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Chapter 12

Association of dissolved organic carbon with stream discharge and dissolved metals concentrations in black shale-draining streams

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Abstract

Watershed characteristics influence the concentrations of dissolved organic carbon (DOC) that affects the levels, fate, partitioning, bioavailability, and toxicity of dissolved metals in aquatic ecosystems. Despite increasing interest in black shales research, there are limited data relating influence of bedrock type upon DOC and dissolved metals in streams whose watersheds are dominated by black shales. Four streams in North-Central Arkansas, USA, were selected for study, three of which (Trace Creek, Begley Creek, and Cove Creek) drain black shales-dominated watersheds. A fourth nearby stream (Mill Creek) that flows over a geologically distinct limestone bedrock, was selected as a reference site to allow comparisons between these watersheds and the assessment of the role of bedrock lithology on DOC and metal concentrations. Spatial and temporal variations in DOC and dissolved metals among stream sites were determined. Streams draining black shales had significantly higher conductivity, and lower pH than the stream draining limestone. Dissolved metal concentrations at all sites were highest in June 2003 and lowest in September 2003, which coincided with a stormflow and a baseflow, respectively. The concentrations of DOC and metals (e.g. Cd, Cu, Hg, Ni, Pb, and Zn) in water collected from Trace, Begley, and Cove creeks were significantly higher than those of Mill Creek. Metals in streams draining black shales whose concentrations approached or exceeded US EPA's surface water criteria included Cr, Cu, Hg, Pb, and Se. A linear regression analysis of DOC with discharge as the predictor variable showed that variations in DOC concentrations were strongly explained by stream discharge with r^2-values ranged from 0.85 to 0.95, whereas DOC was inversely related to conductivity ($r^2 = 0.47$–0.89). The study also revealed that bedrock type was a significant predictor of the observed spatial variations in DOC. Streams draining black shale watersheds transported significantly higher ($p < 0.05$) amounts of DOC than those draining limestone, thereby emphasizing the important role of geology in determining the amount of DOC in streams. Owing to the strong positive correlations between DOC and dissolved metals, any attempt to quantify metals and predict their effect on the aquatic biota in these types of streams should consider DOC levels in addition to other physical and chemical variables.

12.1. Introduction

Watershed characteristics (e.g. hydrologic events, type of vegetation and geology) and anthropogenic activities in catchments influence the concentration of dissolved metals and dissolved carbon (inorganic and organic) in streams (Taylor et al., 1990; Shafer et al., 1997; Shiller, 1997; Sherrell and Ross, 1999; Meyer et al., 2004). Sherrell and Ross (1999) observed that both temporal and spatial variations in dissolved metal concentrations were related to hydrologic flow paths during high discharge. Whereas Shiller and Boyle (1987) and Taylor et al. (1990) have shown that dissolved metals in large rivers can be derived from natural rock weathering in the catchment, other studies have additionally demonstrated that discharge can be a strong predictor of dissolved metals with higher metal concentrations occurring during high discharge (Rember and Trefry, 2004).

Dissolved organic carbon (DOC) can comprise over 95% of total organic carbon (Bishop and Pettersson, 1996) and also constitutes between 40 and 50% of dissolved organic matter (DOM) in forested headwater streams (Allan, 1995; Kaplan and Newbold, 1993). It is a significant energy source for stream biota including macroinvertebrates that commonly form the energy base for food chains in aquatic ecosystems (Elder, 1988; Allan, 1995). DOC also plays an important role in the transport of metals within aquatic ecosystems thereby altering dissolved metal concentrations and, eventually, bioavailability to aquatic organisms. The ability of DOC to form soluble complexes with many metal ions is critical in the analysis of the distribution, accumulation, and effects of metals on biota in aquatic ecosystems. The role of DOC in metal complexation as a primary mechanism in the transport of metals into aquatic ecosystems has been proposed by a number of researchers (e.g. Allen and Hansen, 1996; Davies et al., 1998; Kim et al., 1999; Mounier et al., 1999). Interactions of DOC with metals lead to formation of DOC–metal complexes (Spitzy and Leenheer, 1988; Shafer et al., 1997) that affect the partitioning, fate, and bioavailability of metals (Apte and Batley, 1995; Gardner and Gunn, 1989). DOC–metal complexation renders the metals less bioavailable and less toxic to the aquatic organisms (Allen and Hansen, 1996).

Variations in levels of DOC in streams have also been linked to variations in precipitation in catchments with the highest DOC concentrations coinciding with maximum discharge in temperate and tropical streams (*this study*, Cauwet and Meybeck, 1987; Moore, 1989; Droppo and Jaskot, 1994; Hurley et al., 1996; Shafer et al., 1997; Rember and Trefry, 2004). Degens et al. (1988) also linked changes in stream DOC to climate; Thurman (1985) estimated the range of DOC concentrations for cool temperate and warm temperate climate streams to be between 2–8 and 3–15 $\mathrm{mg\,l^{-1}}$, respectively. Differences in DOC in streams may also be attributed to geologic differences in the watersheds (Sherrell and Ross, 1999; Meyer et al., 2004). For instance, black shales have been shown to be organic carbon- and metal-enriched (Coveney and Martin, 1983; Kim and Thornton, 1993; Chon et al., 1996; Petsch et al., 2000; Ogendi et al., 2004b). These studies found that concentrations of As, Cd, Cr, Cu, Mn, Ni, Pb, V, and Zn in surface waters exceeded surface water criteria for metals in the United States, thus a threat to aquatic life. Throughout the United States, fractured black shales host shallow ground and surface waters with the water and soil in these regions often containing elevated metal concentrations in excess of US EPA maximum contaminant levels (Blette and Newton, 1996; Chon et al., 1996; US EPA, 2002b). The potential importance of metal release from black shales impacts areas of central and western Arkansas, eastern Missouri, Oklahoma, and Kansas as well as in western and central New York and northern Montana. Black shales also occur throughout central and northern Appalachians (Ayotte et al., 1999; Foley et al., 2002) and the southeastern United States (Seal et al., 2000). Despite the known impact of trace metals to aquatic biota and humans (e.g. Mize and Deacon, 2002; Jagoe et al., 2002; Riley et al., 2003; Moore, 2004), quantification of DOC and its relation to dissolved metal concentrations in streams is poorly understood. Increased knowledge of the relation between DOC on the spatial and temporal metal concentrations in headwater streams is critical to the linkages between chemical weathering of metal rich bedrock and metal bioavailability and toxicity.

Whereas a number of studies have shown that black shales are non-point sources for metals whose concentrations are sufficient to elicit toxicity (Kim and Thornton, 1993; Chon et al., 1996), there are limited data to the best of our knowledge, that show the role of DOC in metal transport and complexation in streams draining watersheds dominated by black shales. Increased metal concentrations in surface waters and stream sediments have been attributed to chemical weathering of the shales (Kim and Thornton, 1993; Chon et al., 1996; Hannigan, 1997; Loukola-Ruskeeniemi et al., 1998; Ogendi et al., 2004a). Increased metal concentrations significantly reduce water and sediment quality (Taylor et al., 1990) that may lead to fish kills (e.g. Pasava et al., 1995), reduced survival and growth of midge larvae (Ogendi et al., 2004b), and decreased taxa richness of other benthic macroinvertebrates (Mize and Deacon, 2002). In addition, adverse effects on the reproduction and recruitment of two endangered fish species (razorback sucker, *Xyrauchen texanus* and pike minnow, *Ptychocheilus lucius*) have also been attributed to elevated metal concentrations in surface water and sediments (Hamilton and Waddell, 1994; Deacon and Stephens, 1998). In this study, four bedrock headwater streams in two geologically distinct, but nearby catchments, were selected to assess the impact of DOC, discharge, and pH on spatial and temporal variations in dissolved metal concentrations.

12.2. Materials and methods

12.2.1. Study sites description

The study area consists of four headwater bedrock streams that are tributaries of the Little Red River, Arkansas, USA. The first three streams: Trace Creek, Begley Creek, and Cove Creek (Fig. 12.1) drain an extensive late Mississippian period (~350 mya) Fayetteville Shale outcrop of north-central Arkansas. The Fayetteville Shale is considered to rest conformably on the Batesville Sandstone (Hudson et al., 2001). The Fayetteville Shale consists of black shale that contains medium- to light-gray fetid septarian concretions as large as 0.6 m in diameter (Hudson et al., 2001; Murthy et al., 2004). In this region, the Fayetteville Shale embeds dark-gray, fine-grained limestones, and ranges in thickness from 3 to 120 m (AGC, 2005; Fig. 12.1). The lower part of the Fayetteville Shale outcrops along stream gullies, and is in intimate contact with surface and ground waters throughout the length of Trace, Begley, and Cove creeks (Ogendi et al., 2004a,b). The fourth stream, the Mill Creek drains the Mississippian Pitkin Limestone of north-central Arkansas that rests conformably on the Fayetteville Shale. The Pitkin Limestone is medium- to dark-gray, and its texture varies from micritic to coarse-grained. The Pitkin Limestone generally forms a prominent cliff, and its beds contain abundant crinoids, brachiopods, and corals (Hudson et al., 2001). Its thickness ranges from 0 to 18 m.

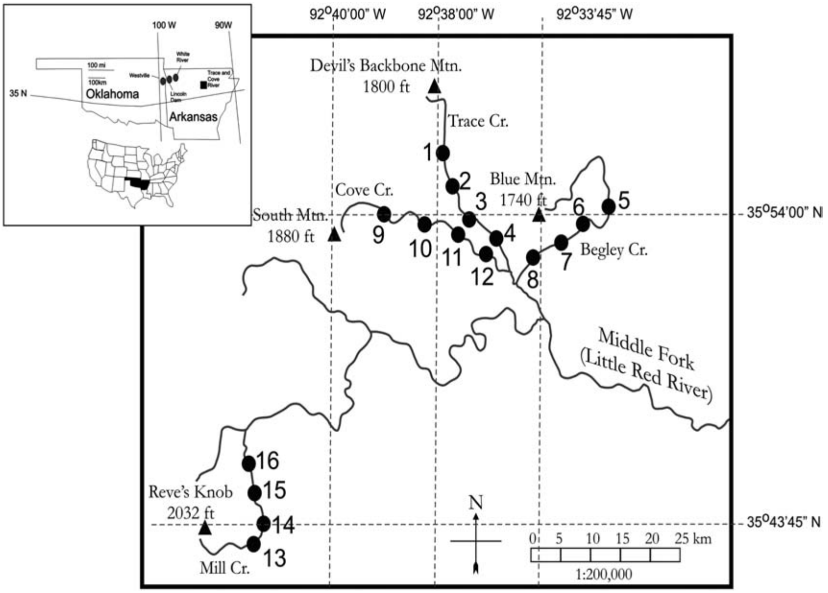

Figure 12.1. Location of sampling sites (numbered-solid circles) on streams draining black shales (i.e. Trace, Begley, and Cove creeks), and on a limestone-draining stream (Mill Creek). The streams are part of the Little Red River watershed (HUC 11010014) in north-central Arkansas, USA (shown on the top-left corner).

The mineralogy of the Fayetteville shale, based on X-ray diffraction (XRD) (Murthy, 2003) showed a dominance of quartz, micas, and feldspars dominate the bulk mineral composition with illite, kaolinite, and smectite the most abundant clay minerals. There is no significant spatial or temporal variation in the mineralogy of the shales exposed in the study area. The limestone mineralogy at Mill Creek, typical of intercalated limestones, is dominated by calcite with some illite. In the case of the organic carbon content, the shales contain 5–8 wt.% and the limestone contains no more than 1% (Murthy, 2003). Carbonate content in the shales is less than 10 wt.%. No vitrinite reflectance data are available and so thermal diagentic history is not well known. Based on organic matter content and petrography of the units the shales appear, on first order, to be mature to post-mature (Hannigan and Basu, 1997).

The Devil's Backbone (92° 38′ 00″ W, 35° 54′ 00′ N), Blue Mountain (92° 33′ 45″ W, 35° 51′ 35″ N), South Mountain (92° 40′ 33″ W, 35° 48′ 35″ N), and Reves Knob (92° 45′ 00″ W, 35° 43′ 45″ N) constitute the catchments for Trace, Begley, Cove, and Mill creeks, respectively. The Fayetteville shale bedrock streams were selected because they drain black shales that are potential non-point sources of metals (Ogendi et al., 2004b). The nearby Mill Creek, draining a geologically distinct limestone bedrock, was selected as a reference site to allow comparisons between these watersheds and for the assessment of the role of bedrock lithology on DOC and dissolved metals. The watersheds were identical in terms of principal land cover and hydrology, and consisted of over 90% forest riparian habitat with negligible anthropogenic disturbances. The natural vegetation along the study streams is primarily oak-hickory, oak-hickory-pine forests, and locally interspersed with cedar glades and short-leaf pines growing on steep slopes. The study area is characterized by a temperate climate with mild winters (summer maximum temperature 27.1°C and a winter minimum 4.8°C) with an annual average rainfall of 1370 mm.

12.2.2. Trace metal analysis

Water samples were collected from four randomly selected sites per stream (Fig. 12.1) using trace-metal clean procedures (Shelton and Capel, 1994; Shafer et al., 1997; APHA, 1998). Six selective sample collections representing the broad range of seasonal variations in DOC, dissolved metals, discharge, and other water quality parameters were carried out between June 2003 and May 2004. All equipment used for sample collection, storage, and analysis of trace metals were pre-cleaned using high-purity nitric acid (GFS Chemicals Inc.) and thoroughly rinsed with Milli-Q water. Such cleaning and storage procedures ensure that there are no detectable metal contaminants in the sampling equipment (Shafer et al., 1997). The samples were collected in polypropylene bottles and filtered immediately through 0.45 μm Gelman in-line filters and acidified with ultra-pure HNO_3 to $pH < 2$ and stored at 4°C prior to trace metal analyses. Other water quality parameters known to affect dissolved metals and DOC were measured (i.e. dissolved oxygen, pH, and conductivity). DOC and trace metals in the filtrate (0.45 μm) are here operationally defined as "dissolved". We centered our attention on the dissolved fraction as this fraction is more likely to have measurable biological effects on aquatic organisms (Di Toro et al., 2000). In addition, the dissolved metals are also similar to the exposure conditions used in toxicity tests (US EPA, 2002a), allowing for comparisons between standard toxicity tests and field community surveys (Ogendi et al., 2004a,b). This study is part of a broader investigation on the Little Red River watershed designed to determine the impact of trace metals on the stream water and sediment quality, and the resident macroinvertebrate communities. Metal concentrations were determined by the dynamic reaction cell inductively coupled plasma mass spectrometry (DRC-ICP-MS; Elan 9000 PerkinElmer) following EPA 200.8 methodology. In brief, 15 ml of water sample was transferred into an autosampler vial into which an internal standard containing 40 $\mu g\,l^{-1}$ Li-6, Ge, In, and Bi was added. A standard calibration curve for all the analytes was established on standards prepared in a linear range from 1 ppb to 100 ppb. National Institute of Standards and Technology reference material (NIST 1640) and procedural blanks were analyzed for trace metals. The dissolved metal concentrations were within 3% of the reported values for the standards. Finally, the relative standard deviations (RSD) for sample dissolved metal concentrations were $<5\%$ for all analytes.

12.2.3. Determination of dissolved organic carbon

Water samples were collected in 1-liter glass bottles (I-Chem Nalge Company) equipped with TFE-backed septa. These bottles were washed scrupulously and rinsed thoroughly with water before drying. The Gelman in-line filters were flushed with sample water before collection and the same was done for the sample containers that were rinsed with an aliquot of sample before collection. Water samples for DOC analysis were taken from the same stations that trace metal samples were collected. They were also filtered through 0.45 μm (Gelman in-line filters) and stored in the dark at 4°C. The water samples were analyzed for DOC within 48 h of collection.

DOC analyses were accomplished by UV-persulfate analysis (EPA 415.2) using a Tekmar-Dohrman Phoenix 8000^{TM} TOC analyzer. Briefly, the inorganic carbon (IC) is removed from the sample by acidification with phosphoric acid and sparging using nitrogen (99.999 pure nitrogen). Organic carbon (OC) is oxidized to CO_2 by sodium persulfate in the presence of ultraviolet (UV) light. The CO_2 produced is then purged from the sample, dried, and carried in a stream of nitrogen to a nondispersive infrared (NDIR) detector that was specifically tuned to the absorptive wavelength of CO_2 ($\sim$4.5 μm). This instrument can detect very low amounts ($\sim$2 ppb) of carbon while not sacrificing the ability to analyze widely varying amounts (Phoenix 8000^{TM} User Manual, 1998). The instrument was calibrated every ten samples and the persulfate solution was prepared fresh each day of analysis. For every ten samples, procedural blanks, a quality control check standard, and a check standard duplicate were also analyzed to ensure quality control. The RSD for replicate standards and samples ranged between 2% and 3 % whereas the r^2-values for the calibration curves ranged between 0.9998 to 0.9999 for these analyses.

12.2.4. Determination of pH, conductivity, and discharge

Stream water pH and discharge were determined at the sites of sample collection. The stream pH was measured using a field pH meter and a glass electrode that was standardized immediately before each reading. Conductivity in microsiemens per centimeter ($\mu S\,cm^{-1}$) was measured using a YSI conductivity meter. The instrument was calibrated before use in the field. The values of conductivity are reported as conductivity of the water samples at 25°C. Discharge measured as $m^3\,s^{-1}$ was determined manually with the use of a flow meter, wading rod, and tape measure. In this study, a stream cross-section was divided into a number of smaller sections of equal width and uniform bed conditions. Velocity was measured at 60% (from the surface) of the depth of each unit and then multiplied by the unit area to give the unit discharge. Total discharge was then calculated as the sum of the discharges of the smaller sections.

12.2.5. Statistical analyses

The data were tested for normality and homogeneity of variance using Kolmogorov-Smirnov Normality Test ($p \leq 0.05$) and Levene's Test for equal variances ($p \leq 0.05$), respectively (MINITAB® Statistical Software for Windows ver. 14). Using data that satisfied the assumptions normality we compared the DOC and metal concentrations amongst the four study sites using analysis of variance (ANOVA) to test for differences among sites and sampling occasions ($\alpha = 0.05$). Linear regression analyses ($y = mx + b$) were carried out on the data that yielded regression slopes, coefficient of determination values (r^2-values), and p-values. In these analyses, except where defined, the criterion for significance was a p-value of ≤ 0.05.

12.3. Results

Both spatial and temporal variations in DOC, discharge, pH, and conductivity were observed among the study sites (Table 12.1). Significant variations in DOC concentrations among sites ($F_{(7,\ 179)} = 49.3$; $p < 0.001$) and sampling occasions ($F_{(5,\ 179)} = 1410.5$; $p < 0.001$) were observed with the highest and lowest values recorded in Trace Creek and Mill Creek, respectively (Fig. 12.2a). The average DOC values in Cove Creek were between 15% and 35% less than those observed in Trace Creek and Begley Creek. Despite its relatively lower DOC levels compared to Trace and Begley creeks, DOC levels at Cove Creek were 1.5 times higher than those of Mill Creek. On average, the highest and lowest DOC

Table 12.1. Means (± SD, in *italics*) of discharge ($m^3 s^{-1}$), pH, dissolved organic carbon ($mg l^{-1}$) and conductivity ($\mu S cm^{-1}$) measured at the study sites in north-central Arkansas (USA). TRA, TRB (Trace Creek A and B), BGA, BGB (Begley Creek A and B), CVA, CVB (Cove Creek A and B), MLA and MLB (Mill Creek A and B)

	TRA	TRB	BGA	BGB	CVA	CVB	MLA	MLB
Discharge								
6/16/03	0.95	0.95	0.80	0.83	0.77	0.78	1.02	1.05
	0.12	*0.07*	*0.03*	*0.03*	*0.02*	*0.03*	*0.06*	*0.10*
8/11/03	0.33	0.34	0.33	0.33	0.30	0.32	0.49	0.54
	0.02	*0.02*	*0.02*	*0.04*	*0.03*	*0.03*	*0.04*	*0.02*
9/17/03	0.07	0.07	0.06	0.06	0.04	0.05	0.11	0.13
	0.01	*0.01*	*0.02*	*0.01*	*0.01*	*0.01*	*0.02*	*0.01*
11/27/03	0.34	0.33	0.30	0.34	0.29	0.31	0.44	0.45
	0.01	*0.01*	*0.01*	*0.03*	*0.04*	*0.02*	*0.03*	*0.02*
1/9/04	0.19	0.19	0.21	0.19	0.18	0.15	0.30	0.31
	0.02	*0.02*	*0.02*	*0.02*	*0.04*	*0.02*	*0.02*	*0.02*
5/23/04	0.15	0.14	0.12	0.13	0.12	0.10	0.22	0.20
	0.01	*0.02*	*0.02*	*0.02*	*0.02*	*0.02*	*0.02*	*0.02*
pH								
6/16/03	4.83	5.10	5.80	5.60	6.68	6.78	7.60	7.60
	0.13	*0.08*	*0.08*	*0.08*	*0.05*	*0.05*	*0.08*	*0.08*
8/11/03	5.78	5.85	6.13	6.13	7.10	6.95	7.45	7.55
	0.05	*0.06*	*0.10*	*0.10*	*0.08*	*0.06*	*0.06*	*0.06*
9/17/03	5.95	5.93	6.33	6.38	7.35	7.23	7.70	7.70
	0.06	*0.10*	*0.05*	*0.05*	*0.06*	*0.05*	*0.08*	*0.05*
11/27/03	5.50	5.55	5.83	5.80	6.83	6.88	7.53	7.55
	0.08	*0.06*	*0.05*	*0.08*	*0.05*	*0.05*	*0.05*	*0.06*
1/9/04	5.65	5.63	5.95	5.98	6.83	6.85	7.50	7.58
	0.06	*0.05*	*0.06*	*0.05*	*0.05*	*0.06*	*0.08*	*0.05*
5/23/04	5.63	5.68	6.05	6.05	6.88	6.85	7.45	7.58
	0.05	*0.05*	*0.06*	*0.06*	*0.05*	*0.06*	*0.06*	0.05
DOC ($mg l^{-1}$)								
6/16/03	13.53	12.62	16.05	15.87	10.44	10.37	6.60	6.66
	0.15	*0.64*	*0.26*	*0.23*	*0.46*	*0.60*	*0.21*	*0.16*
8/11/03	10.68	10.90	10.64	9.96	7.57	7.07	5.81	5.56
	0.33	*0.42*	*0.43*	*0.35*	*0.35*	*0.14*	*0.17*	*0.16*
9/17/03	7.67	9.27	6.64	7.03	6.49	6.42	3.96	3.87
	0.11	*0.35*	*0.15*	*0.08*	*0.05*	*0.05*	*0.23*	*0.24*
11/27/03	10.89	10.56	9.77	9.93	7.48	7.23	5.50	5.24
	0.27	*0.28*	*0.43*	*0.31*	*0.28*	*0.19*	*0.59*	*0.03*
1/9/04	8.14	8.18	6.72	7.09	6.85	6.75	4.88	4.72
	0.20	*0.19*	*0.10*	*0.27*	*0.08*	*0.07*	*0.19*	*0.16*
5/23/04	8.31	7.79	9.06	8.42	7.03	7.11	4.52	4.56
	0.37	*0.16*	*0.22*	*0.44*	*0.08*	*0.15*	*0.24*	*0.19*
Conductivity								
6/16/03	165.00	173.75	165.50	169.50	161.25	156.00	55.75	58.75
	9.97	*5.62*	*8.39*	*4.65*	*9.22*	*2.94*	*2.63*	*2.22*

Table 12.1. (*Continued*)

	TRA	TRB	BGA	BGB	CVA	CVB	MLA	MLB
8/11/03	212.00	208.50	205.75	197.50	195.50	196.25	72.00	72.25
	4.97	*4.20*	*6.95*	*2.08*	*5.57*	*7.80*	*2.94*	*4.99*
9/17/03	365.50	362.25	368.50	365.50	333.00	334.00	170.00	165.25
	5.00	*3.50*	*3.51*	*7.55*	*5.94*	*6.78*	*3.56*	*8.46*
11/27/03	216.50	225.75	212.00	211.00	203.25	205.50	86.00	89.50
	4.43	*1.71*	*4.90*	*7.02*	*4.27*	*1.29*	*5.10*	3.51
1/9/04	248.25	241.75	237.75	233.00	245.50	249.50	130.50	130.50
	12.40	*14.20*	*4.20*	*4.51*	*4.80*	*5.07*	*2.38*	*7.14*
5/23/04	239.50	237.25	260.50	258.50	224.50	221.50	110.50	113.75
	3.10	*4.43*	*5.38*	*3.65*	*2.08*	*3.11*	*4.04*	*7.55*

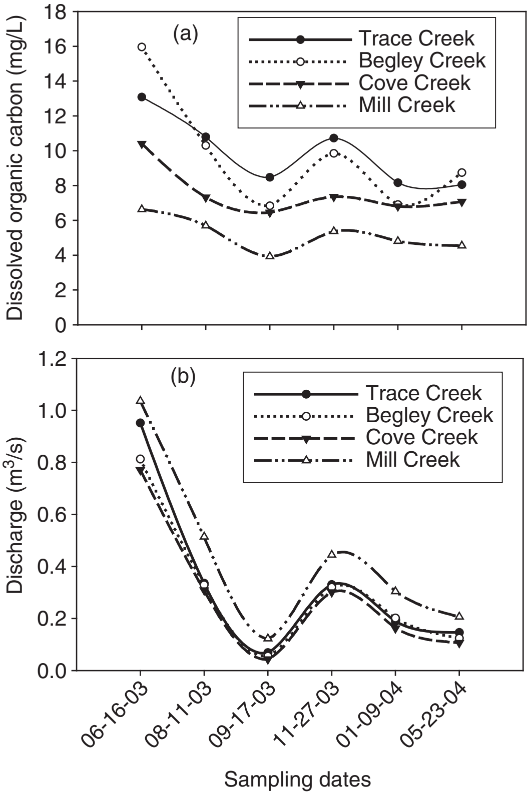

Figure 12.2. Temporal variations in (a) dissolved organic carbon and (b) stream discharge for Trace, Begley, Cove, and Mill creeks. Each point on the scatter plot is a mean of four sample measurements per sampling site during each sampling occasion.

concentrations were measured in June and September 2003, respectively (Table 12.1). The DOC concentrations for June 2003 were approximately twice as much as those measured in September 2003 for sampling sites. Discharge at Mill Creek was consistently greater than that observed at Trace, Begley, and Cove creeks (Fig. 12.2b). The highest and lowest flows occurred in June and September, 2003, respectively. However, the reverse was true of pH and conductivity with minimum and maximum measurements made in June and September, respectively (Table 12.1). A linear regression analysis of DOC with discharge as the predictor variable showed that variations in DOC concentrations were adequately explained by stream discharge with r^2-values ranging from 0.85 to 0.95 (Fig. 12.3). In addition, significant ANOVAs ($F_{(1,10)} = 43$, $p < 0.001$, Trace Creek; $F_{(1,10)} = 115$, $p < 0.001$, Begley Creek; $F_{(1,10)} = 144$, $p < 0.001$, Cove Creek; $F_{(1,10)} = 109$, $p < 0.001$, Mill Creek) were obtained for the corresponding DOC-discharge measurements. The concentrations of DOC were inversely related to specific conductivity with high r^2-values ranging from 0.47 to 0.89 (Fig. 12.4).

Dissolved metal concentrations at all sites were highest in June 2003 and lowest in September 2003 samples (Table 12.2). Except for manganese, dissolved metals in black shale-draining water samples were

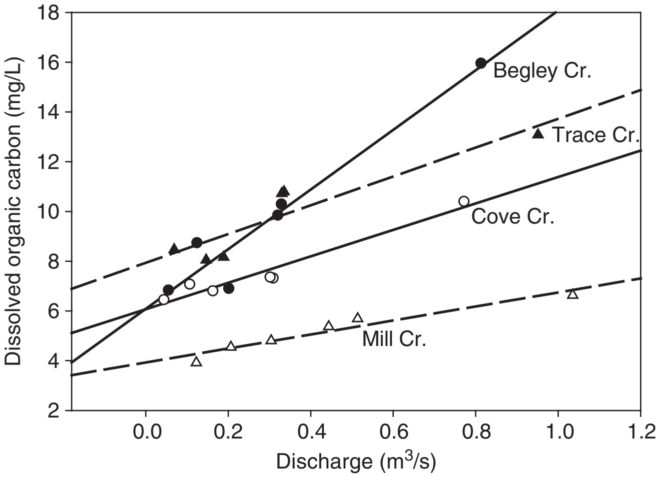

Figure 12.3. Linear regression plots of DOC vs. discharge for Trace Creek (solid triangle; $y = 7.9 + 5.8x$; $r^2 = 0.85$), Begley Creek (solid circle; $y = 6.1 + 12x$; $r^2 = 0.93$), Cove Creek (open circle; $y = 6.1 + 5.3x$; $r^2 = 0.95$), and Mill Creek (open triangle; $y = 3.9 + 2.8x$; $r^2 = 0.93$). Each point on the scatter plot is a mean of four sample measurements per sampling site per sampling occasion.

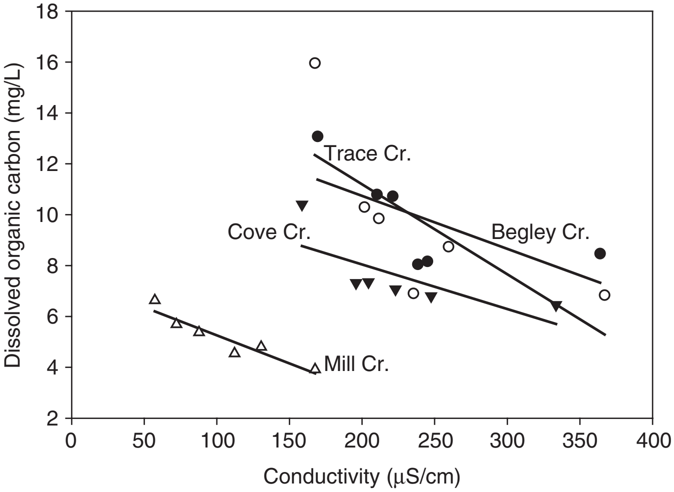

Figure 12.4. Linear regression plots of DOC vs. conductivity Trace Creek (solid circle; $y = 14.8–0.02x$; $r^2 = 0.47$), Begley Creek (open circle; $y = 12.3–0.03x$; $r^2 = 0.53$), Cove Creek (solid triangle; $y = 11.5–0.02x$; $r^2 = 0.54$), and Mill Creek (open triangle; $y = 7.5–0.02x$; $r^2 = 0.89$). Each point on the scatter plot is a mean from four sample measurements per sampling site per sampling occasion.

significantly higher ($p < 0.05$) than those in the stream-draining limestone (Fig. 12.5). The concentrations of both Fe and Mn in all streams were consistently higher than those of other elements in all the sampling occasions. The mean dissolved V and Co were two to three times higher in Trace Creek than in Mill Creek, whereas dissolved Cr in both Trace Creek and Begley Creek was 2–36 times higher than Mill Creek. Dissolved mercury was significantly higher ($p < 0.001$) in samples drawn from streams draining black shales than those collected from the limestone-draining stream (Table 12.2). Dissolved Ni and Pb were between 2 and 42 times higher in Trace, Begley, and Cove creeks than in the Mill Creek samples. In contrast, the concentrations of Zn and Sn were relatively higher in Mill Creek than the streams draining black shales (Table 12.2). Except for the November 2003 samples, dissolved Zn was between 10% and 30% higher in Mill Creek samples than those of Trace, Begley, and Cove creeks. Significant differences ($p < 0.05$) were observed in dissolved Mn between the study streams (Fig. 12.5) with the highest concentrations occurring in Mill Creek. The concentration of Cd in June 2003 in Trace Creek was significantly higher ($p < 0.05$) than that observed in the other streams (Table 12.2). Significantly higher ($p < 0.05$) dissolved Cu was noted in Begley Creek than that of Trace, Cove, and Mill creeks. The

Table 12.2. Dissolved concentrations ($\mu g\, l^{-1}$) of selected elements in stream water as determined by inductively coupled plasma mass spectrometry. TRA, TRB (Trace Creek A and B), BGA, BGB (Begley Creek A and B), CVA, CVB (Cove Creek A and B), MLA and MLB (Mill Creek A and B). *CCC* is criteria continuous concentration—four-day average not to be exceeded more than once every three years on average, and *CMC* is criteria maximum concentration—one-hour average not to be exceeded more than once every three years on average (US EPA, 2002b). nd: not defined

	TRA	TRB	BGA	BGB	CVA	CVB	MLA	MLB	CCC	CMC
6/16/03										
V	5.04	5.34	3.53	3.12	1.21	0.60	1.11	0.50	nd	nd
Cr	14.52	15.93	10.99	8.16	5.14	1.31	0.60	0.40	11.00	16.00
Mn	14.92	20.16	7.06	9.58	14.52	13.41	31.75	56.85	nd	nd
Fe	336.47	338.47	258.15	259.05	184.24	170.13	159.13	96.32	nd	nd
Co	0.30	0.30	0.20	0.20	0.20	0.20	0.10	0.10	nd	nd
Ni	3.02	3.73	3.43	3.83	1.41	1.81	1.51	1.51	52.00	470.00
Cu	7.56	10.48	18.95	6.65	3.83	4.23	4.54	4.13	9.00	13.00
Zn	16.93	16.33	13.61	16.13	7.86	18.35	24.60	12.00	120.00	120.00
As	59.57	45.56	34.37	36.69	47.68	90.22	38.71	53.32	150.00	340.00
Se	3.63	5.95	9.48	8.67	5.24	9.17	3.12	2.32	5.00	nd
Cd	0.30	0.30	0.20	0.20	0.10	0.10	0.10	0.10	0.25	2.00
Hg	1.21	8.37	5.04	1.51	2.02	11.39	0.14	0.03	0.77	1.40
Pb	28.36	44.79	11.72	11.02	4.71	4.21	6.01	7.82	2.50	65.00
8/11/03										
V	1.04	1.11	0.75	0.65	0.27	0.16	0.26	0.12		
Cr	1.60	1.77	1.20	0.88	0.53	0.11	0.08	0.06		
Mn	2.76	3.99	0.94	1.52	2.68	2.41	6.69	12.58		
Fe	232.00	209.51	159.79	160.31	114.01	105.27	98.46	59.62		
Co	0.47	0.49	0.36	0.39	0.28	0.26	0.21	0.19		
Ni	1.79	1.99	1.67	1.87	0.77	0.91	0.85	0.85		
Cu	1.53	2.15	4.09	1.37	0.79	0.89	0.94	0.89		
Zn	9.22	8.45	7.51	8.29	4.68	8.02	11.33	5.38		
As	2.61	2.00	1.50	1.61	2.09	3.95	1.69	2.33		
Se	2.84	4.69	7.41	6.78	4.09	7.19	2.48	1.79		
Cd	0.06	0.06	0.09	0.09	0.03	0.04	0.06	0.06		
Hg	0.26	1.91	1.20	0.31	0.48	2.67	0.03	0.06		
Pb	17.01	0.37	0.34	0.15	0.12	0.14	0.22	0.24		
9/17/03										
V	1.11	1.22	0.78	0.67	0.33	0.11	0.33	0.11		
Cr	1.33	1.33	1.00	0.78	0.67	0.56	0.67	0.67		
Mn	9.77	13.43	4.55	6.22	9.55	8.77	21.20	38.41		
Fe	209.24	210.55	160.60	161.10	114.57	105.83	98.99	59.90		
Co	0.56	0.56	0.44	0.44	0.33	0.33	0.22	0.22		
Ni	2.66	3.22	2.89	3.33	1.22	1.55	1.33	1.33		
Cu	1.78	2.44	4.44	1.55	0.89	1.00	1.11	1.00		
Zn	8.77	7.99	7.10	7.88	4.44	7.66	10.77	5.11		
As	2.00	1.55	1.11	1.22	1.55	3.00	1.33	1.78		
Se	2.55	4.22	6.66	6.11	3.66	6.44	2.22	1.55		

Table 12.2. (*Continued*)

	TRA	TRB	BGA	BGB	CVA	CVB	MLA	MLB	CCC	CMC
Cd	0.11	0.11	0.11	0.11	0.00	0.00	0.11	0.11		
Hg	0.33	2.00	1.33	0.33	0.56	2.89	0.03	0.07		
Pb	12.93	0.30	0.30	0.10	0.10	0.10	0.20	0.20		
11/27/03										
V	3.72	3.96	2.64	2.30	0.91	0.47	0.85	0.35		
Cr	11.62	12.76	8.82	6.58	4.14	1.07	0.46	0.36		
Mn	14.81	20.05	7.06	9.51	14.44	13.33	31.52	56.54		
Fe	311.77	313.68	239.24	240.03	170.70	157.61	147.41	89.27		
Co	0.27	0.29	0.21	0.23	0.16	0.15	0.12	0.11		
Ni	2.77	3.39	3.06	3.44	1.25	1.68	1.37	1.40		
Cu	6.48	8.97	16.32	5.74	3.27	3.68	3.93	3.55		
Zn	16.82	16.20	13.57	16.08	7.77	18.23	24.43	11.97		
As	47.28	36.22	27.28	29.18	37.84	71.62	30.71	42.34		
Se	3.28	5.42	8.56	7.82	4.73	8.30	2.86	2.06		
Cd	0.25	0.28	0.26	0.24	0.08	0.09	0.08	0.07		
Hg	1.02	6.82	4.13	1.20	1.66	9.37	<0.01	<0.01		
Pb	31.82	50.30	13.22	12.39	5.30	4.75	6.76	8.83		
1/9/04										
V	1.98	2.11	1.43	1.26	0.55	0.33	0.52	0.27		
Cr	2.92	3.20	2.22	1.66	1.05	0.28	0.13	0.11		
Mn	3.64	4.83	1.87	2.43	3.55	3.30	7.45	13.16		
Fe	415.67	418.22	318.96	320.02	227.58	210.13	196.54	119.02		
Co	0.28	0.30	0.22	0.23	0.17	0.16	0.13	0.12		
Ni	1.86	2.27	2.05	2.31	0.84	1.13	0.92	0.94		
Cu	1.45	2.05	3.90	1.31	0.75	0.85	0.90	0.84		
Zn	8.94	8.19	7.28	8.03	4.54	7.77	10.99	5.22		
As	2.21	1.70	1.28	1.37	1.77	3.35	1.44	1.98		
Se	3.19	5.26	8.31	7.60	4.59	8.06	2.78	2.01		
Cd	0.08	0.09	0.09	0.08	0.03	0.03	0.03	0.02		
Hg	0.35	2.37	1.43	0.42	0.58	3.26	0.04	<0.01		
Pb	16.68	0.36	0.33	0.14	0.12	0.14	0.22	0.24		
5/23/04										
V	1.56	1.66	1.13	0.99	0.43	0.26	0.41	0.21		
Cr	2.23	2.45	1.69	1.27	0.80	0.22	0.10	0.08		
Mn	3.04	4.04	1.56	2.03	2.97	2.76	6.23	11.00		
Fe	326.29	328.30	250.38	251.21	178.65	164.95	154.28	93.43		
Co	0.22	0.23	0.16	0.18	0.13	0.12	0.10	0.09		
Ni	1.36	1.66	1.49	1.68	0.61	0.82	0.67	0.69		
Cu	1.10	1.54	2.94	0.99	0.57	0.64	0.68	0.64		
Zn	5.69	5.48	4.59	5.44	2.63	6.16	8.26	4.05		
Se	2.30	3.79	5.99	5.48	3.31	5.81	2.00	1.45		
Cd	0.07	0.07	0.05	0.06	0.02	0.02	0.01	0.02		
Hg	0.28	2.05	1.28	0.33	0.52	2.85	0.03	0.01		
Pb	11.50	0.25	0.23	0.10	0.08	0.10	0.15	0.17		

nd, not defined.

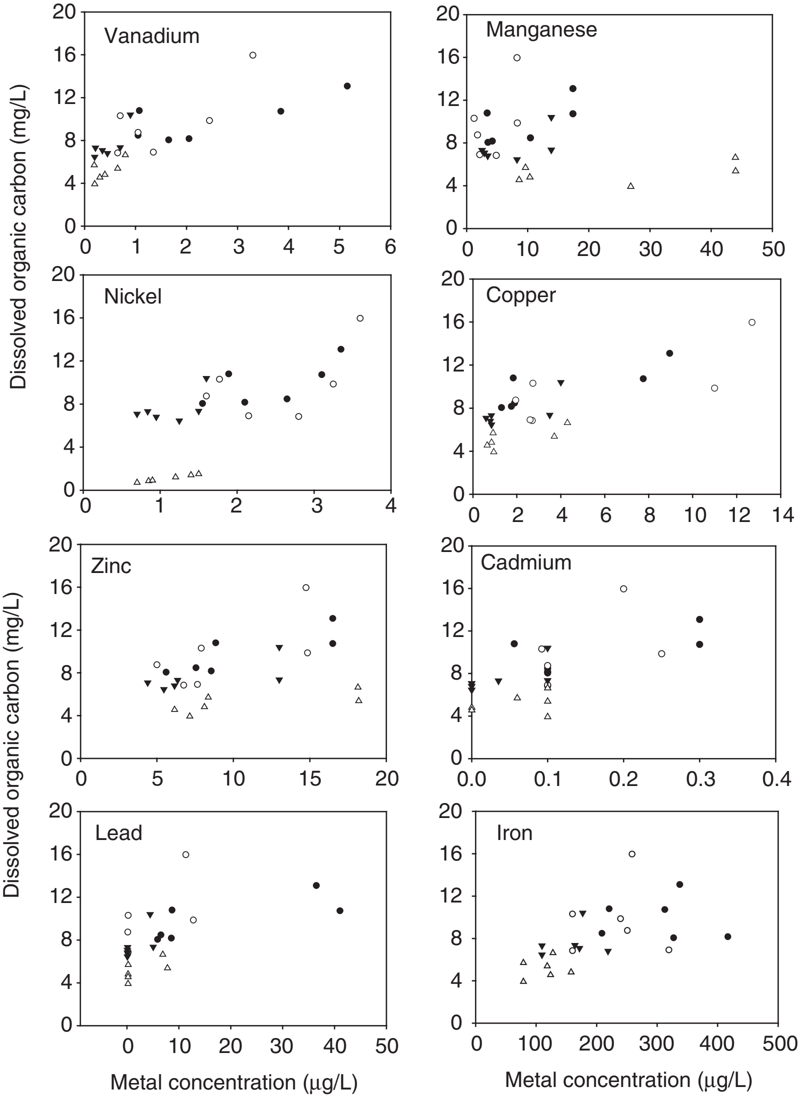

Figure 12.5. Plots of some selected elements vs. dissolved organic carbon for Trace Creek (solid circles), Begley Creek (open circle), Cove Creek (solid triangle), and Mill Creek (open triangle). Each point on the scatter plot is a mean from four sample measurements per sampling site per sampling occasion.

concentration of Ni in Begley Creek was consistently higher than those of Trace, Cove, and Mill creeks. Dissolved metals exhibited weak to strong positive relationships with DOC. The relationships were moderate to strong for V, Cu, Zn, and Pb as shown by the corresponding r^2-values (Table 12.3). Except for Mill Creek, significant temporal variations ($p < 0.05$) in water pH were noted. DOC was inversely related to pH with weak to fairly strong relationships (Fig. 12.6).

12.4. Discussion

The pH and conductivity differences between the streams would be attributed to the geologic differences in their watersheds. The low pH values in Trace and Begley creeks may be explained by the dominance of organic-rich clay soils and unweathered materials derived from black shales in their watersheds. Low pH values have been encountered in streams whose watersheds are dominated by the organic-rich black shales (Loukola-Ruskeeniemi, 1994; Jambor et al., 2000; Tuttle et al., 2001; Foley et al., 2002; Hammarstrom et al., 2003). Overall, these studies noted that the observed low pH in streams draining shales was related to weathering and oxidation of the sulfide minerals in these rocks. Hammarstrom et al. (2003) observed that physical and chemical weathering of metal-enriched rocks not only contributes acidity into the streams but also metals, sediments, and secondary minerals which may sequester metals. The high conductivity values in the black shale-draining streams would be due to the presence of easily ionized materials in the watersheds. The notable conductivity increases during baseflow were attributed to groundwater, which derives its high conductivity signature from the black shale bedrock through which it flows. Whereas our conductivity values for streams flowing through blacks shales are 3 to 4 times higher, our pH values are comparable to those measured in Beech Flats Creek by Hammarstrom et al., 2003. In general bedrock type can significantly influence water quality as was shown by Flum and Nodvin (1995) at the Great Smoky Mountains National Park.

Time-series results (Fig. 12.2, 12.5; Table 12.2) reveal marked spatial and temporal variations in both dissolved organic carbon and dissolved metals. The DOC and metal concentrations in Trace, Begley, and Cove creeks, whose watersheds are dominated by black shales were significantly higher than those of the limestone-draining Mill Creek (Table 12.2). The highest and lowest V, Cu, Mn, Cr, Zn, and Pb concentrations coincided with the highest and lowest DOC values which in turn corresponded with the highest and lowest discharge, respectively. On average, the three

Table 12.3. R^2-square values of linear regression plots of dissolved metals vs. DOC; dissolved metals vs. pH; and dissolved metals and metalloids vs. discharge in Trace Creek, Begley Creek, Cove Creek, and Mill Creek in north-central Arkansas (USA)

	Metal	Trace Creek	Begley Creek	Cove Creek	Mill Creek	Metal	Trace Creek	Begley Creek	Cove Creek	Mill Creek
DOC										
	V	0.58	0.63	0.65	0.50	Zn	0.69	0.49	0.50	0.53
	Cr	0.48	0.52	0.75	0.24	As	0.49	0.68	0.84	0.45
	Mn	0.45	0.31	0.34	0.21	Se	0.71	0.58	0.67	0.52
	Co	0.10	0.15	0.10	0.15	Cd	0.48	0.31	0.53	0.11
	Ni	0.47	0.30	0.35	0.89	Pb	0.59	0.46	0.43	0.43
	Cu	0.70	0.61	0.60	0.53					
pH										
	V	0.84	0.71	0.61	0.63	Zn	0.63	0.59	0.65	0.28
	Cr	0.77	0.68	0.35	0.33	As	0.71	0.66	0.67	0.33
	Mn	0.33	0.34	0.23	0.61	Se	0.76	0.66	0.66	0.51
	Co	0.27	0.13	0.30	0.25	Cd	0.57	0.33	0.51	0.38
	Ni	0.67	0.38	0.61	0.51	Pb	0.64	0.49	0.38	0.29
	Cu	0.66	0.65	0.51	0.39					
Discharge										
	V	0.71	0.70	0.65	0.58	Zn	0.59	0.67	0.61	0.56
	Cr	0.67	0.69	0.64	0.14	As	0.66	0.69	0.69	0.63
	Mn	0.33	0.35	0.36	0.31	Se	0.66	0.59	0.64	0.33
	Co	0.12	0.10	0.09	0.34	Cd	0.33	0.56	0.65	0.17
	Ni	0.48	0.41	0.38	0.45	Pb	0.49	0.48	0.50	0.45
	Cu	0.65	0.65	0.66	0.61					

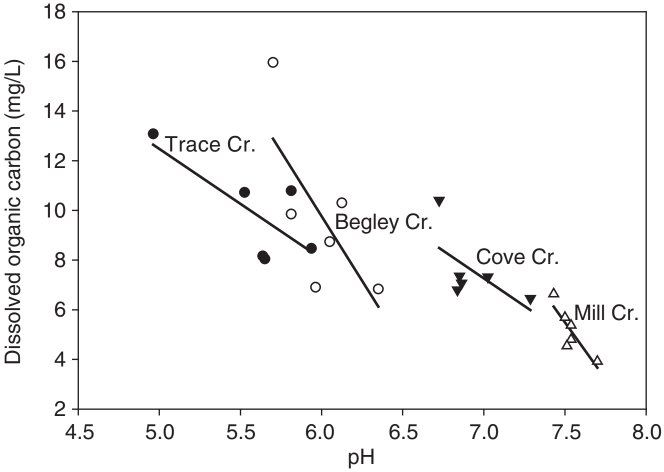

Figure 12.6. Linear regression plots of dissolved organic carbon vs. pH for Trace Creek (solid circle; $y = 34.6–4.4x$; $r^2 = 0.56$), Begley Creek (open circle; $y = 72.1–10.4x$; $r^2 = 0.51$), Cove Creek (solid triangle; $y = 38.4–4.4x$; $r^2 = 0.38$), and Mill Creek (open triangle; $y = 73.9–9.1x$; $r^2 = 0.73$). Each point on the scatter plot is a mean from four sample measurements per sampling site per sampling occasion.

streams draining through black shales had significantly higher dissolved metal levels than that draining limestone. Elevated metal concentrations have been encountered in soils and sediments derived from black shales as well as in streams whose watersheds are dominated by black shales (Coveney and Martin, 1983; Kim and Thornton, 1993; Chon et al., 1996; Loukola-Ruskeeniemi et al., 1998; Hammarstrom et al., 2003; Ogendi et al., 2004a, b). The elevated metal concentrations in Trace, Begley, and Cove creeks would be linked to weathering of the metal-enriched black shales over which these streams flow. Foley et al. (2002) attributed the high concentrations of As, Cu, and Mn in shale-draining streams in the Great Smoky Mountains National Park to near-surface reactions of sulfide minerals and water. Similar observations were made by Seal et al. (2000), and Hammarstrom et al. (2003). Short term perturbations in water quality due to acidity and elevated metal concentrations in creeks were also observed (Hammarstrom and Smith, 2002). Other studies that have documented elevated metal contents in surface waters draining pyritic-rich rocks include Bacon and Maas (1979) and Trumpf et al. (1979). In their study, Trumpf et al. (1979) found out that mass mortalities of native brook trout over an eight-km distance was due to metal toxicity notably aluminum. Ground waters in areas underlain by black shales may also be enriched in dissolved metals. A study by Ayotte et al. (1999) of shale bedrock wells in the Northern Appalachians of Maine and New Hampshire found that groundwaters contained elevated concentrations of dissolved metalloids (e.g. As) that exceeded the US EPA guidelines for drinking well water. The concentrations of Cr, Cu, Hg, Pb, and Se in streams draining black shales either approached or exceeded US EPA's metals criteria for surface waters (US EPA, 2002b). The elevated metals and metalloids in Trace, Begley, and Cove creeks during baseflow may be attributed to the groundwater inputs that contain these elements derived from soils and rocks through which the water flows. Ogendi et al. (2004b) measured between 4 and 10 ppm, and between 0.1 and 0.8 ppm of Hg in bedrock and sediments collected from streams draining black shales in the study area. Weathering of metal-enriched shales may thus lead to increased loading of toxic metals in surface waters. Enrichments of Hg up to 7.5 ppm in Proterozoic black shales have been encountered (Loukola-Ruskeeniemi, 1990). Chon et al. (1996) also encountered enrichments of AS, Mo, and Se in soils developed from black shales. The high concentrations of Fe in the black shale-draining streams are an inherent signature of the pyrite-rich black shales in the watersheds. Oxides of Mn play a significant role in metal sorption. Fe may alter the concentrations and partitioning of Co, Cu, Ni, and Zn, thus modifying metal bioavailability and toxicity to aquatic organisms (Jenne, 1968; Warren and Zimmerman, 1994; Erickson et al., 1996). Under aerobic conditions oxides of Fe and Mn can efficiently act as complexing ligands for metals (Hare et al., 1994; Erickson et al., 1996; Di Toro et al., 2001).

The study demonstrated that bedrock type and the amount of precipitation in the watersheds were strong predictors of the amount of DOC and dissolved metals in surface waters. On average, DOC concentrations in Trace Creek and Begley Creek were two times higher than those of Mill Creek for all the sampling occasions. Whereas the DOC-discharge correlations were very strong, the DOC-conductivity relationships were moderate to strong in the study streams. DOC levels in the streams draining black shales (with mean DOC ranging from 7 to 16 $\mathrm{mg\,l^{-1}}$) are significantly higher ($p \leq 0.05$) than those of typical warm temperate streams (mean = 7; range = 3–15 $\mathrm{mg\,l^{-1}}$) (Mulholland and Kuenzler, 1979; Thurman, 1985; Meybeck, 1993; Shafer et al., 1997). The higher DOC concentrations in our study sites may partly be explained by the presence of the organic-rich black shales in the watersheds. Black shales are rich in organic carbon (Petsch et al., 2000) and therefore may explain the significantly higher DOC in Trace, Begley, and Cove creek surface waters. In contrast, the DOC levels in Mill Creek are within the range of estimates for warm temperate streams (Thurman, 1985). Bedrock differences in the catchments appear to account for the spatial DOC differences because the vegetation types and principal land cover are the same for these watersheds. Temporal DOC variations are strongly correlated with changes in stream discharge (e.g. this study; Cauwet and Meybeck, 1987; Moore, 1989). The DOC data from this study were strongly positively correlated with the observed stream discharge with low- and high-DOC concentrations being encountered during baseflow and stormflow conditions, respectively. During storm events, DOC is likely accumulated by waters in contact with the organic matter-rich shale rock materials and soils, and then transported to the adjacent streams (Hendershot et al., 1992; Peters et al., 1995). The inverse relation between DOC and conductivity suggest that conductivity may indirectly influence metal transport in these streams (Fig. 12.4). The observed decline in conductivity with increased discharge and DOC levels suggests that DOC–metal complexes may be flushed from the watershed and banks into streams augmenting baseflow contents. Similarly, the strong positive linear relationships between discharge and DOC imply that significantly more dissolved metals are transported during peak discharge than during baseflow. Our findings are in agreement with similar studies by Depetris and Paolini (1991), Cauwet and Sidorov (1996), and Boyer et al. (1997) that also showed positive linear relations between discharge and the concentrations of DOC, with maximum DOC levels coinciding with peak discharge.

Metal–DOC relationships ranged from weak (Co, Cd, and Fe) to strong (Cu, Ni, V, and Pb) in the streams draining black shales. This tendency for dissolved metals to increase with increasing DOC concentration in the streams draining black shales supports the supposition that DOC is a major transport vector for dissolved metals. In Trace and Begley creeks, relatively high-DOC levels ranging from 8 to $16\,\mathrm{mg\,l^{-1}}$ in relatively low pH environments (pH range: 4.8–5.8) were noted. Higher concentrations of DOC and dissolved metals in streams draining black shale than in streams draining limestone are most likely related to differences in lithology with lithology similarly influencing pH. These findings suggest that black shales in this region may be undergoing more intense chemical weathering as evidenced by higher concentrations of DOC and acid-generating potential, whereas the limestone buffers (e.g. Walker and Webber, 1979).

12.5. Conclusions

Our study found that the difference in lithology was a significant predictor of the observed spatial variations in DOC concentrations in headwater bedrock streams. Streams draining black shale watersheds transport significantly higher amounts of DOC than those draining over limestones thereby emphasizing the important role of geology in determining the amount of DOC in streams. Second, all streams exhibited a DOC maxima and minima that coincided with a stormflow and a baseflow, respectively. The watershed soils and/or rock surfaces are significant contributors of DOC to streams particularly during stormflow conditions. Third, our results indicate that the total variation in DOC in streams can be explained by discharge. It is also evident from this study that black shales are enriched in metals, which are transported in significantly large amounts during stormflow events as compared to the baseflow conditions. Oxidative weathering of the Mississippian Fayetteville Shale plays a crucial role in the release of metals that are subsequently transported into surface and groundwaters. Findings from numerous studies strongly suggest that DOC plays a significant role in altering the potential toxicity of metals to aquatic organisms (Diamond et al., 1997; Di Toro et al., 2001). The bioavailable fraction of a metal may be decreased significantly through complexation by DOC resulting in a reduction in the overall impact of metals on aquatic organisms (Newman and Jagoe, 1994; Erickson et al., 1996; Di Toro et al., 2001; Heijerick et al., 2003). The bioavailable fraction of the metal has been shown to correspond to the observed metal toxicity to aquatic organisms (Di Toro et al., 2001; De Schamphelaere and Janssen, 2004). Owing to the strong positive correlations between DOC and dissolved metals, we envisage low-metal impact upon resident aquatic communities in the streams draining black shales in this region. Thus, any attempt to quantify metals and predict their effect on aquatic biota in streams draining black shales should consider DOC levels in addition to other physical and chemical variables.

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