S. V. Fend. 1992. Aquatic insects as bioindicators of trace element contamination in cobble-bottom rivers and streams. Can. J. Fish. Aqu. Sci. 49: 2141-2154.

Di-Giovanni, C., J. B. Disnar, and J. J. Macaire. 2002. Estimation of the annual yield of organic carbon released from carbonates and shales by chemical weathering. Global Planetary Change 32: 195–210.

Forth, H. D., L. V. Withee, H. S. Jacobs, and S. J. Thien. 1982. Laboratory Manual for Introductory Soil Science. Brown Company, Dubuque IA, 13-26 pp.

Garrels, R., and F. T. Mackenzie. 1971. Evolution of Sedimentary Rocks. Norton, New York. 247 pp.

Kemble, N. E., J. M. Besser, W. G. Brumbaugh, E. L. Brunson, F. J. Dwyer, C. G. Ingersoll, D. P. Monda, and D. F. Woodward. 1994. Toxicity of metal-contaminated sediments from the upper Clark Fork River, MT., to aquatic invertebrates in laboratory exposures. Environ. Tox. Chem. 13: 1985-1997.

Kennedy M. J., D. R. Pevear, and R. J. Hill. 2002. Mineral surface control of organic carbon in black shale. Science 295: 657-660.

Kim, K.W., and I. Thornton. 1993. Influence of uraniferous black shales on cadmium,molybdenum and selenium in soils and crop plants in the Deog-Pyong area of Korea. Envir. Geochem. Health 15: 119-133.

Lee, J., Chon, H., Kim, J., Kim, K., and Moon, H. 1998. Enrichment of toxic elements underlain by black shales and slates in Korea. Envir. Geochem. Health, 20:135-147

Long, E. R., and L. G. Morgan. 1990. The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program. NOAA Technical Memorandum NOS OMA 52. National Oceanic and Atmospheric Administration. Seattle, Washington. 72 pp.

Loukola-Ruskeeniemi, K. 1994. Environmental geochemistry of Proterozoic black shales in eastern Finland: a pilot study. In, T.J. Bornhorst & S.D. McDowell (eds.), Institute on Lake Superior Geology; Proc. 40th Ann. Meeting, Michigan Technological University: Houghton MI. 24-33.

Loukola-Ruskeeniemi, K., A. Uutela, M. Tenhola, and T. Paukola. 1998. Environmental impact of metalliferous black shales at Talvivaara in Finland, with indication of lake acidification 9000 years ago. J. Geochem. Explor. 64: 395-407.

Mize, S. V., and J. R. Deacon. 2002. Relations of benthic macroinvertebrates to concentrations of trace metals in water, stream sediments, and transplanted bryophytes and stream habitat conditions in non-mining and mining areas of the Upper Colorado River Basin, Colorado, 195-1998. U.S. Geological Survey: Water Resources Investigations Report 02-4139.

Moore, M. T., C. D. Milam, and J. L. Farris. 1996. Reference Sediment Selection in the Lower Mississippi Delta. Proc. Arkansas Acad. Sci., 50:84-90.

Mudroch, A., and S. D. MacKnight. 1994. Handbook of Techniques for Aquatic Sediments Sampling. 2nd edition. Lewis Publishers, New York. 236 pp.

NOAA. 1999. Sediment Quality Guidelines developed for the National Status and Trends Program.

Nordstrom D. K., and C. N. Alpers. 1999. Geochemistry of acid mine waters. In Plumlee G.S.and Logsdon M.J. [eds.] The Environmental Geochemistry of Mineral Deposits. Part A: Processes, Techniques, and Health Issues. Reviews in Economic Geology 6A: 133-160.

Pasava, J., I. MacInnis, M. Graves, and M. Zentilli. 1995. Black slates- a source of acid drainage at the Halifax International Airport, Nova Scotia, Canada. In Pasava, J., Kribek, B., Zak, K. (Eds). Mineral Deposits: from their origin to their Environmental Impacts. Proceedings of the Third Biennial SGA Meetings, 28-31 August, Prague, Balkema, Rotterdam. p. 785-788.

Piispanen, R., and Nykryi, T. 1997. Acidification of groundwater in water-filled gravel pits – a new environmental and geomedical threat. Envir. Geochem. Health, 19:111-126.

Plumb, R. H. 1981. Procedure for Handling and Chemical Analysis of Sediment and Water Samples, Technical Report EPA/CE-81-1, prepared by Great Lakes Laboratory, State University College at Buffalo, Buffalo, N.Y., for the E.S. Environmental Protection Agency/Corps of Engineers Technical Committee on Criteria for Dredge and Fill Material. Published by U.S. Army Engineer Waterways Experiment Station, CE, Vicksburg, MS.

Shelton, L. R., and P. D. Capel. 1994. Guidelines for collecting and processing samples of streambed sediment for analysis of trace elements and organic contaminants of the National Water-Quality Assessment Program: Survey Open–File Report 94-0166, 15pp.

Tuttle, M. L. W., M. B. Goldhaber, and G. N. Breit. 2001. Mobility of Metals from Weathered Black Shale: The Role of Salt Efflorescences. Geological Society of America Annual Meeting, November 5-8, 2001 [Abstract].

USEPA. 2000. Methods for Measuring the Toxicity and Bioaccumulation of Sediment-Associated Contaminants with Freshwater Invertebrates. Office of Research and Development, Mid-Continent Ecology Division, U.S. EPA, EPA/600/R-94/024, Duluth, Minnesota 55804