

Dissolved metals and associated constituents in abandoned coal-mine discharges, Pennsylvania, USA. Part 1: Constituent quantities and correlations

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Abstract

Complete hydrochemical data are rarely reported for coal-mine discharges (CMD). This report summarizes major and trace-element concentrations and loadings for CMD at 140 abandoned mines in the Anthracite and Bituminous Coalfields of Pennsylvania. Clean-sampling and low-level analytical methods were used in 1999 to collect data that could be useful to determine potential environmental effects, remediation strategies, and quantities of valuable constituents. A subset of 10 sites was resampled in 2003 to analyze both the CMD and associated ochreous precipitates; the hydrochemical data were similar in 2003 and 1999. In 1999, the flow at the 140 CMD sites ranged from 0.028 to 2210 L s⁻¹, with a median of 18.4 L s⁻¹. The pH ranged from 2.7 to 7.3; concentrations (range in mg/L) of dissolved (0.45- μ m pore-size filter) SO₄ (34–2000), Fe (0.046–512), Mn (0.019–74), and Al (0.007–108) varied widely. Predominant metalloid elements were Si (2.7–31.3 mg L⁻¹), B (<1–260 μ g L⁻¹), Ge (<0.01–0.57 μ g L⁻¹), and As (<0.03–64 μ g L⁻¹). The most abundant trace metals, in order of median concentrations (range in μ g/L), were Zn (0.6–10,000), Ni (2.6–3200), Co (0.27–3100), Ti (0.65–28), Cu (0.4–190), Cr (<0.5–72), Pb (<0.05–11) and Cd (<0.01–16). Gold was detected at concentrations greater than 0.0005 μ g L⁻¹ in 97% of the samples, with a maximum of 0.0175 μ g L⁻¹. No samples had detectable concentrations of Hg, Os or Pt, and less than half of the samples had detectable Pd, Ag, Ru, Ta, Nb, Re or Sn. Predominant rare-earth elements, in order of median concentrations (range in μ g/L), were Y (0.11–530), Ce (0.01–370), Sc (1.0–36), Nd (0.006–260), La (0.005–140), Gd (0.005–110), Dy (0.002–99) and Sm (<0.005–79). Although dissolved Fe was not correlated with pH, concentrations of Al, Mn, most trace metals, and rare earths were negatively correlated with pH, consistent with solubility or sorption controls. In contrast, As was positively correlated with pH.

None of the 140 CMD samples met all US Environmental Protection Agency (USEPA) continuous-concentration criteria for protection of freshwater aquatic organisms; the samples exceeded criteria for Al, Fe, Co, Ni, and/or Zn. Ten percent of the samples exceeded USEPA primary drinking-water standards for As, and 33% exceeded standards for Be. Only one sample met drinking-water standards for inorganic constituents in a public water supply. Except for S, the nonmetal elements (S > C > P = N = Se) were not elevated in the CMD samples compared to average river water or seawater. Compared to seawater, the CMD samples also were poor in halogens (Cl > Br > I > F), alkalis (Na > K > Li > Rb > Cs), most alkaline earths (Ca > Mg > Sr), and most metalloids but were enriched by two to four orders of magnitude with Fe, Al, Mn, Co, Be, Sc, Y and the lanthanide rare-earth elements, and one order of magnitude with Ni and Zn.

The ochre samples collected at a subset of 10 sites in 2003 were dominantly goethite with minor ferrihydrite or lepidocrocite. None of the samples for this subset contained schwertmannite or was Al rich, but most contained minor

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aluminosilicate detritus. Compared to concentrations in global average shale, the ochres were rich in Fe, Ag, As and Au, but were poor in most other metals and rare earths. The ochres were not enriched compared to commercial ore deposits mined for Au or other valuable metals. Although similar to commercial Fe ores in composition, the ochres are dispersed and present in relatively small quantities at most sites. Nevertheless, the ochres could be valuable for use as pigment.

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1. Introduction

1.1. The problem

Drainage from abandoned mines affects the quantity, quality and potential uses of water supplies in coal and metal mining regions worldwide (Marcus, 1997; Nordstrom, 2000; Blowes et al., 2003; Wolkersdorfer and Bowell, 2004, 2005a,b). Metals in the mine drainage degrade the aquatic habitat and can be toxic to aquatic organisms (Elder, 1988; Hyman and Watzlaf, 1997; Earle and Callaghan, 1998; MacDonald et al., 2000; US Environmental Protection Agency, 2002a). For example, historical mining of coal in the Northern Appalachian Coalfield of the USA has transformed the local landscape and caused widespread degradation of water resources (Herlihy et al., 1990). Such environmental problems in Pennsylvania represent 1/3 of the abandoned mine related problems in the USA (Pennsylvania Department of Environmental Protection, 2002). In Pennsylvania, abandoned coal-mine discharges (CMD) have degraded more than 5000 km of streams (Pennsylvania Department of Environmental Protection, 2002, 2004; US Environmental Protection Agency, 2006) and account for lost revenues of approximately \$67 million annually because recreational fishing cannot be supported in many of those streams (US Geological Survey, 1999). The present cost of cleanup of CMD and the reclamation of abandoned mine lands in Pennsylvania has been estimated to require capital expenditures of approximately \$5 billion and \$15 billion, respectively (Pennsylvania Department of Environmental Protection, 2002). Worldwide, cleanup of drainage and solid wastes at abandoned mines has been estimated in the tens to hundreds of billions of dollars (Nordstrom, 2000; Blowes et al., 2003).

During the past 200 a, the coal deposits in Pennsylvania have been extensively mined as sources of industrial and domestic fuel (Northern and Central Appalachian Basin Coal Regions Assessment Team, 2000). Although the predominant producer of coal

in the USA during the 19th and early 20th centuries, presently, Pennsylvania is fourth behind Kentucky, West Virginia and Wyoming, in order of increasing production (US Office of Surface Mining, Reclamation, and Enforcement, 2005a). Presently, active mining operations must meet land reclamation and water-quality criteria for environmental protection (Commonwealth of Pennsylvania, 1998a,b; US Office of Surface Mining, Reclamation, and Enforcement, 2005b). However, historical coal mining was conducted with little regard for the environment; upon closure, mine voids were left open and surrounding landscapes were covered with unreclaimed spoil. Storm runoff from widely distributed, unreclaimed spoil and discharges from abandoned, flooded mines can contribute sediment, H_2SO_4 , and metals to streams for decades (e.g. Cravotta and Bilger, 2001; Cravotta and Kirby, 2004; Cravotta, 2005).

Although CMD commonly has elevated concentrations of dissolved solids compared to background, CMD from various sources can range widely in quality from strongly acidic and corrosive to alkaline and encrusting (Rose and Cravotta, 1998; Plumlee et al., 1999; Nordstrom and Alpers, 1999) and can range widely in volume from small, ephemeral seeps to large, perennial discharges comparable to third-order streams (Growitz et al., 1985; Cravotta et al., 1999). The oxidation of Fe-sulfide minerals and the subsequent dissolution of carbonate, oxide, and aluminosilicate minerals by acidic water generally account for the elevated concentrations of SO_4 , Fe, Al, Mn and associated metals in CMD (Cravotta, 1994; Rose and Cravotta, 1998; Nordstrom and Alpers, 1999; Cravotta et al., 1999; Plumlee et al., 1999; Blowes et al., 2003). (Hereinafter, the use of an elemental or molecular formula without charge notation indicates the total analytical concentration in solution without regard to valence or the possible existence of aqueous species.) Dissolved Fe, Al and associated metals in the CMD can precipitate as rust-colored (ochreous) or white encrustations on the streambed, especially where the CMD is aerated or mixes with neutral

streamwater (Winland et al., 1991; Bigham and Nordstrom, 2000; Cravotta and Bilger, 2001; Williams et al., 2002).

The pH and concentrations of alkalinity, acidity, Fe, Al and Mn in mine effluent and receiving water bodies routinely are measured to identify potential for environmental effects (Commonwealth of Pennsylvania, 1998a,b; US Environmental Protection Agency, 2000, 2002a,b). The Commonwealth of Pennsylvania (1998a,b) stipulates that effluent discharged from active mines must have pH 6.0–9.0 and alkalinity that exceeds its acidity concentration and must not have an instantaneous maximum concentration of Fe, Mn or Al that exceeds 7.0, 5.0, or 0.75 mg L⁻¹, respectively. Additional water-quality criteria established by the US Environmental Protection Agency (2002b) for the protection of freshwater aquatic life include recommended continuous and maximum exposure levels for trace metals and other constituents that could be present in CMD. Freshwater aquatic criteria and drinking-water standards apply to 15 of the elements analyzed in this study (Al, Sb, As, Ba, Cl, Cr, Co, Cu, Fe, Pb, Hg, Se, Ag, Tl, Zn); drinking-water standards (Be, F, Mn, NO₃, NO₂, SO₄, U) or freshwater aquatic criteria (B, Ni, V) apply to 10 other constituents. Nevertheless, most of these constituents are not routinely measured or reported for abandoned CMD or active coal-mining operations in the USA.

Various trace elements, such as As, Co, Cu, Pb, Ni, Se, U and Zn, are concentrated in coal and coal-bearing rocks (Bragg et al., 1997; Northern and Central Appalachian Basin Coal Regions Assessment Team, 2000) and can be present in CMD at levels harmful to the health of aquatic and terrestrial organisms (Hyman and Watzlaf, 1997; Rose and Cravotta, 1998; Smith and Huyck, 1999; US Environmental Protection Agency, 2002a,b; Cravotta, 2005). Most trace elements tend to adsorb or coprecipitate with solid compounds of Fe, Mn and Al that form as acidic solutions become neutralized or oxygenated (McKenzie, 1980; Elder, 1988; Kooner, 1993; Coston et al., 1995; Broshears et al., 1996; Webster et al., 1998; Smith et al., 1998; Cravotta and Trahan, 1999; Kairies et al., 2005). Removal from solution decreases the direct aquatic exposure of fish to these elements; however, organisms that ingest contaminated sediments, such as macroinvertebrates and bottom-feeding fish, and, consequently, aquatic and terrestrial animals at higher trophic levels, can accumulate toxic levels of some elements in tissue (Elder, 1988; Smith and

Huyck, 1999; US Environmental Protection Agency, 2002a,b). Regardless of trace-element composition, the accumulation of Fe or Al precipitates can encrust streambeds and aquatic plants, destroying physical habitat (Earle and Callaghan, 1998).

Despite their potential for toxicity, various constituents in CMD effluent and encrustations, if recoverable, could have economic value for metal production, pigmentation, and pollution treatment. For example, global demand for precious metals and rare-earth elements for high technology and environmental applications has grown dramatically since 1950, while production from exploitable domestic deposits has diminished (Haxel et al., 2002; Sibley, 2005). Considering that hundreds to thousands of kilograms of common metals can be transported annually from large CMD sources, it has been suggested that valuable quantities of rare-earth elements and precious metals could be present at some CMD sites and that economic recovery of these constituents could offset CMD treatment costs (Southern Alleghenies Conservancy, 1998; Cheney and Swinehart, 1998; Hedin, 2003; Bowell, 2004).

1.2. Purpose and scope

This report summarizes data for pH and a wide range of constituents, including trace metals and rare-earth elements, that were determined in 1999 in abandoned coal-mine drainage from 102 bituminous and 41 anthracite mine sites in Pennsylvania to document the concentrations and transport (loads) of dissolved constituents. For the present study, clean-sampling and low-level analytical methods were used to quantify trace concentrations of constituents previously evaluated and to document the occurrence and distribution of previously unreported constituents. One goal of the study was to acquire data that would be useful for evaluating the potential for recovery of dissolved constituents from CMD. Additional goals were to evaluate potential for toxicity, to evaluate correlations and geochemical controls on element concentrations, and to evaluate the relations between the chemistry of CMD and associated coal deposits. A companion report by Cravotta (2008) compares the anthracite and bituminous CMD sample subsets, examines relations among the pH, SO₄, and metal concentrations in the samples, and evaluates the thermodynamic potential for aqueous and surface complex formation and the precipitation of possible secondary

phases. The present report describes the data-collection methods, summarizes the chemical and hydrological data, estimates the constituent loads, and examines the correlations among flow, pH and constituent concentrations. This report does not attempt to describe the CMD at individual sites; detailed characterization of individual CMD sources is beyond the scope of this report.

2. Study area and methods

2.1. Description of study area

Bituminous coal deposits underlie western and north-central Pennsylvania, and anthracite deposits underlie east-central and northeastern Pennsylvania (Berg et al., 1980) (Fig. 1). The mineable coals are interbedded with shale, siltstone, sandstone, conglomerate and local limestone. Pennsylvania's Bituminous Coalfield lies within the Appalachian Plateaus Physiographic Province, which is characterized by gently dipping strata; nearly horizontal

coalbeds commonly crop out in the incised stream valleys (Berg et al., 1989; Edmunds, 1999; Briggs, 1999). Pennsylvania's Anthracite Coalfield lies within the Ridge and Valley Physiographic Province and is characterized by complexly deformed strata; mineable coalbeds typically extend beneath valleys in steeply folded and fractured synclinal troughs (Wood et al., 1986; Berg et al., 1989; Eggleston et al., 1999). The temperate, humid climate of Pennsylvania sustains a relatively shallow, perched water table in the coal-bearing uplands and a deeper, regional ground-water flow system that discharges as perennial streamflow in the valleys (Ladwig et al., 1984; Stoner et al., 1987; Williams et al., 1989; Trapp and Horn, 1997; Callaghan et al., 1998). The ground and stream water in historically mined areas of Pennsylvania are degraded by thousands of CMD sources.

Data on the concentrations and transport of Fe, Al, Mn, other metals, and rare-earth elements in selected CMD samples were reported by Wood (1996) for the Anthracite Fields and by Hyman

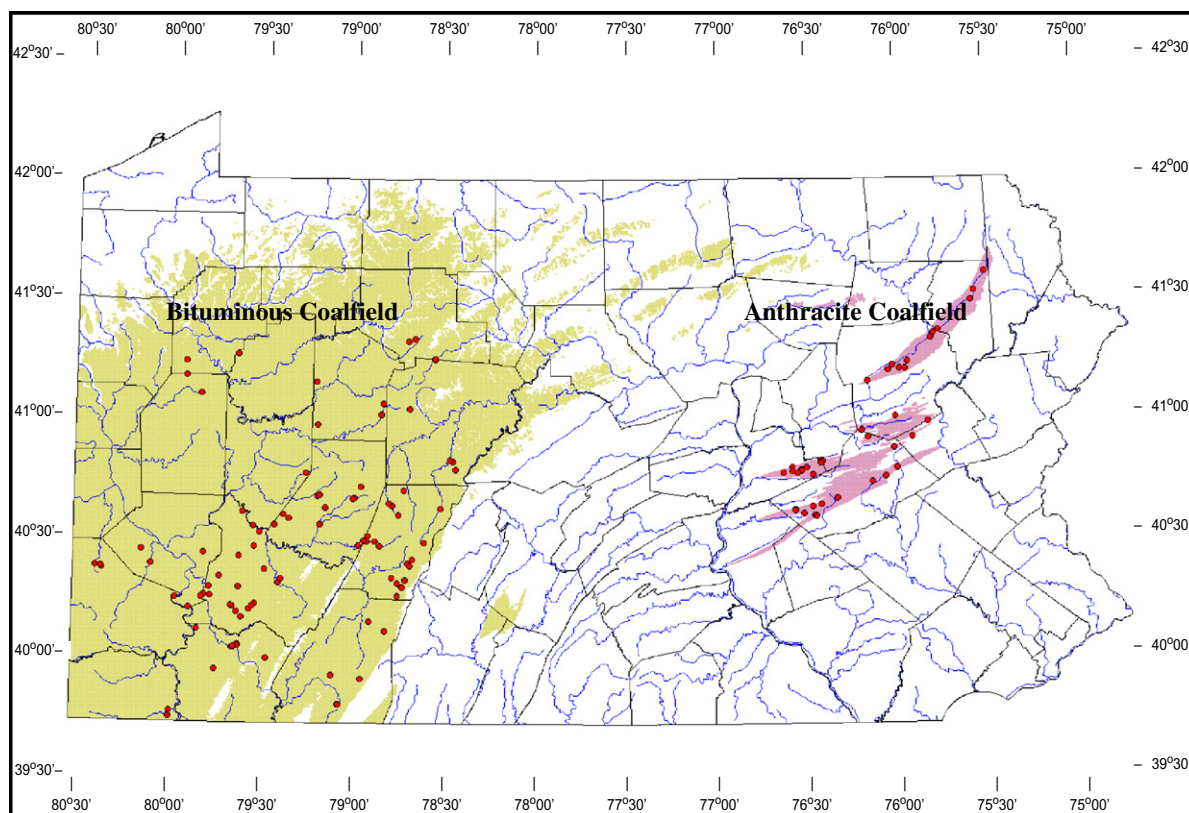


Fig. 1. Map of Pennsylvania showing locations of 140 abandoned coal-mine discharge sites in the Anthracite and Bituminous Coalfields that were sampled in 1999. Coalfield boundaries based on distribution of Pennsylvanian Age bedrock (Berg et al., 1980).

and Watzlaf (1997) and Southern Alleghenies Conservancy (1998) for the Bituminous Field of Pennsylvania. However, conventional sampling and analytical methods that were used for these surveys did not enable the evaluation of low levels of analytes. Furthermore, inconsistent methods of sampling and analysis make it difficult to compare results between the studies.

2.2. Sample site selection

During base-flow conditions in summer and fall 1999, a total of 143 sites in the Anthracite and Bituminous Coalfields of Pennsylvania were sampled for analysis of chemical concentrations and loading (Fig. 1). Additionally, in 2003, a subset of 10 of the bituminous sites, where Au had been detected in the original water samples, was resampled for analyses of ochre compositions and quantities. The 143 discharge sites were selected among thousands of CMD sources statewide on the basis of their geographic distribution, accessibility, and potential for substantial loads of dissolved metals. Most of the sampled discharges were from underground mines. The 41 anthracite discharges had previously been studied by the US Geological Survey (USGS) (Growitz et al., 1985; Wood, 1996). The 102 bituminous discharges had previously been studied by the Southern Alleghenies Conservancy (1998).

2.3. Water-quality sampling and analysis

To minimize effects from aeration, electrodes were immersed and samples were collected as close as possible to the point of discharge. Field data for flow, temperature, specific conductance (SC), dissolved O₂ (DO), pH and redox potential (Eh) were measured at each site when samples were collected in accordance with standard methods (Rantz et al., 1982a,b; Wood, 1976; US Geological Survey, variously dated; Ficklin and Mosier, 1999). All meters were calibrated in the field using electrodes and standards that had been thermally equilibrated to sample temperatures. Field pH and Eh were determined using a combination Pt and Ag/AgCl electrode with a pH sensor. The electrode was calibrated in pH 2.0, 4.0, and 7.0 buffer solutions and in Zobell's solution (Wood, 1976; US Geological Survey, variously dated). Values for Eh were corrected to 25 °C relative to the standard hydrogen electrode in accordance with methods of Nordstrom

(1977). Water samples were collected into 3-L Teflon bottles and then split into sample-rinsed polyethylene bottles.

An unfiltered subsample for analysis of acidity and alkalinity was capped leaving no head space and stored on ice. Other samples were processed using clean-sampling methods for analysis of dissolved constituents (Horowitz et al., 1994) (The goal was to achieve the following minimum reporting levels in mg/L, where X indicates lowest decimal place: 0.000000X for Au; 0.00000X for Co, Cs, Dy, Er, Eu, Gd, Hf, Ho, In, La, Lu, Nd, Os, Pr, Rb, Re, Sm, Tb, Th, Tl, Tm, U, V, Y, Yb; 0.0000X for As, Bi, Cd, Ce, Ga, Ge, Nb, Pb, Pd, Pt, Ru, Sb, Sr, Ta, W, Zr; 0.000X for Ag, Ba, Be, Cr, Cu, Hg, Mo, Mn, Ni, Se, Sn, Te, Ti, Zn; 0.00X for Al, B, Br, Fe, I, Li, Mg, Ni, P, Sc; 0.0X for Ca, K, Na, NO₃N, Si; 0.X for Cl, F; and X for SO₄.) Two subsamples for analysis of “dissolved” constituents were filtered through a 0.45- μ m pore-size nitrocellulose capsule filter inside an enclosed glove box. The subsample for cations and Si analyses was preserved with trace-element grade HNO₃ to pH < 2. The subsample for anion analyses was stored on ice or refrigerated until analyzed.

A total of 83 constituents were analyzed using a variety of analytical methods (Table 1). The noble gases and short-lived radioactive elements were not analyzed. The unfiltered subsamples were analyzed for alkalinity within 48 h of sampling at the USGS Pennsylvania Water Science laboratory in Pittsburgh or Lemoyne, Pennsylvania, by titration with H₂SO₄ to the endpoint pH of 4.5 (American Public Health Association, 1998b). The “hot” acidity was determined on aged, oxidized samples by titration with NaOH to the endpoint pH of 8.3, after the addition of H₂SO₄ and H₂O₂, boiling, and cooling (American Public Health Association, 1998a; Kirby and Cravotta, 2005b). The pH before and during titrations was measured using a liquid-filled combination Ag/AgCl pH electrode calibrated in pH 4.0, 7.0 and 10.0 buffer solution. Sulfate, Cl, F, NO₃, NO₂ and PO₄ in filtered, refrigerated samples were analyzed by ion chromatography (IC) (Fishman and Friedman, 1989; Crock et al., 1999). Concentrations of major cations, Si and trace elements in filtered, acidified samples were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AE) and quadrupole inductively coupled plasma emission mass spectrometry (ICP-MS) (Fishman and Friedman, 1989; Crock et al., 1999). For samples collected in 1999, Au was

Table 1
Summary of hydrochemical data for discharges from 140 abandoned coal mines in Pennsylvania, 1999

Constituent	Element ^a		Method ^b	Units ^{c,d}	BDL % ^e	Percentile						
	G	N				0	10	25	50	75	90	100
Flow rate (<i>Q</i>)	n.a.	n.a.	F/V	L s ⁻¹	0	0.028	2.29	5.81	18.4	65.1	201	2210
Temperature (<i>T</i>)	n.a.	n.a.	T	C	0	8.8	10	10.9	12	13	14	26.6
Specific Conductance (SC)	n.a.	n.a.	E	μS cm ⁻¹	0	131	464	846	1280	1760	2338	3980
Dissolved Oxygen (DO)	n.a.	n.a.	E	mg L ⁻¹	0	0.2	0.3	0.4	1.1	4.2	8.4	11.5
Redox (Eh)	n.a.	n.a.	E	mv	0	140	180	220	390	540	670	800
pH, field	n.a.	n.a.	E	units	0	2.7	3.1	3.7	5.2	6.1	6.4	7.3
Hardness	n.a.	n.a.	CALC	mg L ⁻¹	0	23	145	248	382	545	808	1811
Acidity, net	n.a.	n.a.	CALC	mg L ⁻¹	0	-326	-78.9	-21.8	51.5	193	311	1587
Alkalinity, lab	n.a.	n.a.	ET	mg L ⁻¹	0	0	0	0	9.5	100	199	510
Aluminum (Al)	7	13	MS/AE	μg L ⁻¹	0	7.0	14	34.2	1250	9450	23,900	108,000
Antimony (Sb)	5	51	MS/AE	μg L ⁻¹	34	<0.01	<0.01	<0.01	0.01	0.02	0.04	0.43
Arsenic (As)	5	33	MS/AE	μg L ⁻¹	5	<0.03	0.14	0.39	1.7	5.8	11	64
Barium (Ba)	4	56	MS/AE	μg L ⁻¹	0	2.0	7.5	11	15	19	24	39
Beryllium (Be)	4	4	MS/AE	μg L ⁻¹	10	<0.05	<0.05	0.20	1.6	5.1	10	52
Bismuth (Bi)	7	83	MS	μg L ⁻¹	30	<0.01	<0.01	<0.01	0.01	0.02	0.04	0.35
Boron (B)	5	79	MS/AE	μg L ⁻¹	1	<1	13	23	44	85	139	260
Bromide (Br)	2	35	MS	mg L ⁻¹	1	<0.003	0.009	0.015	0.036	0.060	0.12	0.60
Cadmium (Cd)	6	48	MS/AE	μg L ⁻¹	7	<0.01	0.01	0.025	0.12	0.528	1.48	16.0
Calcium (Ca)	4	20	MS/AE	mg L ⁻¹	0	3.3	27	52	88	130	190	410
Cerium (Ce)	3	58	MS	μg L ⁻¹	0	0.01	0.08	0.58	6.6	19	58	370
Cesium (Cs)	3	55	MS	μg L ⁻¹	0	0.019	0.052	0.085	0.11	0.19	0.32	0.85
Chloride (Cl)	2	17	IC	mg L ⁻¹	0	0.1	1.5	2.8	7.3	20	57	460
Chromium (Cr)	6	24	MS/AE	μg L ⁻¹	27	<0.5	<0.5	<0.5	1.2	2.5	7.9	72
Cobalt (Co)	6	27	MS/AE	μg L ⁻¹	0	0.27	4.1	20	58	130	210	3100
Copper (Cu)	6	29	MS/AE	μg L ⁻¹	0	0.4	0.5	0.8	2.0	7.9	29	190
Dysprosium (Dy)	8	66	MS	μg L ⁻¹	0	0.002	0.031	0.14	1.80	5.7	14	99
Erbium (Er)	8	68	MS	μg L ⁻¹	0	0.003	0.021	0.081	0.88	3.0	6.4	58
Europium (Eu)	8	63	MS	μg L ⁻¹	0	0.002	0.007	0.028	0.34	1.2	2.6	22
Fluoride (F)	2	9	IC	mg L ⁻¹	99	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2
Gadolinium (Gd)	8	64	MS	μg L ⁻¹	0	0.005	0.031	0.16	1.8	6.2	14	110
Gallium (Ga)	7	31	MS	μg L ⁻¹	5	<0.01	0.03	0.06	0.12	0.26	0.58	7.3
Germanium (Ge)	5	32	MS	μg L ⁻¹	7	<0.01	0.02	0.04	0.07	0.10	0.19	0.57
Gold (Au)	6	79	INAA	μg L ⁻¹	3	<0.0005	0.0006	0.0008	0.0010	0.0014	0.0044	0.0175
Hafnium (Hf)	6	72	MS	μg L ⁻¹	9	<0.002	0.002	0.006	0.026	0.087	0.32	7.1
Holmium (Ho)	8	67	MS	μg L ⁻¹	0	0.001	0.0081	0.031	0.35	1.1	2.69	21
Indium (In)	7	49	MS	μg L ⁻¹	23	<0.001	<0.001	0.001	0.003	0.009	0.019	0.34
Iodide (I)	2	53	MS	mg L ⁻¹	1	<0.001	0.003	0.005	0.009	0.018	0.024	0.10
Iron (Fe)	6	26	MS/AE	μg L ⁻¹	0	46	938	14,000	32,000	61,800	97,000	512,000
Lanthanum (La)	8	57	MS	μg L ⁻¹	0	0.005	0.037	0.32	2.2	6.4	19	140
Lead (Pb)	7	82	MS/AE	μg L ⁻¹	29	<0.05	<0.05	<0.05	0.20	1.0	3.1	11

(continued on next page)

Table 1 (continued)

Constituent	Element ^a		Method ^b	Units ^{c,d}	BDL % ^e	Percentile						
	G	N				0	10	25	50	75	90	100
Lithium (Li)	3	3	MS/AE	µg L ⁻¹	0	11	23	40	69	110	160	390
Lutetium (Lu)	8	71	MS	µg L ⁻¹	2	<0.001	0.004	0.011	0.10	0.34	0.60	6.9
Magnesium (Mg)	4	12	MS/AE	mg L ⁻¹	0	3.6	14	24	38	54	82	210
Manganese (Mn)	6	25	MS/AE	µg L ⁻¹	0	19	632	1400	2350	5000	10,900	74,000
Mercury (Hg)	6	80	MS	µg L ⁻¹	100	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Molybdenum (Mo)	6	42	MS/AE	µg L ⁻¹	4	<0.1	0.08	0.10	0.20	0.35	0.55	2.6
Neodymium (Nd)	8	60	MS	µg L ⁻¹	0	0.006	0.051	0.38	4.9	14	29	260
Nickel (Ni)	6	28	MS/AE	µg L ⁻¹	0	2.6	12	28	85	190	290	3200
Niobium (Nb)	6	41	MS	µg L ⁻¹	71	<0.01	<0.01	<0.01	<0.01	0.010	0.019	0.030
Nitrate (NO ₃ -N)	1	7	IC	mg L ⁻¹	99	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.15
Nitrite (NO ₂ -N)	1	7	IC	mg L ⁻¹	100	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Osmium (Os)	6	76	MS	µg L ⁻¹	100	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Palladium (Pd)	6	46	MS	µg L ⁻¹	89	<0.02	<0.02	<0.02	<0.02	<0.02	0.02	0.11
Phosphate (PO ₄ -P)	1	15	MS/AE	mg L ⁻¹	66	<0.001	<0.001	<0.001	<0.001	0.005	0.014	2.8
Platinum (Pt)	6	78	MS	µg L ⁻¹	100	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Potassium (K)	3	19	MS/AE	mg L ⁻¹	0	0.5	1.1	1.8	2.8	3.8	5.1	12
Praseodymium (Pr)	8	59	MS	µg L ⁻¹	0	0.002	0.012	0.074	1.0	2.9	7.5	54
Rhenium (Re)	6	75	MS	µg L ⁻¹	56	<0.001	<0.001	<0.001	<0.001	0.002	0.003	0.011
Rubidium (Rb)	3	37	MS	µg L ⁻¹	0	1.0	2.6	4.1	6.3	9.9	14	28
Ruthenium (Ru)	6	44	MS	µg L ⁻¹	91	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.17
Samarium (Sm)	8	62	MS	µg L ⁻¹	4	<0.005	0.015	0.097	1.3	4.2	8.7	79
Scandium (Sc)	8	21	MS	µg L ⁻¹	0	1.0	3.1	4.0	5.0	9.4	15	36
Selenium (Se)	1	34	MS	µg L ⁻¹	16	<0.2	<0.2	0.3	0.6	1.1	2.0	7.6
Silicon (Si)	5	14	MS/AE	mg L ⁻¹	0	2.7	4.7	6.5	7.9	11.1	18.2	31.3
Silver (Ag)	6	47	MS/AE	µg L ⁻¹	91	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.5
Sodium (Na)	3	11	MS/AE	mg L ⁻¹	0	0.69	1.7	3.9	15	66	140	500
Strontium (Sr)	4	38	MS/AE	µg L ⁻¹	0	27	110	300	720	1400	1900	3600
Sulfate (SO ₄)	1	16	IC	mg L ⁻¹	0	34	160	340	520	760	1100	2000
Tantalum (Ta)	6	73	MS	µg L ⁻¹	80	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.11
Tellurium (Te)	5	52	MS	µg L ⁻¹	98	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.4
Terbium (Tb)	8	65	MS	µg L ⁻¹	0	0.001	0.007	0.024	0.32	1.1	2.6	18
Thallium (Tl)	7	81	MS	µg L ⁻¹	0	0.006	0.020	0.034	0.072	0.17	0.34	1.5
Thorium (Th)	9	90	MS	µg L ⁻¹	1	<0.003	0.008	0.014	0.033	0.15	0.96	24
Thulium (Tm)	8	69	MS	µg L ⁻¹	2	<0.001	0.003	0.01	0.12	0.42	0.84	8.3
Tin (Sn)	7	50	MS	µg L ⁻¹	95	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.2
Titanium (Ti)	6	22	MS/AE	µg L ⁻¹	0	0.65	2.2	3.9	5.8	7.7	10	28
Tungsten (W)	6	74	MS	µg L ⁻¹	16	<0.02	<0.02	0.03	0.05	0.10	0.18	0.52

Uranium (U)	9	92	MS	$\mu\text{g L}^{-1}$	22	<0.006	<0.006	0.056	0.17	0.42	0.99	100
Vanadium (V)	6	23	MS/AE	$\mu\text{g L}^{-1}$	0	0.006	0.042	0.097	0.30	0.93	2.3	18.0
Ytterbium (Yb)	8	70	MS	$\mu\text{g L}^{-1}$	0	0.002	0.018	0.055	0.64	2.3	4.5	48
Yttrium (Y)	8	39	MS	$\mu\text{g L}^{-1}$	0	0.11	0.40	1.4	8.7	27	61	530
Zinc (Zn)	6	30	MS/AE	$\mu\text{g L}^{-1}$	0	0.60	4.7	16	140	380	620	10,000
Zirconium (Zr)	6	40	MS	$\mu\text{g L}^{-1}$	20	<0.03	<0.03	0.03	0.04	0.07	0.13	0.84

^a G, element group (1, non metal; 2, halogen; 3, alkali earth; 4, alkaline earth; 5, metalloid; 6, transition metal; 7, other metal; 8, lanthanide rare earth; 9, actinide rare earth); N, element number, and symbol after periodic table of the elements.

^b Method of analysis: F, flow meter; V, volumetric; T, thermometer; E, electrometric; ET, electrometric titration; MS, inductively coupled plasma mass spectrometry; AE, inductively coupled plasma atomic emission spectrometry; IC, ion chromatography; INAA, individual neutron activation analysis; CALC, calculated. Hardness = $(C_{Ca} \cdot 2.5 + C_{Mg} \cdot 4.1)$; Acidity, net = (Acidity, computed – Alkalinity, lab).

^c Units: L s^{-1} , liters per second; C, degrees Celsius; mv, millivolts; mg L^{-1} , milligrams per liter; $\mu\text{g L}^{-1}$, micrograms per liter; $\mu\text{S cm}^{-1}$, microsiemens per centimeter. Alkalinity, acidity, and hardness expressed as calcium carbonate.

^d Element concentrations for 0.45- μm pore-size filtered samples.

^e BDL %, percentage below detection limit.

concentrated on charcoal sachets added to unfiltered samples and then analyzed by instrumental neutron activation analysis (INAA) (Crock et al., 1999). For samples collected in 2003, Au was analyzed in unfiltered samples by INAA and in filtered, acidified samples by high resolution magnetic sector ICP-MS.

All samples collected in 1999 were analyzed in replicate by one or more methods and at two or more laboratories. Split samples were analyzed at the USGS Mineral Resources Laboratory (MRL) in Denver, Colorado, and Activation Laboratories (Actlabs) in Ontario, Canada, and a subset was analyzed at the USGS National Water Quality (NWQL) Laboratory in Denver, Colorado. A comparison of the replicate results by different laboratories is beyond the scope of this report; results for replicate analyses were similar and were averaged for evaluation in this report. If the different results had different detection limits (e.g. ICP-AE and ICP-MS), the lowest noncensored value or the lowest censored value, if all values were below detection limits, was retained as the “average” result. Charge imbalances for the averaged data routinely were less than 10% relative to the mean of cation and anion equivalents in each sample. Nevertheless, to achieve charge balance in some samples, the SO_4 concentrations were adjusted by as much as 33% of the original value; this adjustment attempts to correct for potential errors associated with the analytical method for SO_4 (Cravotta, 1994). The averaged data used in this report are available in text and spreadsheet formats (Appendix, Tables A.1, A.2, and A.3) on the World Wide Web at <http://www1.elsevier.com/homepage/sad/annexes/ag.html/>.

The original hydrologic and chemical data are maintained in the USGS National Water Information Storage (NWIS) database and are accessible by station number (Appendix, Table A.1) on the World Wide Web at <http://www.pah2o.er.usgs.gov/>. To distinguish results from different laboratories in the NWIS database, a fixed-value parameter code was assigned for each laboratory (P00028 = 80020 for USGS NWQL, 1028 for USGS MRL, 89203 for Actlabs), and the actual sample time was altered. The true sample time was retained for results from the USGS NWQL or USGS Pennsylvania Water Science Centers; however, the time was increased by 1 min for the ICP-MS and IC results from Actlabs, 2 min for the ICP-MS results from the USGS MRL, and 3 min for the ICP-AE results from the USGS MRL. The averaged data described

hereinafter, also included in NWIS, are reported with the time increased by 4 min.

The net acidity was computed considering positive acidity contributions from pH and dissolved Fe, Mn and Al concentrations (C_{Fe} , C_{Mn} , C_{Al} , respectively), in mg/L, and negative contributions from alkalinity as:

$$\begin{aligned} \text{Acidity}_{\text{computed}} (\text{mg L}^{-1} \text{CaCO}_3) &= 50 \cdot (10^{(3-\text{pH})}) + 2 \cdot C_{\text{Fe}}/55.85 \\ &+ 2 \cdot C_{\text{Mn}}/54.94 + 3 \cdot C_{\text{Al}}/26.98 \\ &- \text{Alkalinity} (\text{mg L}^{-1} \text{CaCO}_3). \end{aligned} \quad (1)$$

Kirby and Cravotta (2005a,b) demonstrated with data for 140 samples evaluated in this paper that acidity computed with Eq. (1) is comparable in value to the standard method “hot peroxide” acidity where the H_2SO_4 added to the sample is subtracted from the NaOH added (American Public Health Association, 1998a).

The instantaneous transport or loading of the constituents at each CMD site was computed by multiplying the flow by the constituent concentration. If the concentration was below detection limits, the value was assumed to be zero.

2.4. Ochre sampling and analysis

In September 2003, corresponding samples of water and ochreous precipitates were collected at 10 of the previously sampled CMD sites that had higher loads of dissolved Au than most other sites in 1999. Ochres were not collected in 1999 to avoid problems with contamination of water-sampling equipment. Nevertheless, in 2003, water samples were collected using clean-sampling methods and analyzed as described above taking appropriate precautions. After water samples were processed at each site, ochreous coatings were scraped from submerged rocks using a polyethylene scoop to a depth of 2.5 cm or less at 4–6 points across the discharge location. The ochre samples were combined and stored with “native” water in sealed plastic bags, excluding air, at 4 °C until laboratory processing could be completed.

The ochre samples were processed and analyzed for mineralogy and chemistry at the USGS Minerals Resources Laboratory in Reston, Virginia (Jane M. Hammarstrom, US Geological Survey, pers. comm., 2004). The composite ochre sample for each site was wet-sieved with deionized water

through a 100-mesh (0.182-mm) stainless-steel screen. The material smaller than 100 mesh was centrifuged for 1 h at 10,000 rpm and then oven dried at 32 °C. Dried sediments were disaggregated by crushing gently with a ceramic mortar and pestle and then analyzed for chemical and mineralogical composition. The dried powder was sieved to less than 37 μm and mounted in the 2.5-cm diameter well of a stainless-steel holder for mineralogical analysis by X-ray diffraction (XRD) (Whittig and Allardice, 1986; Taggart, 2002). The XRD patterns were collected on a Scintag theta–theta diffractometer using Cu radiation over the range 5–80° 2θ at a 1°/min continuous scan rate. Major, minor, and trace elements in a 1-g subsample of the dried sediment were determined by ICP-MS and ICP-AE after decomposition with a mixture of HCl, HNO_3 , and HF at low temperature (Crock et al., 1999; Taggart, 2002).

3. Results and discussion – constituent quantities and correlations in CMD samples

Three of the 102 bituminous CMD sources that were targeted for sampling were not flowing when visited in 1999. Thus, data reported hereinafter apply only to the 140 flowing discharges (99 bituminous and 41 anthracite) that could be sampled. The data for all constituents analyzed are summarized in Table 1 as the percentage of samples with values “below detection limits” and the cumulative frequency percentage of the 140 CMD samples, or percentile (quantile), that had values less than or equal to specific values. Accordingly, the 0, 50, and 100 percentile values correspond to the minimum, median, and maximum, respectively.

The summary data for the 140 CMD samples are also illustrated as log-probability plots in Fig. 2 where the horizontal axis indicates the probability that corresponding data values will be observed; these probabilities, expressed as %, equal 100 minus the percentile in Table 1. For example, the constituent concentration corresponding to the 10 percentile in Table 1 would have a 90% probability of being exceeded as shown in Fig. 2. A straight line through data displayed on a log-probability plot indicates a log-normal frequency distribution (Rose et al., 1979; Helsel and Hirsch, 1992).

To provide a basis for evaluation of the results, the chemical concentration data for the anthracite and bituminous CMD subsets are summarized in

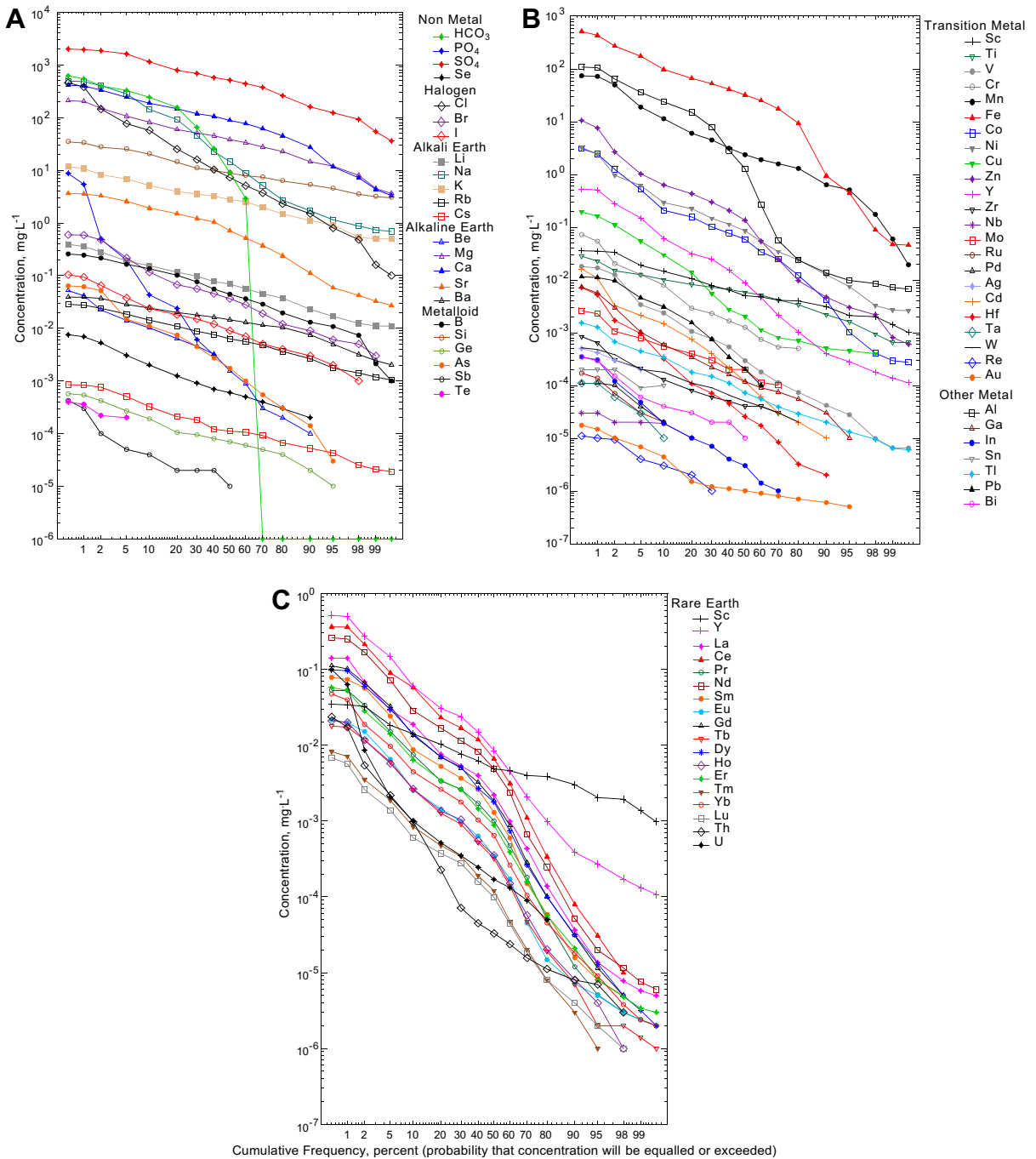


Fig. 2. Log-probability plots of constituents in 140 abandoned coal-mine discharge samples, Pennsylvania, 1999, showing frequency that concentration will be equalled or exceeded: (A) Nonmetals, halogens, alkalis, alkaline earths, and metalloids; (B) Transition metals and other metals; (C) Rare earths.

Table 2 with reference values for average concentrations of the elements dissolved in river water and seawater and contained in relevant types of coal and sedimentary rock. The median values for the

CMD from anthracite and bituminous sites are summarized separately and averaged for comparison with the reference materials (Table 2). Additionally, the concentrations of specific constituents in

Table 2

Element concentrations, in parts per million, in mine-drainage effluent, ochre, and coal from the anthracite and bituminous coalfields, Pennsylvania, compared to global average concentrations in sedimentary rocks, river water, and seawater

Element	Mine effluent and ochre ^a			Coal ^b		Average sedimentary rock, river water, seawater ^c				Enrichment ratios ^d						
	Anthracite CMD (median; N = 41)	Bituminous CMD (median; N = 99)	Ochre (median; N = 12)	Anthracite (median; N = 52)	Bituminous (median; N = 731)	Average shale	Average carbonate	Average river water	Average seawater	Ochre/ Shale	Ochre/ Coal	Bitumin coal/ Anthracite coal	Bitumin CMD/ Anthracite CMD	Coal/ CMD _S	CMD/ River water	CMD/ Seawater
<i>1. Nonmetal elements</i>																
P	<0.001	<0.001	490	96	130	733	281	n.a.	0.075	0.7	3.8	1.4	n.a.	n.a.	n.a.	n.a.
S	87	193	n.a.	6500	22,200	1850	4550	3.57	905	n.a.	n.a.	3.4	2.2	1.0	39.3	0.2
Se	0.0004	0.0006	n.a.	2.7	2.9	0.60	0.32	0.00007	0.000145	n.a.	n.a.	1.1	1.5	54.6	7.1	3.5
<i>2. Halogen elements</i>																
F	<0.1	<0.1	n.a.	34.5	56	560	112	0.1	1.3	n.a.	n.a.	1.6	n.a.	n.a.	n.a.	n.a.
Cl	6.3	7.7	n.a.	130	950	170	305	7.8	18,900	n.a.	n.a.	7.3	1.2	0.8	0.9	<0.1
Br	0.014	0.045	n.a.	14	40	4.3	6.6	n.a.	67	n.a.	n.a.	2.9	3.2	8.9	n.a.	<0.1
I	0.005	0.011	n.a.	n.a.	n.a.	3.8	1.6	n.a.	0.06	n.a.	n.a.	n.a.	2.2	n.a.	n.a.	0.1
<i>3. Alkali earth elements</i>																
Li	0.047	0.074	0.75	20.5	16	46	5.2	0.00184	0.175	<0.1	<0.1	0.8	1.6	2.9	33	0.3
Na	6.1	23	442	110	220	4850	393	6.3	10,635	0.1	2.0	2.0	3.8	0.1	2.3	<0.1
K	1.8	3.3	340	1850	1900	24,900	2390	2.3	385	<0.1	0.2	1.0	1.8	7.2	1.1	<0.1
Rb	0.0041	0.0074	2.5	18	21	243	46	0.00163	0.12	<0.1	0.1	1.2	1.8	33	3.5	<0.1
Cs	0.00018	0.00011	0.19	1.1	1.0	6.2	0.77	0.000011	0.00035	<0.1	0.2	0.9	0.6	71	13	0.4
<i>4. Alkaline earth elements</i>																
Be	0.0015	0.0017	2.2	1.5	2.2	2.1	0.18	0.0000089	0.0000006	1.1	1.0	1.5	1.1	11	180	2670
Mg	35	38	390	265	440	16,400	45,300	4.1	1320	<0.1	0.9	1.7	1.1	<0.1	8.9	<0.1
Ca	37	110	4160	415	1000	22,500	272,000	15	411	0.2	4.2	2.4	3.0	<0.1	4.9	0.2
Sr	0.19	1.0	82	43	81	290	617	0.06	8.0	0.3	1.0	1.9	5.3	1.0	9.9	0.1
Ba	0.018	0.013	69	86	57	250	30	0.023	0.011	0.3	1.2	0.7	0.7	45	0.7	1.4
<i>5. Metalloid elements</i>																
B	0.016	0.062	n.a.	6.75	14	194	16	0.0102	4.45	n.a.	n.a.	2.1	3.9	2.6	3.8	<0.1
Si	6.08	8.88	n.a.	27,000	25,000	260,000	34	6.5	2.50	n.a.	n.a.	0.9	1.5	34	1.2	3.0
Ge	0.00004	0.000085	n.a.	0.87	4.3	1.3	0.036	0.0000068	0.00006	n.a.	n.a.	4.9	2.1	404	9.2	1.0
As	0.00062	0.002	75	3.2	23	9.0	1.8	0.00062	0.00335	8.3	3.3	7.2	3.2	98	2.1	0.4
Sb	0.00002	0.00001	n.a.	0.62	0.90	0.81	0.2	0.00007	0.00027	n.a.	n.a.	1.5	0.5	493	0.2	<0.1
Te	<0.0002	<0.0002	n.a.	38	39	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.0	n.a.	n.a.	n.a.	n.a.
<i>6. Transition metals</i>																
Ti	0.0032	0.0066	70	1250	860	4440	377	0.000489	0.001	<0.1	0.1	0.7	2.1	2100	10	4.9
V	0.00016	0.00032	4.7	26	23	101	13	0.00071	0.00225	<0.1	0.2	0.9	2.0	996	0.3	0.1

Cr	<0.0005	0.0019	4.1	21	19	423	7.1	0.0007	0.000175	<0.1	0.2	0.9	>3.8	103	2.7	10.9
Mn	2.9	2.3	210	11	15	575	842	0.034	0.0011	0.4	14.0	1.4	0.8	<0.1	76	2360
Fe	15	43	390,000	3300	17,000	38,800	8190	0.066	0.0025	10.1	22.9	5.2	2.9	3.4	439	11,600
Co	0.059	0.052	3.2	5.75	5.6	8.1	0.12	0.000148	0.000225	0.4	0.6	1.0	0.9	1.0	375	247
Ni	0.083	0.090	7.3	16	17	29	13	0.000801	0.00435	0.3	0.4	1.1	1.1	1.9	108	19.9
Cu	0.00095	0.0022	6.5	15	14	45	4.4	0.00148	0.00175	0.1	0.5	0.9	2.3	90	1.1	0.9
Zn	0.13	0.14	37	5.4	18	130	16	0.0006	0.00745	0.3	2.1	3.3	1.1	0.8	225	18.1
Zr	0.00004	0.00005	n.a.	30.5	22	142	18	0.000039	0.00003	n.a.	n.a.	0.7	1.3	5690	1.1	1.5
Nb	<0.00001	<0.00001	n.a.	3.1	2.4	20	0.44	0.0000017	0.00001	n.a.	n.a.	0.8	n.a.	n.a.	n.a.	n.a.
Mo	0.00014	0.0002	3.1	2.1	3.2	4.2	0.75	0.00042	0.01	0.7	1.0	1.6	1.4	151	0.4	<0.1
Ag	<0.0002	<0.0002	37	0.09	0.07	0.27	0.19	n.a.	0.00017	137	529	0.8	n.a.	n.a.	n.a.	n.a.
Cd	0.00012	0.00012	0.07	0.075	0.07	0.18	0.048	n.a.	0.000105	0.4	1.0	0.9	1.0	5.9	n.a.	1.1
Hf	0.000015	0.000044	n.a.	1.7	0.7	3.1	0.23	0.0000059	0.000007	n.a.	n.a.	0.4	2.9	397	5.0	4.2
Ta	<0.00001	0.00001	n.a.	0.54	0.22	3.5	0.1	0.0000011	0.000001	n.a.	n.a.	0.4	n.a.	n.a.	n.a.	n.a.
W	0.0001	0.00004	n.a.	0.87	0.80	1.9	0.56	0.0001	0.0001	n.a.	n.a.	0.9	0.4	116	0.7	0.7
Au	0.0000009	0.0000010	0.014	0.83	0.75	0.0034	0.0018	n.a.	0.000007	4.1	<0.1	0.9	1.1	8090	n.a.	0.1
Hg	<0.0002	<0.0002	n.a.	0.10	0.22	0.27	0.046	n.a.	0.000115	n.a.	n.a.	2.2	n.a.	n.a.	n.a.	n.a.

7. Other metals

Al	0.28	1.5	11,500	19,500	16,000	80,100	8970	0.032	0.0015	0.1	0.7	0.8	5.4	195	27.8	593
Ga	0.00012	0.00012	1.3	6.35	7.1	23	2.7	0.00003	0.00003	0.1	0.2	1.1	1.0	547	4.0	4
In	0.000001	0.000004	n.a.	0.475	0.61	0.22	0.068	n.a.	0.0000001	n.a.	n.a.	1.3	4.0	2120	n.a.	25
Sn	<0.0001	<0.0001	n.a.	1.9	0.87	4.1	0.17	n.a.	0.000405	n.a.	n.a.	0.5	n.a.	n.a.	n.a.	n.a.
Tl	0.000039	0.00012	n.a.	0.45	0.58	1.6	0.065	n.a.	0.00001	n.a.	n.a.	1.3	3.1	63	n.a.	8.0
Pb	0.00068	0.0001	3.4	6.05	8.6	80	16	0.000079	0.00003	<0.1	0.4	1.4	0.1	183	4.9	13
Bi	0.00002	0.00001	n.a.	0.605	1.1	n.a.	n.a.	n.a.	0.00002	n.a.	n.a.	1.8	0.5	554	n.a.	0.8

8. Scandium, yttrium, and lanthanide rare earth elements

Sc	0.004	0.006	3.2	4.0	4.3	16	0.68	0.0012	0.0000006	0.2	0.7	1.1	1.5	8.1	4.2	8330
Y	0.0029	0.015	40	9.5	8.5	27	15	0.00004	0.000002	1.5	4.7	0.9	5.2	9.8	224	4480
La	0.0029	0.0021	7.1	14	10	38	9.4	0.00012	0.000003	0.2	0.7	0.7	0.7	47	21	833
Ce	0.0061	0.0067	18	29	20	80	11	0.000262	0.000001	0.2	0.9	0.7	1.1	37	24	6400
Pr	0.00073	0.0011	n.a.	2.1	5.2	8.8	1.3	0.00004	0.0000006	n.a.	n.a.	2.5	1.5	39	23	1530
Nd	0.0031	0.0053	n.a.	13	11	34	8.0	0.000152	0.000003	n.a.	n.a.	0.8	1.7	28	28	1400
Sm	0.00064	0.0018	n.a.	1.85	1.9	5.6	1.1	0.000036	0.00000005	n.a.	n.a.	1.0	2.8	15	34	24,400
Eu	0.00016	0.00052	n.a.	0.51	0.42	1.1	0.19	0.0000098	0.00000001	n.a.	n.a.	0.8	3.3	13	35	34,000
Gd	0.00063	0.0028	n.a.	1.9	2.0	4.7	0.77	0.00004	0.0000007	n.a.	n.a.	1.1	4.4	11	43	2450
Tb	0.000096	0.00051	n.a.	0.55	0.31	0.77	0.14	0.0000055	0.00000001	n.a.	n.a.	0.6	5.3	14	55	3030
Dy	0.00056	0.0027	n.a.	1.35	1.7	4.7	0.53	0.00003	0.0000009	n.a.	n.a.	1.3	4.8	9.1	54	1810
Ho	0.00011	0.00053	n.a.	0.34	0.52	0.99	0.18	0.0000071	0.0000002	n.a.	n.a.	1.5	4.8	13	45	1600
Er	0.00034	0.0014	n.a.	0.82	0.76	2.9	0.45	0.00002	0.0000008	n.a.	n.a.	0.9	4.1	8.8	43	1090
Tm	0.000046	0.00018	n.a.	0.30	0.36	0.41	0.075	0.0000033	0.0000002	n.a.	n.a.	1.2	3.9	28	34	565
Yb	0.00029	0.00092	n.a.	0.85	1.0	2.8	0.20	0.000017	0.0000008	n.a.	n.a.	1.2	3.2	15	36	756
Lu	0.000047	0.00014	n.a.	0.25	0.15	0.43	0.11	0.0000024	0.0000002	n.a.	n.a.	0.6	3.0	21	39	468

(continued on next page)

Table 2 (continued)

Element	Mine effluent and ochre ^a		Coal ^b		Average sedimentary rock, river water, seawater ^c Enrichment ratios ^d									
	Anthracite CMD (median; N = 41)	Bituminous CMD (median; N = 99)	Ochre (median; N = 12)	Anthracite (median; N = 52)	Bituminous (median; N = 731)	Average shale carbonate	Average river water	Average seawater	Ochre/ Shale Coal	Bituminous coal/ Anthracite coal	Bituminous CMD/ Anthracite CMD	Coal/ CMD _S River water	Coal/ CMD _S Seawater	
<i>9. Actinide rare earth elements</i>														
Th	0.000033	0.000033	0.5	5.9	2.6	13	0.2	0.000041	0.00001	<0.1	0.2	0.4	1.0	1260
U	<0.000006	0.00025	1.7	1.4	1.2	4.5	2.2	0.000372	0.0031	0.4	1.4	0.9	>42	51

^a Effluent data are medians for 41 anthracite and 99 bituminous coal-mine drainage (CMD) samples, Pennsylvania, 1999 (this study, Table 1). Ochre data are medians for 12 samples from ten bituminous CMD sites, Pennsylvania, 2003 (this study, Table 3). N, number of samples; n.a., not applicable.

^b Coal data are medians for "Pennsylvania Anthracite" and "Pennsylvania Main Bituminous" sample subsets reported by Bragg et al. (1997).

^c Data for shale and carbonate rocks are world averages from Hem (1985, Table 1) except as noted. Values for rare-earth elements in shale are from McLennan (1989, Table 2). Seawater data are the average of values reported by Krauskopf (1979, Appendix III) and Hem (1985, Table 2). These averages are consistent with data ranges reported by Hood (1972). Values for rock and seawater are consistent with data reported by Mason (1966), Green (1972), Krauskopf (1979), and Veizer (1983). Values for trace elements in river water are from Gallardet et al. (2003); major elements are from Meybeck (2003).

^d Enrichment ratios indicate relative quantities of elements in various media. Ratios involving "Coal" or "CMD" are the averages of the medians for anthracite and bituminous coal or CMD, respectively. The ratio of Coal/CMD_S is the ratio of the element in coal and CMD normalized to the ratio of S in the same materials, e.g. (Pb_{Coal}/Pb_{CMD})/(Sc_{Coal}/Sc_{CMD}).

the individual anthracite or bituminous CMD samples are plotted relative to the pH in Fig. 3 with reference lines for the applicable USEPA criteria for protection of human health and freshwater aquatic organisms. Although some differences between the anthracite and bituminous CMD may be apparent by inspection of Fig. 3 and Table 2, detailed discussion of these differences is beyond the scope of this report. Notable differences between the anthracite and bituminous CMD are addressed by Cravotta (2008).

To facilitate searching for information on specific constituents, data are shown alphabetically by element name in Table 1 and Fig. 3. To facilitate the discussion and evaluation of constituent associations, the data in Table 2 and Fig. 2 are organized by element group and atomic number from the periodic table. The element group and atomic number are identified in Table 1. Although sometimes grouped with the transition metals, Sc and Y are discussed hereinafter with the rare-earth elements, consistent with Brookins (1989) and McLennan (1989).

3.1. Flow, temperature, and chemical composition of 140 CMD samples, 1999

Flows ranged from 0.028 to 2210 L s⁻¹, with a median of 18.4 L s⁻¹ (Table 1). Except for one outlier (warmed by summer heat to 26.6 °C in a shallow ditch containing diffuse CMD seepage), temperature ranged from 8.8 to 16.5 °C, with a median of 12.0 °C (Table 1). These temperatures are comparable to the mean annual air temperatures across Pennsylvania (National Oceanic and Atmospheric Administration, 1981) and, hence, are consistent with the subsurface origin of the CMD samples. Although approximately 10% of the samples had concentrations of DO near equilibrium with the atmosphere (8.4–11.5 mg L⁻¹), most of the CMD samples had low concentrations of DO (<2 mg L⁻¹). High values of DO typically were associated with rapidly flowing CMD from large, open drainage tunnels.

The field pH of the 140 CMD samples ranged from 2.7 to 7.3, with two modes at acidic pH (2.5–4) or near-neutral pH (6–7) values (Table 1, Fig. 3). This bimodal frequency distribution of pH for the CMD samples has been discussed in detail by Cravotta et al. (1999) and Kirby and Cravotta (2005a,b). Alkalinity concentrations ranged from 0 (pH < 4.4; 50 samples) to 510 mg L⁻¹ as CaCO₃. As explained in more detail by Cravotta

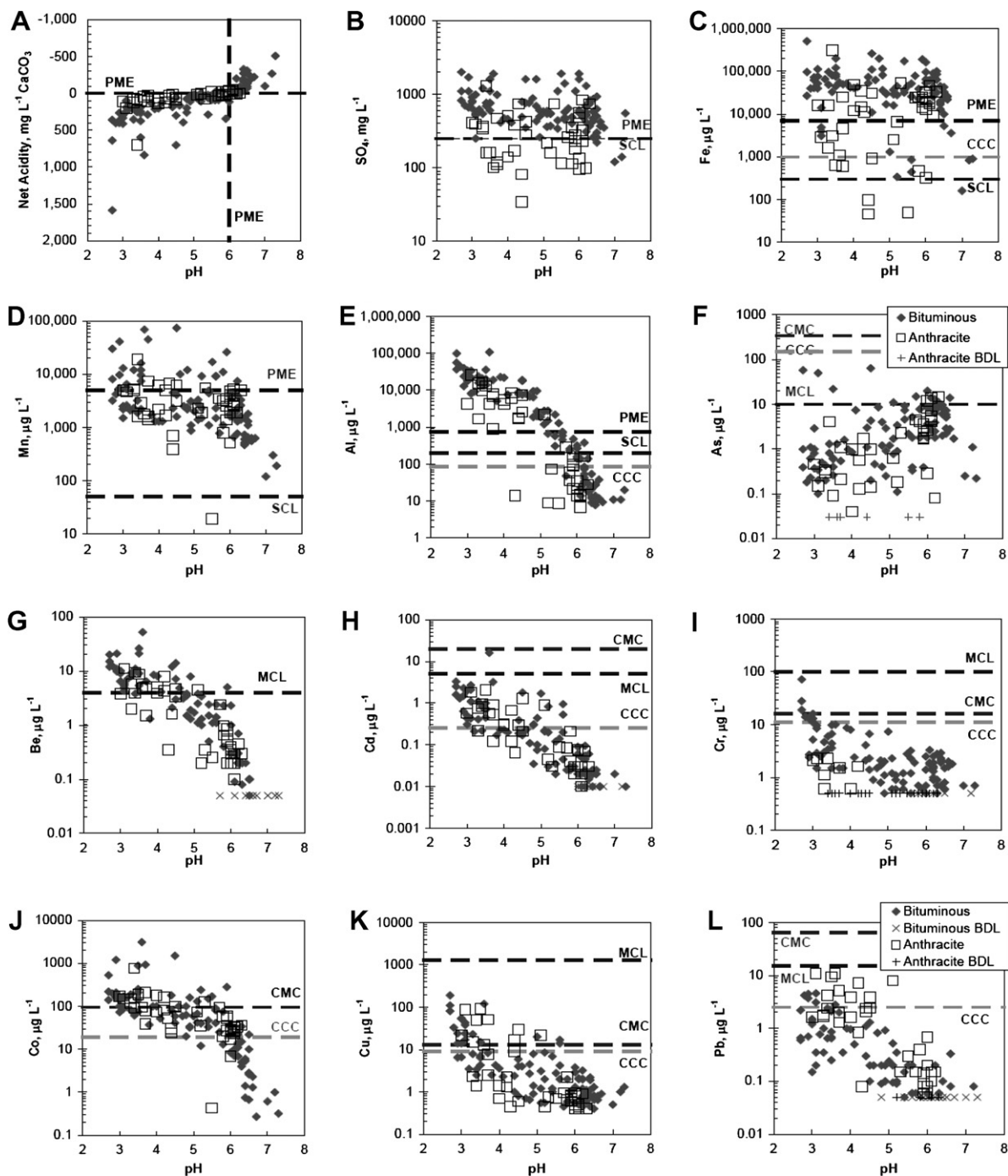


Fig. 3. Contaminant concentration and pH of 140 coal-mine discharge samples, Pennsylvania, 1999, with reference to criteria for permitted mine effluent (PME) in Commonwealth of Pennsylvania (1998a,b), maximum contaminant level (MCL) or secondary contaminant level (SCL) for US drinking water (US Environmental Protection Agency, 2000, 2002a), and criteria maximum concentration (CMC) and continuous concentration (CCC) for freshwater aquatic organisms (US Environmental Protection Agency, 2002b). Values below detection limit (BDL) plotted at the BDL value.

(2008), the nonzero alkalinity values were consistent with partial pressures of CO₂ P_{CO_2} that are 10–1000 times greater than a P_{CO_2} of 10^{-3.5} atm for the ambi-

ent atmosphere. Computed “net” acidity concentrations, excluding contributions from dissolved CO₂, were –326 to 1587 mg L⁻¹ as CaCO₃ (Table 1,

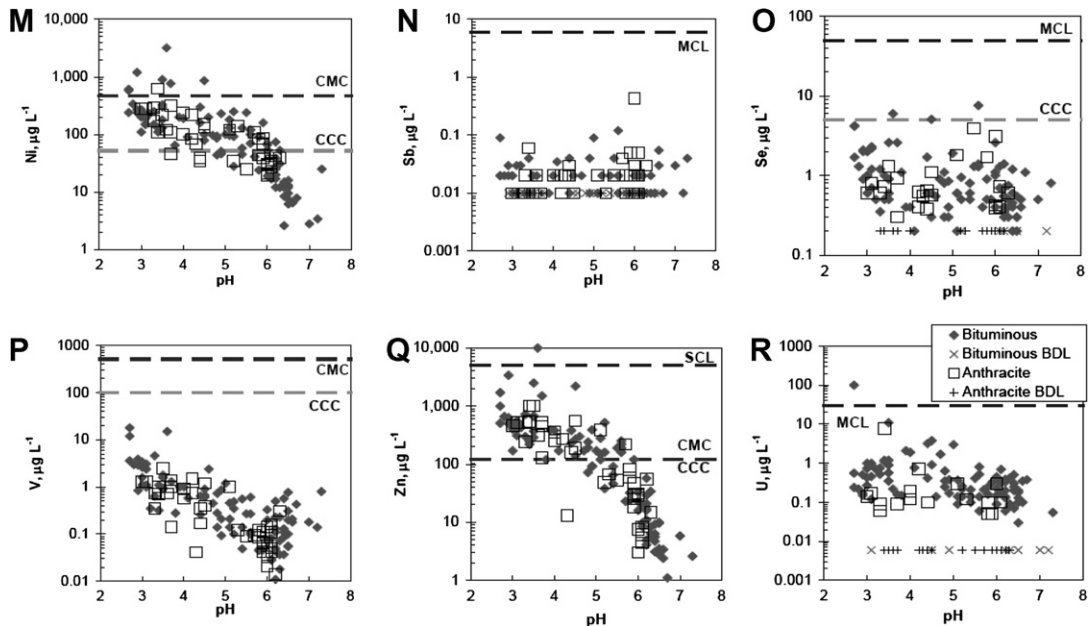


Fig. 3 (continued)

Fig. 3A). More than 2/3 of the CMD samples did not meet permitted mine effluent (PME) criteria for net acidity < 0 and pH \geq 6 (Fig. 3A). Hardness ranged from 23 to 1811 mg L⁻¹ with a median of 382 mg L⁻¹ as CaCO₃ (Table 1). The specific conductance, which is an indirect measure of dissolved solids or hardness (Hem, 1985; Langmuir, 1997), ranged from 131 to 3980 μ S cm⁻¹ (Table 1) and is not correlated with pH but is highly correlated with SO₄ concentration.

The concentrations of dissolved SO₄, Fe, Mn, Al and other constituents varied considerably (Figs. 2 and 3). The subheadings and descriptions below indicate the order of predominance of the median concentrations of these solutes for the respective element groups.

3.1.1. Nonmetals: SO₄ > HCO₃ > PO₄ = NO₃ > Se

Sulfur (34–2000 mg L⁻¹ as SO₄) was the most abundant nonmetal constituent in the CMD samples; the median SO₄ concentration was 520 mg L⁻¹ (Table 1, Fig. 2A). Eighty-four percent of the CMD samples exceeded the 250 mg L⁻¹ PME criteria and USEPA drinking-water “secondary contaminant level” (SCL) for SO₄ (Table 1 and Fig. 3B). Although SO₄ in the CMD samples was elevated compared to the global average concentration of 10.7 mg L⁻¹ in river water, the maximum SO₄ concentration in the CMD was substantially less than

the average concentration of 2715 mg L⁻¹ (905 mg L⁻¹ as S) in seawater (Table 2). The SO₄ concentration exceeded the HCO₃ concentration, estimated as 1.22 times the alkalinity, in all but the three CMD samples that had the highest pH values of 7.0–7.3. The other nonmetal elements (C, N, O, P, Se) generally were only moderately elevated in the CMD compared to average river water or seawater (Tables 1 and 2). Phosphate and NO₃ concentrations in most of the samples were less than detection limits of 0.001 mg L⁻¹ as P and 0.03 mg L⁻¹ as N; maximum concentrations were 2.8 and 0.15 mg L⁻¹, respectively. Although low concentrations of dissolved elements could reflect limited abundance or solubility of source minerals, low concentrations of PO₄ are consistent with its adsorption or precipitation with Fe and Al compounds, whereas low concentrations of NO₃ are consistent with suboxic conditions and potential for NO₃ reduction by Fe^{II} and/or sulfide.

Eighty-four percent of the CMD samples had Se concentrations greater than the 0.2 μ g L⁻¹ detection limit, which is comparable to the average concentration of Se in seawater (Table 2); the maximum concentration was 7.6 μ g L⁻¹. Although less than the drinking-water “maximum contaminant level” (MCL) of 50 μ g L⁻¹, Se concentrations in three samples exceeded the CCC value of 5 μ g L⁻¹ (Table 1 and Figs. 2A and 3O).

3.1.2. Halogens: $Cl > Br > I > F$

Chloride ($0.1\text{--}460\text{ mg L}^{-1}$) was the dominant halogen, with a median concentration of 7.3 mg L^{-1} (Table 1, Fig. 2A). Bromide and I were detected at concentrations greater than 0.003 mg L^{-1} in more than 90% of the samples; maximum concentrations of Br and I were 0.6 and 0.1 mg L^{-1} , respectively (Table 1, Fig. 2A). Fluoride was detected at a concentration greater than 0.1 mg L^{-1} in only three samples, with a maximum concentration of 0.2 mg L^{-1} . The CMD samples with elevated Cl typically had the highest concentrations of Br, I, Na, and K, possibly reflecting contributions from subsurface brines (e.g. Whittemore, 1988). Nevertheless, the maximum concentrations of Cl and Br were orders of magnitude less than the average concentrations in seawater (Table 2) and oilfield brines (Dresel, 1985). Only two samples exceeded the drinking-water SCL for Cl of 250 mg L^{-1} and none exceeded the SCL for F of 2 mg L^{-1} .

3.1.3. Alkalies: $Na > K > Li > Rb > Cs$

The dominant alkali cations were Na ($0.69\text{--}500\text{ mg L}^{-1}$) and K ($0.5\text{--}12\text{ mg L}^{-1}$) (Table 1, Fig. 2A). The maximum concentrations of Li ($390\text{ }\mu\text{g L}^{-1}$), Rb ($28\text{ }\mu\text{g L}^{-1}$) and Cs ($0.85\text{ }\mu\text{g L}^{-1}$) were substantially less than the minimum concentrations of Na or K (Table 1). Median concentrations of Na, K, and Rb were comparable to average concentrations in river water but were orders of magnitude less than the average concentrations in seawater. In contrast, median concentrations of Li and Cs in CMD were elevated compared to river water, and the upper 5% of concentrations were greater than the average concentrations in seawater (Table 2, Fig. 2A). Water-quality criteria have not been established for the alkali earths.

3.1.4. Alkaline earths: $Ca > Mg > Sr > Ba > Be$

Calcium ($3.3\text{--}410\text{ mg L}^{-1}$) and Mg ($3.6\text{--}210\text{ mg L}^{-1}$) were the dominant alkaline earth cations with median concentrations of 88 and 38 mg L^{-1} , respectively (Table 1, Fig. 2A). The maximum concentrations were 3.6 mg L^{-1} for Sr, 0.052 mg L^{-1} for Be, and 0.039 mg L^{-1} for Ba (Table 1). Although Mg, Ca and Sr concentrations were elevated in CMD compared to average river water, the CMD was an order of magnitude less concentrated than seawater (Table 2). The concentrations of Ba in CMD were comparable to average river water or seawater. Cravotta (2008) argues that

relatively low concentrations of Ba in CMD could result because of solubility control by barite (BaSO_4). In contrast, concentrations of Be in CMD were two to three orders of magnitude greater than average concentrations in river water or seawater (Table 2). The maximum Ba concentration in the CMD samples was well below the freshwater CCC value of $4100\text{ }\mu\text{g L}^{-1}$ and the drinking-water MCL of $2000\text{ }\mu\text{g L}^{-1}$; however, 1/3 of the samples had Be concentrations that exceeded the $4\text{ }\mu\text{g L}^{-1}$ drinking-water MCL (Table 1).

3.1.5. Metalloids: $Si > B > As > Ge > Sb > Te$

Silicon was the dominant metalloid element, ranging in concentration from 2.7 to 31.3 mg L^{-1} (Table 1, Fig. 2A). Boron, As, Ge and Sb had median and maximum concentrations of 44 and $260\text{ }\mu\text{g L}^{-1}$; 1.7 and $64\text{ }\mu\text{g L}^{-1}$; 0.07 and $0.57\text{ }\mu\text{g L}^{-1}$; and 0.01 and $0.43\text{ }\mu\text{g L}^{-1}$, respectively, in the CMD samples. Tellurium concentrations were below the detection limit of $0.0002\text{ }\mu\text{g L}^{-1}$ in 98% of the samples. The median Si concentration of 7.9 mg L^{-1} in CMD was comparable to the average for river water but exceeded the average of 2.5 mg L^{-1} for seawater (Table 2). Concentrations of B and Ge in CMD were elevated compared to average river water but were less than or equal to average concentrations in seawater. Concentrations of As and Sb in the CMD samples were less than average concentrations in seawater; however, As was elevated in bituminous CMD compared to river water (Table 2). Although concentrations of As, B and Sb were substantially less than freshwater CCC values (150 , 1600 and $200\text{ }\mu\text{g L}^{-1}$, respectively), approximately 10% of the CMD samples had As concentrations greater than the drinking-water MCL of $10\text{ }\mu\text{g L}^{-1}$ (Fig. 3F). None of the CMD samples exceeded the drinking-water MCL for Sb of $6\text{ }\mu\text{g L}^{-1}$ (Fig. 3N).

3.1.6. Transition metals: $Fe > Mn > Zn > Ni > Co > Ti > Cu > Cr > V > Mo > Cd > W > Zr > Hf > Au$

Iron ($0.046\text{--}512\text{ mg L}^{-1}$), Mn ($0.019\text{--}74\text{ mg L}^{-1}$), Zn ($0.6\text{--}10,000\text{ }\mu\text{g L}^{-1}$), Ni ($2.6\text{--}3200\text{ }\mu\text{g L}^{-1}$), Co ($0.27\text{--}3100\text{ }\mu\text{g L}^{-1}$), Ti ($0.65\text{--}28\text{ }\mu\text{g L}^{-1}$), Cu ($0.4\text{--}190\text{ }\mu\text{g L}^{-1}$) and Cr ($<0.5\text{--}72\text{ }\mu\text{g L}^{-1}$) were the predominant transition metals, in order of abundance (Table 1 and Figs. 2B and 3). The median concentrations of these elements were elevated compared to river water, seawater, and various aquatic protection criteria (Tables 1 and 2, Figs. 2B and 3).

Except for Hf, the median concentrations of subordinate transition metals ($V > Mo > Cd > W > Zr > Hf > Au$) in the CMD samples were less than average concentrations in river water or seawater (Tables 1 and 2). However, the maximum concentrations of V ($18 \mu\text{g L}^{-1}$), Cd ($16 \mu\text{g L}^{-1}$), W ($0.52 \mu\text{g L}^{-1}$), Zr ($0.84 \mu\text{g L}^{-1}$), Hf ($7.1 \mu\text{g L}^{-1}$) and Au ($0.0175 \mu\text{g L}^{-1}$) exceeded the average for seawater (Tables 1 and 2). Maximum concentration of Mo ($2.6 \mu\text{g L}^{-1}$) was greater than the average for river water but less than the average of $10 \mu\text{g L}^{-1}$ in seawater (Tables 1 and 2). No samples had detectable concentrations of Hg, Os or Pt, and less than 1/2 of the samples had detectable Pd, Ag, Ru, Ta, Nb, Re, or Sn.

Gold was detected at concentrations greater than $0.0005 \mu\text{g L}^{-1}$ in 97% of the CMD samples, with a median of $0.001 \mu\text{g L}^{-1}$ and a maximum of $0.0175 \mu\text{g L}^{-1}$ (Table 1). Median concentrations of Au in CMD were about an order of magnitude less than the average concentration $0.007 \mu\text{g L}^{-1}$ in seawater. One CMD sample had a Au concentration of $0.0175 \mu\text{g L}^{-1}$, 12 samples had more than $0.005 \mu\text{g L}^{-1}$, and 54 of the discharges had more than $0.001 \mu\text{g L}^{-1}$. Although these concentrations are extremely dilute, the presence of Au in a few of the high-volume discharges could result in the accumulation of significant quantities of Au with the ochre over time.

Approximately 80% of the CMD samples exceeded the PME criteria for Fe of 7.0 mg/L (Fig. 3C); 26% exceeded the PME criteria for Mn of 5.0 mg/L (Fig. 3D). Although more than 95% of the CMD samples exceeded the drinking-water

SCL values for Fe of 0.3 mg/L and for Mn of 0.05 mg/L, only one sample exceeded drinking-water criteria for other transition metals ($Cd > 5 \mu\text{g L}^{-1}$ and $Zn > 5000 \mu\text{g L}^{-1}$). Most of the CMD samples exceeded freshwater CCC values for multiple transition metals (Fig. 3C, D, H–K, M, Q); only the CCC value for V was not exceeded (Fig. 3P).

Although dissolved Zn, Ni, Co and, to a lesser extent, Cd and Cu in the CMD samples from Pennsylvania commonly exceeded global average concentrations in river water or seawater (Tables 1 and 2), the CMD samples had lower concentrations of “total” base metals (Zn, Cu, Cd, Pb, Co, Ni) compared to drainage from many metal mines in the western USA (Fig. 4). The narrow range in the composition of CMD compared to drainage from metal mines results because the mineralogy of typical coal-bearing sedimentary rocks has limited variability, sulfide minerals are less abundant, and some metals may be present as relatively inert organic compounds. Although Fe-sulfide and calcareous minerals typically comprise only a few %, or less, of the coal-bearing rock, these minerals are highly reactive and are mainly responsible for the CMD chemistry (Brady et al., 1998; Cravotta, 1994; Cravotta et al., 1999). In contrast, metal deposits in diverse geologic settings can contain disseminated to massive concentrations of pyrite, pyrrhotite, other metal-bearing sulfides, and a wide variety of associated minerals (Plumlee et al., 1999; Blowes et al., 2003). The wide variety of minerals in various ore deposits and host rocks influences the resultant drainage composition. Furthermore, the rate of weathering

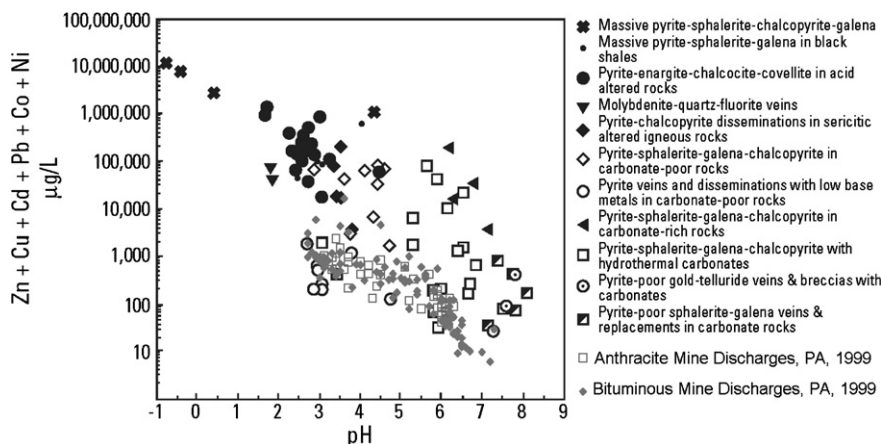


Fig. 4. Sum of the concentration of base metals (Zn, Cu, Cd, Pb, Co and Ni) compared to pH of 140 coal-mine discharges, Pennsylvania, 1999, and of metal-mine discharges reported by Plumlee et al. (1999).

of minerals extracted from metal mines can be accelerated because of ore processing methods that greatly reduce grain size and concentrate the reactive sulfides in mine tailings (Hammarstrom and Smith, 2002; Blowes et al., 2003).

3.1.7. Other metals:

$Al > Pb > Ga > Tl > Bi > In > Sn$

After Fe, Al was the second most abundant metal ($0.007\text{--}108\text{ mg L}^{-1}$), typically in mg/L range in acidic samples (Table 1, Figs. 3A and 2E). Most of the other metals were below limits of detection in various CMD samples. Lead was detected at a concentration greater than $0.1\text{ }\mu\text{g L}^{-1}$ in 71% of the samples, with a maximum concentration of $11\text{ }\mu\text{g L}^{-1}$. Gallium was detected at a concentration greater than $0.01\text{ }\mu\text{g L}^{-1}$ in 95% of the samples, with a maximum concentration of $7.3\text{ }\mu\text{g L}^{-1}$. Thallium was detected at a concentration greater than $0.006\text{ }\mu\text{g L}^{-1}$ in all the samples, with a maximum concentration of $1.5\text{ }\mu\text{g L}^{-1}$. Bismuth was detected at a concentration greater than $0.01\text{ }\mu\text{g L}^{-1}$ in 70% of the samples, with a maximum concentration of $0.35\text{ }\mu\text{g L}^{-1}$. Indium was detected at a concentration greater than $0.001\text{ }\mu\text{g L}^{-1}$ in 77% of the samples, with a maximum concentration of $0.34\text{ }\mu\text{g L}^{-1}$. Tin was less than the detection limit of $0.1\text{ }\mu\text{g L}^{-1}$ in 95% of the samples, with a maximum concentration of $0.2\text{ }\mu\text{g L}^{-1}$. Except for Sn, the median concentrations of the metals in this group were elevated compared to seawater (Tables 1 and 2).

3.1.8. Rare earths: $Y > Ce > Sc > Nd > La >$

$Gd > Dy > Sm > Pr > Er > Yb > Eu > Ho > Tb > U > Tm > Lu > Th$

The majority of CMD samples had concentrations of Sc, Y, and lanthanide and actinide rare-earth elements ranging from $0.01\text{--}1\text{ }\mu\text{g L}^{-1}$ (Table 1, Fig. 2C). Yttrium, Ce, Sc, Nd, La, Gd, Dy and Sm were the predominant rare earths, with median and maximum concentrations of 8.7 and $530\text{ }\mu\text{g L}^{-1}$; 6.6 and $370\text{ }\mu\text{g L}^{-1}$; 5.0 and $36\text{ }\mu\text{g L}^{-1}$; 4.9 and $260\text{ }\mu\text{g L}^{-1}$; 2.2 and $140\text{ }\mu\text{g L}^{-1}$; 1.8 and $110\text{ }\mu\text{g L}^{-1}$; 1.8 and $99\text{ }\mu\text{g L}^{-1}$; and 1.3 and $79\text{ }\mu\text{g L}^{-1}$, respectively. Median concentrations of Th ($0.033\text{ }\mu\text{g L}^{-1}$) and U ($0.17\text{ }\mu\text{g L}^{-1}$) in the CMD were less than average river water or seawater; however, the other rare-earth elements were orders of magnitude more concentrated in CMD than in average river water and seawater (Tables 1 and 2).

3.2. Compositions of ochre samples from selected sites, 2003

The mineralogy of the ochre samples collected at 10 CMD sites in 2003 was dominantly goethite, with minor ferrihydrite or lepidocrocite (Table 3). The ferrihydrite and lepidocrocite were identified in ochres formed at pH greater than 5. Cravotta (2008) shows that the observed ochre mineralogy and associated CMD compositions are consistent with mineral stabilities as reported by Bigham et al. (1996), Yu et al. (1999) and Williams et al. (2002). Many of the ochre samples also contained quartz, kaolinite, muscovite, and/or chlorite, probably derived as detritus; none of the samples for this study was Al rich (Table 3). Although schwertmannite was present at some of the anthracite sites (Williams et al., 2002), this mineral was not identified in the ochres collected in 2003. Although its origin is uncertain, minor gypsum in two samples may have formed upon sample drying.

The ochre chemistry was dominated by Fe, with subordinate concentrations of Al and Ca ($Al > Ca > K > P > Na > Mg > Mn$) (Table 3). The contents of 24–45% Fe are equivalent to 46–72% FeOOH by weight, and 0.02–2.23 wt% Al are equivalent to 0.1–6.7 wt% $Al(OH)_3$, respectively (Table 3). The maximum concentrations of Ca, K, P, Na, Mg and Mn, in order of decreasing median concentrations, were less than 2 wt% (Table 3). The concentrations of Si and S were not determined but could have been greater than Al or other minor elements considering that quartz, aluminosilicates, and/or gypsum were present in the samples.

The ochre samples contained numerous elements at trace levels with maximum concentrations less than 0.1 wt%, in order of decreasing median concentrations: $Sr > As > Ba > Zn > Y > Ag > Ce > V > Cu > Ni > La > Pb > Cr > Co > Sc > Mo > Rb > Be > Nb > U > Ga > Th > Cs > Li > Cd > Ti > Sb > Au$ (Table 3). Strontium ($5.4\text{--}450\text{ mg kg}^{-1}$), As ($2\text{--}190\text{ mg kg}^{-1}$), and Ba ($4\text{--}509\text{ mg kg}^{-1}$) were ubiquitous in the samples. Detectable concentrations of potentially valuable metals also were present in the ochre samples. Generally, the ochres were enriched in Fe, Ag, Au and Y compared to average shale or coal (Tables 2 and 3). However, the ochres were not enriched in these or other trace elements analyzed compared to commercial ores.

The maximum measured concentrations of Zn (183 mg kg^{-1}), Cu (32.4 mg kg^{-1}), Ni (59.9 mg kg^{-1}), Pb (14.3 mg kg^{-1}) and Au (0.044 mg kg^{-1}) in

Table 3

Major minerals and concentrations of various elements, in parts per million, in ochre samples^a from 10 coal-mine discharge sites in the Bituminous Coalfield, Pennsylvania, September, 2003

Element	Site 62 pH = 3.0	Site 62 pond pH = 6.0	Site 97 pH = 4.6	Site 18 pH = 5.3	Site 83 pH = 5.7	Site 91 pH = 5.8	Site 40 pH = 6.0	Site 101 pH = 6.2	Site 101 pile pH = 6.2	Site 5 pH = 6.5	Site 25 pH = 6.9	Site 59 pond pH = 6.9
	Gt, Qz, Gy, Mu	Sh?, Qz, Mu, Ka, Ch	Gt, Qz, Mu	Gt, Lp, Qz	Gt	Gt	Gt	Gt	Gt, Lp, Qz	Gt, Fh	Gt, Qz, Mu, Ka, Ch?	Gt, Qz, Fh?
Ag	33	34	35	21	37	38	38	38	38	38	30	37
Al	24,000	23,300	14,900	12,600	15,900	1,600	409	180	12,900	391	10,400	2590
As	2	17	72	100	64	85	190	5.6	22	78	160	170
Au	0.043	<0.001	0.007	0.017	0.006	0.044	0.011	0.008	<0.001	0.043	0.035	0.016
Ba	205	180	93	4	14	11	28	39	45	124	509	203
Be	4.2	4.2	2.1	9.2	8.8	1.4	2	1.5	8.8	0.7	1.6	2.3
Ca	10,800	4380	295	429	2320	1680	3940	9060	925	7320	8980	16,000
Cd	0.06	0.23	0.02	0.08	0.35	0.02	0.04	0.01	0.31	0.12	0.28	0.03
Ce	21.6	24.2	16.6	34.7	220	13.3	13.5	3.8	41.5	1.4	18.6	6.6
Co	6.7	15.5	1.5	2.8	3.6	1	0.59	1.1	4.2	6	35.6	1.4
Cr	40.1	21	32.7	2.8	5.3	1.9	0.69	<0.2	6.9	<0.2	19	2.7
Cs	1.2	1.8	1.2	0.03	0.004	0.03	0.01	<0.003	0.56	0.03	1.1	0.34
Cu	32.4	19.4	6.6	8.4	6.4	<0.5	5	<0.5	4	1.1	8.7	11
Fe	240,000	290,000	320,000	380,000	400,000	450,000	430,000	440,000	450,000	410,000	310,000	380,000
Ga	4.8	4.9	3.1	0.42	1.4	0.28	0.3	0.1	1.6	0.2	3.1	1.1
K	4270	4270	2810	45	<20	70	46	21	995	52	2470	610
La	9.1	10.9	7.1	7	51.8	2.8	5.3	1	7.5	0.54	8.4	3.2
Li	11.1	15.3	8.5	<0.2	<0.2	<0.2	<0.2	<0.2	3.9	<0.2	9.4	1.5
Mg	4620	1670	865	112	136	131	370	386	380	402	1640	801
Mn	130	259	58	40	109	89	204	217	294	1340	5830	7000
Mo	0.98	3.3	1.6	2.3	5.3	5.5	5.5	1.7	2.4	3.1	6.2	3
Na	674	480	750	18	153	270	277	1760	196	403	1270	587
Nb	2.2	3.3	3.3	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Ni	14.7	59.9	4.6	4.2	11.1	3.8	2	2.3	14.2	9.9	24.6	2
P	390	6500	660	35	74	880	4000	490	190	150	1800	490
Pb	8.3	14.3	7.5	5.1	<0.2	1.6	1.3	<0.2	10.6	0.2	14.2	0.98
Rb	23.7	28.6	17.9	0.4	0.06	0.45	0.23	0.05	7.1	0.35	16.3	4.6
Sb	0.31	1.3	0.1	<0.02	<0.02	<0.02	0.1	<0.02	<0.02	<0.02	0.31	<0.02
Sc	11.5	6.0	3.4	4.9	4.4	0.5	0.3	0.3	2.5	0.4	3.8	3.0
Sr	85.9	77.7	18.4	5.4	56.8	53.3	91.5	388	21.5	384	381	450
Th	7.9	3.2	3.0	0.14	0.44	0.06	0.05	<0.03	0.85	0.03	2.2	0.55
Ti	0.052	0.062	0.06	<0.004	<0.004	<0.004	<0.004	<0.004	0.018	<0.004	0.041	0.014
Tl	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
U	1.6	2.2	1.1	1.4	3.4	0.74	0.77	0.66	2.3	1.8	1.7	1.7
V	22.2	26.4	31.8	14.9	1.1	3.6	<0.4	<0.4	5.7	<0.4	16.3	3.2
Y	28	41	10	57	227	41	66	40	153	9.4	18	17
Zn	122	160	42.5	31.5	81.8	15.6	16	<5.0	183	15.5	106	6.6

^a Samples dry sieved <100 mesh before analysis of mineralogy by X-ray diffraction and chemistry by ICP-MS after digestion in mixture of HCl, HNO₃, and HF. Gt, goethite; Fh, ferrihydrite; Lp, lepidocrocite; Qz, quartz; Mu, muscovite; Ka, kaolinite; Ch, chlorite; Gy, gypsum.

the ochre samples were 1–3 orders of magnitude less than concentrations in typical commercial deposits of these constituents (Brobst and Pratt, 1973; Press and Siever, 1978, Table 22-4; Evans, 1980, Table 1.1). Preliminary estimates of Au concentrations in the ochres at these 10 CMD sites, prior to collection of ochre samples, indicated Au concentrations could be greater than a commercial ore threshold of 0.003 oz/ton (0.1 mg kg⁻¹). Assuming a constant proportionality between the concentrations of Au and Fe in solution and in Fe(OH)₃ precipitate, the Au content of ochres at the 10 sites was estimated to range from 0.003 to 0.856 mg kg⁻¹ based on the data for 1999 and from <0.001 to 1.91 mg kg⁻¹ based on data for 2003. The actual range of <0.001–0.044 mg kg⁻¹ Au in the ochre samples was substantially less than these estimates. This implies that Au is not strongly partitioned into the ochres at these sites.

The concentrations of Fe in the ochres were comparable with those of Fe ores. However, the quantities of ochre at the sampled sites were small compared to commercial ore deposits; the maximum quantity of ochre at any of the 10 sites was estimated to be 2000 kg based on sludge volume computations. Nevertheless, this estimate for in-place material at the time of sampling ignores the fact that Hedin (2003) had previously collected more than 200 metric tons of ochre from site 101 reported in Table 3. Hedin (2003) demonstrated that ochres from this site and some other CMD sites in Pennsylvania have high potential value for commercial use as Fe oxide pigment.

3.3. Transport of constituents at CMD sites

With the exception of Au, the chemical concentrations and loading rates at the 10 ochre sample sites were comparable among CMD samples collected in 1999 and 2003 (Figs. 5 and 6). In 1999, the sites had a wide range of flows (5.7–278 L s⁻¹), pH (3.0–7.2), and concentrations of SO₄ (140–1300 mg L⁻¹), Fe (0.83–174 mg L⁻¹) and Au (0.0009–0.0175 µg L⁻¹) (Fig. 5). In 2003, the 10 sites had similar values for flow (11–283 L s⁻¹), pH (3.0–6.9), SO₄ (110–1220 mg L⁻¹) and Fe (1.9–156 mg L⁻¹), but approximately one order of magnitude lower concentrations of Au (<0.0001–0.0011 µg L⁻¹) (Fig. 5). The lower concentrations of Au for samples collected in 2003 could have resulted from different sample storage and analytical methods. In 1999, charcoal sachets were added directly to CMD samples when filling 1-L polyethyl-

ene bottles at the CMD site. Gold that was adsorbed by the charcoal was subsequently analyzed by INAA (Crock et al., 1999). In 2003, a similar sampling and analytical procedure was unsuccessfully employed; the initial INAA results were negative. Because a satisfactory explanation could not be provided for this result, stored CMD subsamples that had been filtered and preserved with HCl for dissolved metals analysis were reanalyzed by ICP-MS for Au. These results for the 2003 samples were positive, but approximately one order of magnitude lower than values for the 1999 data set.

Good agreement between measured concentrations and computed loading rates for CMD samples at the 10 sites sampled in 1999 and 2003 (Figs. 5 and 6) indicate hydrochemical stability at the sites and supports the reporting of instantaneous loading rates, or transport, in mass units/a (Figs. 6 and 7). Accordingly, the product of the instantaneous flow and constituent concentration was assumed to indicate annual transport at each of the 140 CMD sites sampled in 1999.

The median and maximum transport were estimated to be 87,700 and 9,270,000 kg a⁻¹ for S, 15,500 and 1,250,000 kg a⁻¹ for Fe, 1580 and 216,000 kg a⁻¹ for Mn, and 650 and 509,000 kg a⁻¹ for Al, respectively, for the 140 CMD sites in 1999 (Fig. 7A and B). The transport of typical “major” ions in fresh water, such as Ca, Mg, Na, K and Cl, was of the same magnitude as S, Fe, and Mn (Fig. 7A and B). The median and maximum transport estimates for Co (32 and 6970 kg a⁻¹), Cr (0.31 and 22 kg a⁻¹), Ni (51 and 10,400 kg a⁻¹), and Zn (71 and 39,000 kg a⁻¹) were smaller than those for Al, but larger than those for Au, other precious metals, and rare-earth elements. Despite large flows at some sites with the highest concentrations of dissolved Au, the estimated transport of Au was extremely small, ranging from less than 0.001–0.079 kg a⁻¹ (<0.0003 to 2.76 oz a⁻¹). Nevertheless, the estimated transport of Au exceeded that for Re and Ta (Fig. 7B).

The estimated transport rates for the rare-earth elements ranged over six orders of magnitude (Fig. 7C). The median and maximum transport for Sc (3.65 and 279 kg a⁻¹), Y (5.66 and 906 kg a⁻¹), Ce (4.03 and 2580 kg a⁻¹), Nd (2.63 and 1320 kg a⁻¹), La (1.32 and 1180 kg a⁻¹), Eu (0.20 and 62.7 kg a⁻¹), and Sm (0.67 and 279 kg a⁻¹) were larger than estimates for the other rare-earth elements (Fig. 7C). The smallest rates of transport

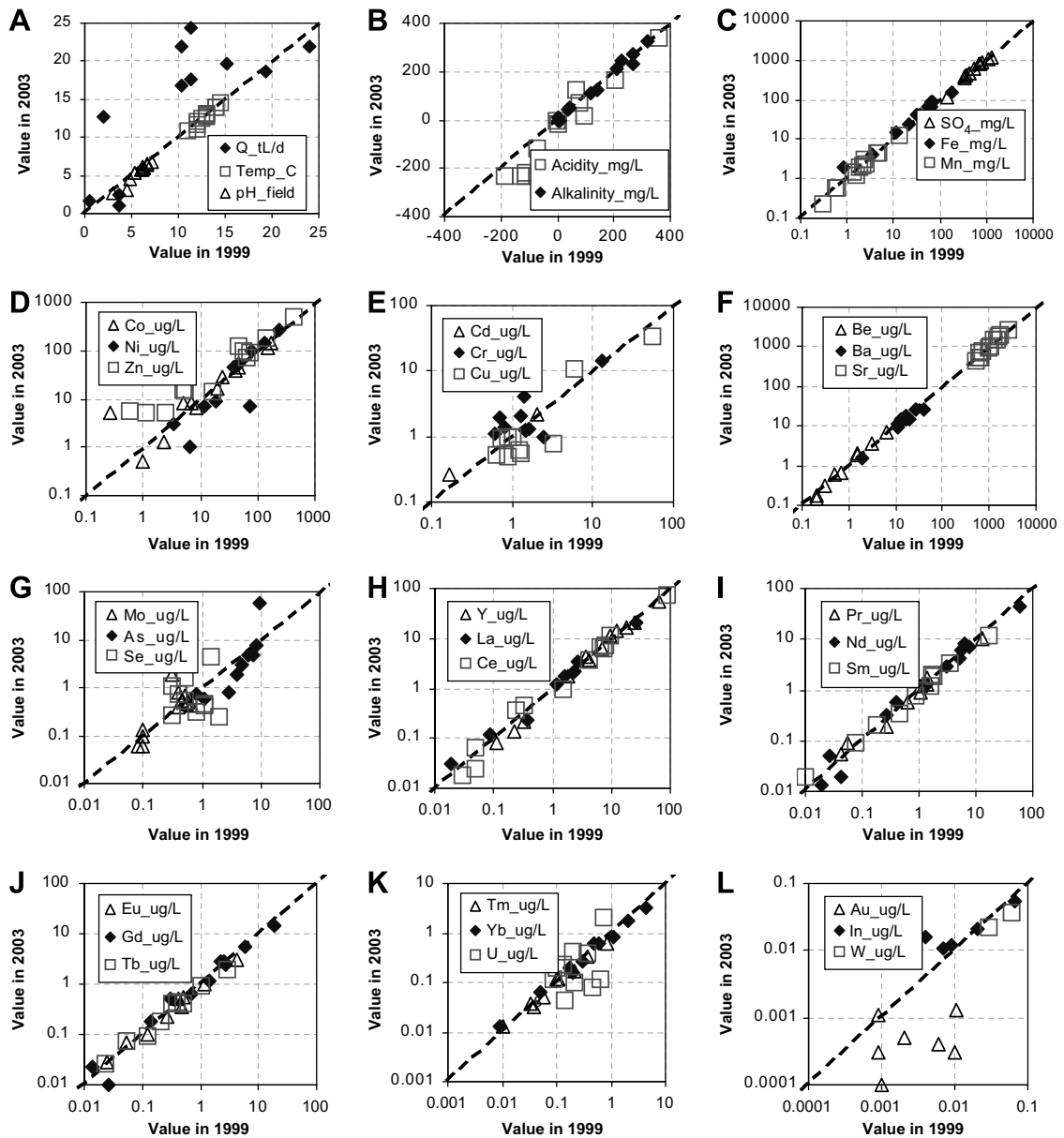


Fig. 5. Comparison of flow rate and water quality at 10 coal-mine discharge sites sampled in 1999 and 2003, Bituminous Coalfield, Pennsylvania. Units are as follows: tL/d, thousand liters per day; C, degrees Celsius; $\mu\text{S}/\text{cm}$, microsiemens per centimeter; mg/L, milligrams per liter; $\mu\text{g}/\text{L}$, micrograms per liter. Dashed line of unity indicates equal values in 1999 and 2003.

among the rare earths were computed for Th, U, Tm and Lu (Fig. 7C).

The potential for constituents to be concentrated or transported with CMD is a function of the abundance of the constituents in source coal and associated rocks coupled with the tendency for the solids to dissolve. For example, bituminous coal and CMD samples from Pennsylvania coal mines had greater concentrations of S, Fe, As and many other

elements than anthracite samples, whereas, the anthracite coal and CMD samples were relatively enriched in Ba, Cs, W and La (Table 2). Apparently, the concentrations of these constituents in CMD are related to the concentrations in coal. However, some constituents, such as Pb, that were elevated in the coal were not elevated in the CMD. Lead and possibly other constituents could have limited mobility in CMD environments because of

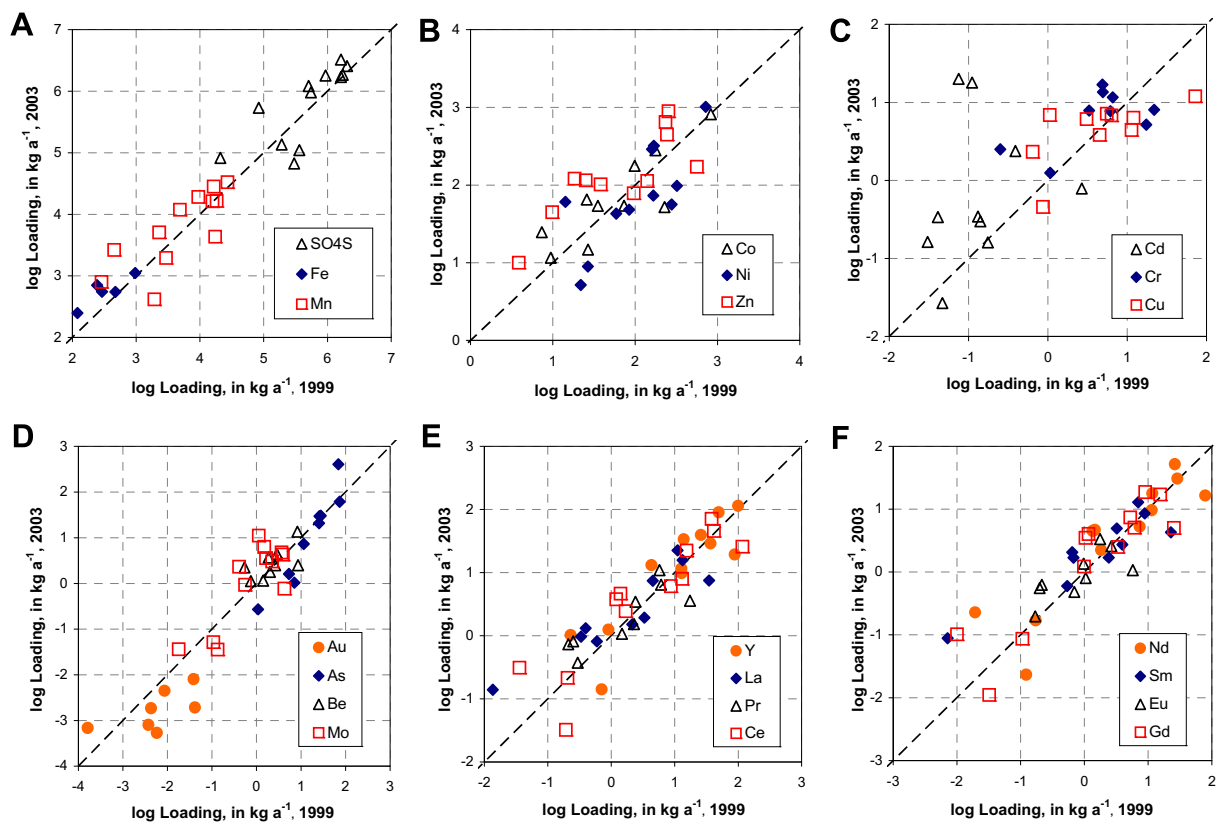


Fig. 6. Comparison of constituent transport, in kilograms per year, at 10 coal-mine discharge sites sampled in 1999 and 2003, Bituminous Coalfield, Pennsylvania. Units are kilograms per year. Dashed line of unity indicates equal values in 1999 and 2003.

solubility or sorption controls imposed by secondary mineral phases (e.g. Cravotta, 2008).

To help distinguish constituent mobilities in coal-mine environments, the ratios of the average concentrations of elements in coal and CMD samples were divided by (normalized to) the ratio of S concentrations in the same materials (Table 2, coal/CMD_S). Normalization to S helps to indicate those elements that are more or less mobile than S, which is among the most abundant and mobile constituents in CMD (Figs. 2, 3 and 7). For example, the coal/CMD_S value for Pb was 183 (Table 2), indicating Pb has limited mobility compared to S in coal-mine environments. In contrast, few elements have coal/CMD_S values less than or equal to 1.0 (Table 2), indicating greater or equal mobility compared to SO₄. The mobile constituents indicated by low values of the normalized coal/CMD_S ratio include Na (0.1), Mg (<0.1), Ca (<0.1), Sr (1.0), Mn (<0.1), Co (1.0), Zn (0.8) and Cl (0.8). The constituents that had the largest coal/CMD_S values were Ti (2100), In (2120), Zr (5690) and Au (8090), in order of decreased mobil-

ity. Thus, despite their enrichment in coal and shale, all of the rare earths, other metals, metalloids, non-metals, and most of the transition metals are difficult to mobilize from geological materials as indicated by their large coal/CMD_S values (Table 2).

3.4. Correlations among constituents in CMD samples

Correlations among the dissolved constituents in the CMD samples and between the compositions of associated CMD and ochre samples are complex. Although the data for the 140 CMD samples collected in 1999 were suitable for rigorous statistical analysis of the correlations among constituents, only generalized data values or a small number of samples were available to describe the relations between corresponding CMD, ochre, coal, and other environmental materials. In these cases, simple bivariate comparisons of listed values (ratios) or bivariate graphs of sample results were used to evaluate correlations (Table 2, Figs. 8 and 9).

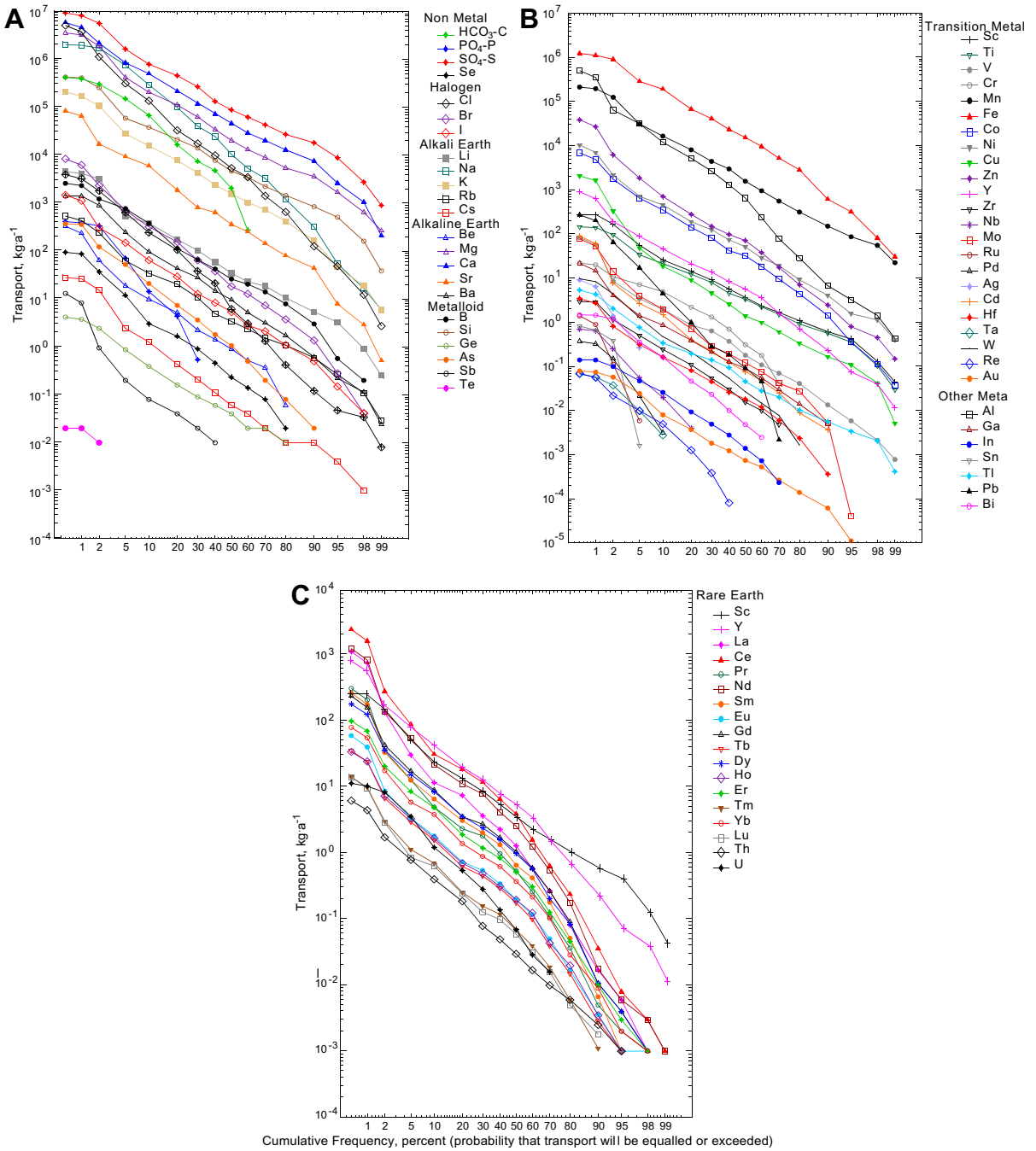


Fig. 7. Log-probability plots of constituents in 140 abandoned coal-mine discharge samples, Pennsylvania, 1999, showing frequency that transport will be equalled or exceeded: (A) Nonmetals, halogens, alkalis, alkaline earths, and metalloids; (B) Transition metals and other metals; (C) Rare earths.

3.4.1. Bivariate correlations

The concentrations of constituents in the ochres generally appear to be a function of the concentrations in the CMD samples, exhibiting a positive

overall relation between concentrations of constituents in the ochre and CMD samples (Fig. 8). Although most trends between concentrations of specific constituents in the solid and aqueous phases

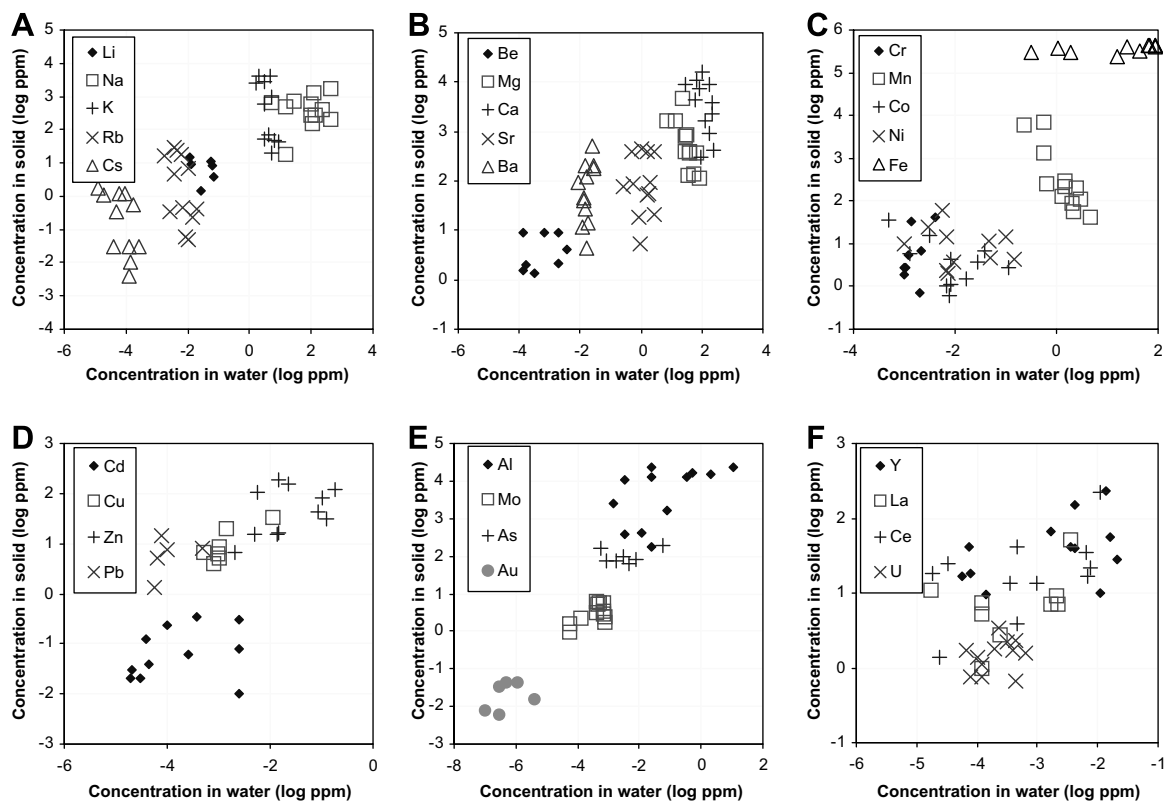


Fig. 8. Element concentrations, in parts per million, in associated aqueous (water) and solid (ochre) phases at 10 coal-mine discharge sites, Pennsylvania, 2003.

are visibly positive, trends for some constituents are visibly negative. Specifically, many metals that were elevated in solution, such as Fe, Al and Zn, were also elevated in the ochres, and the concentrations in associated aqueous and solid samples were positively correlated. Despite being elevated in the CMD, however, some other constituents, such as Na, Ca, Mg, Mn, Ni and Co, exhibited poor or negative correlations between concentrations in the aqueous and solid phases (Fig. 8). The constituents that exhibited poor or inverse correlations between the aqueous and solid phases (Fig. 8) generally had low coal/CMD_S values (Table 2) indicating that differences in the constituent correlations between the aqueous and solid phase probably are related to differences in mobilities of the elements and, to a lesser extent, the element concentration in solution. It is likely that the solubility or adsorption behavior of the elements can explain their relative mobilities. An evaluation of the geochemical behavior of elements generally involves the consideration of additional variables such as the pH or redox potential.

The distribution coefficient, K_d , is the ratio of the element concentrations in associated CMD and ochre samples. When plotted as a function of pH, the K_d value revealed consistent trends for diverse element groups (Fig. 9). With the exception of As, Cr, Mo and U (oxyanions), the K_d values generally decreased with increased pH; ochres associated with a higher pH environment tended to contain proportionally more impurities than those sampled at lower pH. The K_d values for the alkali elements (Li, Na, K, Rb, Cs) and alkaline earth elements (Be, Mg, Ca, Sr, Ba) were larger than those for the transition metals, other metals, and rare earths at a given pH (Fig. 9), indicating relatively smaller proportions of the alkali and alkaline earth elements in the solids. With increased pH, the progressive enrichment with cations (decreased K_d), including the alkali and alkaline earths, and the relative depletion with oxyanions (increased K_d) in the ochres are consistent with the potential formation of metal hydroxides at near-neutral pH and the potential for surface-complexation, or adsorption, reactions between dissolved cations, anions, and solid Fe

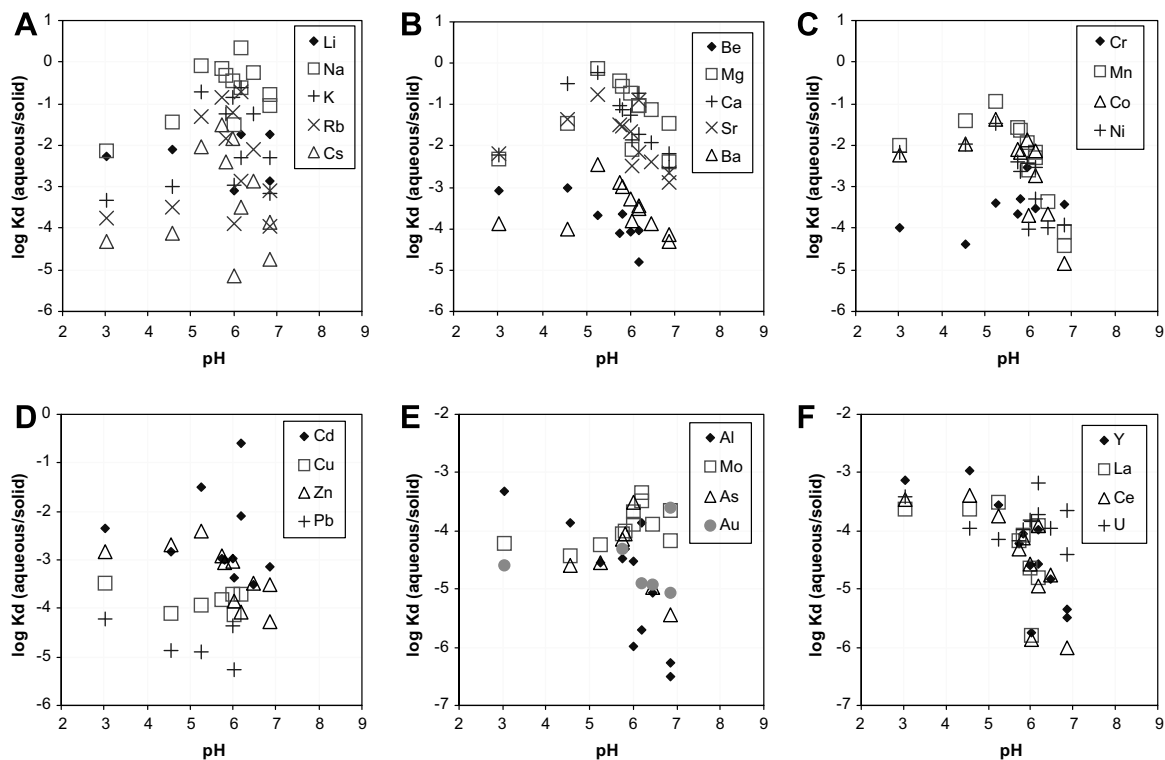


Fig. 9. Element distribution between associated aqueous (water) and solid (ochre) phases as function of pH at 10 coal-mine discharge sites, Pennsylvania, 2003. The distribution coefficient, K_d , is the concentration in solution divided by that in the solid.

hydroxide (e.g. Dzombak and Morel, 1990). On the basis of data from this study, Cravotta (2008) examines possible solubility controls of the metals and surface-complexation reactions between the cations and anions on hydrous ferric oxides.

The graphs showing concentration values plotted against pH for the 140 CMD samples collected in 1999 (Fig. 3) clearly show that the concentrations of most potentially “toxic” metals, such as Al, are negatively correlated with pH, whereas other potentially toxic elements, such as As, are positively correlated with pH. Furthermore, these and other constituents do not exhibit a simple linear trend with pH; most exhibit a break in slope or curvature.

Nonparametric statistical measures were employed to establish the significance of relations among the pH and dissolved constituents. Although geochemical data commonly are described as log-normal (e.g. Kimball et al., 2004), the bimodal frequency distribution for pH, nonlinear trends in the log-probability plots for most elements (Fig. 2), and nonlinear associations between constituent concentrations (log scale) and pH (Fig. 3) indicate the

chemical data were not log-normal. Furthermore, some elements of interest were not detected in all samples (Table 1). Thus, all the data were rank transformed prior to the computation of correlation coefficients and associated principal components analysis.

The Spearman-rank correlation coefficient matrix, computed with SAS (1982a,b), for the hydrochemical data (Table 4) was organized to display elements within the same group in the periodic table, in order of increasing atomic mass. This organization facilitates the evaluation of relations between these elements and the primary field parameters including flow, Eh, pH, specific conductance, alkalinity and DO. Highly significant positive correlations are apparent between the elements within certain groups, such as the rare-earth elements (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U), the first-row transition metals (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn), the halides (Cl, Br, I), and some nonmetals (SO_4 , Se) (Table 4). Generally, the elements within these groups are consistently positively or negatively correlated with pH; the rare earths, first-row transition

metals, and SO₄ and Se are inversely correlated with pH, whereas the halides are positively correlated with pH. Other element groups, such as the alkalis, alkaline earths, the second and third row transition metals, other metals and the metalloids, have variable correlations with pH and among the constituent elements.

The alkaline earth elements did not exhibit consistent correlations within the group or with pH (Table 4). The concentration of Ca was not correlated with pH; Mg and Be were inversely correlated with pH; and Sr and Ba were positively correlated with pH. Calcium, Mg, Sr and Be concentrations were positively correlated with SO₄, whereas Ba

Table 4
Spearman-rank correlation coefficient (*r*) matrix for hydrochemical data on discharges from 140 abandoned coal mines in Pennsylvania, 1999

	Flow	Eh	pH	SC	ALK	DO	SO ₄	Se	Cl	Br	I	Li	Na	K	Rb	Cs	Be	Mg	Ca	Sr	Ba	B	Si	Ge	As	Sb	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
Flow	100																																			
Eh		100																																		
pH			100																																	
SC				100																																
ALK					100																															
DO						100																														
SO ₄							100																													
Se								100																												
Cl									100																											
Br										100																										
I											100																									
Li												100																								
Na													100																							
K														100																						
Rb															100																					
Cs																100																				
Be																	100																			
Mg																		100																		
Ca																			100																	
Sr																				100																
Ba																					100															
B																						100														
Si																							100													
Ge																								100												
As																									100											
Sb																										100										
Ti																											100									
V																													100							
Cr																														100						
Mn																															100					
Fe																																100				
Co																																	100			
Ni																																		100		
Cu																																			100	
Zn																																				100
Zr																																				100
Nb																																				100
Mo																																				100
Pd																																				100
Cd																																				100
Hf																																				100
Ta																																				100
W																																				100
Re																																				100
Au																																				100
Al																																				100
Ga																																				100
In																																				100
Tl																																				100
Pb																																				100
Bi																																				100
Sc																																				100
Y																																				100
La																																				100
Ce																																				100
Pr																																				100
Nd																																				100
Sm																																				100
Eu																																				100
Gd																																				

Table 4 (continued)

Zr	Nb	Mo	Pd	Cd	Hf	Ta	W	Re	Au	Al	Ga	In	Tl	Pb	Bi	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U				
																																		Flow			
																																			Eh		
																																			pH		
																																			SC		
																																			ALK		
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																																			SO ₄		
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																																			Fe		
																																			Co		
																																			Ni		
																																			Cu		
																																			Zn		
100																																			Zr		
	100																																		Nb		
		100																																	Mo		
			100																																Pd		
30				-51	-36	100																													Cd		
43			-40	-35	73	100																													Hf		
41				-22		60	61	100																											Ta		
			19	17	-29				100																										W		
17				36	34	-26				100																									Re		
											100																								Au		
39				-50	-38	87	83	66		-25																										Al	
47				-40	-18	65	60	59			62	100																								Ga	
48				-22		51	53	57			65	34	100																							In	
33				-33	-20	65	66	50			74	38	57	100																					Tl		
24				-47	-32	77	51	43	30	-41	74	41	42	54	100																				Pb		
																																				Bi	
				46												100																				Sc	
44				-17	-17	50	70	62			68	43	63	57	38		100																		Y		
42				-47	-41	81	90	66		-18	94	67	59	74	59			70	100																La		
40				-52	-46	89	78	60		-27	90	72	52	62	75				54	88	100														Ce		
40				-52	-45	89	82	63		-24	93	72	56	66	72					59	92	99	100												Pr		
41				-51	-45	89	83	63		-22	93	71	57	67	71					61	93	98	100	100											Nd		
41				-51	-44	88	84	63		-21	94	71	58	68	69						63	95	97	99	100	100									Sm		
41				-50	-44	86	87	65		-20	95	68	59	71	66						66	97	94	97	98	99	100								Eu		
40				-50	-44	85	87	64		-19	95	67	60	72	64						67	98	93	96	97	98	100	100							Gd		
41				-49	-44	84	89	65		-20	95	67	60	73	63						68	99	92	95	96	97	99	100	100						Tb		
41				-48	-43	83	89	66		-20	95	65	60	74	63						69	99	90	93	95	96	99	99	100	100					Dy		
41				-48	-43	82	89	66		-21	95	65	60	74	63						69	99	90	93	94	96	98	99	100	100	100					Ho	
41				-48	-42	82	89	67		-21	95	65	60	74	63						70	99	89	93	94	95	98	99	99	100	100	100				Er	
41				-48	-43	83	89	67		-23	96	66	61	74	65						69	99	90	93	94	96	98	99	99	100	100	100				Tm	
40				-49	-42	83	88	67		-23	96	66	61	74	67						68	99	90	93	95	96	98	98	99	99	100	100	100				Yb
41				-50	-41	83	88	68		-23	96	66	62	73	68						68	98	91	94	95	96	98	98	99	99	99	100	100	100			Lu
41				-50	-40	84	88	68		-23	96	66	63	74	69						68	98	91	94	95	96	97	98	98	99	99	99	100	100	100		Th
41				-28	-17	58	52	63		-18	72	46	68	50	52	26					62	63	63	64	64	63	64	64	64	65	65	66	66	67	67	100	U
35						27	46	42			46	23	52	50							55	52	29														

(Table 2, Fig. 2) as a framework to describe potential similarities, differences, and correlations among the element concentrations in CMD samples. However, classification of the data with this framework could bias interpretations by establishing boundaries where commonalities exist.

A principal components analysis (PCA) model, computed with SAS (1982a,b), was used to evaluate multivariate correlations among the elements (Table 5) without prior classification of the CMD samples. The goal was to identify the environmental factors that could explain the primary element asso-

Table 5
Principal components analysis of factors controlling the chemistry of coal-mine drainage in Pennsylvania

Constituent	Factor 1: "low pH"	Factor 2: "Sulfate"	Factor 3: "Manganese"	Factor 4: "Tungsten"	Factor 5: "Brine"	Factor 6: "Gold"	Communalities
Aluminum (Al)	96	13	1	5	-8	14	0.96
Zinc (Zn)	95	-4	17	9	-11	2	0.95
Cadmium (Cd)	93	-9	16	-1	2	-13	0.92
Beryllium (Be)	93	7	12	20	-12	10	0.95
Neodymium (Nd)	93	13	18	6	-3	3	0.92
Ytterbium (Yb)	93	23	12	9	-10	9	0.95
Europium (Eu)	92	23	12	3	-7	4	0.93
Lanthanum (La)	91	-1	27	12	-2	1	0.92
Redox potential (Eh)	90	-14	-1	0	-11	6	0.84
Yttrium (Y)	89	33	15	2	-11	6	0.94
Nickel (Ni)	88	10	32	15	-13	2	0.92
Copper (Cu)	83	-6	7	-28	20	-9	0.83
Vanadium (V)	83	6	13	-6	14	1	0.74
Cobalt (Co)	83	7	38	21	-19	2	0.91
Lead (Pb)	81	-31	-4	31	2	4	0.85
Hafnium (Hf)	80	33	15	-6	-15	6	0.80
Thallium (Tl)	73	37	-17	4	0	0	0.71
Thorium (Th)	67	3	8	0	0	50	0.70
Scandium (Sc)	62	52	-4	-2	-8	32	0.77
Selenium (Se)	49	22	13	-28	40	-25	0.61
Sodium (Na)	-54	45	-30	-11	52	-11	0.88
Chloride (Cl)	-60	16	-13	2	53	-2	0.68
pH (pH)	-92	5	-8	-12	14	-9	0.90
Sulfate (SO ₄)	25	85	34	-8	8	-5	0.92
Specific conductance (SC)	11	83	23	-19	30	-3	0.88
Iron (Fe)	15	81	10	22	-8	25	0.81
Calcium (Ca)	-8	81	28	-26	-4	-21	0.85
Rubidium (Rb)	17	80	11	39	2	7	0.84
Acidity (Acid)	45	77	5	13	-1	21	0.85
Potassium (K)	-28	74	-5	13	16	-17	0.70
Germanium (Ge)	4	70	3	0	30	25	0.65
Strontium (Sr)	-42	70	-13	-18	15	-12	0.75
Titanium (Ti)	50	67	14	-30	-7	16	0.84
Lithium (Li)	58	63	20	14	3	7	0.80
Iodine (I)	-38	62	5	11	47	-1	0.76
Silicon (Si)	61	61	-13	-5	-11	22	0.82
Arsenic (As)	-55	58	3	9	9	19	0.69
Uranium (U)	40	57	-18	-19	0	19	0.59
Boron (B)	-33	54	-43	-48	24	-7	0.88
Barium (Ba)	-37	-59	-15	36	24	-7	0.69
Manganese (Mn)	43	25	75	17	-16	8	0.87
Magnesium (Mg)	14	55	70	-6	-8	-14	0.84
Gallium (Ga)	62	16	62	-7	22	0	0.85
Tungsten (W)	12	-7	-8	68	8	-10	0.51
Cesium (Cs)	25	28	35	67	18	0	0.74
Bromine (Br)	-47	49	-25	6	55	-16	0.86
Gold (Au)	-4	10	-5	-7	-8	69	0.50
Zirconium (Zr)	36	24	30	-6	39	44	0.63
Eigenvalue	21.25	10.21	2.47	1.92	1.70	1.15	
Variance explained	19.22	10.38	3.01	2.29	2.13	1.66	38.70
Cumulative percent variance explained:	44.26	65.52	70.68	74.67	78.21	80.61	

Varimax rotation factor pattern for rank-transformed data (SAS, 1982b); minimum eigenvalue ≥ 1 ; loading values multiplied by 100 and rounded; shading indicates significant loadings ($p < 0.0001$).

ciations. The data for all 140 CMD samples were used in the PCA analysis. The Spearman-rank correlation coefficient matrix (Table 4) provided the input for the PCA model; however, those constituents that were below detection in more than 10% of the samples, including alkalinity, were excluded. Furthermore, to avoid producing a PCA model that mainly indicated the rare earths were strongly associated with one another, only a subset of the rare-earth elements was included in the PCA model. The final model, after varimax rotation, indicated the data could be adequately described by six principal components or factors (Table 5). This PCA model explained more than 80% of the data variability. Following the example of Kimball et al. (2004), standardized scores for individual samples were computed for each of the six PCA factors and then plotted with the scaled loadings of significant constituents against other PCA factors (Fig. 10). These scores indicate how well the sample variability can be explained by the PCA models.

Factor 1 of the PCA model explains 44.26% (19.22/38.70) of the data variability and was identified as the “low pH” factor (Table 5, Fig. 10A). On factor 1, pH was strongly negatively loaded whereas the Eh and concentrations of Al, Zn, Cd, Be, Nd, Yb, and many other metals, metalloids, and rare earths were strongly positively loaded. Concentrations of As, Sr, Na, Cl, I and Br were negatively loaded on factor 1. Sulfate and Fe were not loaded on this factor. Factor 1 explains the variability of dissolved Al and other trace-metal and rare-earth concentrations that were elevated at low pH but not at near-neutral pH; concentrations of these con-

stituents are controlled by solubility and sorption reactions and are sensitive to pH variations. The negative loading of As, Na and halides on this factor results because concentrations of these elements were elevated in high-pH, low-Eh samples. These constituent associations could indicate As mobilization under reducing conditions, possibly because of interactions with deep, saline ground water. Sulfate and Fe were not loaded on this factor because neither SO_4 nor Fe concentrations varied substantially over the range of pH (Fig. 3). Bituminous and anthracite CMD samples had similar scores on factor 1 reflecting their similar ranges in pH and associated relations between pH and constituent concentrations.

Factor 2 of the PCA model explains 10.38% of the data variability and was identified as the “sulfate” factor (Table 5, Fig. 10A). Sulfate, Fe, Ca, Mg, Sr, Rb, K, Li, Si and As were strongly positively loaded, whereas Ba was negatively loaded on factor 2. Generally, factor 2 explains the variability of SO_4 , Fe, Ca and other major constituent concentrations that are poorly correlated or not correlated with pH. Constituents that were positively loaded on this factor tend to exhibit high concentrations at acidic and near-neutral pH conditions and are not sensitive to pH variations. The negative loading of Ba on this factor results because of its negative correlation with SO_4 , probably because of solubility control of Ba by barite at high SO_4 concentrations (Cravotta, 2008). Generally, the bituminous CMD samples had larger scores on factor 2 than anthracite CMD samples, reflecting higher concentrations of

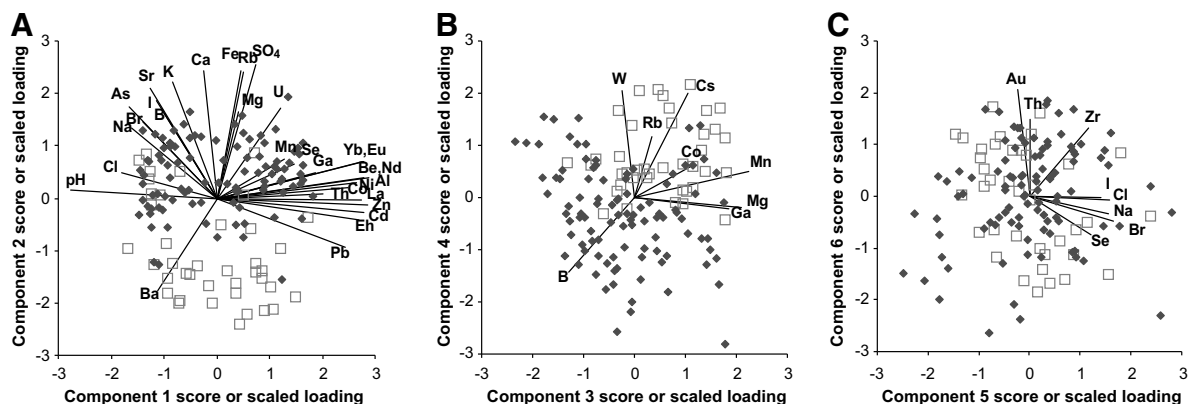


Fig. 10. Biplots of principal component scores and loadings of dissolved elements for 140 coal-mine discharge samples, Pennsylvania, 1999: (A), “factor 1 – low pH” and “factor 2 – sulfate”; (B), “factor 3 – manganese” and “factor 4 – tungsten”; (C), “factor 5 – brine” and “factor 6 – gold”. Element loadings are shown only if loadings are significant on one of the two plotted principal components (Table 5 shaded cells). Open squares, anthracite CMD; solid diamonds, bituminous CMD.

SO₄ and other dissolved solids in the bituminous samples (Fig. 10A).

Factor 3 of the PCA model explains 3.01% of the data variability and was identified as the “manganese” factor (Table 5, Fig. 10B). Manganese, Mg, Ga and Co were positively loaded, whereas B was negatively loaded on factor 3. Generally, factor 3 identifies constituents that are not strongly correlated with pH or SO₄ concentrations. Constituents that were positively loaded on this factor could be associated with the dissolution of impure carbonate minerals such as ankerite or mangano-siderite or the dissolution of Mn-oxide phases. Most bituminous CMD had lower scores on factor 3 than anthracite CMD (Fig. 10B). Anthracite CMD had greater median concentrations of Mn than bituminous CMD but comparable concentrations of Mg and Ga (Table 2).

Factor 4 of the PCA model explains 2.29% of the data variability and was identified as the “tungsten” factor (Table 5, Fig. 10B). Tungsten, Cs and Rb were positively loaded, whereas B was negatively loaded on factor 4. Most bituminous CMD samples had lower scores on factor 4 than anthracite CMD (Fig. 10B). Anthracite CMD had greater median concentrations of W and Cs than bituminous CMD (Table 2).

Factor 5 of the PCA model explains 2.13% of the data variability and was identified as the “brine” factor (Table 5, Fig. 10C). Chloride, I, Br, Na, Se and Zr were positively loaded on factor 5. Bituminous CMD samples had a wider range of scores on factor 5 than anthracite CMD (Fig. 10C). Bituminous CMD had greater median concentrations of halogens and Na than anthracite CMD (Table 2). Zirconium, which is relatively insoluble, may be mobilized by the formation of complexes with Cl or other halogens.

Factor 6 of the PCA model explains 1.66% of the data variability and was identified as the “gold” factor (Table 5, Fig. 10C). Gold, Th and Zr were positively loaded on factor 6. These constituents are highly insoluble, but tend to be present in the same CMD samples. Bituminous CMD samples had a wider range of scores on factor 6 than anthracite CMD (Fig. 10C).

3.5. Implications for aquatic ecology, CMD treatment, and resource recovery

Dissolved constituents in CMD samples result from: (1) weathering of pyrite and other minerals

associated with coal and associated rocks under oxidizing conditions, and (2) reductive dissolution of oxides along flow paths of deep, reducing ground waters. Although few constituents in CMD are as mobile as SO₄, a wide variety of potentially toxic trace constituents commonly are elevated in CMD compared to average river water and aquatic protection criteria (Fig. 3, Tables 1 and 2). Most of the harmful constituents tend to partition into Fe-rich sediments that accumulate at the CMD discharge or downstream locations. Such ochres precipitated by mine discharges can accumulate in wetlands and other accessible water bodies where they are subject to ingestion by aquatic organisms. Although sediment-quality criteria have been recommended for protection of benthic organisms (MacDonald et al., 2000), the USEPA has not yet adopted sediment-quality standards.

Utilization of the CMD to sustain aquatic life or for domestic water supply generally would require removal of SO₄, Fe, Mn, Al, Be, As and/or Zn. None of the 140 CMD samples met USEPA criteria for protection of freshwater organisms; the samples exceeded the criteria continuous-concentration values for Al (120 µg L⁻¹), Fe (1000 µg L⁻¹), Co (19 µg L⁻¹), Ni (52 µg L⁻¹), and/or Zn (120 µg L⁻¹). Furthermore, only three samples met permitted mine-effluent criteria for pH (6–9), net acidity (<0), SO₄ (<250 mg L⁻¹), Fe (<7 mg L⁻¹), Mn (<5 mg L⁻¹) and Al (<0.75 mg L⁻¹). Only one sample met drinking-water standards for SO₄ (<250 mg L⁻¹), Fe (<0.3 mg L⁻¹), Mn (<0.05 mg L⁻¹), Al (<0.2 mg L⁻¹) and other inorganic constituents. Ten percent of the samples exceeded primary drinking-water standards for As (<10 µg L⁻¹), and 33% exceeded those for Be (<4 µg L⁻¹). Nevertheless, all 140 samples met primary or secondary drinking-water standards for NO₃ (<10 mg L⁻¹), F (<4 mg L⁻¹), Sb (<6 µg L⁻¹), Ba (<2000 µg L⁻¹), Cr (<100 µg L⁻¹), Cu (<1000 µg L⁻¹), Pb (<15 µg L⁻¹), Hg (<2 µg L⁻¹), Se (<50 µg L⁻¹), Ag (<100 µg L⁻¹) and Tl (<2 µg L⁻¹).

Treatment of CMD could be conducted with an aim to recover the dissolved metals, rare earths, or other constituents for beneficial use and to meet water-use standards. The recovery of potentially valuable elements from CMD may be possible utilizing various physical and chemical methods. Passive treatment of the CMD may be effective for the recovery of Fe oxide (Hedin et al., 1994; Hedin, 2003), whereas active treatment methods may be

appropriate for the recovery of other elements (Che-ney and Swinehart, 1998). Elevated concentrations of rare earths and certain transition metals in CMD warrant investigation for their recovery and marketing. Nevertheless, quantities of the target elements or minerals must be adequate to justify the expense associated with their separation and recovery from CMD.

The compositions of ochres from 10 CMD sites varied with the pH of the CMD, with greater concentrations of trace impurities associated with higher pH samples (Table 3). Trace-metal enrichment of the ochres with increased pH is consistent with expectations for sorption control of dissolved metals by hydrous ferric oxides (e.g. Dzombak and Morel, 1990; Kairies et al., 2005). However, such impurities in the ochres could affect the potential for their use as pigment. Hedin (2003) has suggested that the production of relatively pure Fe oxides needed for pigment is favored by Fe-laden CMD with near-neutral pH, because the near-neutral effluents tend to be poor in Al as indicated by data for this study (Fig. 3E, Table 4). Although Al and Ca are undesirable in the ochres used for Fe oxide pigments, the effect of trace impurities on the pigment quality is unknown.

4. Summary and conclusions

This report summarizes data on the flow volume and chemical composition of 140 abandoned coal-mine discharge (CMD) sites that were sampled in 1999 in the Anthracite and Bituminous Coalfields of Pennsylvania. Clean-sampling and low-level analytical methods were used to document concentrations and instantaneous loads of dissolved major and trace constituents and to identify potential opportunities for CMD remediation and resource recovery. Flows ranged from 0.028–2210 L s⁻¹. The pH of the 140 CMD samples ranged from 2.7–7.3. Net acidity concentrations, excluding contributions from dissolved CO₂, ranged from –326–1587 mg L⁻¹ as CaCO₃. Alkalinity ranged from 0 (pH < 4.4; 50 samples) to 510 mg L⁻¹ as CaCO₃. Concentrations of dissolved SO₄, Fe, Al, and Mn ranged from 34 to 2000 mg L⁻¹, 0.046–512 mg L⁻¹, 0.007–108 mg L⁻¹, and 0.019–74 mg L⁻¹, respectively. Silicon concentrations ranged from 2.7 to 31.3 mg L⁻¹. The alkalinity was positively correlated with pH; acidity, Al and Si concentrations were inversely correlated with pH; SO₄ and Mn concentrations had inverse, but poor correlations with

pH; and Fe was not correlated with pH. Median concentrations of DO generally were low (<2 mg L⁻¹) throughout the range of pH, consistent with the predominance of dissolved Fe^{II} and Mn^{II} species compared to their oxidized species.

Calcium and Mg were the dominant alkaline earths with median and maximum concentrations of 88 and 410 mg L⁻¹ and 38 and 210 mg L⁻¹, respectively. Maximum concentrations were 3.6 mg L⁻¹ for Sr, 0.052 mg L⁻¹ for Be and 0.039 mg L⁻¹ for Ba. The concentration of Ca was not correlated with pH; Mg and Be were inversely correlated with pH; and Sr and Ba were positively correlated with pH. Calcium, Mg, Sr and Be concentrations were positively correlated with SO₄, whereas Ba concentration was inversely correlated with SO₄. Positive correlations between the cations and SO₄ could result from enhanced dissolution of minerals containing these elements by H₂SO₄ and the consequent formation of SO₄ complexes, whereas the inverse correlation between Ba and SO₄ could result from Ba solubility control by the precipitation of barite.

The dominant alkalis were Na and K with median and maximum concentrations of 15 and 500 mg L⁻¹ and 2.8 and 12 mg L⁻¹, respectively. Maximum concentrations of Li, Rb and Cs were 390, 28, and 0.85 µg L⁻¹, respectively. Chloride was the dominant halide, with a median concentration of 7.3 mg L⁻¹ and a maximum of 460 mg L⁻¹. The CMD samples with elevated Cl typically had the highest concentrations of Na, K, Br and I, possibly reflecting influence from deep brines. Bromide and I were detected at concentrations greater than 0.003 mg L⁻¹ in most samples; maximum concentrations of Br and I were 0.6 and 0.1 mg L⁻¹, respectively. Fluoride was detected at a concentration greater than 0.1 mg L⁻¹ in only three samples.

Except for S, the nonmetal elements (C, N, O, P, S, Se) were not elevated in the CMD samples compared to uncontaminated ground water. Phosphate and NO₃ concentrations were less than detection limits of 0.001 as P and 0.03 mg L⁻¹ as N in most of the CMD samples; maximum concentrations were 2.8 and 0.15 mg L⁻¹, respectively. Although low concentrations of dissolved elements could reflect limited abundance or solubility of source minerals, low concentrations of PO₄ are consistent with its adsorption or precipitation with Fe and Al compounds, whereas low concentrations of NO₃ are consistent with suboxic conditions and potential for NO₃ reduction by Fe^{II} and/or sulfide.

Selenium had a maximum concentration of $7.6 \mu\text{g L}^{-1}$ and was detected at concentrations greater than $0.2 \mu\text{g L}^{-1}$ in 84% of the samples. Selenium concentrations were inversely correlated with pH and positively correlated Cu, Cd, Cr and V.

The metalloid elements (B, Si, Ge, As, Sb, Te) were ubiquitous but rarely elevated in the CMD samples. Arsenic had a median concentration of $1.7 \mu\text{g L}^{-1}$ and maximum concentration of $64 \mu\text{g L}^{-1}$ at a pH of 4.5 and DO of 0.3mg L^{-1} . Arsenic concentrations were positively correlated with pH, Cl, Br and I, and inversely correlated with DO and Eh. These constituent associations could indicate As mobilization under reducing conditions, possibly because of interactions with deep, saline ground water. Boron, Ge and Sb had median and maximum concentrations of 44 and $260 \mu\text{g L}^{-1}$; 0.07 and $0.57 \mu\text{g L}^{-1}$; and 0.01 and $0.43 \mu\text{g L}^{-1}$, respectively. Boron concentrations were positively correlated with pH, Na, K, Br, I and Cl and inversely correlated with Pb, Co, Ni and Zn. Tellurium concentrations were below the detection limit of $0.0002 \mu\text{g L}^{-1}$ in 98% of the CMD samples.

Concentrations of most trace metals and rare earths were inversely correlated with pH, consistent with sorption or solubility control mechanisms. Zinc, Ni and Co were the most abundant trace metals, in order of predominance, with median and maximum concentrations of 140 and $10,000 \mu\text{g L}^{-1}$; 85 and $3200 \mu\text{g L}^{-1}$; and 58 and $3100 \mu\text{g L}^{-1}$, respectively. Titanium, Cu, Cr, Pb and Cd, in order of predominance, had median and maximum concentrations of 5.8 and $28 \mu\text{g L}^{-1}$; 2.0 and $190 \mu\text{g L}^{-1}$; 1.2 and $72 \mu\text{g L}^{-1}$; 0.20 and $11 \mu\text{g L}^{-1}$; and 0.12 and $16 \mu\text{g L}^{-1}$, respectively. Gallium was detected at a concentration greater than $0.01 \mu\text{g L}^{-1}$ in 95% of the samples, with a maximum concentration of $7.3 \mu\text{g L}^{-1}$. Thallium was detected at a concentration greater than $0.006 \mu\text{g L}^{-1}$ in all the samples, with a maximum concentration of $1.5 \mu\text{g L}^{-1}$. Bismuth was detected at a concentration greater than $0.01 \mu\text{g L}^{-1}$ in 70% of the samples, with a maximum concentration of $0.35 \mu\text{g L}^{-1}$. Indium was detected at a concentration greater than $0.001 \mu\text{g L}^{-1}$ in 77% of the samples, with a maximum concentration of $0.34 \mu\text{g L}^{-1}$. Tin was less than the detection limit of $0.1 \mu\text{g L}^{-1}$ in 95% of the samples. Gold was detected at concentrations greater than $0.0005 \mu\text{g L}^{-1}$ in 97% of the samples, with a maximum of $0.0175 \mu\text{g L}^{-1}$. No samples had detectable concentrations of Hg, Os or Pt, and less than 1/2 of the samples had detectable Pd, Ag, Ru, Ta, Nb

or Re. The majority of samples had concentrations of Sc, Y, and associated rare-earth elements ranging from $0.01\text{--}1 \mu\text{g L}^{-1}$. Yttrium, Ce, Sc, Nd, La, Gd, Dy and Sm were the predominant rare earths, with median and maximum concentrations of 8.7 and $530 \mu\text{g L}^{-1}$; 6.6 and $370 \mu\text{g L}^{-1}$; 5.0 and $36 \mu\text{g L}^{-1}$; 4.9 and $260 \mu\text{g L}^{-1}$; 2.2 and $140 \mu\text{g L}^{-1}$; 1.8 and $110 \mu\text{g L}^{-1}$; 1.8 and $99 \mu\text{g L}^{-1}$; and 1.3 and $79 \mu\text{g L}^{-1}$, respectively.

Generally, the CMD samples in this study were rich in rare-earth elements and many transition metals but poor in most alkali, alkaline earth, halogen, and certain other elements compared to seawater. Compared with average concentrations in seawater, the CMD samples were enriched by 2–4 orders of magnitude with Fe, Al, Mn, Co, Be, Sc, Y and the lanthanide rare-earth elements, and one order of magnitude with Ni and Zn. Median concentrations of Sm and Eu in the CMD were more than 20,000 times the average for seawater. Median concentrations of Fe were more than 10,000 times the average for seawater, and median concentrations of Mn, Cr, Co, Ni and Zn were more than 10 times the average for seawater.

Treatment of CMD could be conducted with an aim to recover the dissolved metals, rare earths, or other constituents for beneficial use and to meet water-use standards. The recovery of potentially valuable elements from CMD may be possible utilizing various physical and chemical methods. Nevertheless, quantities of valuable elements or minerals must be adequate to justify the expense associated with the separation and recovery of specific constituents that may be obtained from competing, traditional sources that have established markets and less expense.

Utilization of the CMD to sustain aquatic life or for domestic water supply generally would require treatment to remove SO_4 , Fe, Mn, Al, Be, As and/or Zn. None of the 140 CMD samples met USEPA criteria for protection of freshwater aquatic organisms; the samples exceeded the criteria continuous-concentration values for Al, Fe, Co, Ni and/or Zn. Furthermore, only three samples met permitted mine-effluent criteria for pH, net acidity, SO_4 , Fe, Mn and Al. Only one sample met drinking-water standards for SO_4 , Fe, Mn, Al, and other inorganic constituents. Ten percent of the samples exceeded primary drinking-water standards for As, and 33% exceeded those for Be. Nevertheless, all 140 samples met primary or secondary drinking-water standards for NO_3 , F, Sb, Ba, Cr, Cu, Pb, Hg, Se, Ag and Tl.

To investigate quantities of Au and other potentially valuable constituents in aqueous and solid phases at CMD sites, 10 of the 140 sites with relatively large Au loading rates in 1999 were revisited in 2003. In 1999, these 10 sites had wide ranges of flows, pH, and concentrations of SO₄, Fe and Au. In 2003, the 10 sites had comparable flows, pH, SO₄ and Fe, but approximately one order of magnitude lower concentrations of Au, possibly an artifact of different analytical methods. With the exception of Au, the dissolved chemical concentrations and loading rates at these sites were comparable for the different years. This indicates hydrochemical stability at the sites and supports the expression of instantaneous loading rates, or transport, in mass units/a.

Assuming the instantaneous flow and concentration values in 1999 represent the annual averages at each of the 140 CMD sites, the median and maximum transport were computed to be 87,700 and 9,270,000 kg a⁻¹ for S, 15,500 and 1,250,000 kg a⁻¹ for Fe, 1580 and 216,000 kg a⁻¹ for Mn, and 650 and 509,000 kg a⁻¹ for Al, respectively. The transport of Ca, Mg, Na, K and Cl was of the same magnitude as S, Fe and Mn. Median and maximum transport for Co (32 and 6970 kg a⁻¹), Cr (0.31 and 22 kg a⁻¹), Ni (51 and 10,400 kg a⁻¹), and Zn (71 and 39,000 kg a⁻¹) were larger than those for rare-earth elements, such as Y (5.66 and 906 kg a⁻¹), Sc (3.65 and 279 kg a⁻¹), La (1.32 and 1180 kg a⁻¹), Eu (0.20 and 62.7 kg a⁻¹) and Sm (0.67 and 279 kg a⁻¹).

Ochre samples collected in 2003 at ten of the CMD sites were dominantly goethite with minor ferrihydrite or lepidocrocite. Although some of the ochres also contained quartz, kaolinite, muscovite and/or chlorite, probably derived as detritus, none of the samples for this study was Al rich. The ratio of element concentrations in the associated ochre and CMD samples revealed consistent trends for various element groups as a function of pH. With increased pH, the distribution of elements in the aqueous phase compared to the solid phase generally decreased. Although the distribution ratios for the alkali elements (Li, Na, K, Rb, Cs) and alkaline earth elements (Be, Mg, Ca, Sr, Ba) were larger than those for the transition metals, other metals, and rare earths, the ochres formed at higher pH tended to contain proportionally greater concentrations of most trace impurities than those formed at lower pH. This progressive enrichment of the ochres with impurities is consistent with the solubility control of

metals by hydroxides and the adsorption of dissolved elements by Fe oxides with increased pH.

Compared to concentrations in global average shale, the ochres were rich in Fe, Ag, As and Au, but they were poor in most other metals and rare earths. Despite relative enrichment in Au and other potentially valuable elements, the ochres were not enriched compared to commercial ore deposits mined for Au or other valuable metals. Although comparable to Fe ores in their composition, the ochres are dispersed and present in relatively small quantities at most coal-mine sites. The small size and widespread distribution of ochre deposits at abandoned coal mines could represent an obstacle to the recovery of the Fe oxide for commercial applications.

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