

Relations among Sulfate, Metals, Sediment, and Streamflow Data for a Stream Draining a Coal-Mined Watershed in East-Central Pennsylvania

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ABSTRACT

Streamflow and water-quality data for the northern part of Swatara Creek, which drains a 112-km² area in the Southern Anthracite Field of east-central Pennsylvania, indicate iron, copper, and lead, and to a lesser extent manganese and zinc, are transported with suspended particles during stormflow conditions. During stormflow conditions, concentrations of these constituents typically peak prior to peak stream stage as a result of scour and transport of streambed deposits. In contrast, sulfate is transported mostly as a dissolved ion. Concentrations of sulfate, specific conductance, and pH are inversely related to streamflow, indicating dilution and acidification during stormflow. 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.

INTRODUCTION

More than 100 years of mining in the Southern Anthracite Field has contaminated surface and ground-water supplies in east-central Pennsylvania (Wood et al. 1968; Growitz et al. 1983; Wood 1995; Brady et al. 1998). For example, losses of stream water to and contaminated drainage from abandoned anthracite mines within the upper 112 km² of the 1,492-km² 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 is designated as a "high priority watershed" for reducing nonpoint-source pollution (Pennsylvania Department of Environmental Protection 1998). Current land use in the upper 112-km² area, upstream from Ravine, Pa., is classified as 86.6 percent forested, 4.9 percent agricultural, and only 6.4 percent barren, mined. The land-use classification for this extensively mined area is misleading, however, because underground mines extend beneath much of the surface and "natural" reforestation conceals large tracts of unreclaimed spoil. Agricultural development predominates downstream from the mined area. For example, land use in the 300-km² area of the Swatara Creek Basin upstream from Pine Grove (Fig. 1), which is 11 km downstream from Ravine, is classified as 69.7 percent forested, 25.0 percent agricultural, and 2.4 percent barren, mined.

Although several surface and underground anthracite mines presently are active, most mines in the Swatara Creek Basin were abandoned before 1960. Barren, steep banks of spoil and culm and fine coal debris in siltation basins are sources of sediment (suspended solids), sulfate (SO₄), iron (Fe), aluminum (Al), and other metals in water that infiltrates or runs off the surface during storms. The abandoned underground mines have flooded and have collapsed locally causing subsidence. Surface flow is diverted through subsidence pits, fractures, and mine openings to the underground mines where the water becomes contaminated with acidity, SO₄, and metals (Skelly & Loy, Inc. 1975; Ladwig et al. 1984; Growitz et al. 1985; Wood 1995). In downstream reaches, the contaminated water resurges as "acidic" or "abandoned" mine drainage (AMD) contaminating Swatara Creek and its tributaries, while contributing substantially to baseflow (Fishel 1988).

To neutralize the AMD, with a goal of remediating approximately 40 km (67 percent) of degraded streams in the upper part of the Swatara Creek Basin, a variety of limestone treatment systems recently were

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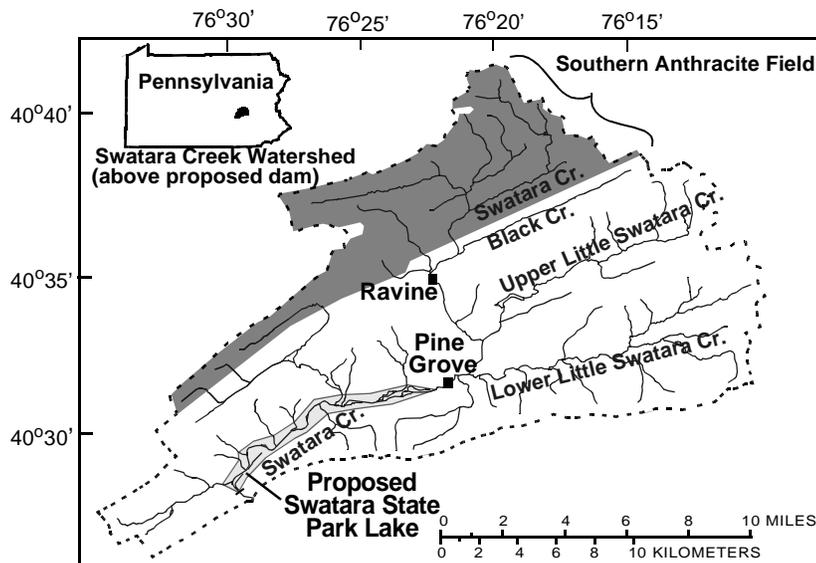


Figure 1 Locations of streamflow and water-quality monitoring stations on Swatara Creek above proposed Swatara State Park Lake near Ravine and Pine Grove, Lebanon and Schuylkill Counties, Pa.

installed at selected locations (Cravotta, 1998). The treatments, which include limestone-sand dosing, open limestone channels, anoxic and oxic limestone drains, limestone diversion wells, and limestone-based wetlands, were constructed mainly during fall 1996 and spring 1997 by the Schuylkill County Conservation District and the Swatara Creek Watershed Association, with technical assistance from the U.S. Geological Survey (USGS) and the Pennsylvania Department of Environmental Protection (PaDEP). To characterize untreated mine drainage and treatment-system performance, data on flow rate and water quality at 54 stations in the Swatara Creek Basin were collected during base-flow and stormflow conditions in 1995-99 (Durlin and Schaffstall 1998, 1999). Data for two of the stations on Swatara Creek, near Ravine (Fig. 1; USGS station 01571820) and Pine Grove (Fig 1; USGS station 01572025), indicate cumulative effects of AMD remediation throughout the northern Swatara Creek Basin and transport of pollutants from the mined part of the watershed to a proposed dam and water-supply reservoir at Swatara State Park (Fig. 1).

Current water-quality data in conjunction with historical data for Swatara Creek at Ravine (with inherent gaps) indicate acidity, SO_4 , and specific conductance (SC) declined monotonically, while pH increased sharply from 3.5-4.4 (median ~4) during 1955-75 to 4.6-7.0 (median ~6) after 1975 (McCarren et al. 1964; Stuart et al. 1967; Skelly & Loy, Inc. 1975; Fishel 1988; Durlin and Schaffstall 1998, 1999). The step trend in pH from acidic to near neutral probably resulted from a decline in pyrite oxidation or transport of oxidation products, unchanged or increased alkalinity production, and a carbonate buffering effect (Cravotta et al. 1999). At near-neutral pH, the transport of dissolved Fe, Al, and trace metals including cobalt (Co), copper (Cu), lead (Pb), and zinc (Zn) typically is attenuated owing to precipitation and adsorption (Bigham et al. 1996; Smith et al. 1998; Webster et al. 1998; Cravotta and Trahan 1999). Nevertheless, substantial transport of dissolved and suspended metals persists in Swatara Creek. This paper evaluates relations among SO_4 , metals, suspended solids, and streamflow data collected during June 1996 through May 1998 for Swatara Creek at Ravine and Pine Grove, Pa., in an attempt to identify and quantify important processes affecting the transport of metals and associated pollutants in a coal-mined watershed.

METHODS OF DATA COLLECTION AND ANALYSIS

The streamflow gaging stations on Swatara Creek at Ravine and Pine Grove were equipped with automatic stage-recording, water-quality monitoring, and (or) water-sampling devices. At Ravine, stream stage was measured continuously with a pressure transducer; temperature, pH, and SC were measured with a multiparameter sonde. At Pine Grove, only stream stage was measured continuously. The continuous stage and water-quality data were recorded at 15-minute intervals with an electronic data logger. In accordance with standard methods (Rantz et al. 1982a, b), instantaneous streamflow for a range of stream stages was determined from streamflow velocity measurements conducted with a vertical-axis current meter. Continuous

streamflow was computed on the basis of a stage-discharge rating developed for each site (Rantz et al. 1982a, b). At both stations, instantaneous data for temperature, SC, dissolved oxygen (DO) and pH also were 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 streamflow for the June 1996 - May 1998 study period (Fig. 2). Baseflow samples were collected manually as grab samples from well-mixed zones in the stream. Stormflow samples were collected automatically using pumping samplers containing 24 1-L 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. Stormflow samples were analyzed for 10 events, including significant storms in October and December 1996.

Water samples were split into subsamples in the field or in the USGS laboratory in Lemoyne, Pa., and stored in sample-rinsed polyethylene bottles at 4°C until analyzed. 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. Samples were analyzed for major ions, metals, and nutrients at the PaDEP Bureau of Laboratories facility in Harrisburg, Pa., following methods of Greenberg et al. (1992) and Fishman and Friedman (1989). The water-quality and streamflow data are maintained in the USGS National Water Information System (NWIS) data base.

Streamflow and water-quality data for baseflow and stormflow conditions were plotted and evaluated for statistical correlations (SAS, Inc. 1990). To estimate baseflow and surface-runoff contributions during stormflow conditions, hydrographs were separated into these components using HYSEP (Sloto and Crouse 1996). To evaluate the chemistry of mixtures of baseflow and runoff, the geochemical models WATEQ4F (Ball and Nordstrom 1991), BALANCE (Parkhurst et al. 1982), and PHREEQC (Parkhurst 1995) were used.

RESULTS AND DISCUSSION

Streamflow

Hydrographs for the study period (Fig. 2) show streamflow for Swatara Creek at Ravine and Pine Grove was correlated and increased downstream in proportion to the respective watershed areas. Daily mean streamflow for Swatara Creek at Ravine ranged from 11 to 1,180 ft³/s (0.31 to 33.4 m³/s) for September 1997 and October 1996, respectively, and at Pine Grove ranged from 24 to 2,970 ft³/s (0.68 to 84.1 m³/s) for September 1997 and December 1996, respectively.

Hydrograph separation by the local minimum method with HYSEP (Sloto and Crouse 1996) indicated that on average during the study, the total streamflow at Ravine was composed of about 60 percent baseflow and 40 percent storm runoff. However, during October and December 1996, baseflow contributed an average of only 25 and 47 percent, respectively, of the monthly total streamflow. Storm runoff was estimated to contribute about 95 percent of the daily total streamflow at Ravine during October 19-21, 1996, and about 76 percent of the daily total streamflow during December 13-15, 1996.

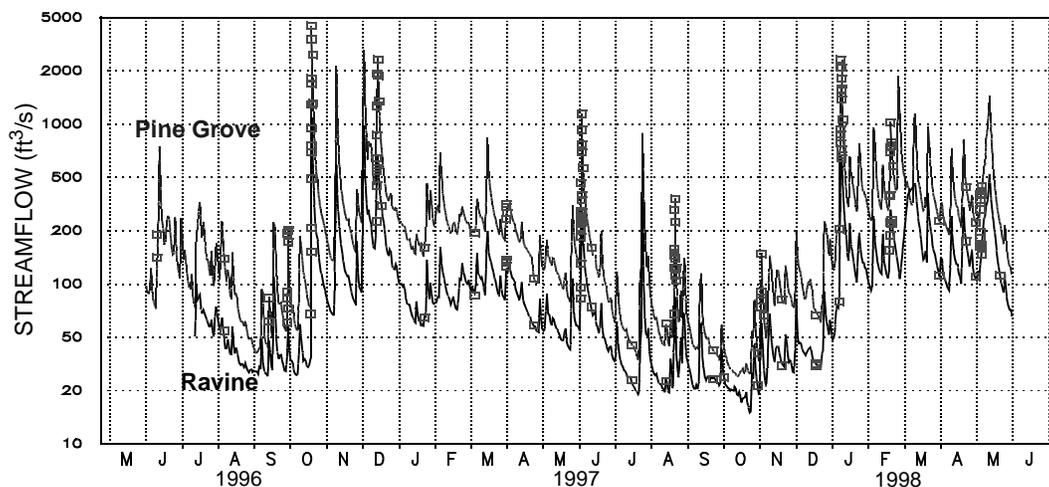


Figure 2 Streamflow hydrographs for Swatara Creek near Ravine and Pine Grove, Pa., June 1996 through May 1998. Square symbols indicate streamflow at times water-quality samples were collected.

Water Chemistry: Relations among Sulfate, Metals, Sediment, and Streamflow Data

Despite significant contributions of AMD and the presence of rusty deposits on the streambed above Ravine, baseflow at Ravine during the study was near neutral (mean pH~6.5; alkalinity>acidity) (Figs. 3 and 4) and supported brook trout and other native fish (Cravotta 1996-99, unpublished data). Generally, pH was positively correlated with SC (Fig. 3A) and negatively correlated with streamflow (Fig. 3D). The SC and pH were more strongly correlated with SO_4 (Figs. 3B and 3C) than with other constituents. Sulfate concentrations at Ravine ranged from 50 to 100 mg/L in baseflow and from 22 to 82 mg/L in stormflow samples.

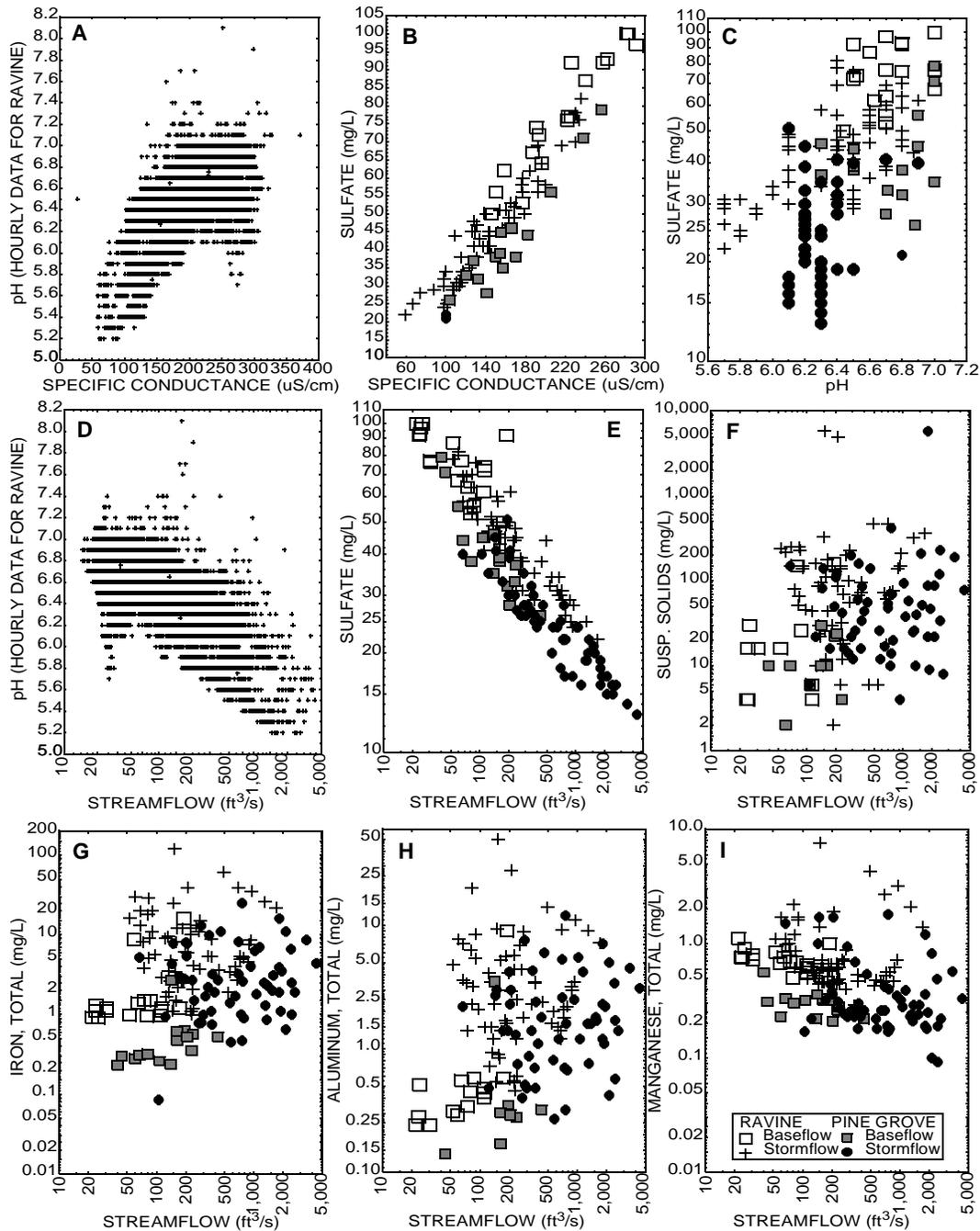


Figure 3 Relations among streamflow, pH, specific conductance, and constituents in stream water during baseflow and stormflow conditions, Swatara Creek at Ravine and Pine Grove, Pa.

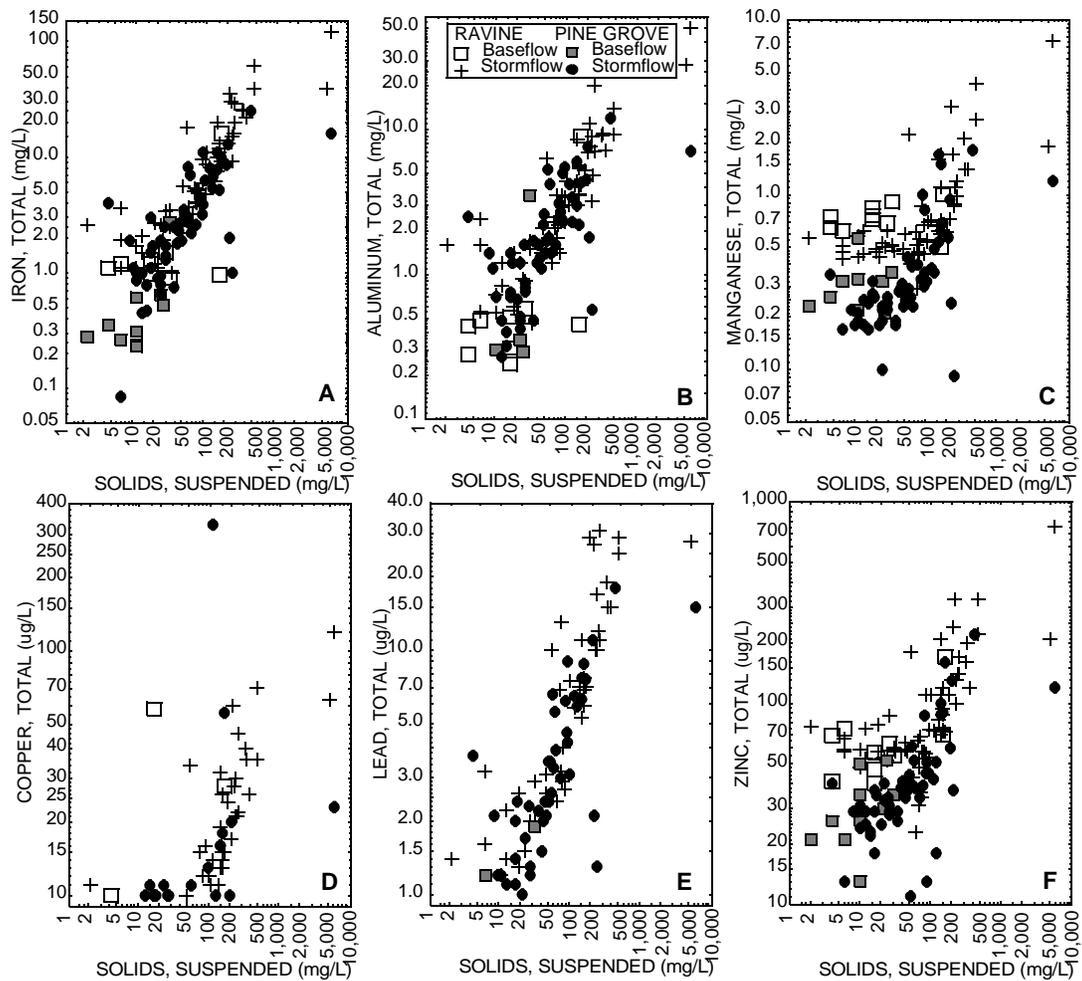


Figure 4 Relations among concentrations of suspended solids and total metals in stream water sampled during baseflow and stormflow conditions, Swatara Creek at Ravine and Pine Grove, Pa.

Concentrations of SO_4 and metals generally were lower at Pine Grove than at Ravine (Figs. 3 and 4) due to attenuation and decreased loading downstream of Ravine. However, because of increased loading from agricultural and municipal sources, concentrations of suspended solids and nutrients typically were greater at Pine Grove than at Ravine (Fishel 1988; this study).

At both stations, the transport of SO_4 , metals, and suspended solids occurs primarily during stormflow events. For example, during the stormflow event December 13-15, 1996 (Fig. 5), the following total quantities, expressed as yields from the watershed, were transported:

	Sulfate	Iron	Manganese	Aluminum	Susp. Solids
Swatara Creek at Ravine:	1,274	82	19	50	55 kg/km ²
Swatara Creek at Pine Grove:	715	69	8	42	878 kg/km ²

The above yields for one storm are about 1/10 of the annual yields of these constituents by baseflow (Fishel 1988; this study).

Correlations, or lack thereof, among the streamflow and water-quality data (Figs. 3 and 4) resulted from the relatively conservative transport of SO_4 and, to a lesser extent, manganese (Mn) and Zn as dissolved species, the accumulation of $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, and associated materials within the streambed during baseflow, and the scour and transport of accumulated metal-rich streambed deposits during the rising stage of stormflow events (Fig. 5). At Ravine and Pine Grove, concentrations of dissolved SO_4 , Mn, and Zn generally decreased with increased streamflow, whereas concentrations of suspended solids and total and dissolved Fe, Al, and trace metals were poorly correlated with streamflow (Fig. 3). For stormflow and baseflow samples, total metals normally were detected at concentrations several times greater than dissolved concentrations. The

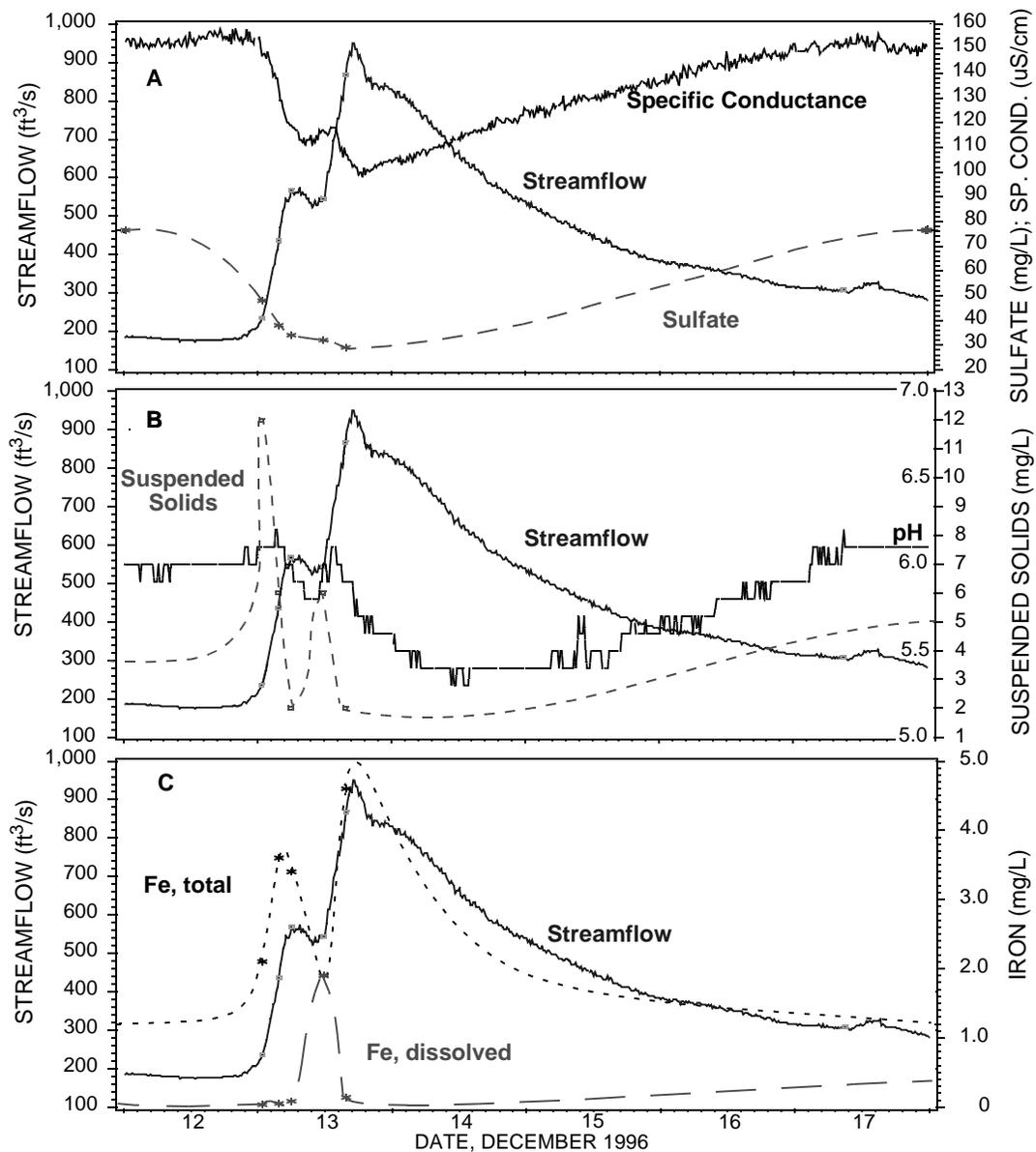


Figure 5 Stormflow hydrograph and associated water quality for Swatara Creek at Ravine, Pa., December 12-17, 1996: A, Specific conductance and sulfate; B, pH (inner scale) and suspended solids; C, total iron and dissolved iron.

concentration of total Mn was positively correlated with that of dissolved Mn, whereas concentrations of total and dissolved Fe, Al, and trace metals were not correlated.

Concentrations of total Fe, Al, Cu, and Pb, and to a lesser extent, Mn and Zn were correlated with the concentration of suspended solids (Fig. 4) indicating a relatively constant source of metal-rich particles over the range of flow conditions. The linear correlations between concentrations of suspended solids and total metals (Fig. 4) are consistent with suspended solids that contained about 10 percent Fe, 5 percent Al, and lesser amounts of Mn and trace metals. Although concentrations of dissolved Al and trace metals commonly approached limits of detection, the metal-rich solids 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 desorption (Webster et al. 1998), and (or) by reductive dissolution of Fe(III) and Mn(III-IV) oxides (Francis and Dodge 1990). These processes could be promoted by decreases in pH and (or) redox potential in the streambed or water column.

Stormflow: Mixing of Surface Runoff and Baseflow

The inverse correlations between streamflow and pH, SC, and concentration of SO_4 (Fig. 3) indicate dilution and acidification commonly result during stormflow. Mixing of poorly buffered, near-neutral stream water with weakly acidic storm runoff having pH 4-5 and low dissolved solids could produce the trends observed for the composite data set (Fig. 3) and individual stormflow data sets (Fig. 5). For example, during the stormflow event on December 13-15, 1996 (Fig. 5), streamflow at Ravine increased rapidly from about 180 to 550 ft^3/s at an intermediate stage during early morning and then rose sharply to about 950 ft^3/s at the peak stage during the afternoon of December 13. During the falling stage on December 14, the pH decreased from 6.2 to a minimum of 5.3 while SC decreased from 160 to a minimum of about 100 $\mu\text{S}/\text{cm}$, gradually recovering to baseflow conditions as stage receded (Figs. 5A and 5B). In contrast, suspended solids and total Fe concentrations increased to peak concentrations during the initial rising stage and declined prior to peak stage (Figs. 5B and 5C). Dissolved Fe concentrations increased following the peak for total Fe.

Inverse geochemical models were developed to evaluate the effects of storm runoff on the composition of stormflow. For this evaluation, stream-water samples near the peak and the beginning of the stormflow hydrograph for Swatara Creek at Ravine on December 13, 1996 (Fig. 5) were considered final and initial solutions, respectively. Rain water was mixed with the initial stream water in various proportions, and plausible geochemical reactions within weathered soil or spoil or within the stream channel were quantified to produce the final stream water. Acceptable mass-balance models, as indicated by the following equation:



were constrained by considering the computed saturation index (SI) for solids, to allow dissolution or precipitation of appropriately saturated phases (Parkhurst et al. 1982; Ball and Nordstrom 1991; Parkhurst 1995). Table 1 shows the input concentrations of elements in the peak stormflow (final solution), initial stormflow (initial solution 1), and rainwater (initial solution 2) are shown in Table 1. The stormflow at peak stage had intermediate pH, SC, and concentrations of Ca, Mg, Na, K, S, and Mn relative to initial storm water and rainfall (Table 1). The stoichiometry of potential reactants or products considered in the models is shown in Table 2. Minerals indicated in Table 2 are commonly associated with coal deposits; römerite [$\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}$] is included in the models instead of pyrite (FeS_2) to simulate the dissolution of soluble products of pyrite oxidation by storm runoff (Bayless and Olyphant 1993; Cravotta 1994). Table 3 shows the results of the mass-balance calculations, indicating the proportion of the initial solutions mixed and the quantities of reactants and products to achieve mass and electron balance in accordance with equation 1.

Seven mass-balance models were developed using NEWBAL, a variation of BALANCE (Parkhurst et al. 1982), to evaluate the mixing of surface runoff with baseflow having the compositions of rainwater and initial stormflow, respectively (Table 1). Although the resultant mixing ratios varied among the seven models (Table 3), all indicated nearly equal or smaller contributions of baseflow than surface runoff. Model 1 indicated a 25:75 mixing ratio (baseflow:surface runoff), which is the same as that computed by hydrograph separation; the other models indicated approximately 50:50 mixtures could produce the observed peak stormflow composition. A 50:50 mixing ratio would be anticipated for conservative mixing of SO_4 (55:45), Mg (55:45), and Mn (53:47). All the models indicated "minimal" reactions (<0.1 mmol/kg) with solids including the dissolution of halite (road salt), dolomite, and microcline, the precipitation of kaolinite (or gibbsite), and cation exchange ($\text{Ca}^{2+} + \text{Na}_2\text{-ex} = \text{Ca-ex} + 2 \text{Na}^+$). The models also involved the dissolution of römerite, $\text{Fe}(\text{OH})_3$, pyrolusite, calcite, or gypsum.

The pH of 25:75 and 50:50 mixtures of baseflow and surface runoff having the compositions of initial stormflow and rainwater, respectively (Table 1) was evaluated using PHREEQC (Parkhurst 1995). Without reactions, the mixtures had simulated pH 4.13 and 4.39, respectively, which is significantly lower than the observed pH 5.85 for peak stormflow. However, by specifying equilibrium with $\text{Fe}(\text{OH})_3$ and dissolution of dolomite and calcite to attain respective saturation indexes of -4.0 and -8.0 computed for the peak stormflow composition, the simulated mixtures attained pH 5.82 and 5.88, respectively. Thus, neutralization reactions such as dissolution of dolomite and/or calcite (Table 3) are needed to produce the observed pH and composition of stormflow. The decline of pH values to less than 5 during stormflow conditions (Figs. 3 and 5) implies that additional buffering capacity is needed to maintain near-neutral pH of Swatara Creek during large storm events. Generally, to maintain stream pH during storms, additional or larger limestone diversion wells could be constructed to begin or increase alkalinity production as the stream stage rises and/or additional or larger limestone drains could be constructed to produce greater amounts of alkalinity and enhance the buffering capacity of baseflow.

**Table 1 Composition of aqueous solutions used in mass-balance computations
[element units millimoles per kilogram of solution]**

Constituent	Rain Water	Initial Stormflow 1996/12/13 @ 0045	Peak Stormflow 1996/12/13 @ 1545
pH	4.10	6.14	5.85
Specific Conductance	32	128	88
Calcium (Ca)	0.023	0.250	0.167
Magnesium (Mg)	.005	.317	.177
Sodium (Na)	.013	.196	.161
Potassium (K)	.002	.046	.041
Sulfur (S)	.062	.500	.302
Iron (Fe)	.001	.001	.003
Manganese (Mn)	.000	.011	.006
Aluminum (Al)	.001	.001	.001
Carbon (C)	.000	.375	.442
Chloride (Cl)	.029	.186	.152
Redox State (RS)	.373	4.521	3.600

**Table 2 Stoichiometry,¹ reactivity,² and operational redox state³ (RS) of potential reactant and product phases used in mass-balance computations
[units moles per mole; +, dissolution or ingassing only; -, precipitation or outgassing only]**

O ₂ Gas	+RS	4.00						
CO ₂ Gas	C	1.00	RS	4.00				
Römerite	+Fe	3.00	S	4.00	RS	32.00		
Ferrihydrite	+Fe	1.00	RS	3.00				
Pyrolusite	+Mn	1.00	RS	4.00				
Calcite	+Ca	1.00	C	1.00	RS	4.00		
Dolomite	+Ca	1.00	Mg	1.00	C	2.00	RS	8.00
Gypsum	+Ca	1.00	S	1.00	RS	6.00		
Ca-Na Exchange	+Ca	-1.00	Na	2.00				
Microcline	+K	.85	Na	.15	Al	1.00	Si	3.00
Kaolinite	Al	2.00	Si	2.00				
Halite	+Na	1.00	Cl	1.00				

1. Stoichiometry excludes hydrogen and oxygen (Parkhurst et al.1982).
2. Reactivity defined by saturation index (SI) determined by WATEQ4F (Ball and Nordstrom 1991): '+' indicates reactant (SI < 0); '-' indicates product (SI > 0); no sign indicates SI positive or negative depending on the particular sample.
3. Redox state computed for redox active components (S, C, Fe, Mn, O) as defined by Parkhurst et al. (1982).

**Table 3 Summary of mass-balance results
[All mineral and gas mass-transfers are in millimoles per kilogram of water; negative for precipitation or outgassing, positive for dissolution or ingassing; '.' indicates no reaction occurred. Input data are values in Table 1; mineral stoichiometry and reactivity in Table 2]**

Model	Mixing ratio ¹	O ₂ gas	CO ₂ gas	Römerite	Fe(OH) ₃	Pyrolusite	Dolomite	Calcite	Gypsum	Microcline	Kaolinite	Halite	Ca-Na Exchange
1	25:75	0.007	0.160	0.033	-0.096	0.003	0.094	•	•	0.033	-0.017	0.084	0.007
2	55:45	.006	.211	.003	.001	•	.002	.022	•	.018	-.009	.037	.004
3	54:46	.007	.211	.007	•	.000	.003	.022	•	.018	-.009	.038	.004
4	50:50	.004	.222	.007	•	.001	.016	•	.019	.020	-.010	.045	.045
5	55:45	.001	.212	•	.002	.000	.001	•	•	.018	-.009	.037	.004
6	50:50	.003	.224	•	.002	.001	.018	•	.019	.018	-.009	.037	.004
7	55:45	.005	.213	•	.002	•	.002	.021	•	.018	-.009	.037	.004

1. Mixing ratio indicates proportions of initial stormflow (initial solution 1) and rain water (initial solution 2), respectively, mixed to produce peak stormflow (final solution).

CONCLUSIONS

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 stormflow conditions. The metals including Fe, Al, Cu, and Pb, and to a lesser extent Mn and Zn, are transported with suspended particles as a result of scour and transport of metal-enriched streambed deposits. Total Fe and associated metals commonly increase in concentration at the onset of stormflow conditions; peak metal concentrations commonly 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. In contrast, SO₄ is transported primarily as a dissolved ion and achieves highest concentrations during low streamflow conditions.

The pH, SC, and concentration of SO₄ for the stream water are inversely related to streamflow, indicating dilution and acidification during stormflow. 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. For an example stormflow event in December 1996, mixing ratios for baseflow and surface runoff determined on the basis of hydrograph separation and geochemical mass-balance techniques were comparable, indicating about half or more of the stormflow was derived from dilute, low-pH surface runoff. The associated decline in stream-water pH to values approaching 5.0 during stormflow events could result in the remobilization of adsorbed or precipitated metals associated with suspended solids.

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