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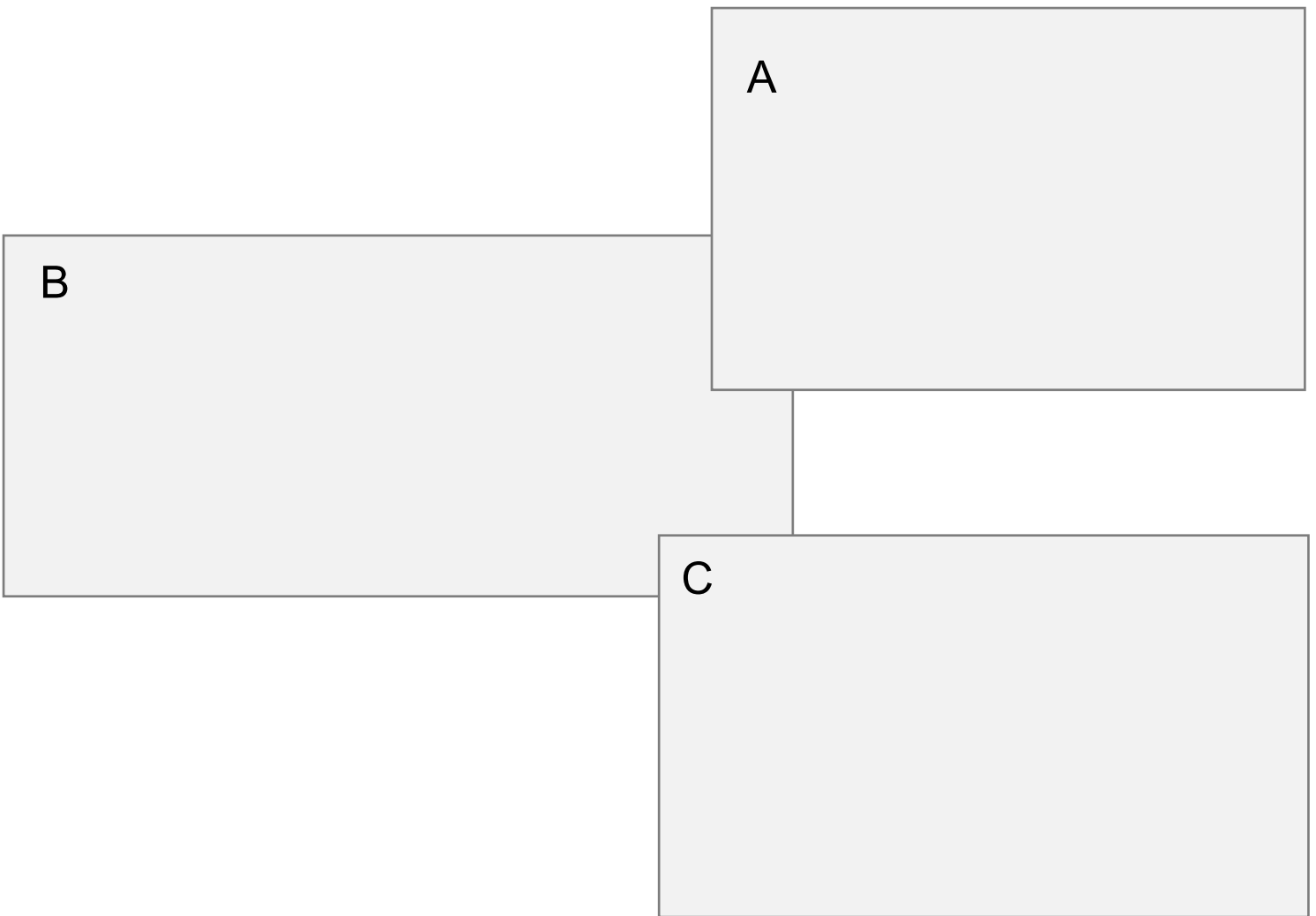
The Ohio Department of Natural Resources, Division of Mineral Resources Management

The Ohio Minelands Partnership

Water Quality and Geochemical Modeling of Water at an Abandoned Coal Mine Reclaimed With Coal Combustion By-Products

Water-Resources Investigations Report 02-4216





Front cover: A. Eroded Lower Kittanning (No. 5) coal and underclay at the Fleming abandoned mine site before reclamation.
B. Graded spoil and topsoil at the Fleming abandoned mine site during reclamation. PFBC by-product and compost are in piles in background.
C. Fleming abandoned mine site three years after reclamation (1997). Small buildings on upper left of photo are shelter houses where water-quality samples were collected from the six test watersheds.

Back cover: American Electric's Tidd Plant in Brilliant, Ohio, with the Ohio River in the foreground. (Photo courtesy of American Electric Power, Columbus, Ohio. Reproduced with permission.)

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By Ralph J. Haefner

U.S. Geological Survey Water-Resources Investigations Report 02-4216

Prepared in cooperation with
West Virginia University,
The Ohio Department of Natural Resources, Division of Mineral Resources Management, and
The Ohio Minelands Partnership

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

Multiply	By	To obtain
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
square foot (ft ²)	0.09290	square meter
square mile (mi ²)	2.590	square kilometer
acre	0.4047	square hectometer
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second
ton	0.9072	megagram

Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation: °F = 1.8(°C) + 32

Vertical datum: In this report, “sea level” refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Abbreviated water-quality units used in this report: Chemical concentrations and water temperature are given in metric units. Chemical concentration is given in milligrams per liter (mg/L) or micrograms per liter (µg/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. For concentrations less than 7,000 mg/L, the numerical value is approximately the same as for concentrations in parts per million.

Specific conductance of water is expressed in microsiemens per centimeter at 25 degrees Celsius (µS/cm). This unit is equivalent to micromhos per centimeter at 25 degrees Celsius (µmho/cm), formerly used by the U.S. Geological Survey.

Stable isotope ratios, as referenced to the Canyon Diablo Troilite, are indicated by use of the delta symbol (δ) and are expressed in parts per thousand (per mil).

Tritium concentration is expressed in tritium units (TU). One tritium unit is equal to one tritium atom per 10¹⁸ hydrogen atoms; in terms of radioactivity, it is equivalent to 3.24 picocuries per liter.

Water Quality and Geochemical Modeling of Water at an Abandoned Coal Mine Reclaimed With Coal Combustion By-Products

by Ralph J. Haefner

ABSTRACT

An abandoned coal mine in eastern Ohio was reclaimed with 125 tons per acre of pressurized fluidized bed combustion (PFBC) by-product. Water quality at the site (known as the Fleming site) was monitored for 7 years after reclamation; samples included water from soil-suction lysimeters (interstitial water), wells, and spring sites established down-gradient of the application area. This report presents a summary of data collected at the Fleming site during the period September 1994 through June 2001. Additionally, results of geochemical modeling are included in this report to evaluate the potential fate of elements derived from the PFBC by-product.

Chemical analyses of samples of interstitial waters within the PFBC by-product application area indicated elevated levels of pH and specific conductance and elevated concentrations of boron, calcium, chloride, fluoride, magnesium, potassium, strontium, and sulfate compared to water samples collected in a control area where traditional reclamation methods were used. Magnesium-to-calcium (Mg:Ca) mole ratios and sulfur-isotope ratios were used to trace the PFBC by-product leachate and showed that little, if any, leachate reached ground water. Concentrations of most constituents in interstitial waters in the application-area decreased during the seven sampling rounds and approached background concentrations observed in the control area; however, median pH in the application area remained above 6, indicating that some acid-neutralizing capacity was still present. Although

notable changes in water quality were observed in interstitial waters during the study period, quality of ground water and spring water remained poor. Water from the Fleming site was not potable, given exceedances of primary and secondary Maximum Contaminant Levels (MCLs) for inorganic constituents in drinking water set by the U.S. Environmental Protection Agency. Only fluoride and sulfate, which were found in higher concentrations in application-area interstitial waters than in control-area interstitial waters, could be related to the PFBC by-product. Concentrations of arsenic, lead, and selenium typically were at or below the detection limits (generally 1 or 2 micrograms per liter).

Elements detected at elevated concentrations in PFBC by-product application-area interstitial waters were not evident in downgradient ground water or spring water. Dilution of leachate by ground water was confirmed with a mixing model generated by the computer code NETPATH. Additionally, thermodynamic modeling of the chemical composition of water samples by use of the computer code PHREEQC indicated favorable conditions for precipitation of secondary minerals in the unsaturated zone and in aquifer materials. Because of low application rates of PFBC by-product and precipitation and sorption of elements in the unsaturated zone, it is improbable that concentrations of any toxic elements of concern (arsenic, lead, or selenium) will exceed drinking-water standards at this site or other sites where similar volumes of PFBC by-products are used.

INTRODUCTION

The Clean Air Act of 1990 directs coal-burning utilities to reduce sulfur emissions by burning low-sulfur coal or by retrofitting with scrubbers that use a sorbent (limestone or dolostone) to remove sulfur from flue gases. The flue-gas desulfurization (FGD) process eliminates up to 99 percent of gaseous sulfur emissions, but it produces a solid by-product. Butalia and Wolfe (2000) estimated that, in Ohio, as much as 10 million tons of FGD and other coal-combustion by-products (CCBs) are generated each year. Eighty percent of CCBs are placed in landfills or surface impoundments, and the remaining 20 percent are used in application technologies. The costs (including trucking and landfilling fees) associated with disposal of CCBs are passed directly to the customers of the electric-power utility.

Beneficial uses are being sought for CCBs, including use as a soil amendment in the reclamation of abandoned coal mines. Many abandoned coal mines in Ohio and throughout the Appalachian coal region are characterized by acid mine drainage (AMD). These mines typically require alkaline amendments such as crushed limestone or agricultural lime to raise the pH of soil so that vegetation can be reestablished (Barton, 1978). Abandoned mine sites also commonly have very little topsoil, and what topsoil remains after mining may be of poor quality; so, soil amendments may be necessary to improve soil texture and water-holding properties. FGD by-products are desirable in this application because they are alkaline and typically have high calcium carbonate equivalents (Stehouwer and others, 1996). Additionally, some CCBs not only have a texture similar to that of silt loam but also may provide necessary elements to nutrient-deficient soils (Stehouwer and others, 1996). Therefore, a potential use exists for CCBs as a soil amendment. Before beneficial uses of FGD by-products will be supported by regulatory agencies and the electric-power industry, however, environmental data must be collected to show potential influences on water quality in the environmental settings of interest. Specifically, questions remain regarding the transport and fate of major elements such as sulfur and trace elements such as arsenic, lead, selenium, and boron that may be derived from the FGD by-product.

In late 1994, an abandoned surface coal mine in eastern Ohio (hereafter referred to as the "Fleming site") was reclaimed with pressurized fluidized bed combustion (PFBC) by-product. Although the PFBC by-product used in this study is not strictly an FGD by-product, chemical reactions in the FGD process are similar to the PFBC process; thus, the PFBC by-product is chemically and physically comparable to FGD by-products. In addition to the PFBC by-product, yard-waste compost was added to the site to provide organic matter for establishment of vegetation. Site instrumentation and monitoring of the chemical character of unsaturated-zone water (hereafter referred to as "interstitial water"), ground water, and spring water began soon after

reclamation to determine the mobility and fate of elements derived from the PFBC by-product. Grants from the Combustion Byproducts Recycling Consortium (a program of West Virginia University in cooperation with the U.S. Department of Energy National Energy Technology Center), the Ohio Department of Natural Resources Minerals Resources Management Division, and the Ohio Minelands Partnership provided support for collection and analysis of data presented in this report.

Purpose and scope

This report documents the effects of a surface application of dry PFBC by-product on water quality in the reclamation of an abandoned coal mine in Tuscarawas County, eastern Ohio. To evaluate the effects of addition of PFBC by-product and (or) reclamation on water, this report presents a summary of data collected from interstitial water, ground water, and spring water during the period September 1994 through June 2001. Additionally, results of geochemical modeling are included to evaluate the potential fate of elements derived from the PFBC by-product. The report is limited to description of the site hydrology and its related water chemistry and to geochemical modeling of solid-phase and water samples.

Acknowledgments

Many individuals and agencies contributed to this work over the 7-year span of the project. In earlier years, the Ohio Department of Development Coal Development Office, Ohio Edison, Dravo Lime Company, The Ohio State University, American Electric Power, the U.S. Bureau of Mines, and the U.S. Department of Energy (Pittsburgh Energy Technology Center) were involved in the planning and financial support of the project. Special thanks go to the landowners, Donald Domer, Walter and Julie Randolph, and Lee Baumberger, for allowing data-collection activities at the Fleming site.

PREVIOUS INVESTIGATIONS

This report represents the culmination of a 7-year effort by the U.S. Geological Survey and The Ohio State University. Data and previous interpretations have been published in a series of technical reports, including Stehouwer and others (1996), Haefner (1998), and Dick and others (1999). The publication by Stehouwer and others (1996) includes chemical and physical characterization of PFBC by-product and other CCBs in Ohio. It also includes the results of greenhouse studies in which plant growth and leachate quality were examined with respect to varying application rates of CCBs. The reports by Haefner (1998) and Dick and others

(1999) provide site characterization and water-quality data from the first 3 years of monitoring. These three reports are referenced extensively throughout this publication and are available for inspection at the U.S. Geological Survey Ohio District Office in Columbus, Ohio.

Abandoned mine sites have been reclaimed with soil amendments for many years in Ohio and throughout the United States. (See, for example, Skousen and others, 1987.) The most common approach is to regrade the land to the approximate premining topographic contour, replace topsoil with soil taken from a borrow area, and apply agricultural lime (CaO) if the soil is too acidic. The land is then seeded with acid-tolerant plants (such as fescue) to encourage revegetation. Trees (pine and oak) also have been used in revegetation (Cordell and others, 2001). Other surface amendments include gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), papermill by-products, and waste materials derived from industrial processes and sewage sludge (Logan, 1992).

Cunningham and Jones (1990) and Sedam and Francy (1993) describe the geochemistry of water in the Appalachian coal region of Ohio. These publications document elevated concentrations of iron and sulfur derived from the oxidation of pyrite contained in the coals and surrounding sedimentary rocks. Many other elements also are found in elevated concentrations in water from this region, including aluminum, chromium, manganese, nickel, and zinc. Surface-water pH in the Appalachian coal region is typically below 5 because of the hydrolysis reaction involved with the oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}). The reaction results in precipitation of iron hydroxide (“yellow boy”) and the liberation of hydronium ions (H^+). The low pH allows many pH-sensitive elements to remain in solution, resulting in elevated total dissolved solids concentrations and elevated specific conductance.

As the Clean Air Act of 1990 dictates, coal-burning utilities are required to reduce sulfur emissions. This has created a large amount of solid CCBs that are primarily disposed of in landfills. Monitoring at a FGD by-product landfill in Conesville, Ohio, indicated that leachate had elevated concentrations of sulfate and chloride (Hupe and Dziubek, 1984). This landfill was used to dispose of wet FGD by-products (as opposed to the dry PFBC material used in this study). The primary difference between wet FGD by-products and dry FGD by-products is that most of the sulfur in wet FGD by-products is present as sulfite (SO_3^{2-}), whereas sulfur in dry FGD (and PFBC) by-products is present as sulfate (SO_4^{2-} ; Stehouwer and others, 1996). Water samples collected downgradient from the Conesville landfill over a 3-year period intermittently exceeded the U.S. Environmental Protection Agency National Primary Drinking Water Regulations for arsenic, cadmium, chromium, and lead, and the National Secondary Drinking Water Regulations for sulfate (from oxidation of sulfite), total dissolved solids, and pH. Therefore, precedent exists for water-quality monitoring at sites that receive high volumes of these materials.

In light of available environmental data on FGD by-products, additional applications are still being sought for abandoned mine reclamation, for agricultural uses, and for civil-engineering applications (Butalia and Wolfe, 2000; Stewart, 1997; Stehouwer and others, 1996). With regard to reclamation of abandoned coal mines, several efforts have been documented in Ohio. Stuart and Novak (2000) investigated the use of FGD by-products as a mine seal along a highwall left by coal mining. The main purpose of the project was to “remine” the area for remaining coal reserves and then eliminate AMD by reducing acidic discharge from mine portals left in the coal at the base of the highwall. The FGD by-product mine seal was successful in that acidic discharge from the mine was greatly decreased after reclamation. Correspondingly, iron and sulfate loading decreased during the study period. For this application, the use of FGD by-products as an impermeable seal precluded issues with degraded water quality.

Use of FGD by-products as a grout in an underground mine in eastern Ohio was described by Mafi and others (1997). The objective of the project was to fill the mine void with FGD by-product grout and thereby limit oxygen availability and prevent pyrite oxidation. Although the initial volume of discharge from the mine decreased, a new hydrologic equilibrium was established that allowed water to flow elsewhere with little improvement in water quality. FGD by-products also were used to cap a coal refuse pile at the Rehoboth mine site in southeastern Ohio (Mafi, 1996). Slope-stability and erosion problems developed at the site after reclamation, compounded by elevated concentrations of boron at downgradient monitoring sites.

The PFBC by-product used in this study was from an experimental test burn at a research facility in eastern Ohio; therefore, no other mine-reclamation applications of this or other PFBC by-products were identified in the literature. The mineralogy, solid-phase chemistry, and physical properties of the PFBC by-product were studied and described in detail by Stehouwer and others (1996); however, a short description of the solid-phase composition also will be given here. Grab-samples of the PFBC by-product and yard-waste compost were obtained immediately before application from piles of the materials stored onsite. The PFBC by-product was dominated by calcium, magnesium, sulfate, and aluminum (table 1). Calcium and magnesium are derived from the dolomitic sorbent, resulting in a calcium carbonate equivalence as high as 60 percent (Stehouwer and others, 1996). Sulfate originates from the coal (the Pittsburgh No. 8) that was burned as the fuel source. The aluminum found in the PFBC by-product is derived from the fly-ash component of the by-product and originates from the clays and shales that are commonly associated with coal seams. Trace-element analysis of the PFBC by-product indicate that it contains elevated arsenic, boron, barium, chromium, nickel, lead, and selenium concentrations. For comparison, table 1 also includes maximum concentrations of trace

elements in spoil and aquifer materials obtained from core samples reported in Dick and others (1999) and the composition of composted yard waste applied at the site. Boron was not quantified in the spoil and aquifer materials in this study; however, Botoman and Stith (1978) published boron analyses from Ohio coals, and their maximum value is included in table 1. These results indicate that, for many constituents, concentrations of elements can be higher in the mine spoil, aquifer materials, and compost than they are in the PFBC by-product. Comparison of PFBC by-product with the surrogate analysis of boron in coal from Botoman and Stith indicate that boron is found at greater concentrations in the PFBC by-product than in the coals.

Table 1. Solid-phase composition of PFBC by-product and maximum concentrations of constituents in mine spoil and aquifer materials from the Fleming abandoned mine site, Tuscarawas County, Ohio

[Modified from Haefner, 1998; --, not applicable]

Constituent	PFBC by-product	Yard-waste compost	Maximum concentration in spoil and aquifer materials
Major Elements (weight percent)			
Al	3.3	3.8	--
Ca	18	3.6	--
Fe	4.4	3.3	--
K	0.59	1.5	--
Mg	9.5	0.93	--
Mn	0.01	2.1	--
Na	0.10	0.52	--
S (as SO ₄)	4.9	<0.05	--
Total C	4.5	13	--
C, Organic	0.73	13	--
C, as CaCO ₃	3.8	0.41	--
Trace Elements (parts per million)			
As	75	11	91
B	190	92	120 ^a
Be	3	1	9
Ba	150	400	730
Cd	<2	<2	<2
Cr	37	290	210
Ni	23	37	100
Pb	15	110	110
Se	1.3	6	21.5
Sr	160	130	720

^a Botoman and Stith, 1978.

Although applied at a rate of only 50 tons per acre over a 7-acre area, the compost may have been a significant source of chromium. Specific details of the source of materials used in the compost were not available, but compost typically contains grass clippings, leaves, and shredded wood from sources that might include treated pallets and telephone poles. The treatment of the wood involves

chemicals that commonly contain trace elements including chromium. No further investigation was done regarding the organic chemistry of the compost; however, it should be noted that transport of elements such as cadmium, chromium, and copper might be enhanced by organic complexation.

STUDY METHODS

To investigate the effectiveness of a CCB as a mine-spoil reclamation amendment, an abandoned surface coal mine was reclaimed with PFBC by-product in 1994. Workers at The Ohio State University, School of Natural Resources, tested the mine spoil from the site and analyzed the PFBC by-product to determine that the mine spoil required approximately 125 tons per acre of PFBC by-product to attain a pH of 7 (Stehouwer and others, 1996). In addition, the mine spoil lacked organic matter necessary for successful plant growth, so approximately 50 tons per acre of yard-waste compost were added at the time of PFBC by-product application. The PFBC by-product and compost were applied to the regraded surface and were disked into the spoil during reclamation. The depth of incorporation was about 6 to 12 in.

The Fleming site was instrumented after reclamation in late 1994 and in early 1995 so that water quality could be assessed through time. Data- and sample-collection activities included the following:

- Four core holes were drilled to define site stratigraphy and obtain lithologic samples for chemical analysis.
- A precipitation station was established to collect wet and dry deposition for chemical analysis during a 1-year period (1995).
- Surface- and borehole-geophysical surveys were done to estimate the thickness of a surficial clay layer and further define site stratigraphy.
- Thirty-five soil-suction lysimeters in five clusters were installed to monitor interstitial-water quality within the shallow unsaturated zone.
- Twenty monitoring wells in 13 well clusters were installed to monitor ground-water levels and water quality at depths ranging from 15 to 100 ft.
- Three sampling sites were established below downgradient springs to monitor the quality of spring water flowing from the site.

Soil-suction lysimeter clusters were installed in the PFBC by-product application area and outside of the application area (hereafter referred to as the "control area"). Reclamation within the control area was done by traditional

methods that included grading of spoil and applying a cover of approximately 1 ft of topsoil. The lysimeters were installed at depths ranging from 1.5 to 4.5 ft below the surface. Attempts were made to extract interstitial water from all lysimeters during each sampling round; however, small sample yields resulted in insufficient sample volumes for some analyses. Monitoring wells were installed at sites surrounding the PFBC by-product application area so that comparisons could be made between upgradient and downgradient water chemistry. Each of the wells was constructed of polyvinyl chloride casing material with 10-ft screens.

Water samples were collected from lysimeters, monitoring wells, and springs during the period 1995-2001. Six of the seven sampling rounds were done in June of each year during relatively dry periods, when base-flow conditions prevailed. One set of samples (interstitial-water sampling round 3) was collected in January, immediately after a snowmelt of approximately 11 in. Discharge of springs was measured at the time of each sampling round by means of volumetric techniques.

Onsite measurements of water characteristics included temperature, alkalinity, pH, reduction-oxidation (redox) potential, specific conductance, and dissolved-oxygen concentration by methods described in Wilde and others (1999). Measurements of ferrous iron (Fe^{2+}), total iron, sulfate, hydrogen sulfide, and turbidity were made in the field by use of a portable spectrophotometer, in accordance with standard methods described in Walters (1989). Air temperature and air pressure were measured at the time of sampling. Water samples were analyzed in the laboratory by the methods described in Stehouwer and others (1996), Haefner (1998), and Dick and others (1999). Both the USGS National Water Quality Laboratory in Denver, Colo., and the Ohio Agricultural Research and Development Center (OARDC) Laboratory in the Department of Natural Resources in Wooster, Ohio, analyzed water samples for major and trace constituents. Water-quality constituents selected for analysis were based on the composition of PFBC by-product and acid mine drainage, as well as on anticipated water-rock interactions. Quality-assurance measures included submitting blank samples, replicate samples, and standard reference water samples (samples of known composition) to both laboratories. Discussion of quality-assurance results is given in Dick and others (1999).

The USGS Isotope Laboratory in Reston, Va., analyzed water samples for sulfur-isotope ratios ($\delta^{34}\text{S}$) in sulfate. Sulfur-isotope ratios are reported in parts per thousand (per mil) relative to the Canyon Diablo troilite (FeS) standard and have a reproducibility of ± 0.3 per mil. The ratio is calculated by the following equation:

$$\delta^{34}\text{S} = \frac{{}^{34}\text{S}/{}^{32}\text{S}_{\text{sample}} - {}^{34}\text{S}/{}^{32}\text{S}_{\text{standard}}}{{}^{34}\text{S}/{}^{32}\text{S}_{\text{standard}}} \times 1000 \quad . \quad (1)$$

Sulfur-isotope ratios were measured to determine whether they could be used as a tool to trace leachate derived from PFBC by-product in an environment where water quality was already influenced by high concentrations of sulfate. Direct comparisons of sulfur-isotope ratios in sulfide and sulfate are possible because no significant fractionation occurs during the oxidation of sulfide minerals (Ohmoto and Rye, 1979; Taylor and others, 1984). Fractionation of sulfur isotopes upon precipitation of relatively soluble sulfate minerals was assumed to be negligible and has been estimated in the laboratory to be less than 2 per mil (Thode and Monster, 1965).

For the purposes of this study, the dissolution and precipitation kinetics (rates of reactions) were assumed to be similar for all sulfur-bearing species with similar oxidation states. The primary form of sulfide at the mine site is pyrite, although minor amounts of marcasite (FeS_2) also may be found. Oxidation of pyrite is relatively slow and may be rate-limited by available oxygen and water. Accelerated pyrite oxidation has likely been occurring since mining began at the site because of exposure to the atmosphere and increased surface area caused by disaggregation of overburden. With the addition of calcium from the PFBC by-product, the most abundant sulfate mineral in the unsaturated zone likely was gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), but alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$), basaluminite ($\text{Al}_4(\text{SO}_4)(\text{OH})_{10} \cdot 5\text{H}_2\text{O}$), ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$), jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$), melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$), schwertmannite ($\text{Fe}_{16}\text{O}_{16}(\text{OH})_{12}(\text{SO}_4)_2$), and other variations also may be present (Jambor and others, 2000). These sulfate minerals are all fairly soluble, and their precipitation or dissolution does not significantly fractionate sulfur isotopes in water.

The sulfur-isotope composition of sulfide minerals in spoil and aquifer materials is reported in Haefner (1998) and ranged from -26.3 to $+13.6$ per mil. The most negative values of $\delta^{34}\text{S}$ are associated with strata that have the highest sulfur content; so, the dominant source of sulfate in water samples has relatively depleted values of $\delta^{34}\text{S}$ (Haefner, 2001). For coal sequences, bacterial reduction of sulfate in sea water during deposition results in coal seams with sulfide that have isotope ratios ranging from -30 to $+20$ per mil (Thode and others, 1949). This wide range of sulfur-isotope ratios is most likely caused by infiltration of sulfate from seawater and nonmarine water.

Two samples of PFBC by-product were analyzed for $\delta^{34}\text{S}$, and values of $+4.6$ and $+4.8$ per mil were determined (Haefner, 1998). These data, along with sulfur-isotope ratios in sulfide from aquifer materials, sulfate in rain water, interstitial water, ground water, and spring water, were combined to construct a sulfur-isotope mixing model for sulfate in water at the Fleming site (Haefner, 2001) following techniques outlined in Faure (1991). An advantage of using isotope ratios in mixing evaluations is that dilution or concentration does not affect isotope ratios, as opposed to

concentrations (mass per unit volume) of individual constituents. Assumptions inherent in the sulfur-isotope mixing model are that the constituent under consideration is conservative, that only two components contribute sulfur to the system, and that the chemical and isotopic compositions of the end-members are constant (Faure, 1991). The isotopic composition of any mixture can be described as a straight line with the form

$$\delta^{34}\text{S} = \frac{a}{S_m} + b, \quad (2)$$

where $\delta^{34}\text{S}$ is the isotope ratio in sulfate, S_m is the concentration of sulfate in the mixture, and a and b are constants specified by the concentrations and $\delta^{34}\text{S}$ values of sulfate in the two end-members. Because the sulfate concentration in equation 2 is in the denominator, the inverse of sulfate was used for all subsequent mixing relations.

For the purposes of this report, results of data-collection activities are reported in the context of their relation to changes caused by reclamation and surface amendment with PFBC by-product. Other than reporting the median values of constituents, additional statistical computations were not done because the water-quality data were characterized by non-normal distributions, diverse sample-size populations, and changing detection limits between laboratories and sampling rounds. Helsel and Hirsch (1992) describe several statistical techniques to characterize censored data (data values below the reporting limit); however, these techniques generally require that the data fit an assumed distribution. To include all water samples in the median calculations and to provide insight into the “worst-case” maximum possible concentrations of constituents in water samples, values with concentrations less than the detection limit were substituted in all calculations without the less-than sign, providing estimates that are greater than the true value.

Water-quality and solid-phase data were used to construct geochemical models with the computer codes NETPATH (Plummer and others, 1994) and PHREEQC (Parkhurst and Appelo, 1999) to examine the fate of elements derived from the PFBC by-product. NETPATH computes the mixing proportions of several initial waters and the net geochemical reactions that can account for the observed composition of a final water. PHREEQC was used to evaluate whether thermodynamic conditions are favorable to either dissolve or precipitate secondary minerals.

HYDROGEOLOGIC SETTING

The Fleming site is within the Pottsville and Allegheny groups of Pennsylvanian-age sedimentary rocks of Tuscarawas County, eastern Ohio (fig. 1). The Lower Kittanning (No. 5) coal was mined from the site by surface operations

over a 20-year period during about 1950-70. (Mining permits and records available from the Ohio Department of Natural Resources were not clear on the exact dates of mining.) The mining records indicate that a clay unit immediately beneath the Lower Kittanning coal also was mined during this period. The mine site was abandoned after depletion of the coal and clay reserves in the early 1970s. Soon thereafter, local residents began to lodge complaints regarding flooding and sedimentation along a nearby road. During a reconnaissance visit in early 1994, the author observed springs discharging AMD with pH less than 4 and high concentrations of dissolved solids, including iron and sulfate.

Reclamation of the Fleming site was completed in the late summer and fall of 1994 by regrading the spoil to the approximate premining topographic contour and applying composted yard waste and PFBC by-product. Parallel studies by workers at the OARDC focused on surface-water runoff from six 1-acre test watersheds at the site (fig. 1). During reclamation and regrading, a continuous clay layer was installed beneath these watersheds to promote surface-water runoff; thus, water quality from the test watersheds was not considered in this report. The reader is directed to Dick and others (1999) for more details on the results of the experiments at the test watersheds.

The stratigraphy at the site is characterized by repeating sequences of sandstone, shale, limestone, coal, and underclay that dip slightly (1-2 degrees) to the southeast (fig. 2). The underclays act as a barrier to the downward movement of ground water; therefore, perched aquifers are common in these settings. As was the case for many other coal-related studies in Ohio, saturated zones are referred to as “aquifers” for convenience, even though they might only yield less than 1 gal/min to wells. Aquifers chosen for investigation in this study included the coals and sandstones immediately above the Brookville (No. 4) underclay and the Tionesta (No. 3b) underclay. These aquifers are hereafter referred to as the “shallow” and “deep” aquifers, respectively.

Ground-water-flow directions were documented through monthly water-level measurements in monitoring wells. Water levels were measured from January 1995 through June 1998 and May 2000 through June 2001. The potentiometric surface for the shallow aquifer in June 2001 is shown in figure 3. Flow directions in the shallow aquifer are from northwest to southeast; however, flow along the northern part of the Fleming site is from west to east. Water in the deep aquifer follows similar flow directions as those in the shallow aquifer. Hydrographs of water levels from 3 wells at well cluster 4 indicate that water levels rose by as much as 4.5 ft during the study period. (Wells 4S and 4D were screened in the shallow and deep aquifer, respectively. Well 4D2 was screened in an aquifer below the deep aquifer and was the only well at the Fleming site screened in this

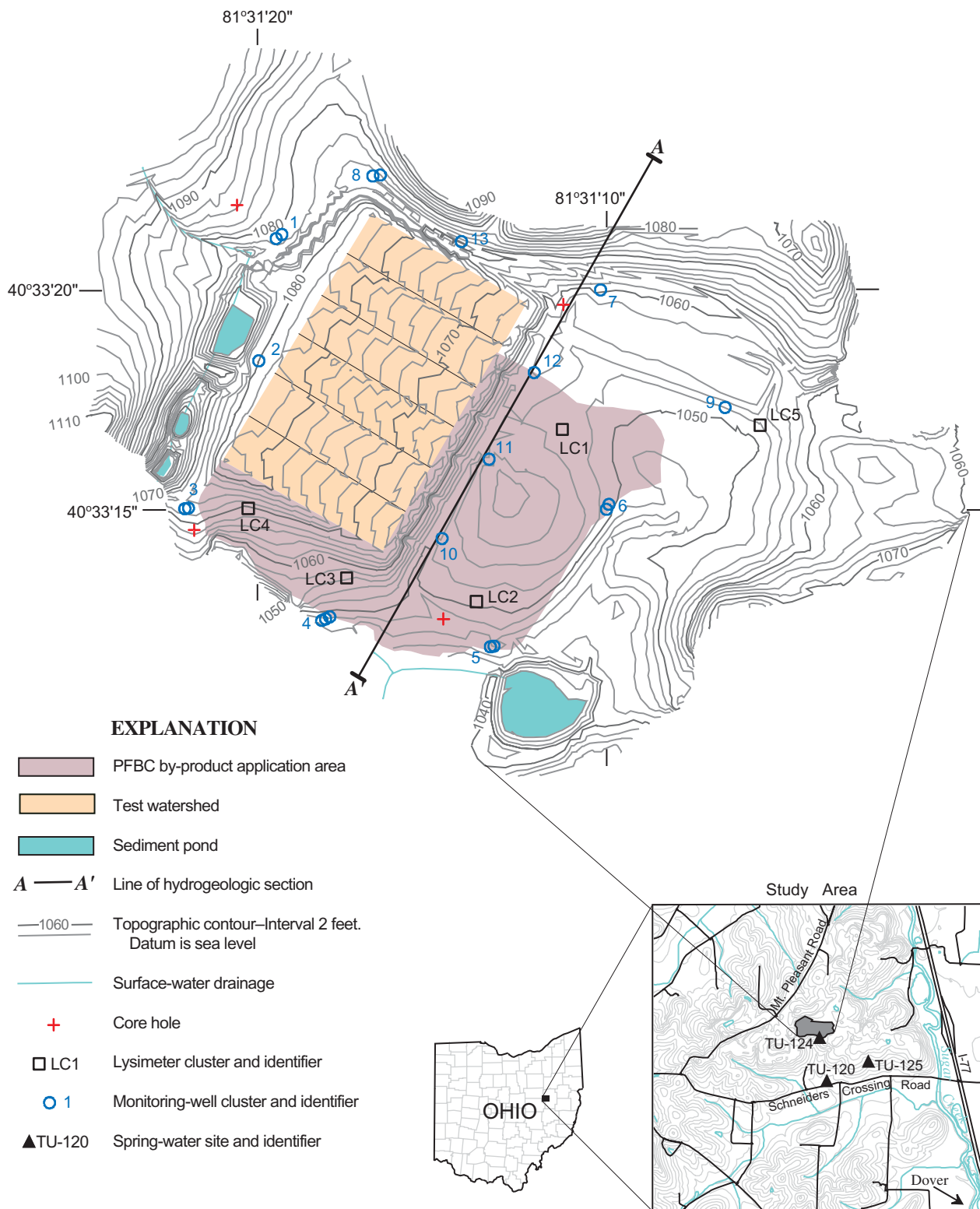


Figure 1. Lysimeters, monitoring wells, and spring sites at the Fleming abandoned mine site, Tuscarawas County, Ohio. (Hydrogeologic section shown in figure 2).

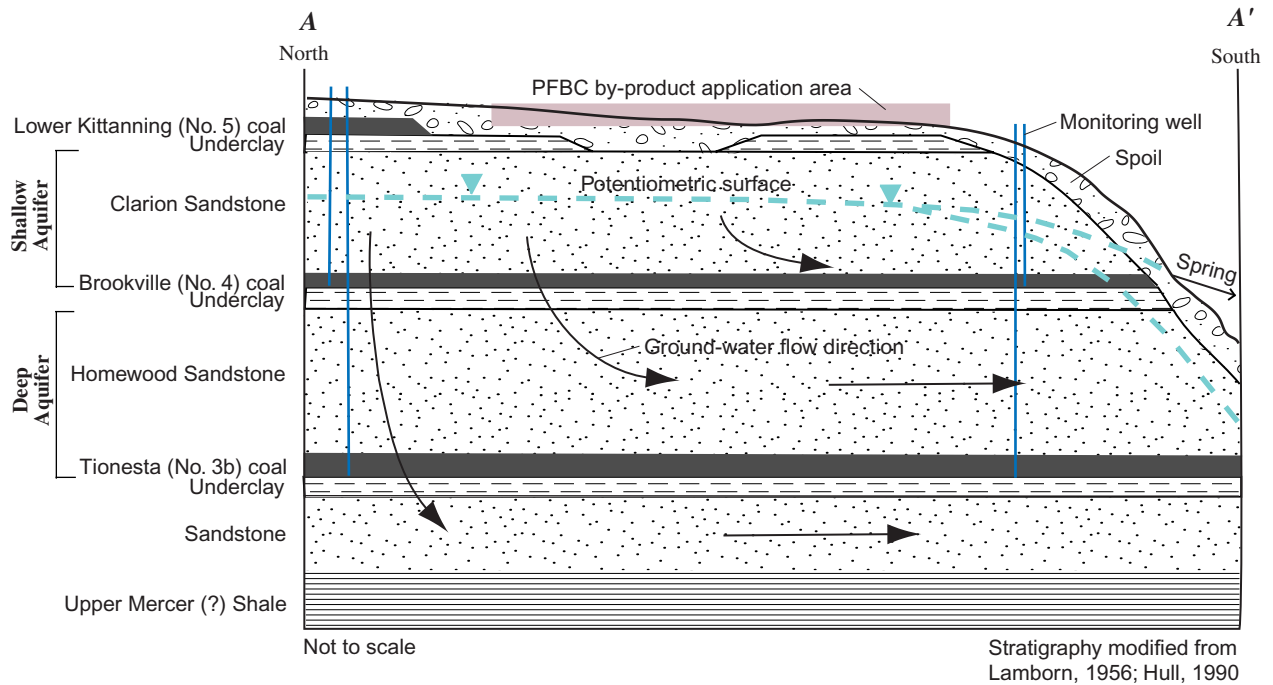


Figure 2. Diagrammatic hydrogeologic section along A-A' showing shallow and deep aquifer at the Fleming abandoned mine site, Tuscarawas County, Ohio.

zone.) Water levels in all other wells followed a similar pattern as those in well cluster 4, except for well 5SP, which was 14 ft deep and was screened in the spoil. Water levels in well 5SP were below the screen bottom for most of 1995 but remained above the screen bottom for most of the study rose to within the screened interval in the spring of 1996 and period (Dick and others, 1999).

Over the 7-year period of water-level measurements, water-level rises were noted in all wells at the Fleming Site. Water-levels in wells 4D and 4D2 shown in figure 4 show a continuous rise throughout the study period; however, water levels in well 4S appear to have stabilized at an elevation of about 1,032 ft. Several factors may have combined to produce the observed rises during the study period. First, reclamation and the establishment of vegetation may have caused changes in the location and amount of recharge entering the shallow aquifer. Reduced runoff and increased infiltration are two desired effects of abandoned mine reclamation. The discharge areas (downgradient springs) were not altered before or during the course of this study. Second, the outlet elevation for a sediment pond southeast of well cluster 5 was raised approximately 5 ft in early 1996, which may have resulted in higher water levels adjacent to the pond. Third, above-average rainfall during the 7-year period may have provided increased recharge to the water table. Average precipitation for eastern Ohio is approximately 38 in/yr; however, the cumulative total of rainfall from October 1994 through September 2001 was 6.75 in above normal (table 2,

Ohio Department of Natural Resources, 2002). Well 4S is the shallowest well of the cluster, and it appears to have responded to changes in the hydrologic system and equilibrated before wells 4D and 4D2.

Table 2. Rainfall amounts for the Northeast Hills, Ohio, 1993 through 2001

[Summarized from Ohio Department of Natural Resources, 2002; water year begins on October 1 and ends on September 30]

Water year	Measured rainfall (in inches)	Departure from average of 38 inches (in inches)	Cumulative total departure (in inches)
1993	42.77	+4.77	+4.77
1994	32.40	-5.60	-0.83
1995	46.14	+8.14	+7.31
1996	39.41	+1.41	+8.72
1997	40.55	+2.55	+11.27
1998	36.19	-1.81	+9.46
1999	41.56	+3.56	+13.02
2000	31.72	-6.28	+6.74

The horizontal hydraulic conductivity of aquifers beneath the site was evaluated with single-well volume-displacement tests (slug tests) in 15 of the 20 wells (Haefner, 1998). The hydraulic conductivity of the shallow aquifer from 33 tests on 8 wells ranged from 1 to 12 ft/d, whereas the hydraulic conductivity of the deep aquifer from 14 tests in 5 wells was 0.3 to 25 ft/d. Aquifer tests in similar

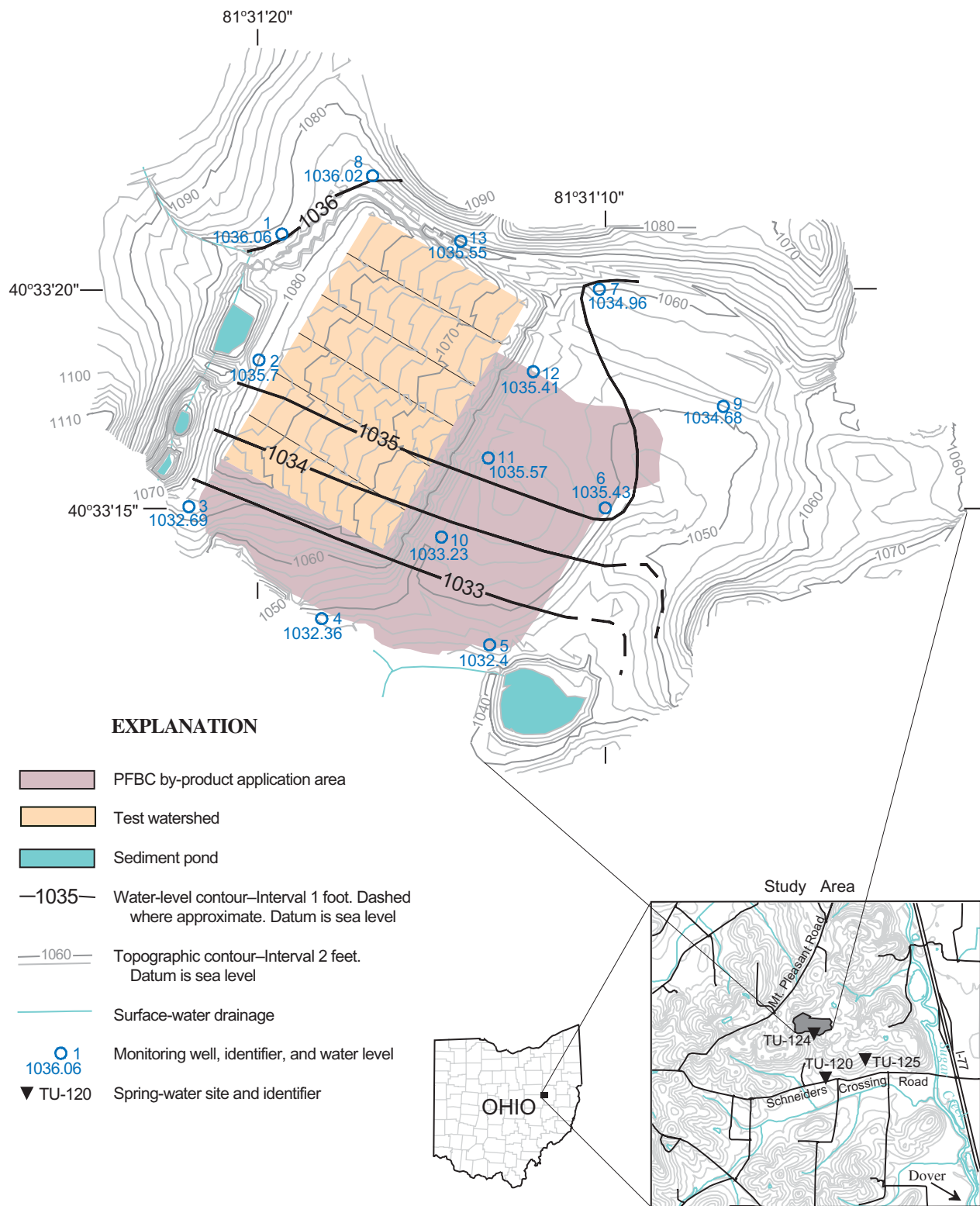


Figure 3. Potentiometric surface in the shallow aquifer on June 25, 2001, at the Fleming abandoned mine site, Tuscarawas County, Ohio.

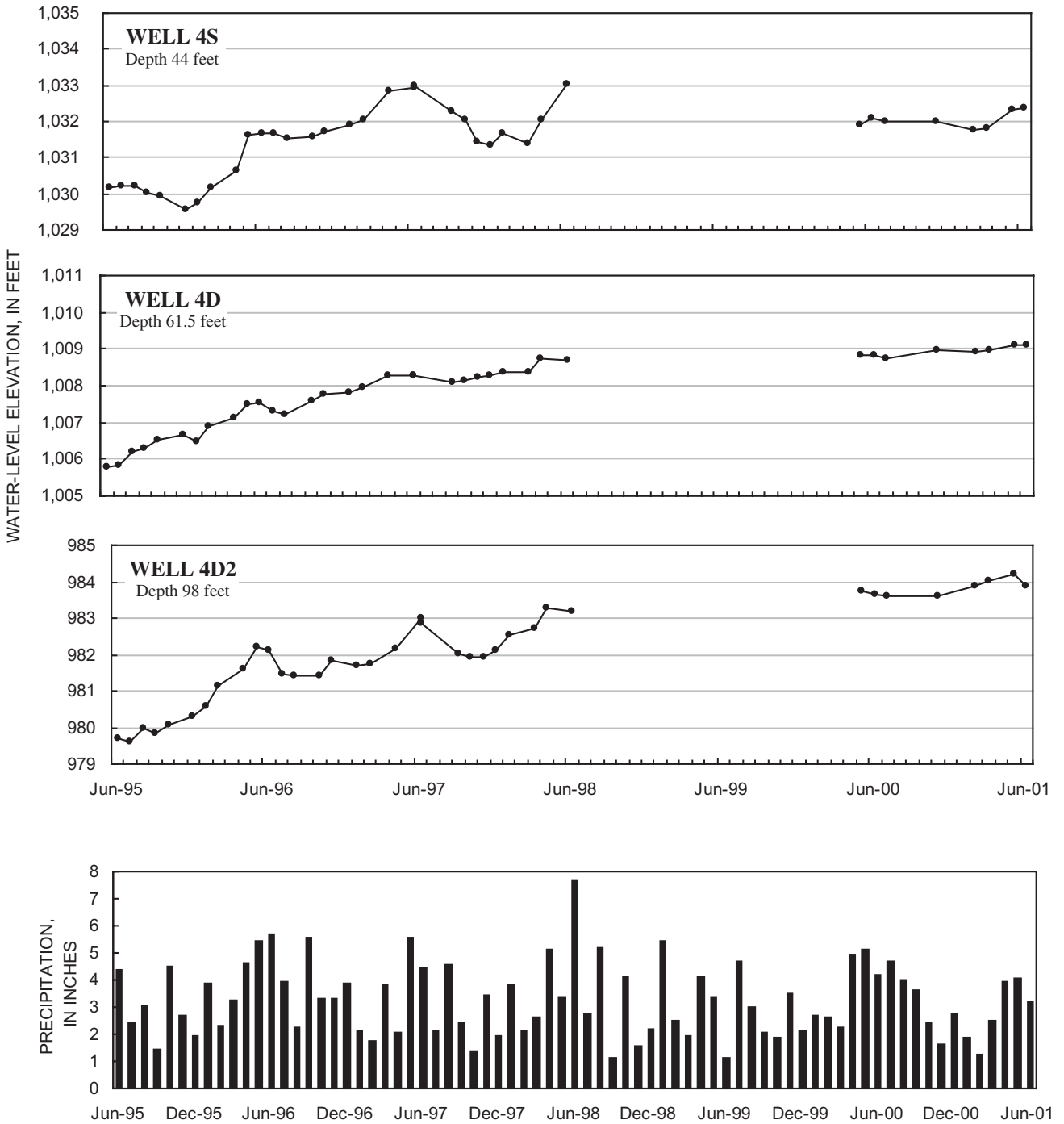


Figure 4. Water levels and precipitation from cluster 4, Fleming abandoned mine site, Tuscarawas County, Ohio. (Precipitation data from Ohio Department of Natural Resources, 2002).

coal-related aquifers in Coshocton, Jefferson, and Muskingum Counties within the Middle Kittanning (No. 6), the Waynesburg (No. 11), and the Meigs Creek (No. 9) coals indicated values ranging from 0.1 to 150 ft/d (Bonta and others, 1992). Hobba (1991) tested an aquifer in the Upper Freeport coal in West Virginia and computed hydraulic con-

ductivity of 11.8 to 13.6 ft/d. Aquifer tests by Martin and others (1990) from aquifers within Indiana coal sequences resulted in ranges of 0.0002 to 0.8 ft/d. The wide ranges of hydraulic conductivities are likely the result of the diversity of rock types in coal sequences. Coal beds have fractures (cleats) that enhance hydraulic conductivity, whereas

Table 3. Discharge measurements at three spring sites at the Fleming abandoned mine site, Tuscarawas County, Ohio

All measurements were made using volumetric techniques and are in cubic feet per second; --, measurement not done; <, actual value is less than that indicated]

Site ^a	Date of measurement					
	June 1995	June 1996	June 1997	June 1998	June 2000	June 2001
TU-120	0.045	0.072	0.095	-- ^b	--	--
TU-124	.005	.008	.010	0.020	0.012	0.013
TU-125	.007	.008	.016	.008	<.001	.004

^a Site location shown on inset map on figure 1.

^b Site TU-120 was altered by installation of a nearby pond in early 1998; therefore, no subsequent samples or discharge measurements were made.

shales, underclays, and some of the tighter sandstones may have lower values of hydraulic conductivity. Springs discharge into a small system of streams along the south border of the site (fig. 1). These springs discharge from the shallow aquifer. Discharge was measured only at times corresponding to water-quality sampling (during base flow) and ranged from less than 0.001 ft³/s at TU-125 to 0.095 ft³/s at TU-120 (less than 0.45 to 43 gal/min; table 3).

Conceptually, precipitation at the Fleming Site can either infiltrate into the unsaturated zone through pores in the spoil and aquifer materials or run off the surface and be collected in one of the four sediment-detention ponds onsite (fig. 1). Water that infiltrates into the spoil (and through PFBC by-product) may react with soluble components, dissolve them, and transport them down to the water table. Because the PFBC by-product was applied to the surface and incorporated into the spoil, water was not expected to flow any differently in the application area than in the control area. Water in the unsaturated zone moves downward only under the force of gravity and could potentially evaporate, precipitate secondary minerals (such as sulfate salts and iron and aluminum hydroxides), and (or) percolate down to the water table. The ground-water quality at this and most other AMD sites is influenced most strongly by chemical reactions in the unsaturated zone. These reactions most typically involve oxidation and dissolution of minerals from the spoil. Because the site sits on a hilltop, the water flows away from topographic highs and discharges to down-gradient springs along the hillside.

The conceptualization of the flow system and the data obtained from wells, core samples, and surface geophysical surveys, were combined to construct a three-dimensional ground-water-flow model documented in Haefner (1998). The objectives of the model were to simulate ground-water-flow directions and estimate advective traveltimes of particles of water from the water table beneath the PFBC by-product application area to spring discharge areas. The model was calibrated to head and flow conditions measured in June 1996 and included a recharge rate of 5.1 in/yr over the entire modeled area. If water-level rises in wells at the site were caused by additional recharge entering the system (as postulated for the rise in water levels

observed at the Fleming site), then the recharge estimate of 5.1 in/yr represents a minimum value because additional recharge would be required to increase the amount of water held in storage. Particle-tracking simulations provided estimated traveltimes of 227 days to 27 years for water to move through the system (Haefner, 1998).

Ground-water-flow-modeling simulation results were substantiated by analyses of tritium (³H) in ground water. At the beginning of this study, it was not known whether recharge rates were fast enough or traveltimes were short enough to detect water-quality changes after application of PFBC by-product on the land surface. Tritium is produced naturally in the upper atmosphere as a result of interactions of cosmic-ray-produced neutrons with nitrogen atoms. Estimated concentrations of naturally occurring tritium in precipitation are as high as 20 tritium units (TU, 1 TU equals one atom of ³H in 10¹⁸ atoms of ¹H). The onset of thermonuclear bomb testing in the early 1950s, however, produced a tritium peak with concentrations up to 1,000 TU, providing a qualitative mechanism to estimate the approximate age of ground-water recharge. All ground-water samples had tritium concentrations greater than 4 TU, and water samples from most wells had greater than 20 TU (fig. 5).

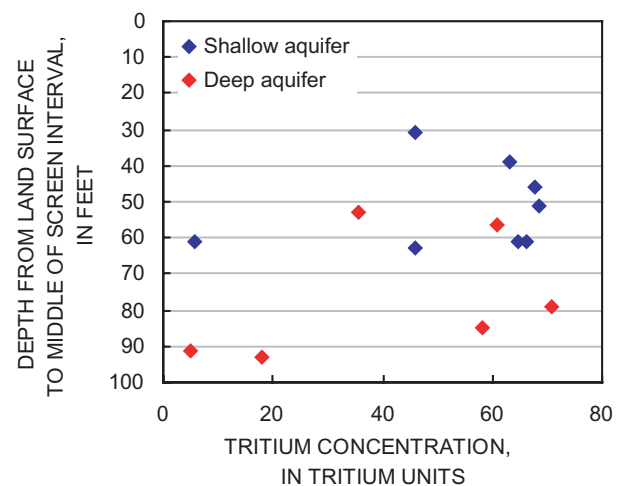


Figure 5. Tritium concentration as a function of depth for ground-water samples collected in 1995 at the Fleming abandoned mine site, Tuscarawas County, Ohio.

Because tritium has a half-life of 12.43 years, Fontes (1980) asserted that any ground waters with detectable concentrations of tritium were recharged after 1952. Results of analyses of ground-water samples from the Fleming site indicate that water recharged after the early 1950s had mixed with ambient ground water (Haefner, 1998). The traveltime of water through the unsaturated zone (precipitation as rain or snow on land surface to the water table) was not evaluated.

The water-table gradient on the north side of the site is relatively gentle, but it steepens closer to the southern part of the site (fig. 3). Accordingly, ground-water velocity is relatively faster through the southern part of the site. This steepening of the gradient is likely caused by stress-relief fractures along the hillside, as noted at other mine sites throughout the Appalachian coal region (Bonta and others, 1992; Saad and Cravotta, 1991; Hobba, 1991).

WATER QUALITY

In terms of surface revegetation and reduction of erosion, reclamation of the Fleming site with PFBC by-product and yard-waste compost was almost immediately successful (Dick and others, 1999). The fescue and alfalfa planted at the site established itself during the first growing season (1995) and continued to reseed itself during the course of this study (through 2001). In contrast, water-quality improvements from reclamation of abandoned mine sites are known to take many years (Eberle and Razem, 1985; Cunningham and Jones, 1990). To evaluate the water quality at the Fleming site, water samples were collected from the shallow unsaturated zone, ground water, and springs over 7 years of study. Major findings are summarized in graphs, tables, and text in the next few pages of this report. Supporting data from all sampling rounds are given in Stehouwer and others (1996), Haefner (1998), Dick and others (1999), and Shindel and others (2001, 2002) and are not reproduced here.

Haefner (1998) and Dick and others (1999) describe the properties and constituents that can be used to evaluate differences between waters that have been influenced by leachate derived from PFBC by-product from those that were not. These include specific conductance, pH, selected major ions and trace elements (calcium, magnesium, sulfate, and boron), magnesium-to-calcium (Mg:Ca) mole ratios, and sulfur-isotope ratios ($\delta^{34}\text{S}$). Several comparisons are included in this report to summarize the effects of PFBC by-product leachate on water quality, including:

- median values of water-quality characteristics in application-area and control-area interstitial water,
- median values of these characteristics in upgradient ground water, downgradient ground water, and spring water,
- median values for selected characteristics in different matrices for each sampling round, presented as a series of bar graphs,
- graphs of sulfate concentrations as a function of magnesium-to-calcium mole ratios and sulfur-isotope ratios, and
- comparisons of water-quality results with U.S. Environmental Protection Agency Maximum Contaminant Levels (MCLs) for drinking water.

Waters from abandoned surface coal mines in Ohio have been generally categorized as calcium-sulfate type waters (Sedam and Francy, 1993). Because magnesium concentrations are approximately equal to calcium concentrations, water samples from the Fleming site are calcium-magnesium-sulfate type waters. When the Fleming site samples are represented on a standard Piper trilinear diagram, the high concentrations of sulfate and low concentrations of sodium in these waters cause most of the data points to be densely clustered towards the sulfate end-member and the calcium and magnesium axes (fig. 6A). To allow for greater differentiation, the standard Piper diagram shown in figure 6A was modified to include different cations and anions, and multipliers were applied to distinguish water types (fig. 6B). Modifications included changing the cation end-members to calcium plus magnesium (Ca + Mg), iron plus aluminum (Fe + Al), and sodium plus potassium (Na+K) multiplied by 10. Anion end-members were modified to include fluoride (F) multiplied by 10, chloride (Cl), and sulfate (SO_4) multiplied by 0.01. When plotted this way, most application-area interstitial waters can be distinguished from all other water samples because their calcium and magnesium concentrations were much greater than those for other water samples. (Not all water samples are included in figures 6A and 6B because of incomplete analyses for some samples.)

Median values of all water-quality characteristics were computed for the five different water matrices (application-area interstitial water, control-area interstitial water, upgradient ground water, downgradient ground water, and spring water; table 4). The median values of most characteristics clearly show the influence of PFBC by-product leachate on application-area interstitial waters. The median specific conductance in application-area interstitial waters was 5,500 $\mu\text{S}/\text{cm}$ as compared to 1,900 $\mu\text{S}/\text{cm}$ for control-area interstitial waters. The neutralizing effect of the PFBC by-product can be seen in median alkalinity and hardness in interstitial waters, which were more than 5 times greater in the application area than in the control area. The median pH of application-area interstitial waters was 6.6 as compared to 5.0 for the control area. Median concentrations of major elements such as calcium, magnesium, and sulfur (as sulfate) were greater in application-area interstitial waters than in control-area interstitial waters. The median concentrations of boron, chloride, fluoride, potassium, and strontium

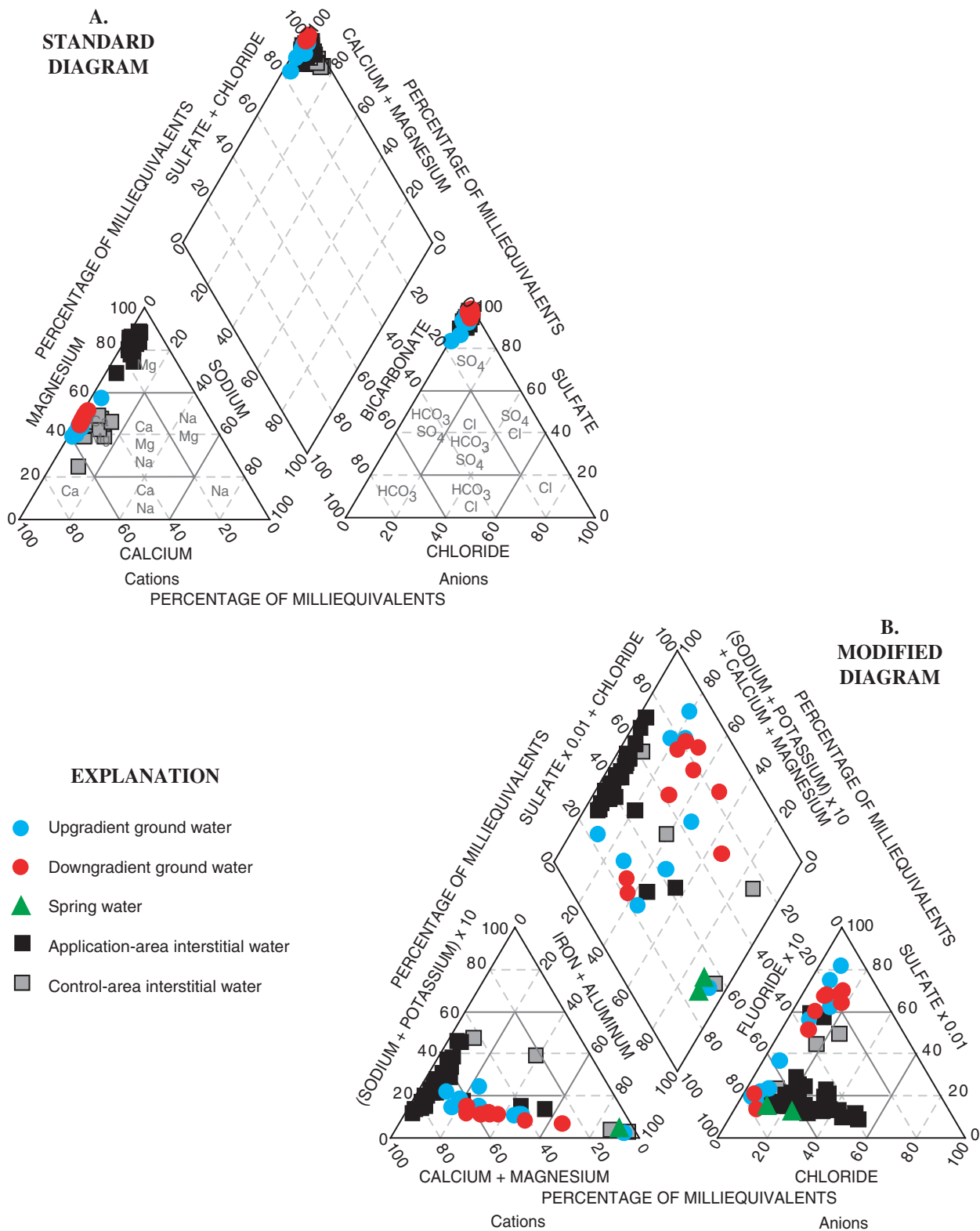


Figure 6. Standard and modified piper trilinear diagrams of selected water samples from the Fleming abandoned mine site, Tuscarawas County, Ohio. (See discussion in text for description of modifications.)

Table 4. Median values of water-quality characteristics from selected water samples collected at the Fleming abandoned mine site, Tuscarawas County, Ohio

[Number of samples used to compute each median is given in parentheses; mg/L, milligrams per liter; redox, reduction-oxidation potential; $\mu\text{S}/\text{cm}$, microsiemens per centimeter; $\mu\text{g}/\text{L}$, micrograms per liter; --, not measured; per mil, parts per thousand relative to a standard]

Property or constituent	Units	Interstitial water		Ground water		Spring water
		Application area	Control area	Up-gradient	Down-gradient	
Onsite Measurements and Analyses						
Alkalinity	mg/L as CaCO_3	195 (6)	35 (1)	68 (27)	52 (26)	5.0 (1)
Oxygen, dissolved	mg/L	-- (0)	-- (0)	<0.1 (23)	<0.1 (22)	7.3 (5)
pH	standard units	6.6 (113)	5.0 (18)	5.6 (27)	5.5 (26)	3.6 (6)
Redox	millivolts	-- (0)	-- (0)	160 (27)	200 (26)	590 (5)
Specific conductance	$\mu\text{S}/\text{cm}$	5,500 (113)	1,900 (19)	3,100 (27)	3,100 (26)	1,400 (6)
Temperature	degrees Celsius	-- (0)	-- (0)	13.0 (27)	13.0 (26)	22.5 (6)
Laboratory Analyses (all values are for the dissolved (filtered) fraction)						
Acidity	mg/L as CaCO_3	0.5 (30)	0.0 (3)	11.5 (19)	10.9 (18)	0.6 (4)
Dissolved solids	mg/L	10,430 (31)	-- (0)	3,290 (27)	3,400 (26)	1,100 (5)
Hardness	mg/L as CaCO_3	5,800 (76)	900 (15)	1,700 (27)	1,800 (26)	750 (6)
Aluminum	mg/L	280 (61)	300 (9)	87 (27)	240 (26)	1,500 (4)
Antimony	$\mu\text{g}/\text{L}$	<106 (51)	<106 (5)	<106 (19)	<106 (18)	<106 (5)
Arsenic	$\mu\text{g}/\text{L}$	<2.0 (39)	<2.0 (11)	<1.0 (27)	<2.0 (26)	<1.0 (6)
Barium	$\mu\text{g}/\text{L}$	15 (51)	16 (5)	20 (19)	13 (18)	22 (4)
Beryllium	$\mu\text{g}/\text{L}$	<1 (51)	2 (5)	3 (19)	4 (18)	2 (4)
Boron	$\mu\text{g}/\text{L}$	690 (77)	65 (14)	280 (27)	300 (26)	220 (6)
Bromide	$\mu\text{g}/\text{L}$	<0.10 (10)	<0.10 (4)	.58 (8)	.50 (8)	<0.01 (2)
Cadmium	$\mu\text{g}/\text{L}$	1 (61)	3 (9)	4 (27)	5 (26)	3 (6)
Calcium	mg/L	430 (77)	180 (15)	360 (27)	370 (26)	150 (6)
Chloride	mg/L	39 (66)	7.4 (14)	2.2 (27)	3.5 (26)	3.0 (6)
Chromium	$\mu\text{g}/\text{L}$	11 (61)	10 (9)	4 (27)	6 (26)	6 (6)
Cobalt	$\mu\text{g}/\text{L}$	80 (61)	120 (9)	200 (27)	270 (26)	90 (6)
Copper	$\mu\text{g}/\text{L}$	23 (61)	11 (9)	<2 (27)	<2 (26)	3.5 (6)
Fluoride	mg/L	1.6 (66)	0.45 (14)	<0.10 (27)	<0.10 (26)	1.1 (6)
Iron	mg/L	.078(77)	12 (15)	270 (27)	280 (26)	1.6 (6)
Lead	$\mu\text{g}/\text{L}$	<2 (49)	<1 (12)	<1 (27)	<2 (26)	<1 (6)
Lithium	$\mu\text{g}/\text{L}$	110 (61)	140 (9)	150 (27)	220 (26)	110 (6)
Magnesium	mg/L	1,200 (77)	100 (15)	200 (27)	210 (26)	91 (6)
Manganese	mg/L	19 (77)	15 (15)	17 (27)	19 (26)	6.0 (6)
Mercury	$\mu\text{g}/\text{L}$	<0.1 (24)	<0.1 (3)	<0.1 (6)	<0.1 (6)	<0.1 (1)
Molybdenum	$\mu\text{g}/\text{L}$	<11 (51)	<7 (5)	<11 (19)	<11 (18)	<11 (4)
Nickel	$\mu\text{g}/\text{L}$	160 (61)	460 (9)	420 (27)	490 (26)	180 (6)
Nitrogen, as NH_4	mg/L	0.13 (27)	0.92 (3)	1.0 (26)	0.95 (25)	0.15 (6)
Nitrogen, as NO_2	mg/L	<0.01 (27)	<0.01 (3)	<0.01 (26)	<0.01 (25)	<0.01 (6)
Nitrogen, as $\text{NO}_2 + \text{NO}_3$	mg/L	0.06 (27)	0.06 (3)	<0.05 (26)	<0.05 (25)	<0.05 (6)
Phosphorous, as PO_4	mg/L	<0.01 (27)	<0.01 (3)	0.02 (26)	0.02 (25)	<0.01 (6)
Potassium	mg/L	47 (67)	16 (12)	13 (27)	11 (26)	6.2 (6)
Selenium	$\mu\text{g}/\text{L}$	<3 (36)	<1 (11)	<1 (26)	<1 (26)	<1 (6)
Silica, as SiO_2	mg/L	29 (77)	32 (15)	11 (27)	11 (26)	10 (6)
Silver	mg/L	<10 (61)	<10 (9)	<10 (27)	<10 (26)	<6 (6)
Sodium	mg/L	44 (77)	34 (15)	11 (27)	10 (26)	3.4 (6)
Strontium	$\mu\text{g}/\text{L}$	750 (61)	300 (9)	2,800 (27)	2,800 (26)	490 (6)
Sulfate	mg/L	4,800 (66)	970 (14)	2,200 (27)	2,200 (26)	810 (6)
Vanadium	$\mu\text{g}/\text{L}$	17 (61)	10 (9)	6 (27)	7 (26)	8 (6)
Zinc	mg/L	74 (61)	310 (9)	310 (27)	540 (26)	200 (6)
Carbon, organic	mg/L	23 (18)	5.7 (2)	0.7 (26)	1.0 (26)	1.2 (6)
$\delta^{34}\text{S}$ in sulfate	per mil	-4.1 (69)	-14.5 (14)	-10.2 (27)	-10.1 (26)	-9.95 (6)

also were greater in the application-area interstitial waters than in the control area. Elevated concentrations of boron may be of concern because at concentrations approaching 10 mg/L, boron is known to be phytotoxic (Pierzinski and others, 1994). The greatest concentration of boron (1.7 mg/L) was detected in a sample of interstitial water in the PFBC by-product application area during sampling round 3. For many of the trace elements of concern (including arsenic, lead, and selenium), the concentrations in most of samples were at or below the detection limit (generally less than 2 µg/L). Elements that have lower median concentrations in application-area interstitial waters than in control-area interstitial waters include iron, nickel, and zinc, presumably because of pH dependence on the solubility of these elements and their related solid phases. The median $\delta^{34}\text{S}$ in dissolved sulfate for waters from the application-area interstitial waters was -4.1 per mil, whereas the median $\delta^{34}\text{S}$ for control-area interstitial waters was -14.5 per mil (table 4). The relatively higher sulfur-isotope ratios in application-area interstitial waters reflect the influence of the positive $\delta^{34}\text{S}$ of the PFBC by-product.

Median values of most characteristics in samples of downgradient ground waters are approximately equal to or greater than those in upgradient ground waters (table 4). Consequently, upgradient and downgradient waters are both influenced by similar geochemical processes. The median value for sulfur (as sulfate) was 2,200 mg/L for upgradient and downgradient ground-water samples alike. Measurements for sulfide made with a field spectrophotometer indicated that only trace amounts of sulfide ($<0.001 \pm 0.003$ mg/L) were present in ground water. Aluminum, nickel, and zinc were found in greater concentrations in downgradient ground waters, presumably because of the influence of mining and reclamation activities at the Fleming site. Calcium, magnesium, and chloride increased slightly between upgradient and downgradient ground-water sampling sites, a possible indication that leachate from the PFBC by-product has mixed with downgradient ground water.

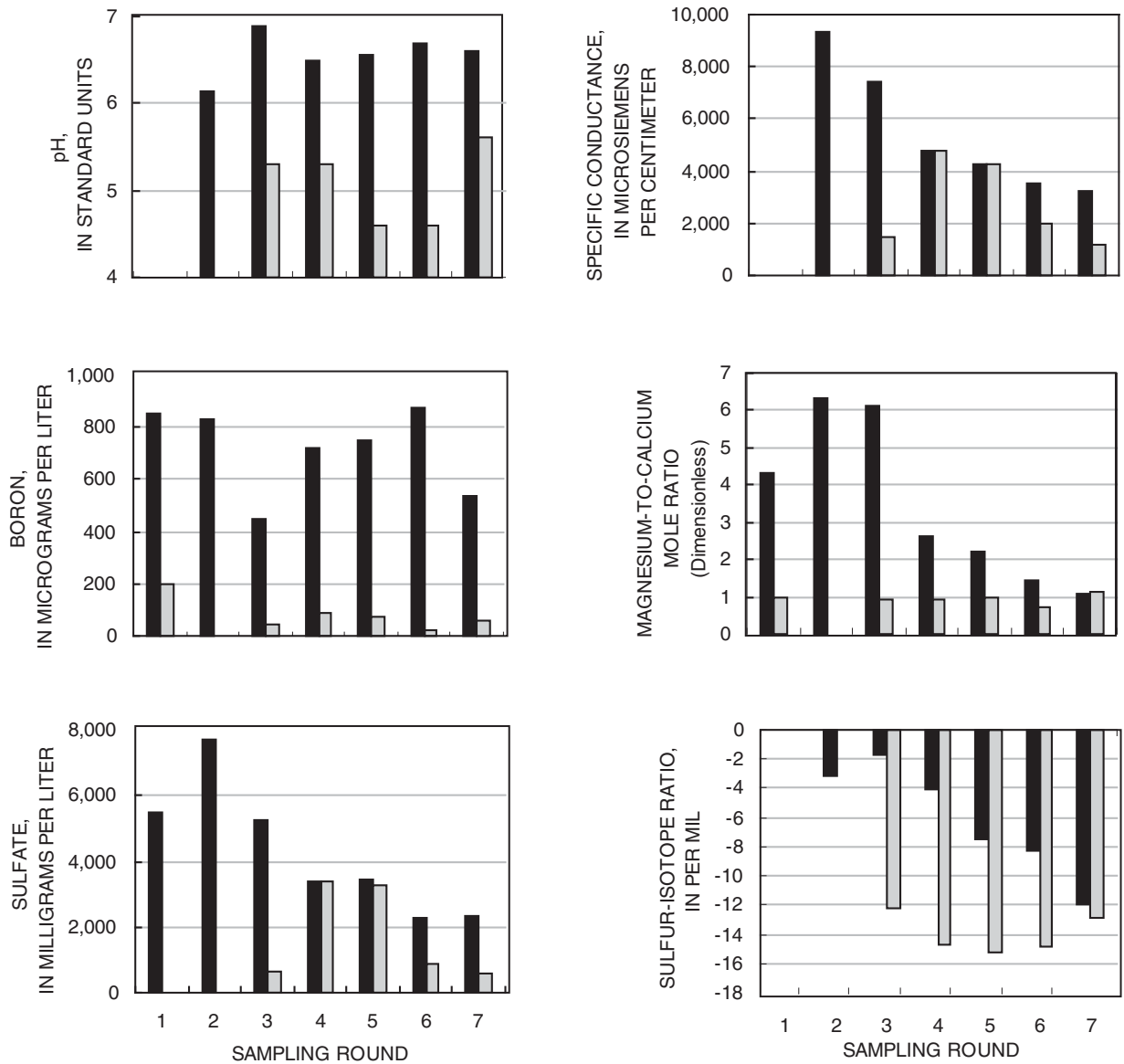
Concentrations of almost all major ions, nutrients, and trace elements decreased between downgradient ground water and spring water except for aluminum, which increased by a factor of more than six (240 µg/L to 1,500 µg/L). At pH less than 4.5, the solubility of aluminum increases dramatically (Hem, 1992; Hamlin and Alpers, 1996). Median pH in spring water was 3.6 but varied considerably throughout the study period, from a minimum of 3.2 to a maximum of 5.5 among six samples. Measurements of pH at TU-125 (which was outside the PFBC by-product application area watershed) ranged from 5.3 to 6.5 for six samples collected on the same date as other spring samples. Large decreases of median concentrations between downgradient ground water and spring water were noted in elements related to AMD, including iron, manganese, nickel, and zinc. Constituents associated with the PFBC by-product, including boron, calcium, and magne-

sium, also decreased between downgradient ground water and spring water. Sulfur-isotope ratios of sulfate in spring water were virtually the same as ratios in both upgradient and downgradient ground waters and represent the relatively negative isotopic composition of aquifer materials and spoil oxidation.

The analysis of median values of characteristics for all water samples, regardless of sampling round, is useful if there are no trends or changes in water quality through time but becomes less meaningful otherwise. Therefore, bar graphs of median values of selected water-quality characteristics by sampling round are shown in figures 7 and 8. For interstitial-water sampling rounds 1 and 2, insufficient water was obtained from the lysimeters; therefore, data are not shown for some characteristics. For interstitial waters (fig. 7), each of the bar graphs shows a distinct difference between medians obtained in the PFBC by-product application area and those in the control area. For the graphs of specific conductance, magnesium-to-calcium (Mg:Ca) mole ratios, sulfate, and sulfur-isotope ratios, the greatest median values obtained from interstitial water within the PFBC by-application area were observed in sampling rounds 2 or 3. For each subsequent sampling round, medians for these characteristics in the application-area interstitial waters approach those for the control area. The trends observed in median values from application-area interstitial waters during the seven sampling rounds is likely a result of the influence of leaching and depletion of soluble elements derived from the PFBC by-product through time. Similar relations were observed in greenhouse studies reported in Stehouwer and others (1996).

The patterns in the bar graphs for the same characteristics in ground water and spring water are different than those for the interstitial waters (fig. 8). For most sampling rounds, median values in upgradient ground waters were similar to downgradient ground waters; therefore, table 4 may represent these data adequately for many constituents. However, median values of Mg:Ca mole ratios were consistently greater in downgradient ground waters. As seen in figure 7, Mg:Ca mole ratios were higher in application-area interstitial waters than control-area interstitial waters; therefore, elevated Mg:Ca mole ratios in downgradient ground waters may provide additional evidence that leachate from the PFBC by-product has reached ground water.

The median values of $\delta^{34}\text{S}$ in both upgradient and downgradient ground water for seven sampling rounds show that the isotope ratios are greatest during the early sampling rounds, but then become more negative in later sampling rounds (fig. 8). This is in contrast to median sulfate concentrations, which increase to a maximum value during round 5. Therefore, an additional source of sulfate must have been reaching ground water. If the source of increased sulfate in ground water was from PFBC by-product leachate, the sulfur-isotope ratio should increase (become less negative). Spoil and aquifer materials at the Fleming site have



EXPLANATION

- Application-area interstitial water
- Control-area interstitial water

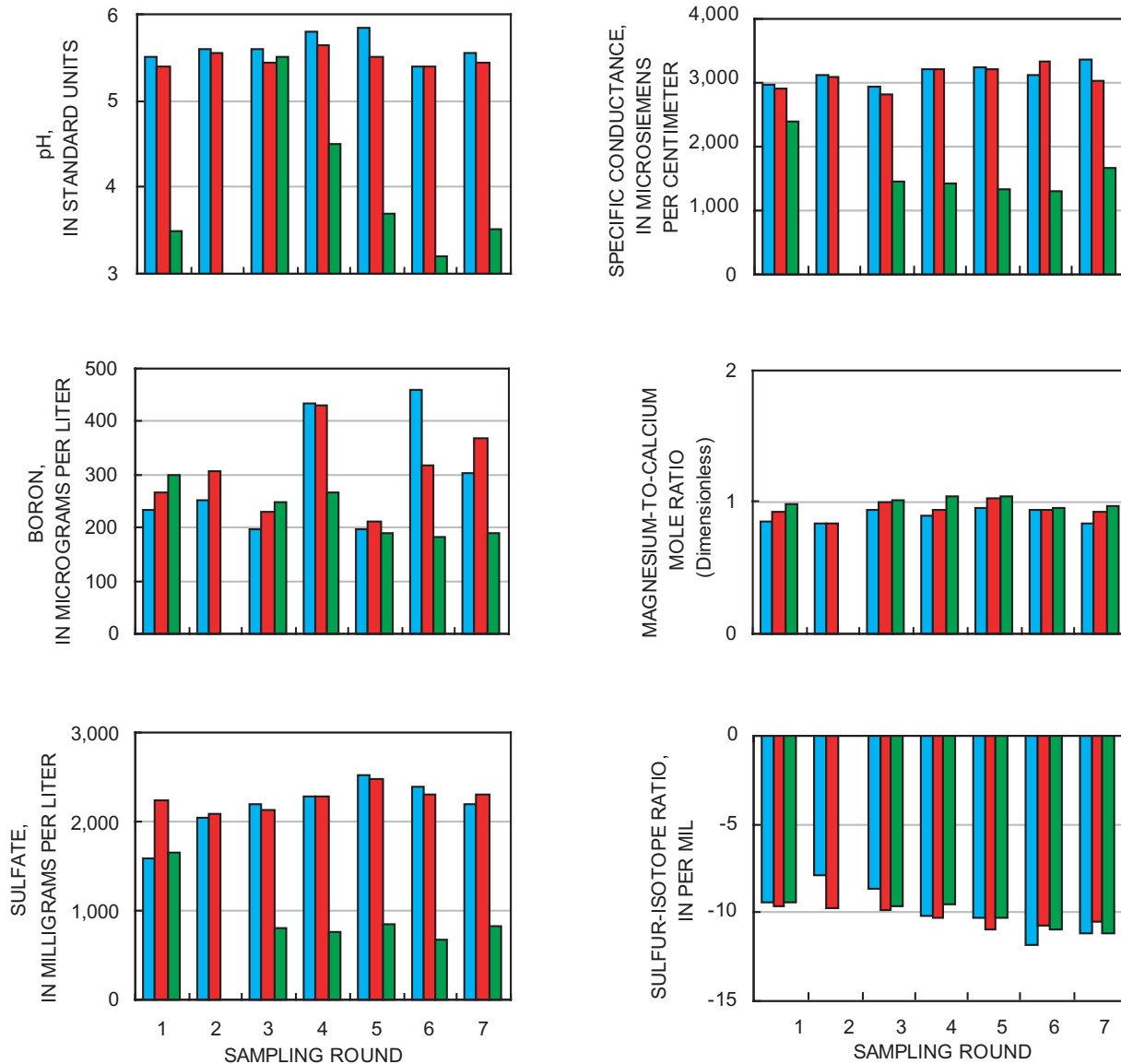
NOTE: No data where bars are absent

Figure 7. Median pH, specific conductance, boron, magnesium-to-calcium mole ratios, sulfate, and sulfur-isotope ratios for interstitial waters for each sampling round from the Fleming abandoned mine site, Tuscarawas County, Ohio.

relatively negative values of $\delta^{34}\text{S}$. The likely source of increased sulfate in ground water is the disturbance of mine spoils during reclamation, not the PFBC by-product.

These results indicate that the quality of interstitial water within the PFBC by-product application area has been influenced by leachate derived from the PFBC by-product. The only improvements in interstitial-water quality that can

be directly attributed to the PFBC by-product include increased pH and reduction in the concentrations of dissolved iron, nickel, and zinc. Median pH obtained from the application-area interstitial waters remained above 6.0 for all sampling rounds, indicating that at least some acid neutralizing capacity remained 7 years after application; however, bar graphs of interstitial water (fig. 7) show that



EXPLANATION

- Upgradient ground water
- Downgradient ground water
- Spring water

NOTE: No data where bars are absent

Figure 8. Median pH, specific conductance, boron, magnesium-to-calcium mole ratios, sulfate, and sulfur-isotope ratios for ground and spring waters for each sampling round from the Fleming abandoned mine site, Tuscarawas County, Ohio.

many of the elements derived from the PFBC by-product have been leached to concentrations approaching the background concentrations observed in the control area. Down-gradient ground-water quality and spring-water quality remain poor and show no sign of improvement 7 years after reclamation.

Chemical tracers of PFBC by-product

In addition to the Piper diagrams shown in figure 6 and the bar graphs in figures 7 and 8, two additional plotting techniques were used to differentiate waters that contain PFBC by-product from waters that are influenced by AMD and the aquifer materials. A scatterplot of sulfate concentration with respect to Mg:Ca mole ratios shows the difference between waters influenced by PFBC by-product leachate and all

other water samples (fig. 9). Samples of interstitial water from the application area typically have Mg:Ca mole ratios greater than 1, whereas most other water samples from the site have ratios approximately equal to or less than 1. As noted previously, downgradient ground waters have slightly higher Mg:Ca mole ratios than upgradient ground waters. The median Mg:Ca mole ratio of all upgradient ground-water samples was 0.89 as compared to 0.95 for downgradient ground waters.

A scatterplot of the inverse of sulfate with respect to $\delta^{34}\text{S}$ also shows a difference between water samples influenced by PFBC by-product leachate and those that are not (fig. 10). These relations were used in an isotope-mixing model reported in Haefner (2001). To estimate the abundance of sulfate derived from PFBC by-product in interstitial waters, an equation for the relation between the inverse of sulfate and $\delta^{34}\text{S}$ was computed for the most concentrated samples by use of least-squares regression. The regression

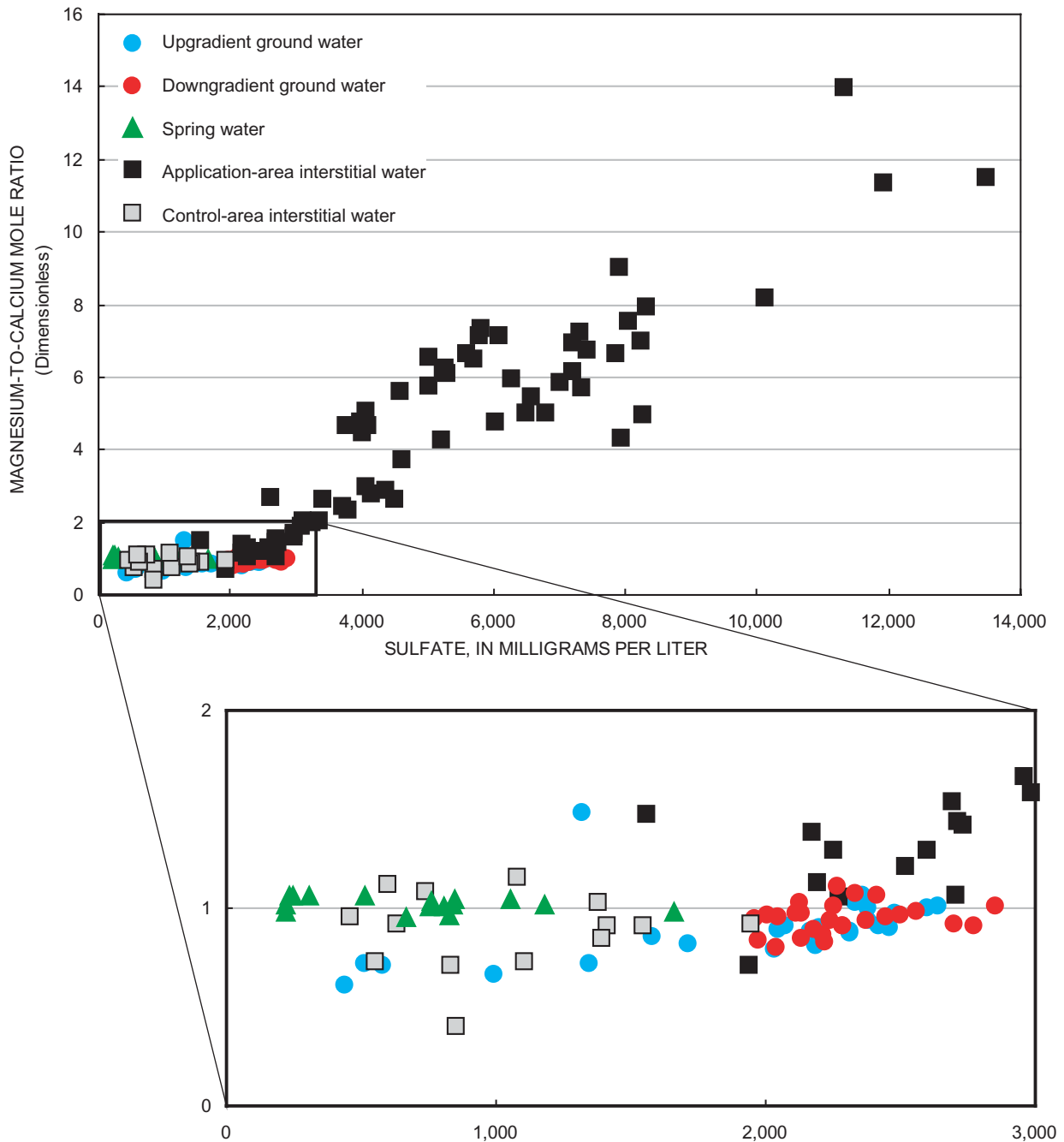


Figure 9. Relation of sulfate concentration to magnesium-to-calcium mole ratios for selected water samples from the Fleming abandoned mine site, Tuscarawas County, Ohio.

line was generated for a selected set of water samples only and does not include data from the end-members. The regression analysis resulted in the following mixing equation:

$$\delta^{34}S = -82,194.5 \left(\frac{1}{SO_4} \right) + 7.302 \quad (3)$$

Estimates based on a positive $\delta^{34}S$ value of the PFBC by-product (+4.8 per mil) as one end-member and the most negative value of $\delta^{34}S$ from control-area interstitial waters (-16.6 per mil) as the other end-member indicate that as much as 75 percent of the sulfate in application-area interstitial waters was derived from the PFBC by-product leachate during interstitial-water sampling round 3 (January 1996). The contribution of sulfate from the PFBC by-product has decreased from 75 percent in round three to a median value of about 20 percent in round 7 (June 2001). The process responsible for this decrease is leaching and subsequent depletion of the soluble sulfate minerals within the PFBC by-product. This same analysis was done for ground-water samples; however, sulfur-isotope ratios in upgradient and downgradient ground waters show that sulfate in ground water was derived from spoil and aquifer materials, not PFBC by-product.

The primary reason that these graphical techniques allow distinction between the waters influenced by leachate

derived from the PFBC by-product and waters that were not is that the coal burned (Pittsburgh No. 8) and the sorbent used (dolomite from northwest Ohio) in the PFBC process were from different formations than those at the Fleming site. These methods may not prove as successful in haul-back situations, where coal and (or) the sorbent were taken from the same mine where the by-product is placed. Therefore, if interstitial water containing leachate from the PFBC by-product were mixing with ground water from the Fleming site, we should see increasing $\delta^{34}S$ ratios approaching +4.8 per mil and increasing Mg:Ca ratios above 1.0 in downgradient ground-water samples.

Comparisons of water-quality data to established drinking-water standards

To put the water-quality data collected in this study in context with established drinking-water regulations, comparisons to the U.S. Environmental Protection Agency (2002) list of Maximum Contaminant Levels (MCLs) are provided in table 5. This table includes data from all water samples collected during the study. Many primary and secondary MCLs were exceeded in the waters collected at the Fleming mine site. The primary standards for beryllium, cadmium, and fluoride were exceeded in 17 to 30 percent of the samples. No upgradient ground-water samples exceeded

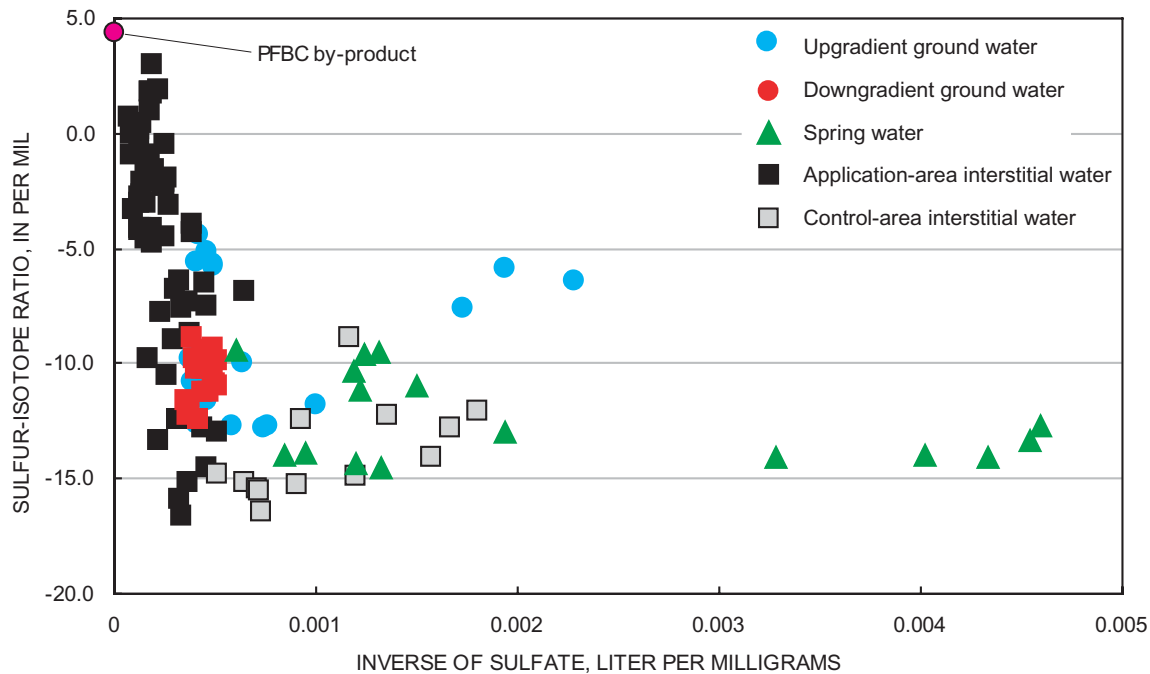


Figure 10. Relation of the inverse of sulfate concentration to sulfur-isotope ratios for selected water samples from the Fleming abandoned mine site, Tuscarawas County, Ohio.

the standard for beryllium; however, 29 of 30 ground-water samples from downgradient of the site exceeded the MCL. Only one sample from the application-area interstitial water exceeded the MCL for beryllium. The MCL for cadmium was exceeded in 61 of 206 samples, but 20 to 40 percent of each water type (including upgradient ground water and control-area interstitial water) also exceeded this MCL. Therefore, the source of beryllium and cadmium is likely related to spoil and (or) the aquifer materials at the mine site. The MCL for fluoride was exceeded in almost half of the application-area interstitial-water samples but no other samples. The source of fluoride is likely from fluorite (CaF₂), which is a common trace mineral associated with

the dolomitic sorbent. The MCL for lead (0.015 mg/L) was exceeded in only one control-area interstitial water sample with a concentration of 0.058 mg/L. No water samples exceeded the MCLs for arsenic and selenium (as of February 2002, both MCLs were at 0.050 mg/L). The greatest concentration of arsenic was detected in one sample of application-area interstitial water with a concentration of 0.010 mg/L. This sample was obtained during sampling round 1 (June 1995). As is the case for many abandoned mine sites in Ohio, the secondary MCLs for aluminum, iron, manganese, pH, sulfate, and total dissolved solids were exceeded in 50 percent or more of the samples.

Table 5. Comparison of Maximum Contaminant Levels for drinking water established by the U.S. Environmental Protection Agency with analyses of all water samples obtained from the Fleming abandoned mine site, Tuscarawas County, Ohio

[mg/L, milligrams per liter; na, not applicable; TDS, total dissolved solids; min, minimum; max, maximum; MCL, Maximum Contaminant Level]

Constituent	Maximum Contaminant Level (mg/L)	Detection limit(s) ^a (mg/L)	Total number of samples	Number of detections above detection limit (percent given in parentheses)	Number of samples that exceed MCL (percent given in parentheses)	Maximum value (mg/L)
National Primary Drinking-Water Regulations						
Antimony	0.006	0.106	160	8 (5)	unknown ^b	0.16
Arsenic	0.05	0.001 - 0.002	185	37 (20)	0 (0)	0.010
Barium	2	0.001	160	160 (100)	0 (0)	0.075
Beryllium	0.004	0.0001 - 0.002	160	79 (49)	30 (19)	0.037
Cadmium	0.005	0.001 - 0.08	206	90 (44)	61 (30)	0.17
Chromium	0.1	0.002 - 0.1	206	118 (57)	0 (0)	0.026
Copper	1.3	0.002 - 0.05	206	66 (32)	0 (0)	0.31
Fluoride	4.0	0.1 - 1.0	216	105 (49)	36 (17)	15.0
Lead	0.015	0.001 - 0.01	196	9 (5)	1 (<1)	0.058
Mercury	0.002	0.0001	61	0 (0)	0 (0)	na
Nitrate	10	0.01 - 0.05	163	34 (21)	0 (0)	4.4
Selenium	0.05	0.001 - 0.005	178	38 (21)	0 (0)	0.006
National Secondary Drinking-Water Regulations						
Aluminum	0.2	0.015 - 0.045	206	188 (91)	104 (50)	29.6
Chloride	250	0.1 - 1.0	216	188 (87)	1 (<1)	261
Copper	1.0	0.002 - 0.05	206	73 (35)	0 (0)	0.31
Fluoride	2.0	0.1 - 1.0	216	124 (57)	0 (0)	0.015
Iron	0.3	0.010	228	219 (96)	164 (72)	920
Manganese	0.05	0.0016	228	228 (100)	224 (98)	150
pH	6.5-8.5	na	267	na	192 (72 ^c)	min 3.2 max 7.9
Silver	0.10	0.003 - 0.046	206	183 (89)	0 (0)	0.063
Sulfate	250	0.11	216	216 (100)	212 (98)	13,500
TDS	500	computed ^d	164	na	157 (96)	20,850
Zinc	5	0.001 - 0.06	206	188 (91)	0 (0)	3.8

^a Detection limits varied depending on which laboratory performed the analysis, the dilution ratio, and the sample matrix.

^b The MCL was below the detection limit.

^c Seventy-two percent of the pH measurements were below the minimum accepted value of 6.5. No samples exceeded the maximum accepted value of 8.5.

^d Total dissolved solids is computed as the sum of all dissolved constituents.

Except for fluoride, all exceedances of the primary and secondary MCLs are due to the influences of AMD, not the PFBC by-product. Additionally, out of all the MCLs that were exceeded, only fluoride and sulfate are found in higher concentrations in the application-area interstitial waters than in control-area waters. A key consideration to comparisons of this type is whether these waters will ever be used as drinking-water sources. Given extremely high iron and sulfate concentrations derived from AMD, it is not likely that ground water from the site will be used as a drinking-water source, even for domestic animals. With regards to grazing by domestic animals, uptake of trace elements by vegetation was evaluated by Stehouwer and others (1996), who found that, with the exception of chromium, concentrations of all other trace elements in plant tissues either decreased or showed no response to application of PFBC by-product in spoil.

The nearest drinking-water supplies in the area are from domestic wells that derive water from the underlying Mississippian sandstones, which include the Blackhand Sandstone (locally referred to as the "Big Injun") and the Berea Sandstone. The domestic wells are at least 0.5 mi downgradient from the Fleming site. The nearest public-supply wells, which are screened in alluvial sands and gravels beneath Sugar Creek, are about 5 mi away and provide drinking water to the city of Dover.

GEOCHEMICAL MODELING

The ultimate fate and transport of elements derived from the PFBC by-product remains in question. The chemistry of interstitial water, ground water, and spring water from the site shows that interstitial-water samples contain leachate derived from the PFBC by-product and that the leachate chemistry has changed greatly during the 7 years of sampling; however, examination of the graphs presented in this report indicate that little, if any, effects of leachate derived from PFBC by-product can be found in ground water or spring water. An objective of this study was to determine the fate and mobility of elements derived from the PFBC by-product in an abandoned mine setting. To address this issue, three hypotheses were examined to determine the fate of elements derived from the PFBC by-product: (1) the sampling schedule missed the highest concentrations of PFBC by-product leachate, (2) the mass of PFBC by-product applied at the site was so small that dilution by rainwater and the overwhelming influence of AMD obscured detection by the methods used in this study, and (3) elements derived from the PFBC by-product leachate have precipitated as secondary minerals in the unsaturated zone. Each of the hypotheses is addressed individually below.

Hypothesis 1. The sampling schedule missed the highest concentrations of PFBC by-product leachate. Immediately after application, the first few rainfall events

may have dissolved readily soluble compounds from the PFBC by-product so that the maximum concentration of elements was mobilized to ground water before monitoring began. Application of PFBC by-product was completed in October 1994; however, the first sampling round was not done until June 1995. Additionally, other than interstitial-water sampling round 3, which coincided with a snowmelt event in January 1996, all sampling rounds were done during periods of little or no precipitation at base-flow conditions. Application-area interstitial waters show the greatest concentrations of elements during interstitial-water sampling round 3; therefore, soluble minerals from the PFBC by-product may dissolve primarily during precipitation events. Greenhouse pot studies by Stehouwer and others (1996) show that the concentrations of many soluble elements decrease rapidly after the first few flushes of water.

This hypothesis is precluded by the relatively slow ground-water-flow rates at the Fleming site. According to the ground-water-flow model by Haefner (1998), estimated traveltimes for ground water to flow from upgradient recharge areas to downgradient springs were on the order of tens of years, well within the sampling period. The shortest ground-water traveltime of 227 days was computed for a hypothetical water particle released on the water table near well cluster 4 that discharged at a downgradient spring. All other particles had traveltimes that exceeded 227 days, and the first sampling round was done within this timeframe. Although the sampling schedule for interstitial waters may have missed the maximum concentrations of elements associated with precipitation events, ground-water-flow rates were slow enough to ensure that any leachate that reached ground water was sampled during the study period.

Hypothesis 2. The mass of PFBC by-product applied at the site was so small that dilution by rainwater and the overwhelming influence of AMD obscured detection by the methods used in this study. The PFBC by-product was applied at 125 tons per acre over a 7-acre area for a total weight of 875 tons. The application mass was determined by calculating the required volume of PFBC by-product to bring the spoil pH up to 7. This represents addition of more than 43 tons of sulfur, 157 tons of calcium, and 82 tons of magnesium over the 7-acre area. Nevertheless, this amount may not have been adequate to influence the ambient concentrations in ground water and allow determination of the contribution of PFBC by-product leachate by analysis of mixing diagrams. As can be seen from median concentrations of many constituents, upgradient ground waters at the site also had relatively high concentrations of dissolved constituents compared to ground-water samples collected in other areas of eastern Ohio (as reported in Sedam and Francy, 1993).

Graphs of water-quality characteristics indicated that several downgradient ground-water samples might have mixed with a small amount of PFBC by-product leachate (figs. 7, 8, and 9). To investigate this possibility further,

water-quality data from rainwater, interstitial water, and ground water were modeled in NETPATH (Plummer and others, 1994). For this simulation, the observed chemical concentrations of selected water samples were combined to produce 12 possible models. Many models were eliminated on the basis of unrealistic output, such as the requirement for precipitation of pyrite. One reasonable model was identified as below:

$$\begin{array}{l} 26 \text{ percent rainwater} \\ + 1 \text{ percent PFBC by-product application-area} \\ \quad \text{interstitial water} \\ +73 \text{ percent upgradient ground water} \\ \hline \text{Downgradient ground water minus precipitation} \\ \quad \text{of jarosite (KFe}_3\text{(SO}_4\text{)}_2\text{(OH)}_6\text{)} \end{array}$$

Therefore, the observed chemistry of downgradient ground water may have been derived from mixing with a very small amount of the PFBC by-product. Other models do not require mixing with any PFBC by-product at all; so, the 1-percent estimate might be a maximum value, and dilution of the PFBC by-product leachate was likely.

Hypothesis 3. Elements derived from the PFBC by-product leachate have precipitated as secondary minerals in the unsaturated zone. High concentrations of dissolved solids derived from the PFBC by-product leachate may lead to precipitation of minerals including calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CaCO}_3)_2$), ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (Stehouwer and others, 1996). To evaluate whether thermodynamic conditions were favorable to precipitate secondary minerals, the geochemical model PHREEQC (Parkhurst and Appelo, 1999) was employed. PHREEQC uses chemical data from water-quality analyses to compute saturation indices for minerals. The saturation index (SI) is defined as the log of the ion activity product (IAP) divided by the solubility constant (K) for a given mineral.

$$SI = \frac{\log IAP}{K} \quad (4)$$

If SI is greater than zero, the mineral could precipitate but not dissolve; if SI is less than zero, the mineral could dissolve but not precipitate; and if SI is equal to zero, the mineral could be dissolving or precipitating. The primary assumption associated with these calculations is that all phases are in equilibrium—an assumption rarely met in natural environmental conditions. Nonetheless, this exercise is useful to evaluate the possibility that secondary minerals can precipitate or dissolve in the unsaturated zone and within aquifers beneath the Fleming site.

The SIs for all minerals given in the PHREEQC databases (phreeqc.dat and llnl.dat) initially were evaluated for each water sample with sufficient chemical data; however, only those minerals that are likely to exist in this

environment or may be associated with the PFBC by-product are described below. In addition to the four minerals named above, gibbsite ($\text{Al}(\text{OH})_3$), ferrihydrite ($\text{Fe}(\text{OH})_3$), jarosite ($\text{KFe}(\text{SO}_4)_2(\text{OH})_6$), and melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were included because these minerals are common in AMD environments. Input data for PHREEQC included concentrations of dissolved major and trace elements in water, alkalinity, pH, water temperature, and pE. (pE is analogous to pH, except that pE is equal to the negative log of the activity of electrons. It is closely related to the reduction-oxidation potential.) pE values for ground-water samples and spring-water samples were calculated from the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple obtained from field measurements of ferrous and total iron (ferric iron was calculated as the difference between ferrous and total iron).

Ferrous and total iron concentrations were not measured in the field in interstitial-water samples because of insufficient sample volumes. It was assumed that interstitial-water samples were in equilibrium with the atmosphere and were saturated with respect to dissolved oxygen. This assumption provided maximum possible pE values and is likely valid only for near-surface samples because oxygen is depleted with depth by processes such as decay of organic matter. Only redox-sensitive minerals (including ferrihydrite, jarosite, and melanterite) are affected by changing pE conditions. The influence of changing pE on SI for a sample of application-area interstitial water is shown in figure 11. The oxygen redox couple resulted in a calculated pE

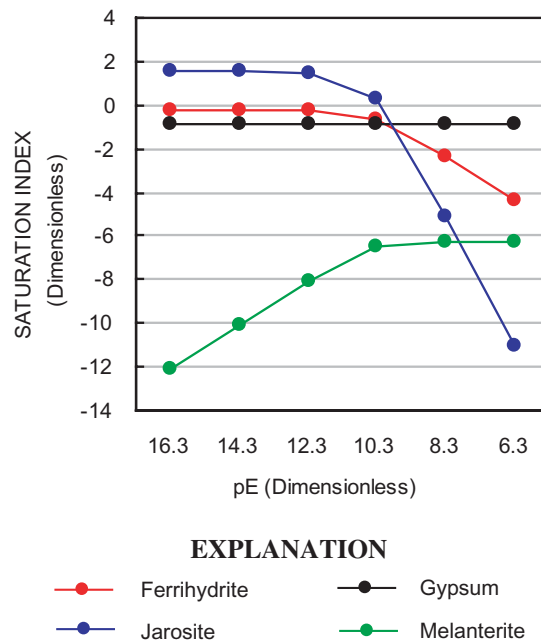


Figure 11. Relation of pE to saturation index calculated for selected minerals from an application-area interstitial-water sample collected at the Fleming abandoned mine site, Tuscarawas County, Ohio.

of 16.3, indicating extremely oxidizing conditions. PHREEQC was run six times with pE values ranging from 16.3 to 6.3 while keeping all other water-quality characteristics constant. The approximate lower limit of pE value of 6.3 was comparable to pE values calculated for anoxic (less than 0.1 mg/L of dissolved oxygen) ground-water samples. The SI for ferrihydrite and jarosite decrease with decreasing pE, whereas the SI for melanterite increases with decreasing pE (fig. 11). Although gypsum is the only pE-insensitive mineral shown in figure 11, the SIs calculated for calcite, dolomite, ettringite, and gibbsite also are insensitive to changing pE within the calculated pE range.

The distributions of SIs for the eight minerals listed above are given as boxplots in figures 12 and 13. Most water samples were supersaturated with respect to the hydroxides of aluminum (gibbsite) and iron (ferrihydrite). These hydroxides are relatively insoluble in oxidizing conditions and are known to adsorb trace elements. Therefore, the favorable conditions for hydroxide precipitation within the unsaturated zone may serve as a trace-element sink. All ground-water samples were anoxic, with median dissolved-oxygen concentrations of less than 0.1 mg/L; therefore, it is unlikely that minerals such as ferrihydrite or jarosite, which favor oxic conditions, could precipitate within pore spaces in aquifer materials. The resulting distribution of supersaturation with respect to ferrihydrite and jarosite in ground water likely is an artifact of the method in which pE was calculated. Ferrous and total iron concentrations of all ground-water samples were measured in the field to calculate pE values based on the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple. In an environment insensitive to changing pE within the calculated pE range, anoxic environment, all iron should tend towards the reduced (Fe^{2+}) form; however, field measurements indicated the presence of some oxidized iron (Fe^{3+}) in almost all samples. Even a small amount of oxidized iron resulted in saturation with respect to ferrihydrite and jarosite. Dissolved oxygen may be at high enough concentrations at the capillary fringe to allow precipitation of these minerals, but fluctuating or rising water levels may once again cause dissolution. Although not given here, the SIs for goethite (αFeOOH) were similar to those for ferrihydrite (all samples except those from spring water had SIs greater than zero). The boxplots show that more samples of control-area interstitial waters were undersaturated with respect to ferrihydrite than those for the application area. This is likely the result of higher pH in the application area caused by the neutralizing effect of the PFBC by-product leachate. More ground-water samples have SIs greater than zero with respect to jarosite than for any other water types. All water samples were undersaturated with respect to melanterite.

Very few water samples were supersaturated with respect to calcite and dolomite. Those samples with SI greater than zero were from the PFBC by-product application-area interstitial waters. Boxplots for ettringite had a similar distribution to gibbsite, although the values of SIs

for ettringite were much lower. The SI values for ettringite for all water samples were well below zero because ettringite precipitation generally requires pH conditions above 10.7 (Myneni and others, 1998). The similarities between the behavior of ettringite and gibbsite are most likely due to controls exerted on mineral precipitation by aluminum solubility. Several application-area interstitial water samples and upgradient ground-water samples had SIs for gypsum that exceeded zero.

These calculations indicate that precipitation of gibbsite, ferrihydrite, jarosite, calcite, dolomite, and gypsum may be occurring in the unsaturated zone and within aquifer materials at the Fleming site.

Of the three hypotheses given above, dilution (hypothesis 2) is the most probable cause of the few detections of elements related to the PFBC by-product in down-gradient ground waters. The small volume of PFBC by-product was virtually insignificant when compared to the overwhelming effects of AMD. It is likely that leachate from the PFBC by-product has mixed with downgradient ground water, but the chemical- and isotopic-detection methods used in this study may have been inadequate to resolve the relatively small amounts of leachate from the ambient ground water. In addition to dilution, precipitation of secondary minerals (hypothesis 3) in the unsaturated zone may have reduced the concentrations of major and trace elements in water. Consequently, it is improbable that any of the toxic elements of concern (arsenic, lead, or selenium) will cause water-quality problems at this site or other sites where similar application rates are used. It should be noted that if these elements were precipitated within or adsorbed by secondary minerals, they could potentially remobilize after recharge events or if geochemical conditions within the unsaturated zone or aquifers change from current conditions.

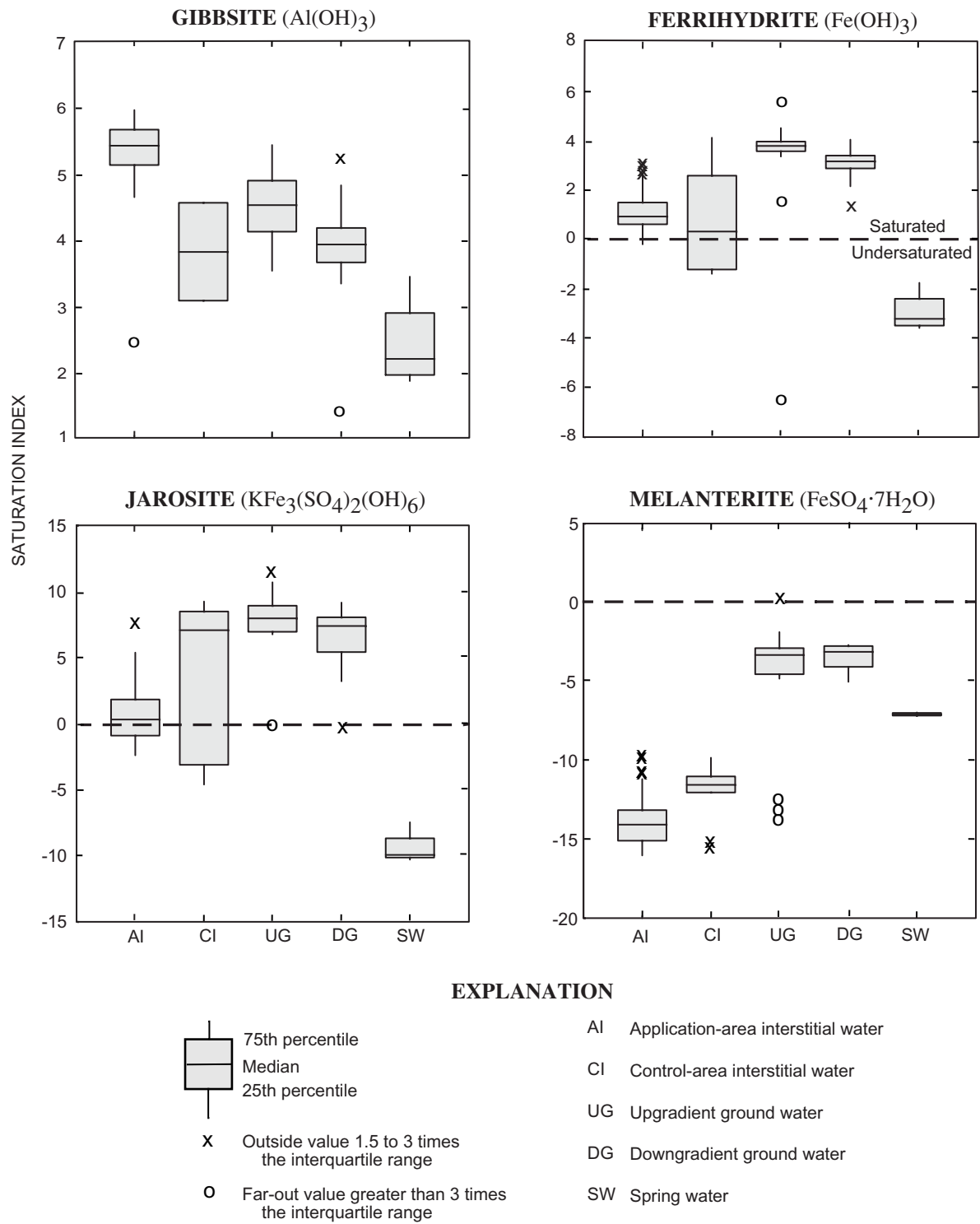
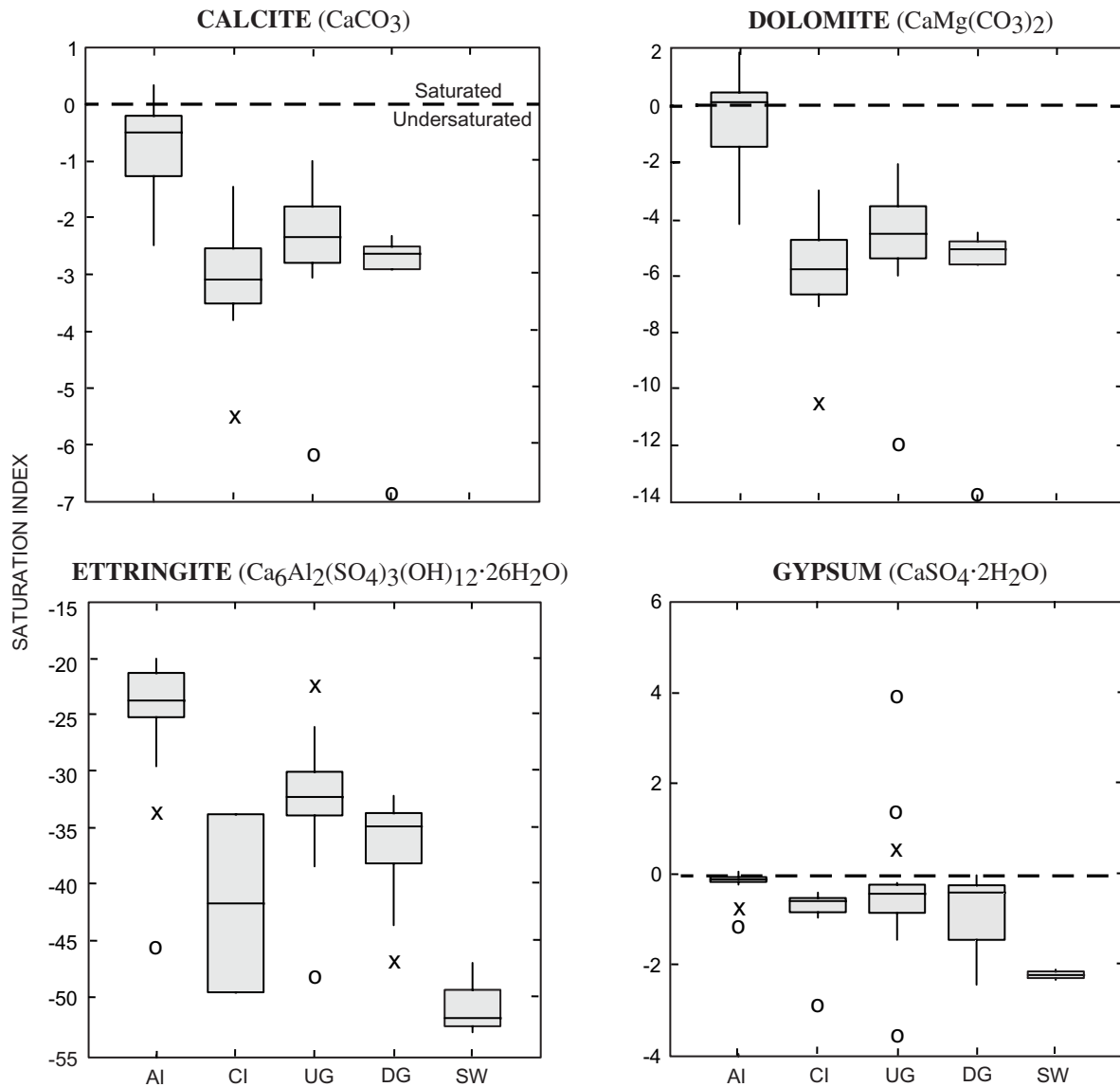
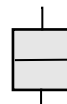






Figure 12. Distribution of saturation indices for gibbsite, ferrihydrite, jarosite, and melanterite for selected water samples from the Fleming abandoned mine site, Tuscarawas County, Ohio.



EXPLANATION

-  75th percentile
-  Median
-  25th percentile
-  X Outside value 1.5 to 3 times the interquartile range
-  O Far-out value greater than 3 times the interquartile range

- AI Application-area interstitial water
- CI Control-area interstitial water
- UG Upgradient ground water
- DG Downgradient ground water
- SW Spring water

Figure 13. Distribution of saturation indices for calcite, dolomite, ettringite, and gypsum for selected water samples from the Fleming abandoned mine site, Tuscarawas County, Ohio.

SUMMARY AND CONCLUSIONS

A 7-acre abandoned mine site (the Fleming site) in eastern Ohio was reclaimed with 125 tons per acre of pressurized fluidized bed combustion (PFBC) by-product and 50 tons per acre of yard-waste compost. The hydrology and water quality at the site was studied over a 7-year period to determine the environmental effects of reclamation with this material. The two main processes of interest in this study were (1) dissolution and leaching of PFBC by-products applied to the surface of the study area, and (2) the generation of acid mine drainage (AMD) in spoil left at the surface of the site after mining ceased. Addition of alkaline PFBC by-product was intended to increase pH, thereby reducing the solubility of major and trace elements in water. This report summarizes water-quality data from the study and presents several hypotheses regarding the fate of elements derived from the PFBC by-product.

Water quality in application-area interstitial waters (samples collected from the unsaturated zone) clearly showed the influence of leachate derived from the PFBC by-product. Application-area interstitial waters had elevated pH and specific conductance along with higher concentrations of boron, calcium, chloride, fluoride, magnesium, potassium, strontium, and sulfate than water samples collected in a control area where the PFBC by-product and compost were not used. Of these elements, only boron presents a potential concern because boron is known to be phytotoxic at high concentrations, and one of the goals of abandoned mine reclamation is reestablishment of vegetation. Sulfur-isotope ratios also showed the influence of PFBC by-product leachate because sulfate derived from the PFBC by-product had relatively positive isotope ratios as compared to those for spoil and aquifer materials. Increases in pH reduce the solubility of some elements; therefore, the median concentrations from application-area interstitial waters were lower for iron, nickel, and zinc than those in the control area. Graphical techniques used to highlight water-quality differences were successful with Fleming-site waters because the coal and sorbent used in the PFBC process were from different formations than those at the Fleming site and therefore had different geochemical signatures.

Comparisons of water-quality data obtained at the Fleming site to the U.S. Environmental Protection Agency Maximum Contaminant Levels (MCLs) show many exceedances of the MCLs. Out of all the MCLs that were exceeded, only fluoride and sulfate were found in higher concentrations in the application-area interstitial waters than in control-area waters. There were no exceedances of MCLs for elements of concern such as arsenic, lead, or selenium. It is not likely that the water at the Fleming site will ever be used as a drinking-water source.

Three plausible hypotheses were developed to investigate the fate and transport of elements derived from the PFBC by-product and the apparently minor influence of the

by-product on water quality: (1) the sampling schedule missed the highest concentrations of PFBC by-product leachate, (2) the mass of PFBC by-product applied at the site was so small that dilution by rainwater and the overwhelming influence of AMD obscured detection by the methods used in this study, and (3) elements derived from the PFBC by-product leachate have precipitated as secondary minerals in the unsaturated zone. Graphical analysis of median concentrations of elements associated with the PFBC by-product show that the concentrations of elements seemed to have peaked at or around the time of interstitial-water sampling round 3 (January 1996, 15 months after reclamation); therefore, changes in water quality (if any) should have been detected during this timeframe. Results from the geochemical models NETPATH and PHREEQC indicate that downgradient ground water may have mixed with a small amount of PFBC leachate and that thermodynamic conditions are favorable for secondary minerals to precipitate in the unsaturated zone and in aquifers at the site. Because the amount of PFBC by-product was small compared to the mass of other elements already in solution at the site, it is likely that dilution caused difficulty in distinguishing constituents from the PFBC by-product in downgradient ground waters.

Reclamation of the site was successful in that vegetation was reestablished and erosion was reduced. It was also successful in the sense that water quality in the PFBC by-product application area shows a raised pH, which was maintained throughout the 7-year period after reclamation. Because of low application rates and sorption onto iron and aluminum hydroxides, it is improbable that any of the toxic elements of concern (arsenic, lead, or selenium) will cause water-quality problems at this site or other sites where similar application rates are used. At the onset of this project, researchers from the U.S. Geological Survey and the Ohio Agricultural Research and Development Center anticipated ground-water-quality improvement as a result of reclamation and soil amendment with PFBC by-products. Seven years later, however, ground-water quality remained poor and showed no signs of improvement during the study period.

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