Water-quality trends for a stream draining the Southern Anthracite Field, Pennsylvania

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ABSTRACT: Stream flow, chemical and biological data for the northern part of Swatara Creek, which drains a 112 km^2 area in the Southern Anthracite Field of eastern Pennsylvania, indicate progressive improvement in water quality since 1959, after which most mines in the watershed had been flooded. Drainage from the flooded mines contributes substantially to base flow in Swatara Creek. Beginning in 1995, a variety of treatment systems and surface reclamation were implemented at some of the abandoned mines. At Ravine, Pa., immediately downstream of the mined area, median SO_4 concentration declined from about 150 mg l^{-1} in 1959 to 75 mg l^{-1} in 1999 while pH increased from acidic to near-neutral values (medians: *c.* pH 4 before 1975; *c.* pH 6 after 1975). Fish populations rebounded from non-existent during 1959–1990 to 21 species identified in 1999. Nevertheless, recent monitoring indicates (1) episodic acidification and elevated concentrations and transport of Fe, Al, Mn, and trace metals during storm flow; (2) elevated concentrations of Fe, Mn, Co, Cu, Pb, Ni, and Zn in streambed sediments relative to unmined areas and to toxicity guidelines for aquatic invertebrates and fish; and (3) elevated concentrations of metals in fish tissue, notably Zn. The metals are ubiquitous in the fine fraction (<0.063 mm) of bed sediment in mining-affected tributaries and the main stem of Swatara Creek. As a result of scour and transport of streambed deposits, concentrations of suspended solids and total metals in the water column are correlated, and those for storm flow typically exceed base flow. Nevertheless, the metals concentrations are poorly correlated with stream flow because concentrations of suspended solids and total metals typically peak prior to peak stream stage. In contrast, SO_4, specific conductance and pH are inversely correlated with stream flow as a result of dilution of poorly buffered stream water with weakly acidic storm runoff derived mainly from low-pH rainfall. Declines in pH to values approaching 5.0 during storm flow events or declines in redox potential during burial of sediment could result in the remobilization of metals associated with suspended solids and streambed deposits.

KEYWORDS: *sulphate, metals, chemistry (water, streambed, sediment, fish, tissue), storm flow, stream flow, mine, drainage.*

INTRODUCTION

The Pennsylvania Anthracite region consists of four large coal fields within an area of about 8850 km^2 in the Appalachian Mountain Section of the Ridge and Valley Physiographic Province in eastern Pennsylvania (Wood *et al.* 1986; Berg *et al.* 1989; Way 2000). The coal fields are the sites of parallel, moderately to deeply downwarped synclinoria. Most mines in the region were developed to access multiple coal beds of the Llewellyn and Pottsville Formations of Pennsylvanian Age. In the Southern Anthracite Field, a total of 38 coal beds with an average thickness of 1 to 11.5 ft (0.3 to 2.5 m) have been identified and mined to depths exceeding 3280 ft (1000 m). Sandstone, siltstone and conglomerate are the dominant lithologies; limestone has not been mapped (Wood *et al.* 1968, 1986; Berg *et al.* 1989; Way 2000).

As a result of more than 150 years of mining in the Southern Anthracite Field, groundwater, surface water and stream sediments have been adversely affected (Growitz *et al.* 1985; Fishel 1988; Wood 1996; Brady *et al.* 1998; Way 2000). For example, losses of stream water to, and contaminated drainage from, abandoned anthracite mines within the upper 112 km^2 of the 1492 km^2 Swatara Creek Basin, degrade the aquatic ecosystem and impair uses of Swatara Creek to its mouth on the Susquehanna River, 95 km downstream from the mined area (Fig. 1). Consequently, the Swatara Creek Basin was designated a 'high priority watershed' for reducing nonpoint-source pollution (Pennsylvania Department of Environmental Protection 1998*a*). Current land use in the upper 112 km^2 area, upstream from Ravine, Pa., is classified as 86.6% forested, 4.9% agricultural, and only 6.4% 'barren, mined' (U.S. Geological Survey 2000). This land-use classification is misleading, however, because underground mines extend beneath much of the surface and 'natural' reforestation conceals large tracts of unreclaimed spoil. Downstream from the mined area, forest

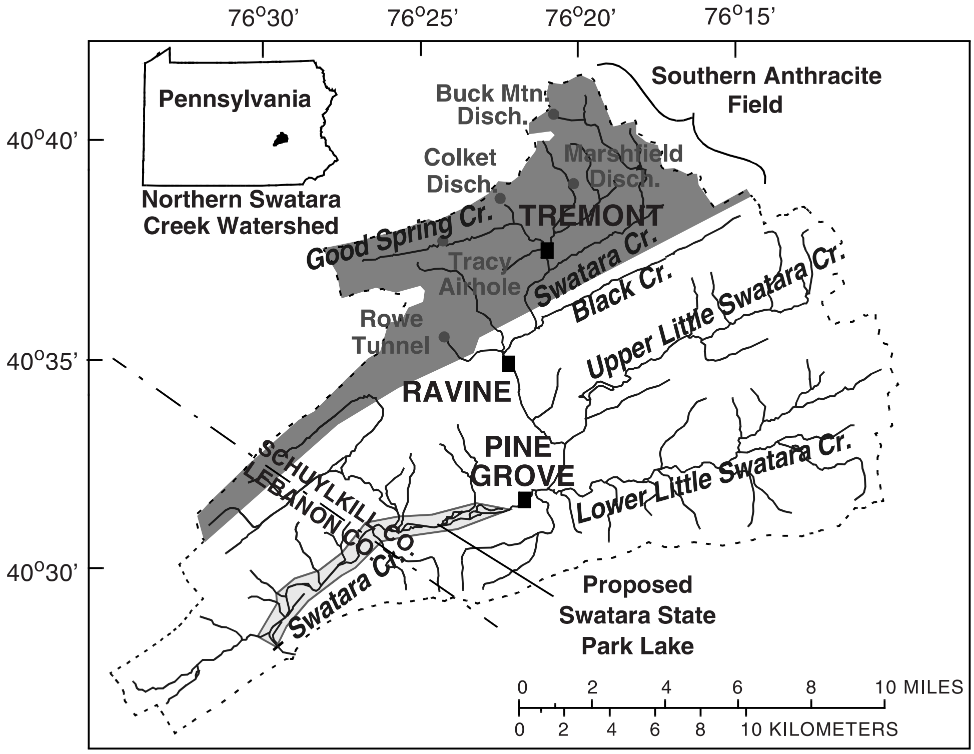


Fig. 1. Locations of selected abandoned mine discharges and key stream flow and water quality monitoring sites on Swatara Creek near Ravine and Pine Grove, Schuylkill County, Pa.

and agricultural land uses predominate. For example, land use in the 300 km^2 area of the Swatara Creek Basin upstream from Pine Grove (Fig. 1), inclusive of the area above Ravine, is classified as 69.7% forested, 25.0% agricultural, and 2.4% 'barren, mined'.

Although several surface and underground anthracite mines are currently active, most underground mines in the Swatara Creek Basin were abandoned before 1960. Barren, steep banks of spoil and culm and fine coal debris in overflowing or incised siltation basins are sources of sediment (suspended solids), acidity, and dissolved sulphate (SO_4) and metals in water that infiltrates or runs off the surface during storms (e.g. Olyphant *et al.* 1991). Many of the abandoned underground mines are flooded and have collapsed locally. Surface flow is diverted through subsidence pits, fractures and mine openings to the underground mines, where the water becomes contaminated (Ladwig *et al.* 1984; Growitz *et al.* 1985; Skelly & Loy, Inc. 1987; Wood 1996). In downstream reaches, the contaminated water resurges as 'acidic' or 'abandoned' mine drainage (AMD) contaminating Swatara Creek and its tributaries, while contributing substantially to base flow (Fishel 1988).

Swatara Creek and other streams in historic coal-mined regions commonly appear rusty owing to elevated concentrations of metals in AMD (Wood 1996; Hyman & Watzlaf 1997; Rose & Cravotta 1998). High concentrations of acidity, iron (Fe) and other metals including aluminium (Al), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), nickel (Ni), and zinc (Zn) in the water column or sediment can be toxic to aquatic macroinvertebrates, fish and piscivorous birds and mammals (Burrows 1977; Baker & Schofield 1982; Elder 1988; Sample *et al.* 1996; Hyman & Watzlaf 1997; U.S. Environmental Protection Agency 1999; Winterbourn *et al.* 2000). Hence, many streams draining coal-mined areas in Pennsylvania are 'fish-less' or contain few fish (Boyer & Sarnoski 1995; Earle & Callaghan 1998). Nevertheless, reproducing populations of brook trout and other native fish have recently been documented in certain AMD-affected streams that had been considered fish-less less than 10 years ago, such as the headwaters of Swatara Creek (this paper), Mahanoy Creek (Lindsey *et al.* 1998), and the West Branch Schuylkill River (Paul Lohen 2000, written communication, Schuylkill Headwaters Association) that drain the Anthracite region. The recent appearance of fish in these streams coincides with increased pH, from acidic (pH<4.5) to near neutral (pH>6), for many of the large AMD sources in the region (Wood 1996). The AMD sources sustain base flow at relatively constant temperature (10–15°C) and volume required for aquatic habitat. Upon aeration and at near-neutral pH, the transport of dissolved 'toxic' metals typically is attenuated owing to precipitation and adsorption (Bigham *et al.* 1996; Smith *et al.* 1998; Webster *et al.* 1998; Cravotta & Trahan 1999). However, because the recolonization of historically 'fish-less' mined areas in the eastern U.S. by aquatic and piscivorous organisms is a relatively recent phenomenon, few data are available on the aquatic ecological conditions or restoration requirements for mined watersheds (e.g. Earle & Callaghan 1998).

A variety of limestone treatment systems were recently installed at selected locations to neutralize the AMD and restore the aquatic ecosystem in the northern Swatara Creek watershed above Ravine, Pa. (Fig. 1) (Cravotta & Weitzel in press). The treatments include limestone-sand dosing, open limestone channels, anoxic and oxic limestone drains, limestone diversion wells, and limestone-based wetlands (Skousen *et al.* 1998; Cravotta & Weitzel in press). Most of these systems were constructed between winter 1995 and winter 1998. To evaluate the cumulative effects of AMD remediation and the transport of pollutants from the mined part of the watershed to unmined areas, stream flow, chemical and biological data were collected

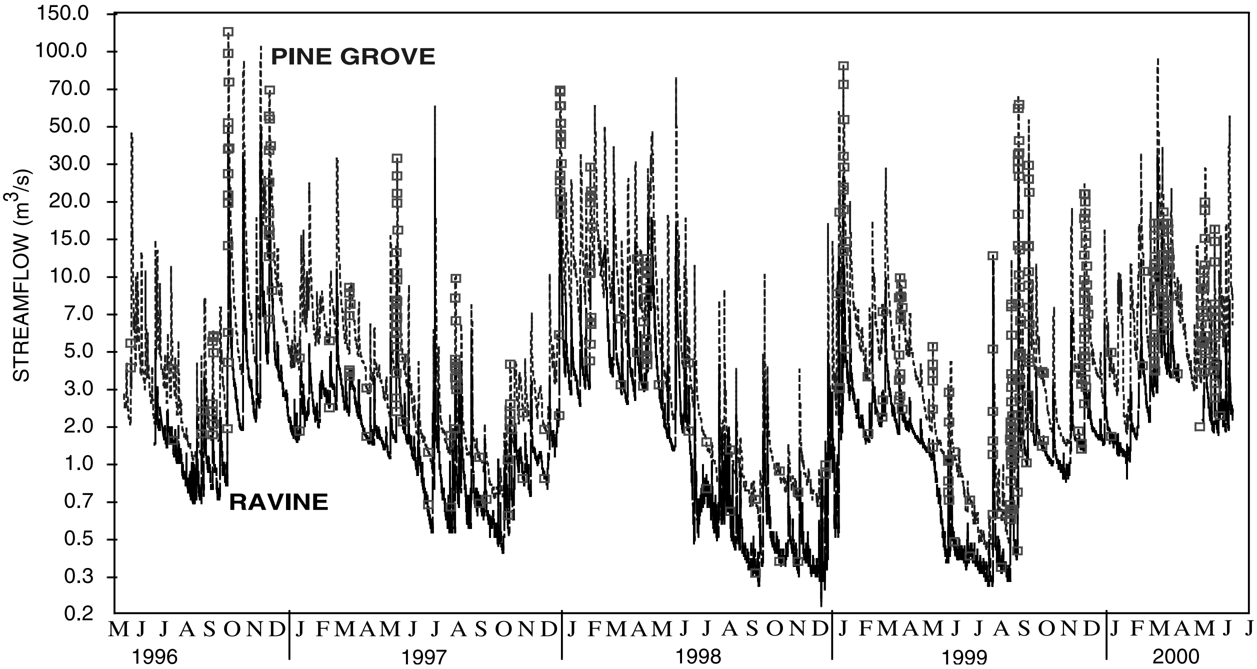


Fig. 2. Stream flow hydrographs for Swatara Creek near Ravine and Pine Grove, Pa., June 1996–June 2000. Square symbols indicate stream flow at times water-quality samples were collected.

by the U.S. Geological Survey (USGS) on the main stem of Swatara Creek near Ravine (Fig. 1; USGS station 01571820) and Pine Grove (Fig. 1; USGS station 01572025), Pa. (Fig. 1). This paper evaluates trends and relations among SO_4, metals, suspended solids and stream flow data collected at these stations between June 1996 and June 2000. Additionally, corresponding data for metals in streambed sediments and fish tissue, and information on fish and macroinvertebrate communities are presented to indicate the potential long-term effects and bioavailability of accumulated metals in the aquatic ecosystem of a coal-mined watershed.

METHODS OF DATA COLLECTION AND ANALYSIS

The stream flow gaging stations on Swatara Creek at Ravine and Pine Grove were equipped with automatic stage recording, water quality monitoring and/or water-sampling devices in 1996. At Ravine, stream stage was measured continuously with a pressure transducer; temperature, pH and specific conductance (SC) were measured continuously with a multiparameter sonde. At Pine Grove, only stream stage was measured continuously for most of the study. The continuous stage and water-quality data were recorded at 15-min intervals with an electronic data logger. In accordance with standard methods (Rantz *et al.* 1982*a*, *b*), instantaneous stream flow for a range of stream stages was determined from stream flow velocity measurements conducted with a vertical-axis current meter. Continuous stream flow was computed on the basis of a stage-discharge rating developed for each site (Rantz *et al.* 1982*a*, *b*). At both sites, instantaneous data for temperature, SC, pH, redox potential (Eh) and dissolved oxygen (DO) were also measured using calibrated instruments when samples were collected or processed (Wilde *et al.* 1998).

Water-quality samples were collected at Ravine and Pine Grove over the range of stream flow for the June 1996–June 2000 study period (Fig. 2). Monthly base flow samples were collected manually as grab samples from well-mixed zones in the stream. Storm flow samples were collected automatically using pumping samplers containing 24 l-l polyethylene bottles. The automatic samplers were programmed to initiate sampling after a specified rise in stream stage above the current base stage and to proceed at intervals based on rate of change in stage until the stream returned to the base stage. Samples submitted for analysis were selected to cover rising, peak and falling stages of the hydrograph for a storm. Storm flow samples were analysed for more than 25 events, including significant storms in October and December 1996, May 1997, January 1998, January, September and December 1999, and May 2000. Bulk precipitation for some of the storms also was collected and analysed.

Water samples were split into sub-samples either in the field or in the USGS laboratory in Lemoyne, Pa., and stored in sample-rinsed polyethylene bottles at 4°C. Samples for dissolved (0.45 μm filter) and total recoverable (whole-water; in-bottle nitric and hydrochloric acid digestion) metal analysis were stored in acid-rinsed polyethylene bottles and acidified with nitric acid (HNO_3). Samples were analysed for major ions, metals and nutrients by inductively coupled plasma atomic emission spectrometry (ICP-AES), ion chromatography (IC), colorimetry and electrometric titration at the Pennsylvania Department of Environmental Protection (PaDEP) following the methods of Greenberg *et al.* (1992), Hoffman *et al.* (1996) and Fishman & Friedman (1989). The water quality and stream flow data are maintained in the USGS National Water Information System (NWIS) data base and published annually (Durlin & Schaffstall 1998, 1999, 2000).

Streambed sediments were collected in October 1999 at water quality sampling sites on Swatara Creek at Ravine and Pine Grove, and on Good Spring Creek at Tremont, Pa. (Fig. 1). At each site, a composite sample was collected using a polyethylene scoop for subsampling to a depth of about 2 cm at 10–12 points across the stream, emphasizing depositional zones behind obstructions. The composite sample for each station was oven dried at 100°C for 72 h. Dried sediments were broken up by gentle crushing with a ceramic mortar and pestle taking care to avoid breaking individual particles. Sub-samples, obtained by cone and quartering on plastic-coated freezer paper, were subjected to particle-size analysis and chemical extraction. Particle-size distribution was determined by weighing fractions obtained using standard stainless steel sieves and a vibratory shaker. Sub-samples of sediment for analysis of metal concentrations were obtained using 2 mm (sand+silt+clay) and 0.063 mm (silt+clay) nylon sieves.

Total recoverable and progressive chemical extractions were performed on the sediment samples following methods of Greeman *et al.* (1999). The total recoverable extraction was performed by in-bottle (pre-cleaned polypropylene), partial digestion of the <2 mm and <0.063 mm fractions with high-purity 'aqua regia' consisting of nitric acid and hydrochloric acid (HNO_3+HCl). A 2–3 g sub-sample was extracted with 20 ml 50% HNO_3+HCl for 30 min and then diluted to 250 ml for continued extraction at 100°C for 48 h. The sequential extractions were performed on a separate 1.5–2 g sub-sample of the <0.063 mm size fraction, only, by adding 10 ml aliquots of reagent or deionized water, agitating for 10 min, centrifuging and decanting supernatant. The following reagents were used in sequence: (1) 1.0 M $MgCl_2$ adjusted to pH 5 with HNO_3='exchangeable ions'; (2) 5% NaOCl adjusted to pH 5 with HNO_3='easily decomposed organic matter'; and (3) 1 g $Na_2S_2O_4$ (sodium–dithionite) with 0.3 M citrate-0.2 M bicarbonate buffer at pH 8 and 75–80°C='Fe–Mn oxides' (Greeman *et al.* 1999). Each extraction step was performed twice with reagent and once with deionized water, and then supernatants were combined, stabilized with HNO_3, and diluted with deionized water. The diluted extracts were analysed for total recoverable metals by ICP-AES at the USGS National Water Quality Laboratory (NWQL) in Denver, Co., following methods of Hoffman *et al.* (1996) and Fishman & Friedman (1989). Concentration of metals in the 0.063–<2 mm fraction were determined from the <2 mm result by subtracting the mass contribution of the <0.063 mm fraction on the basis of the particle-size analysis and the <0.063 mm result.

Stream flow and water quality data for base flow and storm flow conditions were plotted and evaluated for univariate and bivariate distributions (SAS, Inc. 1990). To estimate base flow and surface runoff contributions during storm flow conditions, hydrographs were separated into these components using the local minimum method of HYSEP (Sloto & Crouse 1996). Furthermore, to compare hydrological conditions during the study with the long-term record, the stream flow duration records at the Ravine and Pine Grove gaging stations for the study period were compared with that for Harper Tavern (USGS station 01573000), which is downstream on Swatara Creek and has been gaged continuously by the USGS since 1919. To illustrate the results of sediment analyses, the concentrations of total metals and sequentially extracted fractions were plotted as stacked bar charts. If the sum of the sequential extraction fractions exceeded the total result, the fractional values were adjusted proportionally to normalize their relative contributions to the total. Concentrations of Co, Cu and Pb were below detection in extracts for exchangeable and easily decomposed organic fractions for several samples and hence were estimated as half the detection limit.

Fish were collected annually in Swatara Creek at Ravine (Fig. 1) by electrofishing over a 150 m reach consisting of mixed riffle, run and pool habitats as described by Bilger *et al.* (1999) and U.S. Environmental Protection Agency (1993). Individual fish were identified and measured before releasing most specimens (Table 1). In 1999, selected large specimens (>25 cm) of white sucker (*Catostomus commersoni*), a bottom feeder, were sacrificed for analysis of trace metals in whole fish and in fillet samples. Additionally, selected specimens of legal size (>18 cm) brook trout (*Salvelinus fontinalis*), a predator, were sacrificed for analysis because the species commonly is consumed by anglers and is one of the most widespread species in mine-affected waters in the study area. Six of the white sucker specimens were composited for whole-fish analysis, six others were filleted using a stainless steel knife, and six brook trout were eviscerated, 'gutted and gilled', and then frozen for transport to the laboratory in accordance with preparation protocols (Hoffman 1996). Each set of fish samples was homogenized to form a single composite, and a sub-sample was dried and acid-extracted for analysis of trace metals by ICP-AES, inductively coupled plasma-mass spectrometry, or cold vapour-atomic absorption spectrophotometry at the USGS NWQL in Denver, Co. (Hoffman 1996).

In addition to fish surveys, benthic macroinvertebrates were collected at Ravine during the fall of 1994 and 1996–1999. In accordance with rapid bioassessment protocols (U.S. Environmental Protection Agency 1990; Barbour *et al.* 1999), a rectangular frame kicknet with 0.6-mm screen size was used to capture debris and organisms dislodged from the streambed. An area of approximately 0.5 m^2 was 'kicked' upstream of the net for a total of 30 s for each sample. Samples were collected from three habitats consisting of shallow riffle with exposed cobbles, deeper riffle and run habitats. The three samples were composited and preserved with a formaldehyde solution for subsequent identification in the laboratory.

RESULTS AND DISCUSSION

Stream flow trends

Stream flow hydrographs for the study period were correlated between Swatara Creek at Ravine and Pine Grove (Fig. 2). At each of these sites, stream flow increased in proportion to their respective watershed areas. Compared to the 81-year record (1919–2000) for Swatara Creek at Harper Tavern, the stream flow probability distribution during the 1996–2000 study period was normal. However, annual stream flow was greater than normal in 1996 and 2000, normal in 1997, and lower than normal in 1998 and 1999. Generally, high base flow was sustained during the winter and spring months each year (Fig. 2). Lowest stream flow during the study resulted during droughts in the fall 1998 and summer 1999. These high- and low-flow periods were punctuated by short-duration storm flow events that lasted from hours to several days.

The average daily stream flow by month for Swatara Creek at Ravine ranged from a minimum of 0.31 $m^3\ s^{-1}$ for September 1997 to a maximum of 5.56 $m^3\ s^{-1}$ for February 1998. Hydrograph separation by the local minimum method with HYSEP (Sloto & Crouse 1996) indicated, on average during the study, the total stream flow at Ravine was composed of about 67% base flow and 33% storm runoff. However, base flow contributions were much smaller during relatively dry periods when large storm events occurred. For example, during October and December 1996 and September 1999, base flow contributed an average of only 25, 47 and 36%, respectively, of the monthly total stream flow at Ravine. Storm runoff was estimated to contribute about 95% of the total stream flow during October 19–21, 1996; about 76% during December 13–15, 1996; and about 92 and 73% during September 16–17, 1999, and September 30–October 1, 1999, respectively.

Table 1. *Fish species identified in Swatara Creek at Ravine, Pa., 1985–1999**

Taxa				Month and year of survey					
ORDER Family *Genus species*	Common name	Minimum pH in PA†	Pollution tolerance‡	10/85 8/90	9/94	7/96	10/97	9/98	9/99
				Number of individuals					
CYPRINIFORMES									
Cyprinidae									
Campostoma anomalum	Stoneroller	6.0	M	0	0	0	0	0	2
Cyprinella analostana	Spotfin shiner	6.4	M	0	0	0	0	3	3
Exoglossum maxillingua	Cutlips minnow	6.1	I	0	0	0	1	0	0
Nocomis micropogon	River chub	6.0	I	0	7	1	14	9	44
Notemigonus crysoleucas	Golden shiner	4.6	T	0	0	0	0	1	0
Notropis rubellus	Rosyface shiner	6.0	I	0	0	0	1	0	0
Rhinichthys atratulus	Blacknose dace	5.6	T	0	1	22	47	162	6
Rhinichthys cataractae	Longnose dace	5.9	I	0	1	12	1	17	4
Semotilus atromaculatus	Creek chub	5.2	T	0	3	0	7	22	1
Semolitus corporalis	Fallfish	6.1	M	0	15	0	66	54	30
Catostomidae									
Catostomus commersoni	White sucker	4.6	T	0	2	20	25	52	22
Hypentelium nigricans	Northern hog sucker	6.0	I	0	0	0	0	0	5
SILURIFORMES									
Ictaluridae									
Ameiurus natalis	Yellow bullhead	—	T	0	0	0	1	1	0
Ameiurus nebulosus	Brown bullhead	4.6	T	0	0	0	1	12	2
Noturus insignis	Margined madtom	5.9	M	0	0	0	0	2	9
SALMONIFORMES									
Esocidae									
Esox niger	Chain pickerel	4.6	M	0	0	0	0	0	2
Salmonidae									
Salmo trutta	Brown trout	5.9	M	0	0	2	0	1	2
Salvelinus fontinalis	Brook trout	5.0	M	0	0	19	10	21	5
SCORPAENIFORMES									
Cottidae									
Cottus sp.	Sculpin	5.9	M	0	0	0	0	2	0
PERCIFORMES									
Centrarchidae									
Ambloplites rupestris	Rock bass	6.0	M	0	0	0	0	0	6
Lepomis auritus	Redbreast sunfish	6.2	M	0	0	0	0	2	2
Lepomis gibbosus	Pumpkinseed	4.6	M	0	0	0	1	0	2
Lepomis macrochirus	Bluegill	—	M	0	0	0	0	2	1
Micropterus dolomieu	Smallmouth bass	6.0	M	0	0	0	7	0	52
Micropterus salmoides	Largemouth bass	4.7	M	0	0	0	1	0	0
Percidae									
Etheostoma olmstedi	Tessellated darter	5.9	M	0	0	0	12	16	3
Percina peltata	Shield darter	—	I	0	0	0	0	0	3
Total number of individuals collected:				0	29	76	195	379	206
Total number of species identified:				0	6	6	15	17	21

*Fish collected and identified by M. D. Bilger and R. A. Brightbill of USGS. †Minimum pH of occurrence in freshwater in Pennsylvania as reported by Butler *et al.* (1973). ‡Pollution tolerance: I (intolerant), M (moderate), T (tolerant), adapted from Barbour *et al.* (1999).

Water quality trends

Baseflow

Current and historical data from 1959 to 2000 for Swatara Creek at Ravine indicate progressive improvement in base flow water quality (Fig. 3). Although stream flow at times of collection of historical and current base flow samples was generally comparable, SO_4 declined from a median of about 150 mg l^{-1} in 1959 to 75 mg l^{-1} in 1999, while pH increased sharply from 3.5–4.4 (median *c.* 4) to 4.6–7.0 (median *c.* 6) after 1975 (Fig. 3). The decline in SO_4 concentration was probably caused by a decline in pyrite oxidation after flooding of the abandoned mines had minimized inflows of oxygenated air and water. The associated increase in pH was caused by the onset of carbonate buffering that occurred when the rate of alkalinity production equalled or exceeded acid production (Cravotta *et al.* 1999). Although a variety of environmental factors could affect pH and SO_4 concentrations, consistently near-neutral pH with variable SO_4 concentration at Ravine during 1998–2000 (Figs. 3 and 4) imply that the recently implemented limestone treatments have neutralized acid, further improving water quality.

As a consequence of the improved water quality at Ravine, the fish community composition has progressively improved since 1990, when fish were not recorded (Table 1). During ecological surveys in 1994 and 1996, six species of fish were found. Increased numbers of fish species have been documented annually since 1996; 21 species were found in 1999 (Table 1). The overall fish community structure can be characterized as transitional between cold-water and warm-water classifications. The colonizing fish probably originated from wild stocks in unaffected or marginally affected tributaries and downstream reaches in the watershed. Although species abundance varied from year to year, the majority of the species collected since 1994 is mostly insectivorous and is considered

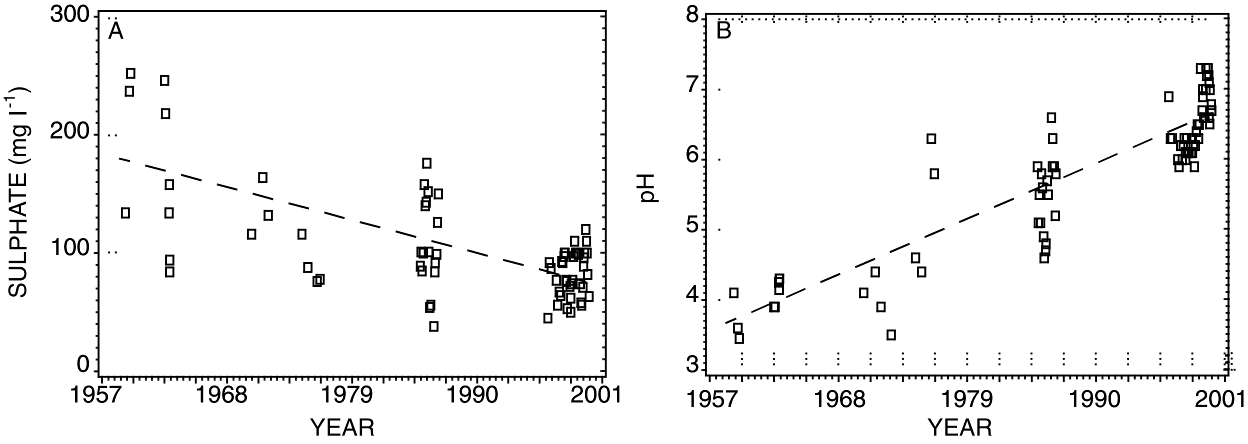


Fig. 3. Long-term water quality trends for base flow of Swatara Creek at Ravine, Pa. A, Sulphate; B, pH. Data from McCarren *et al.* (1964), Stuart *et al.* (1967), Skelly & Loy, Inc. (1987), Fishel (1988) and Durlin & Schaffstall (1998, 1999, 2000).

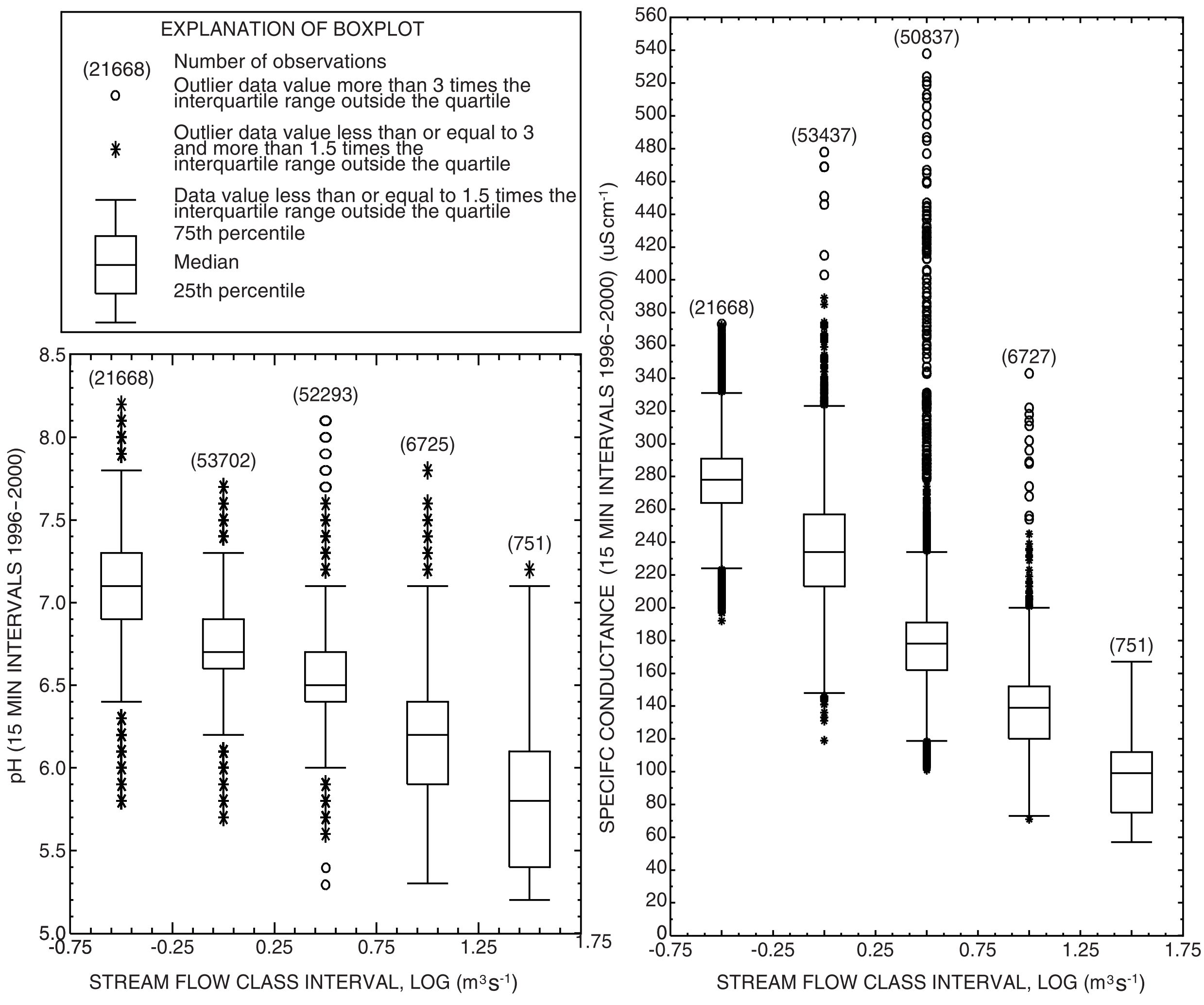


Fig. 4. Boxplots showing continuously measured pH and specific conductance data (recorded at 15 min intervals) by stream flow class interval for Swatara Creek at Ravine, Pa., June 1996–June 2000.

to have moderate tolerance to pollution (Table 1). As populations have increased, competition among species could be a significant factor affecting species abundance. For example, the populations of predator and prey species appear to be inversely and dynamically related. During 1997–1998, the dominant species were blacknose dace (*Rhinichthys atratulus*), fallfish (*Semolitus corporalis*), white sucker (*Catostomus commersoni*), creek chub (*Nocomis atromaculatus*), tessellated darter (*Etheostoma olmstedi*), and brook trout (*Salvelinus fontinalis*). In 1999, smallmouth bass (*Micropterus dolomieu*), river chub (*Nocomis micropogon*), and fallfish were dominant, with significantly fewer blacknose dace, tessellated darter, and brook trout.

Table 2. *Benthic macroinvertebrates identified in Swatara Creek at Ravine, Pa., 1994–1999**

Taxa ORDER Family *Genus*	Pollution tolerance†	8/94	10/96	9/97	9/98	9/99	9/99
		Month and year of survey — Number of individuals					
EPHEMEROPTERA (mayflies)							
Baetidae	4						
Acentrella		0	0	3	2	1	2
Baetis		0	0	14	22	4	5
Heptageniidae	4						1
Stenarcron		0	0	0	0	1	0
Stenonema		0	0	1	0	1	0
PLECOPTERA (stoneflies)							
Leuctridae	0						
Leuctra		1	1	0	2	0	0
MEGALOPTERA (dobsonflies, alderflies)							
Sialidae	4						
Sialis		1	3	0	2	1	1
COLEOPTERA (aquatic beetles)							
Dryopidae	5						
Helichus		0	0	1	0	0	0
Elmidae	4						
Optioservus		0	0	0	1	0	0
Promoresia		0	0	0	0	1	0
Stenelmis		0	0	1	0	0	1
Psephenidae	4						
Psephenus		0	0	0	0	1	0
TRICHOPTERA (caddisflies)							
Hydropsychidae	4						
Ceratopsyche		0	0	0	0	0	33
Cheumatopsyche		0	0	0	14	12	8
Diplectrona		2	0	5	1	0	0
Hydropsyche		18	12	25	59	40	39
Philopotamidae	3						
Dolophilodes		0	0	0	0	0	1
Rhyacophilidae	0						
Rhyacophila		0	0	1	0	0	2
DIPTERA (true flies)							
Chironomidae	6	33	0	63	21	12	6
Empididae	6						
Chelifera		1	5	1	11	0	0
Hemerodromia		2	6	0	0	0	2
Tipulidae	3						
Antocha		0	0	0	1	0	0
Dicranota		0	1	0	3	5	4
Limnophila		0	0	0	0	0	1
NON-INSECT TAXA							
DECAPODA (crayfish)							
Cambaridae	6						
Cambarus		0	1	0	0	0	0
HYDRACHNIDIA (water mites)	4	0	0	0	0	0	2
OLIGOCHAETA (aquatic earthworms)							
Lumbricidae	6	3	0	2	0	0	0
Total number of individuals collected:		61	29	117	139	79	108
Total number of taxa identified (⩾family level):		6	6	9	8	8	11
Hilsenhoff's family-level biotic index†		5.21	4.65	5.10	4.37	4.24	4.02

*Taxa collected/identified in 1994–99 by D. Bogar, PaDEP, and in 1999 by M. D. Bilger, USGS (last column). †Pollution tolerance index values from 0 to 10 and number of individuals used to compute Hilsenhoff's (1988) family-level biotic index: 0.00–3.75 (excellent), 3.76–4.25 (very good), 4.26–5.00 (good), 5.01–5.75 (fair), 5.76–6.50 (fairly poor), 6.51–7.25 (poor), and 7.26–10.00 (very poor) (U.S. Environmental Protection Agency 1993).

The benthic macroinvertebrate community at Ravine has not exhibited the same dynamic as the fish community. However, an improved water-quality trend from 1994 to 1999 is implied by an increased abundance of taxa that are considered intolerant of pollution (Table 2). In 1994 and 1996, six taxa (family level) were recorded; during 1997–1999, 8 to 11 taxa were recorded. The calculated Hilsenhoff's (1988) family-level biotic index (Table 2) indicates water quality at Ravine improved, from fair in 1994 to very good in 1999. Hydropsychidae (caddisflies) and Chironomidae (midges), which are known to tolerate acidic conditions, were consistently dominant during 1994–1999 (Table 2). Although subordinate, the appearance of Ephemeroptera (mayflies), including Baetidae and Heptageniidae, in 1997 and later years is significant in that these insects are sensitive to acidic conditions and considered intolerant to pollution (Table 2). The benthic macroinvertebrate community recorded for 1999 can be characterized as moderately impacted based on total taxa and slightly impacted based on the total mayfly, stonefly and caddisfly taxa.

During the study, pH, SO_4, and other constituent concentrations varied greatly in response to changes in stream flow. Generally, base flow samples had higher pH, SC, alkalinity, hardness, and concentrations of dissolved major ions, and lower concentrations of total metals compared to storm flow (Figs 4, 5 and 6). At Ravine, the pH ranged from 5.2 to 8.2 and SC ranged from 27 to 540 $\mu S\ cm^{-1}$, with values generally decreasing with increased stream flow (Fig. 4). Minimum values of pH and SC were recorded for storm flow. Concentrations of SO_4 and total Fe ranged from 43 to 120 $mg\ l^{-1}$ and 0.21 to 59.5 $mg\ l^{-1}$, respectively, in baseflow and from 22 to 150 $mg\ l^{-1}$ and 0.61 to 130 $mg\ l^{-1}$, repectively, in storm flow samples (Figs 5 and 6).

Six bulk precipitation samples were collected during June 1999–June 2000 at Ravine or Pine Grove. The rain had the following median and range values: pH=4.7 (4.1–6.2), SC= 18 $\mu S\ cm^{-1}$ (6–78 $\mu S\ cm^{-1}$), SO_4=2.4 $mg\ l^{-1}$ (<1–5.9 $mg\ l^{-1}$), and total Fe=0.053 $mg\ l^{-1}$ (0.043–0.077 $mg\ l^{-1}$). The pH, SC and solute concentrations for the precipitation were consistently lower than those for Swatara Creek; only one rain sample had pH>5.

Storm flow

As stream flow at Ravine increased during storm flow events, pH, SC and concentrations of SO_4 and Mn typically decreased, while concentrations of suspended solids, Fe, Al and other metals in whole-water samples typically increased (Figs 5, 6 and 7). Similar trends for dissolved and suspended solids during storm flow on Swatara Creek in 1959 were reported by Stuart *et al.* (1967, fig. 10). However, the trends for pH, SC and SO_4 are inconsistent with work of others who evaluated impacts of acid rain on small streams in forested watersheds of the Appalachian Mountains of northeastern U.S. For example, Corbett & Lynch (1982) and DeWalle (1990) showed pH typically *decreased* while SO_4 *increased* with flow in Appalachian headwater streams during storm events.

Cravotta (2000) showed the decreases in pH, SC and major ion concentrations during storm events for Swatara Creek could result from mixing of weakly acidic storm runoff having pH 4.0–4.5 and low dissolved solids with poorly buffered stream water having pH 6.0–6.5 and high SO_4. The storm runoff is derived from acidic rainfall with minor contributions from pyrite oxidation products and carbonate minerals (e.g. Olyphant *et al.* 1991; Cravotta 1994). For example, during the storm flow event on December 13–15, 1996 (Fig. 5B), stream flow at Ravine increased rapidly from about 5.1 to 15.6 $m^3\ s^{-1}$ at an intermediate stage during early morning and then rose sharply to about 26.9 $m^3\ s^{-1}$ at the peak stage during the afternoon of December 13, while SC decreased from 160 to a minimum of about 100 $\mu S\ cm^{-1}$ and sulphate followed the same trend. Cravotta (2000) showed the peak storm flow composition could result from mixing storm runoff with base flow in proportions ranging from 75:25 to 50:50, which is consistent with hydrograph separation estimates for storm runoff and base flow contributions. During the falling stage on December 14, the pH decreased from 6.2 to a minimum of 5.3, gradually recovering to base flow pH values near 6, as stage receded. These trends are consistent for other storms during the study.

Several examples of storm hydrographs with associated stream flow chemistry during the study are illustrated in Figure 5. The same vertical axes for stream flow, SC and SO_4; pH; and concentrations of suspended solids, total Fe and dissolved Fe were used so that storm characteristics can be compared. Although each storm hydrograph is unique, owing to variations in storm duration, intensity and runoff, some features are consistent among the hydrographs. Typically, the greatest changes in SC and pH occurred with the largest changes in stream flow (greatest dilution by storm runoff). The minimum SC typically occurred with peak stream flow, whereas the minimum pH lagged by several hours, generally occurring during the falling stage. In contrast, suspended solids generally increased to peak concentrations during the initial rising stage and declined prior to peak stage. Although the total Fe concentration included contributions from suspended particles, peaks for total Fe concentrations tended to be achieved after the peaks in suspended solids, possibly reflecting a time lag for Fe-laden water and associated sediment from the upper, mined part of the watershed to reach Ravine. Generally, concentrations of suspended solids and total Fe and other metals at a given stream flow during a storm event were greater during the rising stage than the falling stage (Fig. 5). Furthermore, small storm events can scour Fe deposits from the streambed with little dilution of the concentrations, resulting in concentrations of total metals and suspended solids that are comparable with or greater than those of large storms. Hence, the overall correlation between Fe concentration and stream flow is relatively poor (Fig. 6).

Correlations among stream flow, metals, and suspended solids

Concentrations of Al, Co, Cu, Pb and Ni were commonly detected in the unfiltered samples and not in the corresponding filtered samples. Hence, the 'dissolved' consistent concentrations did not include significant contributions from <0.45 mm colloids (e.g. Schemel *et al.* 2000). Furthermore, when detectable in both filtered and unfiltered samples, the total concentration of Fe, Al, Co, Cu, Pb and Ni generally exceeded those in filtered samples indicating a significant fraction of these metals was associated with suspended particles (Figs 6 and 7). In contrast, comparable values for total and dissolved concentrations of Mn and Zn, particularly in base flow samples, indicate a significant fraction of these metals was transported as dissolved ions (Fig. 7).

At Pine Grove, concentrations of SO_4 and metals were generally lower than at Ravine (Figs 6, 7 and 8) due to attenuation by precipitation, adsorption and dilution, and decreased loading downstream of the mined area. However, because of increased stream flow and loading from agricultural and municipal sources downstream of the mined area, transport of suspended solids, associated metals and nutrients were typically greater at Pine Grove than at Ravine (Fishel 1988; Cravotta 2000).

At Ravine and Pine Grove, suspended solids and total Fe, Al, Mn, Co, Cu, Pb and Zn achieved maximum concentrations during storm flow conditions but typically prior to peak stream flow (Figs 6, 7 and 8). Although concentrations of total Fe, Al, Cu Pb, and, to a lesser extent, Mn and Zn were poorly correlated with stream flow (Fig. 6), these constituents were correlated with the concentration of suspended solids (Fig. 8). These trends generally resulted from the accumulation of metal-rich sediments (Fe(OH)3, Al(OH)3, and clay minerals) within the streambed during base flow conditions, scour and transport of the streambed deposits during rising storm flow stage, and dilution during falling stages. The correlations between concentrations of suspended solids and total metals are consistent with suspended solids that contained approximately 10% Fe, 5% Al, and lesser amounts of Mn and trace metals (Fig. 8), which are present in comparable concentrations in fine streambed sediments (Fig. 9).

The concentrations of dissolved Al and trace metals commonly approached limits of detection (Fig. 7); however, the metal-rich suspended solids and streambed sediments represent a potential source of dissolved metals. Dissolved metals could be derived from the solids by recrystallization of metastable phases to more stable, pure phases (Bigham *et al.* 1996), by dissolution or desorption (Francis *et al.* 1989; Webster *et al.* 1998), and (or) by reductive dissolution of Fe(III) and Mn(III-IV) oxides (Francis & Dodge 1990). These processes could be promoted by decreases in pH and (or) redox potential in the streambed or water column.

Streambed sediments

Concentrations of Fe, Mn, Co, Cu, Pb, Ni and Zn in sediment from northern Swatara Creek (Fig. 9) were elevated, generally exceeding 75% of reported values for freshwater sites in the conterminous U.S. (Rice 1999) and 95% of values for low-order streams in unmined watersheds in the eastern U.S. (e.g. Fitzpatrick *et al.* 1998). However, the concentrations of Al in sediments from Swatara Creek were not elevated.

Total concentrations of metals in the fine sediment fraction (<0.063 mm) exceeded those for the coarser fraction (0.063–<2-mm) for each station (Fig. 9). Although concentrations of Fe for each size fraction decreased with distance downstream from the mined area, in the order Tremont>Ravine>Pine Grove (Fig. 9), concentrations of Mn were higher at Ravine, and concentrations of Al were higher at Pine Grove than at the other sites. The total concentrations of most trace metals showed downstream trends that reflected those for total Mn (Fig. 9). Although Fe, Mn and Co were almost entirely associated with the Fe–Mn-oxide fraction of the sediment, Cu, Pb, Ni and Zn were primarily associated with the Fe–Mn-oxide and easily decomposed organic fractions.

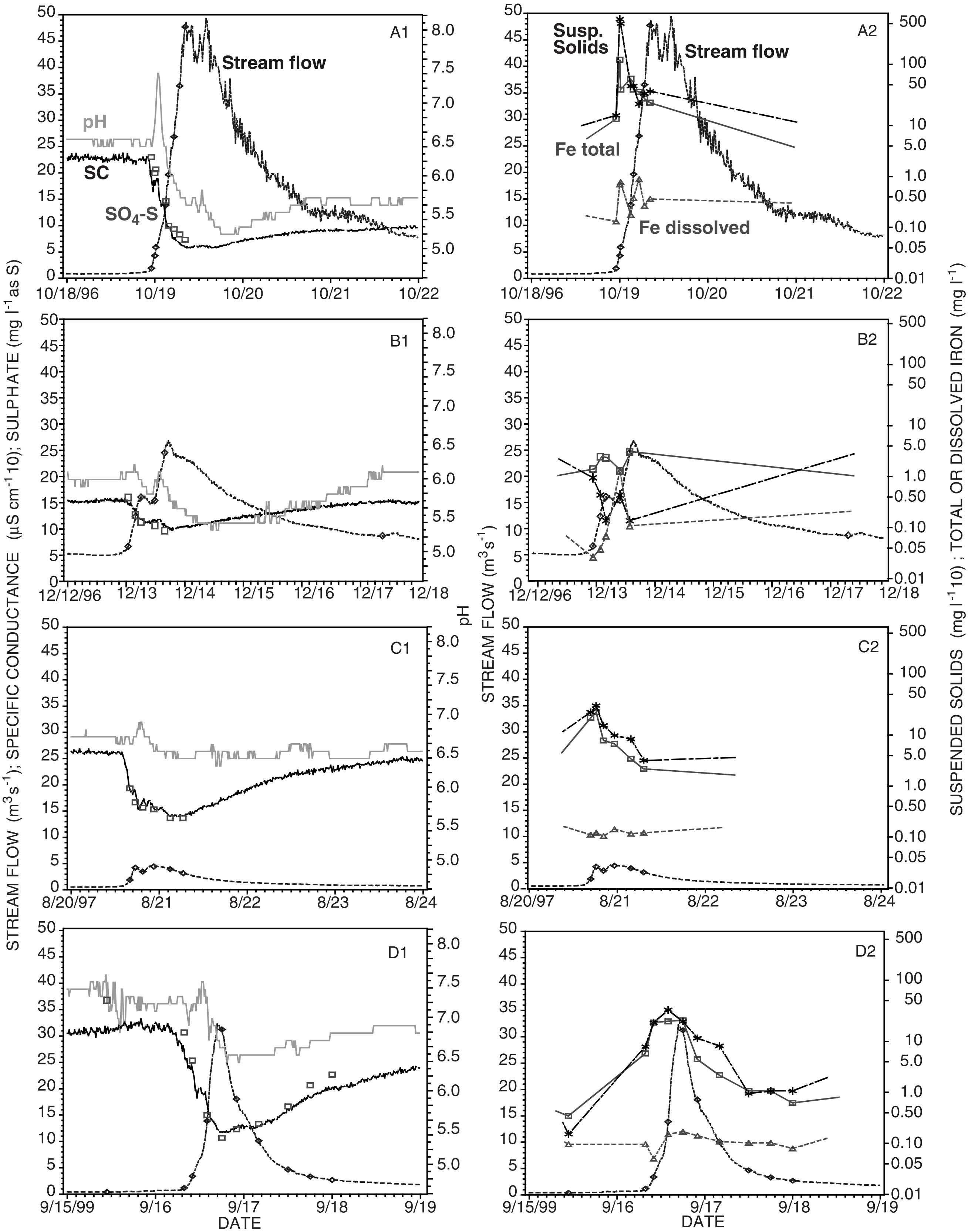
Differences in the concentrations of Fe, Al and Mn among sampling locations (Fig. 9) indicate different sources and depositional environments for the metals in streambed sediments. Highest concentrations of Fe in samples from Good Spring Creek at Tremont are consistent with the proximity of this station to the Tracy, Colket and Marshfield mine discharges which are characterized as large flows (2–10 ft^3 s^{-1} combined) of near-neutral, anoxic water containing significant concentrations of dissolved Fe (5–25 mg l^{-1}) and lesser quantities of Al and other metals (Durlin & Schaffstall 1998, 1999, 2000). Highest concentrations of Mn in sediment from Swatara Creek at Ravine, which is below a series of rapids and small water falls, are consistent with elevated pH, supersaturation with dissolved oxygen, and increased temperatures in this reach compared to upper reaches (e.g. Durlin & Schaffstall 1998, 1999, 2000). These conditions favour microbially mediated oxidation and precipitation of Fe and Mn oxides, which tend to be supersaturated in solution but slow to precipitate (e.g. Cravotta & Trahan 1999). Highest concentrations of Al in samples from Swatara Creek at Pine Grove imply that mine drainage is not the only source of Al in the watershed. Agricultural land use in the southern part of the watershed contributes significant runoff containing fine sediments including illite and other aluminium-bearing minerals. Storm flow samples at Pine Grove tend to be 'muddy' in contrast to their 'rusty' character at Ravine.

Higher concentrations of metals in the fine fraction relative to the coarser fraction are related to the higher surface-to-volume ratio for fine particles compared to coarse particles and imply that the trace elements are associated with Fe–Mn-oxide and organic coatings on mineral particles (e.g. Tessier *et al.* 1982; Horowitz 1991). (Fig. 9). Dissolved Mn^{2+} and trace metals have been reported to adsorb to hydrous Fe, Al, and Mn oxides, with Mn oxides generally more effective sorbents than Fe or Al oxides at near-neutral and lower pH (McKenzie 1980). Hence, as the Mn content of the oxides in the sediment increases, trace-metal removal generally would become more effective. Relatively high proportions of the Cu, Pb, Ni and Zn in the organic fraction imply that these metals could be bioavailable.

Fish tissue

USEPA has recommended screening values for only a few metals, As (3 μg g^{-1}), Cd (10 μg g^{-1}), Hg (0.6 μg g^{-1}) and Se (50 μg g^{-1}), in fish tissue for human consumption (U.S. Environmental Protection Agency 1997). None of these constituents in white sucker or brook trout collected at Ravine in 1999 (Table 3) exceeded these screening values. With the exception of Pb, which was below detection in the trout sample, the metals reported for the streambed sediments, Fe, Al, Mn, Co, Cu, Ni, Pb and Zn, plus Ba, B, Cr, Hg, Se and Sr, were present in the fish collected at Ravine (Table 3). In general, because of metals in gut contents and in organs such as the liver (e.g. Campbell *et al.* 1988), concentrations of most metals in whole fish were greater than those in fish prepared as for consumption (Table 3); however, Pb, B and Se were concentrated in sucker fillet relative to whole sucker. Additionally, Hg, Cr and Mn were concentrated in cleaned trout relative to sucker fillet (Table 3). The following elements were not detected in the fish sample: Sb, As, Be, Cd, Mo, Ag, U and V (Table 3).

The biological uptake of metals and transfer to higher trophic levels has been the subject of numerous investigations (e.g. Lowe *et al.* 1985; Campbell *et al.* 1988; Sharpe & MacKay 2000; Winterbourn *et al.* 2000) and is beyond the scope of this study. Nevertheless, some observations are noteworthy. The fish sampled from Swatara Creek had Zn concentrations that were more than 30 times the national average (geometric mean), Cu and Se concentrations that were equivalent to the national average, and Hg and Pb concentrations that were less than half the national average for freshwater fish in the U.S. (Lowe *et al.* 1985). Compared to other metals, Cu and Zn were partitioned to a greater extent in fish tissue relative to the sediment; tissue concentrations were 2.0 to 4.5% of the Cu and 10 to 13% of the Zn in sediment (Table 3, Fig. 9). This trend implies that ingested forms of Cu and Zn are not as readily excreted or excluded as other metals in the sediments. Furthermore, concentrations of Hg and to a lesser extent Cr, Cu and Fe, were greater in trout, which feed upon invertebrates and other fish, relative to white sucker, which feed primarily on vegetation, detritus and other organic matter (Table 3). In contrast Al, Co, Pb and Sr, and to a lesser extent Zn, were higher in sucker fillet than in trout. These results indicate biomagnification of Hg (Campbell *et al.* 1988) and are consistent with those of Brezina & Arnold (1977) who reported that (1) Hg concentrations in fish collected in Pennsylvania were higher for fish predators than for bottom feeders; and (2) Zn was more concentrated in bottom feeders than in predators.


A1
Stream flow
pH
SC
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A2
Susp. Solids
Stream flow
Fe total
Fe dissolved
B1
B2
C1
C2
D1
D2
STREAM FLOW (m3s-1); SPECIFIC CONDUCTANCE (µS cm-1 10); SULPHATE (mg l-1 as S)
pH
STREAM FLOW (m3s-1)
SUSPENDED SOLIDS (mg l-1 10) ; TOTAL OR DISSOLVED IRON (mg l-1)
10/18/96
10/19
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Fig. 5.

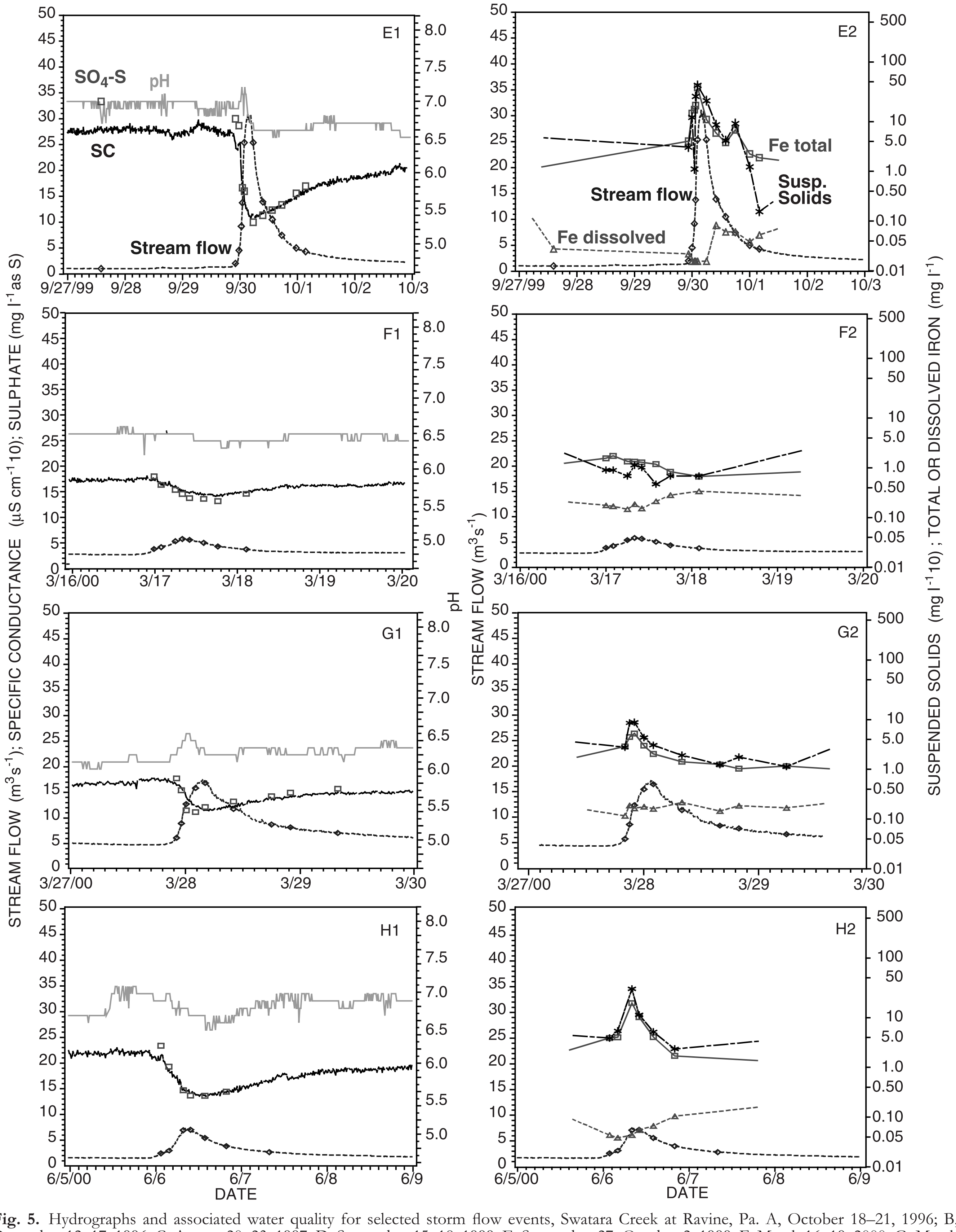

Fig. 5. Hydrographs and associated water quality for selected storm flow events, Swatara Creek at Ravine, Pa. A, October 18–21, 1996; B, December 12–17, 1996; C, August 20–23, 1997; D, September 15–18, 1999; E, September 27–October 2, 1999; F, March 16–19, 2000; G, March 27–29, 2000; and H, June 5–9, 2000. Values plotted for SC and suspended solids were divided by 10 and for SO_4 concentration were divided by 3 (as sulphur).

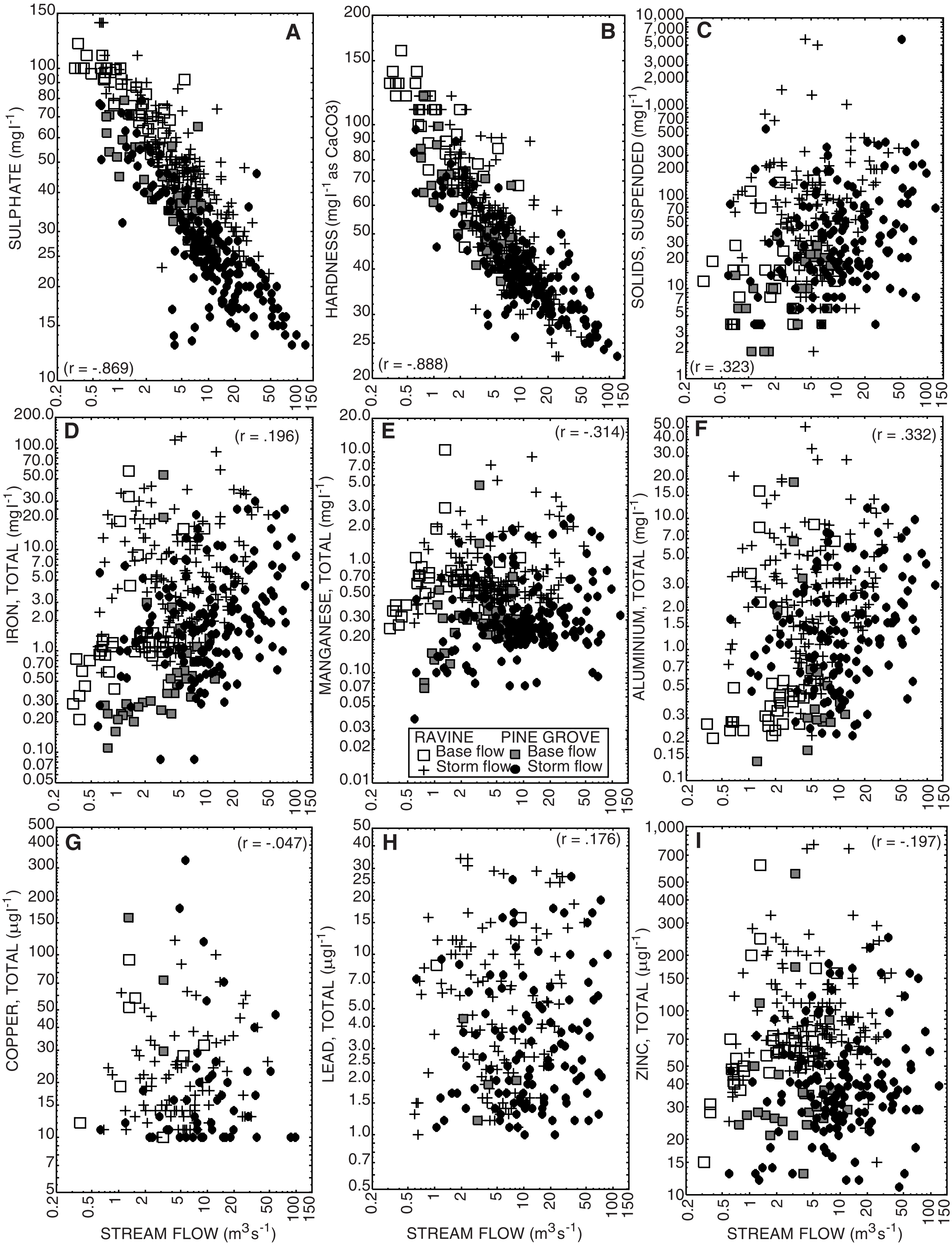

Fig. 6. Relations between stream flow and water quality constituents in base flow and storm flow samples, Swatara Creek at Ravine and Pine Grove, Pa. Spearman correlation coefficient, r, values>absolute value of 0.2 are significant ($P \leq 0.001$).

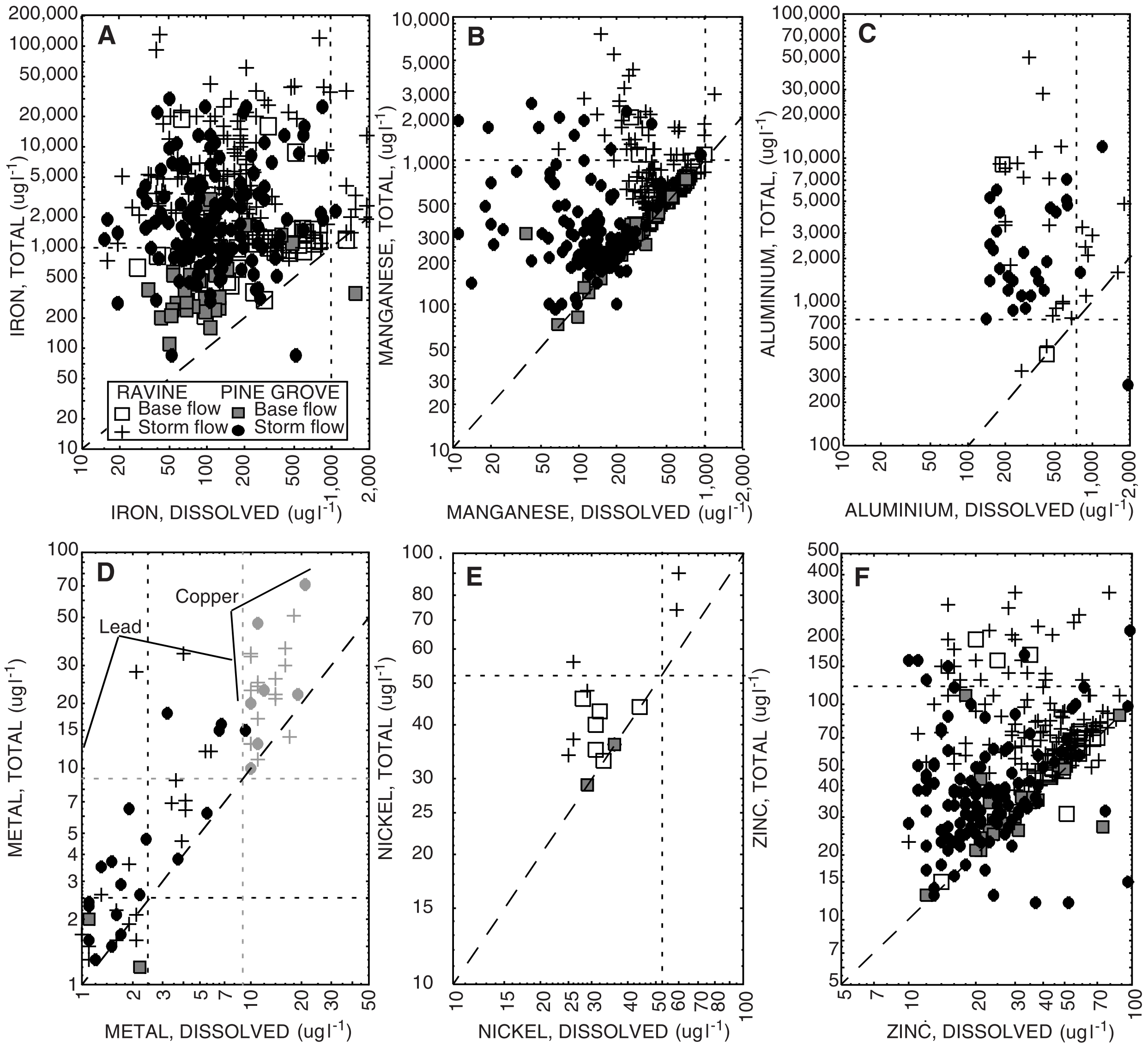

Fig. 7. Relations among concentrations of dissolved and total metals in stream water sampled during base flow and storm flow conditions, Swatara Creek at Ravine and Pine Grove, Pa. Values farther to right of diagonal line indicate decreasing fraction of dissolved ions (<0.45 μm) contributing to total concentration. Data plotted only if dissolved concentrations detectable. Dotted horizontal and vertical lines, except for Mn, indicate National Recommended Water Quality Criteria (U.S. Environmental Protection Agency 1999) for continuous concentration; dotted lines for Mn indicate PaDEP standard for daily average concentration (Pennsylvania Department of Environmental Protection 1998*b*). Symbols and lines for copper shaded gray.

Ecological ramifications

On the basis of temperature, DO and SO_4 concentrations in stream water during the study, Swatara Creek at Ravine and Pine Grove consistently met water quality criteria established to maintain its designated use as a cold water fishery (Pennsylvania Department of Environmental Protection 1998*b*). Sulphate concentrations never exceeded 250 mg l^{-1}. The maximum recorded water temperature at Ravine and Pine Grove was 20.0 and 21.0°C, respectively, during July 1997 (Durlin & Schaffstall 1998). The minimum DO at Ravine was 8.7 mg l^{-1} during July, 1997 (Durlin & Schaffstall 1998) and at Pine Grove was 6.2 mg l^{-1} during September 1998 (Durlin & Schaffstall 1999). Nevertheless, concentrations of metals periodically exceeded water quality criteria for protection of aquatic organisms.

Base flow during the study met PaDEP (1998*b*) water quality standards (Figs 6, 7 and 8); however, *storm flow* commonly *did not* meet standards for pH (6.0 to 9.0) and concentrations of total Fe (1.5 mg l^{-1} daily average), dissolved Fe (0.3 mg l^{-1} maximum), and total Mn (1.0 mg l^{-1} maximum). Furthermore, although concentrations of 'dissolved' metals in 0.45 μm filtered samples generally met USEPA recommended national water quality criteria for maximum concentrations, the concentrations of 'total recoverable' metals in unfiltered storm flow samples (Figs 6, 7 and 8) commonly exceeded continuous exposure criteria for Fe (1.0 mg l^{-1}) and Al (87 μg l^{-1}) and occasionally exceeded criteria for Cu (9 μg l^{-1}), Pb (2.5 μg l^{-1}), Ni (52 μg l^{-1}), and Zn (120 μg l^{-1}) (U.S. Environmental Protection Agency 1999). The continuous exposure criteria indicate potential for adverse effects due to long-term (30 d) exposure. Although storm conditions lasting only hours to days accounted for most exceedances of water quality criteria, impounding the storm water could prolong exposure.

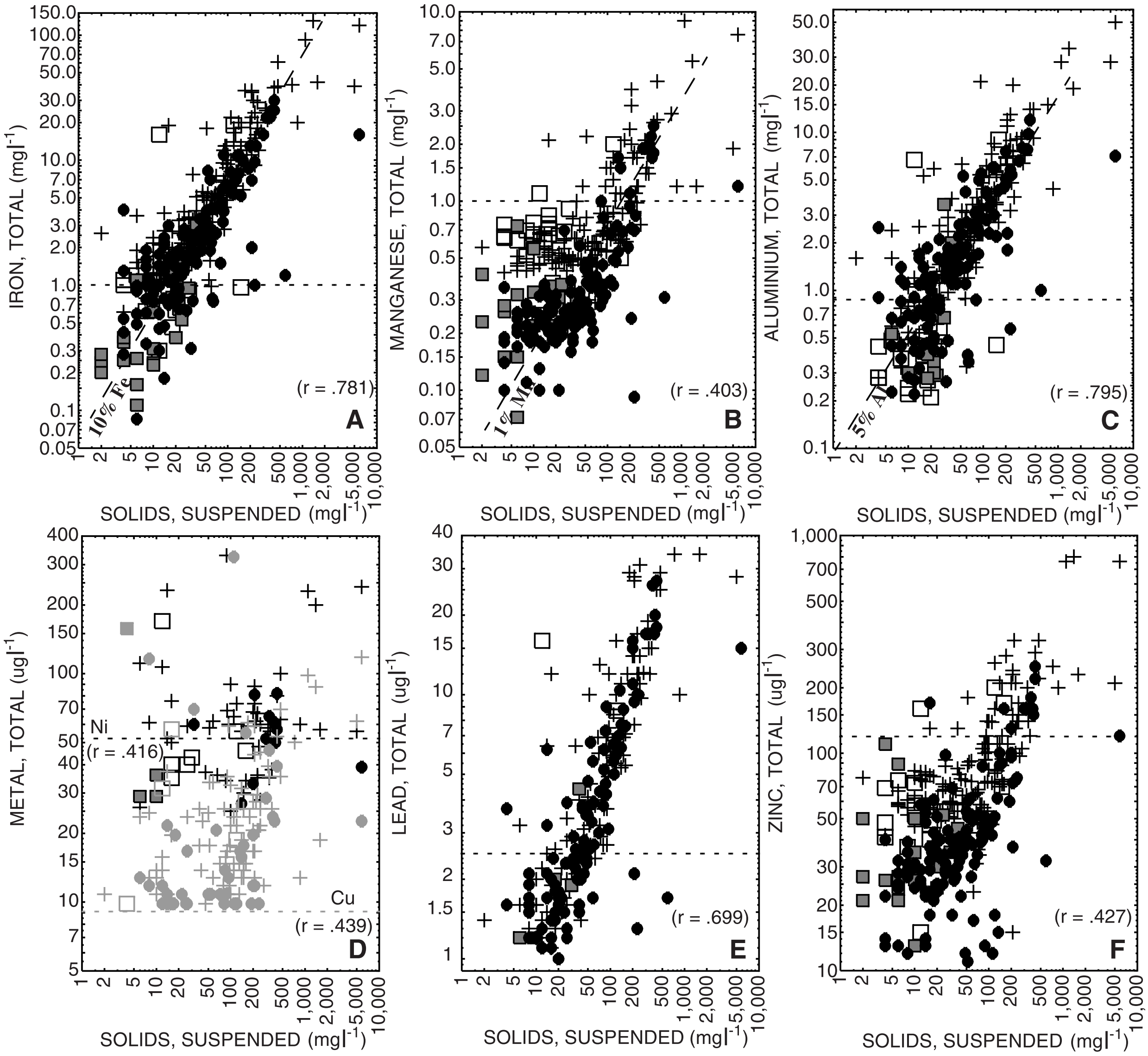

Fig. 8. Relations among concentrations of suspended sediment and total metals in stream water sampled during base flow and storm flow conditions, Swatara Creek at Ravine and Pine Grove, Pa. Spearman correlation coefficient, r, values all are significant ($P \leq 0.0001$). Diagonal trend lines for solids containing 10% Fe, 5% Al and 1% Mn shown for reference. Dotted horizontal lines, except for Mn, indicate National Recommended Water Quality Criteria (U.S. Environmental Protection Agency 1999) for continuous concentration; horizontal line for Mn indicates PaDEP standard for daily average concentration (Pennsylvania Department of Environmental Protection 1998*b*). Symbols the same as in Figures 6 and 7; symbols and lines for copper are shaded gray.

Concentrations of metals in the sediments exceeded sediment-quality guidelines (SQGs) for protection of sediment-dwelling organisms in freshwater ecosystems (Fig. 9). Metals in the fine fraction exceeded the 'probable effect concentration' (PEC) (MacDonald *et al.* 2000) or 'probable effect level' (PEL) (Persaud *et al.* 1993), indicated in parentheses, for Fe (4 wt%), Mn (0.11 wt%), and Ni (48.6 μg g^{-1}) and the 'threshold effect concentration' (TEC) (MacDonald *et al.* 2000) for Cu (31.6 μg g^{-1}), Pb (35.8 μg g^{-1}) and Zn (121 μg g^{-1}). Concentrations of Cd and Cr were below the TEC.

Elevated concentrations of Fe, Mn, Cu, Pb, Ni, or Zn in the fine fraction of sediments relative to SQGs could indicate potential for adverse effects of metals on benthic macroinvertebrates in Swatara Creek, particularly because multiple metals for each sediment sample exceeded the SQGs (Fig. 9). MacDonald *et al.* (2000) concluded that a geometric mean PEC quotient (concentration/PEC) >0.5 accurately indicated sediment toxicity due to multiple contaminants. The geometric mean PEC quotients considering only Cr, Cu, Pb, Ni and Zn for the fine fraction (<0.063 mm) collected at Tremont, Ravine, and Pine Grove were 0.56, 0.65 and 0.60, respectively. However, the bulk sediments (<2 mm) collected at these sites had substantially lower geometric mean PEC quotients of 0.18, 0.40 and 0.17, and comparable PEL quotients, which included Fe and Mn, of 0.21, 0.39 and 0.21, respectively. Hence, risk of metal toxicity would be greatest for benthic macroinvertebrates that reside or forage in the fine sediments.

Twenty-four of the 27 fish species identified in Swatara Creek at Ravine during the study had been previously reported for Pennsylvania streams with pH 4.6 to 6.4 (Table 1). According to Earle & Callaghan (1998), only 18 species of fish native to Pennsylvania have been found in Pennsylvania streams having pH <6; the majority of these species now can be found in Swatara Creek (Table 1) and, presumably, other watersheds

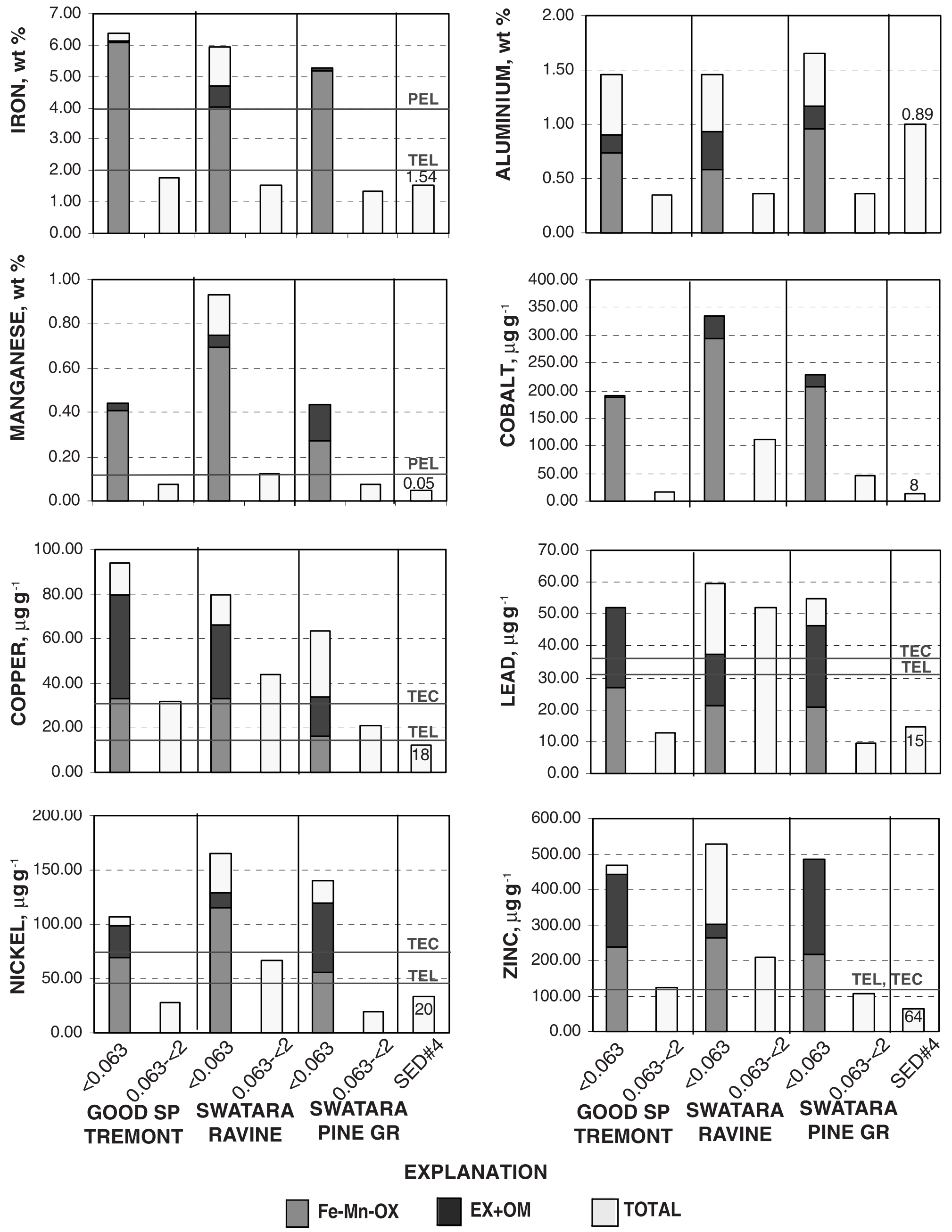

Fig. 9. Metal concentrations in streambed sediment from Good Spring Creek at Tremont, Swatara Creek at Ravine, and Swatara Creek at Pine Grove, Pa. Sediment fractions: <0.063 µm=silt+clay; 0.063 to <2.0 µm=fine sand. For silt+clay fraction, sequential extraction results shown as coloured increments of total bar: Fe-Mn-OX=Na-dithionite extract; EX=OM=exchangeable cations+organic matter. Solid horizontal lines indicate probable effect level or concentration (PEL, PEC) or threshold effect level or concentration (TEL, TEC) for protecting benthic organisms (Persaud *et al.* 1993; MacDonald *et al.* 2000). Expected concentration within bar for USGS Standard Reference Sediment SED#4 analysed for quality assurance.

in Pennsylvania recovering from mining impacts. Although 11 benthic macroinvertebrate taxa (family level), including three genera of Ephemeroptera mayflies now can be found in Swatara Creek at Ravine, a few relatively pollution-tolerant taxa dominate (Table 2). More than half of the individual specimens identified in 1999 were Hydropsyche and Chironomidae that are known to tolerate acidic conditions. This lack of taxa richness and trophic imbalance is consistent with the identified toxic effect levels for Fe, Mn, Ni, Cu, Pb and Zn in streambed sediments (Fig. 9), and implies that contaminants in the aquatic environment that are stressful to macroinvertebrates may not be severely limiting to fish.

SUMMARY AND CONCLUSIONS

Despite near-neutral, aerobic, cold-water conditions in Swatara Creek, which support a diverse fish population, streambed sediments in this and other mining-affected watersheds represent a substantial, long-term source of metals that are likely to impair water quality and complicate aquatic ecological recovery for the future. Although the transport of dissolved Fe, Al and most trace metals typically is attenuated at near-neutral pH, substantial transport of suspended and dissolved metals persists in Swatara Creek, especially during storm flow conditions. Metals including Fe, Al, Cu and Pb, and to a lesser extent Mn

Table 3. *Trace-element content of fish from Swatara Creek at Ravine, Pa., fall 1999*

Element	White sucker, whole fish		White sucker, fillet		Brook trout, gutted and gilled	
	Dry	Wet	Dry	Wet	Dry	Wet
Aluminium (Al)	46.9	11.07	3.0	0.59	1.0	0.18
Antimony (Sb)	<0.2	<0.05	<0.2	<0.04	<0.2	<0.04
Arsenic (As)	<0.2	<0.05	<0.2	<0.04	<0.2	<0.04
Barium (Ba)	4.2	0.99	1.5	0.30	1.5	0.26
Beryllium (Be)	<0.2	<0.05	<0.2	<0.04	<0.2	<0.04
Boron (B)	0.4	0.09	0.5	0.10	0.5	0.09
Cadmium (Cd)	<0.2	<0.05	<0.2	<0.04	<0.2	<0.04
Chromium (Cr)	1.9	0.45	1.4	0.28	2.0	0.35
Cobalt (Co)	0.8	0.19	0.5	0.10	0.3	0.05
Copper (Cu)	3.6	0.85	1.6	0.32	2.8	0.49
Iron (Fe)	103.0	24.31	24.0	4.74	35.6	6.25
Lead (Pb)	0.2	0.05	0.3	0.06	<0.2	<0.04
Manganese (Mn)	70.6	16.66	15.2	3.01	18.2	3.19
Mercury (Hg)	0.10	0.02	0.10	0.02	0.24	0.04
Molybdenum (Mo)	<0.2	<0.05	<0.2	<0.04	<0.2	<0.04
Nickel (Ni)	1.2	0.28	0.4	0.08	0.4	0.07
Selenium (Se)	2.3	0.54	2.5	0.49	2.7	0.47
Silver (Ag)	<0.2	<0.05	<0.2	<0.04	<0.2	<0.04
Strontium (Sr)	62.8	14.82	34.3	6.78	15.5	2.72
Uranium (U)	<0.2	<0.05	<0.2	<0.04	<0.2	<0.04
Vanadium (V)	<0.2	<0.05	<0.2	<0.04	<0.2	<0.04
Zinc (Zn)	70.0	16.52	57.1	11.29	53.1	9.32
Solids (%)		23.6		19.77		17.55

Concentrations reported as micrograms per gram ($\mu g\ g^{-1}$) wet and dry weight.

and Zn, which are associated with fine sediments in the streambed, are transported as suspended particles as a result of scour and transport of metal-enriched streambed deposits. Total Fe, Mn, Al and associated trace metals commonly increase in concentration at the onset of storm flow conditions; peak metal concentrations typically are achieved prior to peak discharge. The metal content of the suspended solids is relatively constant over the range of flow conditions, implying a relatively uniform source of material such as streambed deposits. In contrast, SO_4 is transported primarily as a dissolved ion and achieves highest concentrations during low stream flow conditions.

On the basis of combined methods using fixed-interval base flow and automated storm flow sampling, total concentrations and loads of suspended sediment and metals were shown to be greatest and pH lowest during storm flow conditions in Swatara Creek. In general, temporal variations in water quality of low-order streams such as the northern part of Swatara Creek are difficult to characterize by routine monitoring at fixed time intervals. This routine works well to characterize base flow conditions and to establish long-term trends, but is not appropriate to characterize rapidly changing conditions in response to storms. Automated samplers and continuous water quality and flow monitoring methods, as used in this study, generally will indicate extremes, which can be important with respect to biological or regulatory thresholds, and can indicate significant relations between stream flow, water chemistry and transport of sediment and associated chemicals. Water-quality regulations established to achieve in-stream water quality standards or to maintain designated uses of the water body (water supply, fishing etc.), such as Total Maximum Daily Loads (TMDLs), require baseline characterization of pollutant loads in order to determine required reductions in loading from various contaminant sources. Data that do not adequately represent storm flow conditions will underestimate the transport of sediment and associated metals and will not be useful to establish the data distribution.

The pH, SC and concentration of SO_4 for the stream water are inversely related to stream flow, indicating dilution and acidification during storm flow. This effect is attributed to the mixing of poorly buffered stream water having pH 6.0–6.5 with weakly acidic storm runoff having pH 4.0–4.5 and low dissolved solids. The associated decline in stream water pH to values approaching 5.0 during storm flow events could result in the remobilization of adsorbed or precipitated metals associated with suspended solids.

Declines in pH during storm flow conditions for Swatara Creek imply that additional buffering capacity is needed to maintain near-neutral pH during storm events. Generally, for Swatara Creek and other poorly buffered streams, additional or larger limestone diversion wells could be constructed to begin or increase alkalinity production as the stream stage rises during storms and/or additional or larger limestone drains could be constructed to produce greater amounts of alkalinity and enhance the buffering capacity of base flow. Nevertheless, neutralization and pH buffering alone will not remedy the problem of metals transport. Solid forms of the metals, as particulate and particle coatings, can be ingested and accumulated by aquatic organisms and can be remobilized by reductive dissolution of Fe(III) and Mn(III-IV) oxides in buried sediment. Additional measures are needed to prevent metals transport to the stream.

Fish populations have been recovering and gaining increased attention for development of recreational fishing; however, macroinvertebrate populations are slightly to moderately impacted in the northern part of Swatara Creek and mining affected tributaries. Concentrations of Fe, Mn, Co, Cu, Pb, Ni and Zn in streambed sediment exceed values for equivalent size streams in nonmining areas and exceed consensus based guidelines for the protection of aquatic macroinvertebrates.

Concentrations of Zn in fish tissue exceed the national average for freshwater fish. Although the concentration of Hg, Cd, Se and As in fish tissue did not exceed human consumption advisories, piscivorous organisms such as otter, kingfisher, osprey and eagles, which have begun to recolonize their former ranges in Pennsylvania, could be at risk from consumption of whole fish exclusively from mining affected waters such as Swatara Creek.

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