

# Geochemistry of Water and Mobilization and Transport of Solutes in Coal Mine Spoils, East-Central Texas

By Roger W. Lee<sup>1</sup> and Jennifer T. Wilson<sup>2</sup>

**Abstract.** Reclamation of surface mines in Texas became mandatory in 1978, requiring that overburden removed during surface mining (mine spoils) be emplaced in open mine pits and land surface reshaped to pre-mining topography. The reclaimed land surface then is revegetated to control erosion. Shallow ground-water-flow systems that develop in reclaimed areas have geochemical characteristics substantially different from pre-mining conditions. Because the solutes produced by mine spoils potentially can degrade the quality of ground and surface water, the mining industry has developed methods of spoils emplacement and surface reclamation to mitigate these effects. Comparisons of chemical data from ground water collected from two coal mine reclamation sites in east-central Texas and results of a laboratory-controlled, column-leaching experiment on reclaimed spoil material from the area indicate that large amounts of solutes are mobilized from the spoil material. Increased concentrations of dissolved solids (550 to 6,050 milligrams per liter), dissolved sulfate (73 to 2,800 milligrams per liter), dissolved iron (2,000 to 160,000 micrograms per liter), and dissolved manganese (800 to 13,000 micrograms per liter) and low pH (4.0 to 6.2) in ground water from two reclaimed areas indicate these to be the primary water-quality concerns. However, reclamation practices and establishment of strongly reducing environments in shallow ground water inhibit mobilization and transport of trace elements (including radium-226 and uranium-238, which are present in very small amounts in the ground water). Mass-balance models indicate that pyrite oxidation and dissolution of halite, carbonates, amorphous alumina, amorphous silica, and to a lesser extent, gypsum are reaction processes occurring in reclaimed spoils. Sulfate reduction was apparent in the aquifers from detection of sulfide in ground water; however, the magnitude of sulfate reduction was not substantial in mass-balance models.

## Introduction

In the Gulf Coastal Plain of Texas, shallow coal (lignite) deposits have been extracted for many years by surface-mining methods. In 1978, the Texas Railroad Commission was directed by the U.S. Office of Surface Mining to require reclamation of all active strip mines in Texas. Reclamation of these lands is ongoing, and ground-water flow and subsurface geochemical environments are being re-established as recharge percolates through the mine spoils and saturated flow of ground water develops. Because much of this reclaimed mine land has low topographic relief and low permeability, ground water flows slowly for long distances and reducing conditions favorable for sulfate reduction can develop (Holzmer, 1992).

Spoils emplaced in strip-mined areas typically contain pyrite and its oxidation products, residual coal, and carbonaceous shale. Rewetting of the spoil material occurs primarily through precipitation recharge, but lateral flow of water from undisturbed aquifers and possibly from deeper artesian aquifers can occur. As pyrite

oxidation occurs during the weathering of spoil, dissolution of pyrite oxidation products and other minerals can cause dissolved solids concentrations to increase relative to pre-mining concentrations (Lee, 1981; Davis, 1989; Williams and Clark, 1994). Oxidation-reduction (redox) processes in mine spoils can affect the mobility of trace elements. Trace elements can be mobilized as a result of acid-forming oxidation reactions and as a result of reduction of manganese and iron oxides that contain trace elements. Some trace elements can be immobilized under the strongly reducing conditions of sulfate reduction (facilitated by bacteria such as *Desulfovibrio desulfuricans* (Dockins and others, 1980)). Coal residues and coal-bearing sediment also are known to contain radium and uranium (U.S. Environmental Protection Agency, 1978). The activity of sulfate-reducing bacteria under the field conditions of this study is pertinent to microbiological research in the control of uranium solubility (Lovley and Phillips, 1992).

Ground water with large concentrations of dissolved solids, trace elements, and other constituents eventually could discharge as base flow to streams, thus

<sup>1</sup> Research Hydrologist, U.S. Geological Survey, Austin, TX 78754.

<sup>2</sup> Co-op Student, U.S. Geological Survey, Austin, TX 78754.

affecting quality of surface water. Information on chemical constituents and geochemical environments in ground water in mine spoils and potentially affected surface water is needed to evaluate water-quality changes that result from surface reclamation practices. Study of solutes from mine spoils and their mobility under field and laboratory conditions can improve understanding of geochemical controls on major constituents and trace elements. This study by the U.S. Geological Survey (USGS), in cooperation with the City of Houston, will provide data and information that could result in improved surface-reclamation practices to mitigate potential water-quality problems.

### **Purpose**

The purpose of this paper is to discuss the chemistry of ground water and transport of solutes in mine spoils emplaced in strip-mined areas after surface reclamation. Sampling of ground water in mine spoils and a laboratory column-leaching experiment using mine spoils were done during 1994–95 to determine solute chemistry and to evaluate geochemical controls on trace elements and radionuclides in spoils at a coal mine in east-central Texas.

### **Background**

In aquifers, geochemical conditions can change from oxidizing to reducing along ground-water flowpaths. Redox processes in ground water for some chemical solutes typically are bacterially mediated and can affect the mobility of many solutes, including nutrients, organic compounds, trace elements, and naturally occurring radionuclides such as radium and uranium. In areas where land disturbance from surface mining or contamination of shallow ground water has occurred, geochemical conditions are altered and chemical constituents can mobilize or attenuate as a result of redox processes in the aquifer. Some understanding of aqueous geochemical controls on mobility and transport of solutes has been achieved in undisturbed sediments, in ore deposits, and within uranium mining wastes. For example, radium is more soluble and mobile in more anaerobic ground-water environments (Beaucaire and Toulhoat, 1987), whereas uranium is more soluble and thus more mobile in aerobic ground-water environments (Drever, 1988). However, the conditions that can introduce these solutes into water require more site specific research to improve understanding of geochemical and microbiological processes affecting mobilization, fate,

and transport of radium and uranium in reducing environments in ground water.

Reducing zones can be established in disturbed ground-water systems within a relatively short time (months to years), depending on the nature of the disturbance and local hydrogeologic conditions. Redox conditions are affected by the oxygen content of recharge water, the distribution and reactivity of organic matter and other potential reductants in the aquifer, the distribution of potential redox buffers in the aquifer, and the circulation rate of the ground water (Drever, 1988). Shallow ground water might contain sufficient dissolved oxygen to maintain an oxidizing environment in which reduced species in aqueous and solid phases can be oxidized. Similarly, chemical species in their more highly oxidized states can be reduced in an oxygen-poor reducing environment.

As reduced species (most commonly sulfur, nitrogen, iron, manganese, and carbon) in an aquifer react with dissolved oxygen in recharge water (usually enhanced by bacteria), the oxygen can be consumed more rapidly than it can be supplied by recharge or by diffusion from the atmosphere. Thus, geochemical environments have been observed to change along a ground-water flowpath from oxidizing to reducing for certain chemical species.

In natural environments, reducing zones that occur along ground-water flowpaths can be established for millennia, reaching a degree of chemical "steady-state" within an aquifer (Back, 1966). Geochemical zonation along a ground-water flowpath can occur by buffering redox conditions with reducible solid phases from the aquifer matrix containing sulfur, iron, manganese, or carbon. Bacteria are active in most redox environments, catalytically increasing reaction rates of redox reactions. Rates of redox reactions depend on availability of labile carbon, availability of specific oxidized species, bacterial activity, and reducing conditions, all of which can be affected by ground-water flow.

Trace elements commonly are present in association with organic and inorganic compounds in sedimentary rocks. When the sediments are contaminated or disturbed, some of these trace elements can be mobilized and transported by ground-water flow. The mobility of a specific trace element typically depends on the mineral phases, sorptive properties of the solid phase, solubility of the stable species of the element, pH of the aqueous phase, redox potential (Eh) of the aqueous phase, and the availability of complexing agents. Knowledge of which trace elements are present in the mine spoils from east-central Texas is needed to assist in the design of mine reclamation for the purpose of mitigating potential degradation of water quality from excessive amounts of certain trace elements.

In sulfate-reducing environments, attenuation of uranium transport is expected, but site specific documentation has not been obtained. Uranium solubility in natural environments is controlled principally by the mineral uraninite ( $UO_2$ ) (Langmuir, 1978). In aquifers where the partial pressure of  $CO_2$  ( $P_{CO_2}$ ) is large, aqueous carbonate complexes mobilize uranium in zones of higher pH and Eh (Runnels and Lindberg, 1981). Complexes involving sulfate, fluoride, and phosphate also can enhance uranium mobility. Recent microbiological research has shown that sulfate-reducing bacteria (*Desulfovibrio desulfuricans*) enzymatically metabolize dissolved uranium, converting it to solid uraninite (Lovley and Phillips, 1992). Reduction of more soluble uranium (VI) to less soluble uranium (IV) by dissimilatory iron (III)-reducing microorganisms also has been observed (Lovley and others, 1991).

Radium mobility is less well understood but has been associated with barite (barium sulfate) as a coprecipitate (Beaucaire and Toulhoat, 1987). Radium tends to be mobile in reducing environments, but the chemical processes involved are not well understood.

### **Description of Study Area**

The study area is a surface coal mine located in east-central Texas (Fig. 1). Specifically, two areas of reclamation were studied, one reclaimed mostly in 1987 and a second area reclaimed mostly in 1991. Coal seams were mined to depths of about 150 feet (ft) below land surface. Mine spoils were emplaced in the mined-out pits, and the surface reclaimed to approximate original topography. The 1991 site had at least one layer of sediment removed from the spoil before emplacement owing to large pyrite concentrations in the layer. Current reclamation practices at the mine include surface placement of about 10 ft of sandy topsoil with fertilizer and lime added (Joel Trouart, NW Resources, oral commun., 1994). Revegetation typically is done with varieties of prairie grasses or coastal bermuda grass. The following descriptions summarize the geologic and hydrologic characteristics of the mine site.

**Geology.** The mined areas are within the "Lignite Belt" of the Wilcox Group, a thick sequence of alternating fluvial-deltaic deposits. The lignite beds are contained in the upper unit known as the Calvert Bluff Formation. The Calvert Bluff Formation (900 ft thick) was deposited in the upper part of a transition zone between a lower alluvial plain and an upper deltaic plain. Three mineable lignite beds are in the lower part of the Calvert Bluff Formation of the Wilcox Group, ranging from 1 to 13 ft thick, with an average thickness of 10 ft. Overburden thickness ranges from 0 to 280 ft above the deepest

lignite bed in the permitted mine area. Overburden lithology is primarily interbeds of sand, silt, and clay with several minor lignite beds. Principal mineralogy of the coal-bearing sediment in the Wilcox Group includes quartz, feldspars, and clay minerals, with variable amounts of calcite, dolomite, and pyrite (Dutton, 1986; T.U. Services, 1992). X-ray diffraction analysis of bulk spoil material recovered from the mine contained appreciable amounts of quartz, feldspars, and clay minerals (smectite), with lesser amounts of aragonite, dolomite, and pyrite although proportions can vary locally. The mineral r merite, an acidic iron sulfate derived from pyrite oxidation, also was present in the sample.

**Hydrology.** The principal source of recharge to local aquifers in the Calvert Bluff Formation is from precipitation. Most discharge from local aquifers is to area streams, although locally, thin clay layers divert some of the percolating water to springs and seeps. Development of a water-table aquifer in the re-emplaced spoils at the mine site as a result of recharge from precipitation has been estimated to require about 7 years (Wade Robinson, NW Resources, oral commun., 1995). In some areas, rehydration of mine spoils can result from ground water either rising from deeper aquifers or moving in laterally from adjacent, undisturbed sediments.

### **Methods**

**Observation Wells.** In March 1995, nine observation wells were installed in different parts of the reclaimed mine area using mud-rotary drilling (Fig. 1). Each well was constructed of 4-inch (in.) inside-diameter PVC casing with a 10-ft screen at the bottom of the borehole. The annular space was grouted from 2 ft to 12 ft above the screen, then backfilled with cuttings to land surface. Well APM-3OB was installed as a monitoring well in 1987 using similar drilling and installation methods. The observation wells were installed along two traces of section (*A-A'* and *B-B'*) approximately parallel to probable respective ground-water-flow directions through the mine spoils (Fig. 1). Section *A-A'* represents a ground-water-flow direction in the older spoils at the mine; emplacement and initial surface reclamation occurred mostly in 1987. Section *B-B'* represents a ground-water-flow direction in younger mine spoils; emplacement and initial surface reclamation occurred mostly in 1991. Both mine-spoil areas have small detention ponds at the down-gradient end of their respective flowpaths. These ponds were constructed downgradient from the spoils to receive ground-water seepage and to impound surface runoff temporarily.

The observation wells along each trace of section were distributed originally as three nests of two



wells each—a shallow well screened near the water table and a deep well screened about 10 ft below the bottom of the shallow well. Three of the shallowest wells were screened above the present (1995) water table and produced no water for sampling.

**Ground-Water Sampling Procedures.** One-time sampling of observation wells in the area was done in September 1993 for APM-3OB and in April 1995 for the newer wells. Sampling followed the procedures described in Wood (1976) and Claassen (1982). Observation wells were purged of at least 3 casing volumes and sampled using a 2-in. submersible pump. Where water levels were less than 25 ft below the top of the well casing, a peristaltic pump was used for purging and sampling. The USGS National Water-Quality Laboratory in Arvada, Colo., analyzed ground-water samples for major cations and anions, nutrients, and trace elements, including radium and uranium using methods described in Fishman and Friedman (1989). pH, water temperature, alkalinity, and dissolved oxygen were measured on site for all samples. Dissolved oxygen concentrations were measured using Chemets<sup>1</sup> (Chemetrics Inc., Calverton, Va.), which has a lower detection limit of 0.1 milligram per liter (mg/L).

**Column Experiment.** The column experiment consisted of flow of a solution, representing recharge water and containing a conservative tracer, through a column packed with 65-percent quartz sand and 35-percent mine spoil by dry weight. The sand fraction was a medium-grained Ottawa quartz sand that was acid-washed before mixing with the spoil material and was included to increase velocity upward through the spoils. The spoil-material fraction (275 grams (g) wet weight) was sampled from emplaced mine spoils prior to reclamation about 1 ft below land surface at the mine site. Moisture content of the spoil material was measured as 17.6 percent by weight. Distilled water, sand, and spoil material were thoroughly blended to create a thick, smooth mixture. The mixture was poured into a 30.5-in. (length) × 1.25-in. (inside diameter) clear plastic column. After pumping approximately 1,000 milliliters (mL) of distilled/deionized water upward through the vertically oriented column at a rate of 0.5 milliliter per minute (mL/min), the height of the sand-spoil-water mixture stabilized. Total volume of the column was 620 mL.

The influent solution simulating recharge contained 9 mg/L bromide tracer, and had a  $P_{CO_2}$  of  $10^{-1}$  atmospheres and a pH of 4.5 (no other solutes were present). The  $P_{CO_2}$  ( $10^{-1}$  atmospheres) was selected

<sup>1</sup> The use of brand or product names is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

based on data collected on site that show concentrations of  $CO_2$  of more than 5 percent (volume/volume) in unsaturated-zone gases in reclaimed areas. In the buried spoils,  $CO_2$  is produced by the oxidation of residual coal and the release of  $CO_2$  from acid dissolution of carbonate minerals. The solution was pumped through the column from bottom to top at a flow rate of 0.5 mL/min. The total flow through the column of about 2 liters (L) of influent solution represents about 9 pore volumes in 2.8 days. For the packed column, assuming 35-percent porosity for the medium, 1 pore volume is about 220 mL. The column leachate was filtered through a 0.45-micrometer ( $\mu$ m) in-line filter and collected in 70-mL increments. Sample fractions were analyzed for specific conductance, pH, major cations and anions, and trace metals. The specific conductance and pH were measured soon after the collection of the leachate in the USGS laboratory in Austin, Tex. Concentrations of major cations and anions and trace elements were analyzed at laboratories of the University of Texas at Austin. Anions (sulfate, chloride, bromide, and nitrate) were analyzed using an ion chromatograph; and cations (calcium, magnesium, sodium, and potassium) and trace elements (aluminum, barium, boron, chromium, cobalt, iron, lead, manganese, nickel, strontium, and zinc) were analyzed using inductively coupled plasma-emission spectroscopy. Silicon (Si) was analyzed using atomic-absorption spectroscopy.

The initial column leachates of distilled/deionized water used to prepare and stabilize the column medium were not analyzed. It is assumed that some solutes were leached from the column in the preparation phase when approximately 3 pore volumes of fluid were passed through the medium before doing the column experiment.

## **Geochemistry of Water in Mine Spoils**

### **pH and Dissolved Oxygen**

The pH of the water from all the wells sampled ranges from 4.0 to 6.2 (Table 1). Typically, lower pH occurs in water from wells that are deeper in the mine spoils. Dissolved oxygen concentrations decrease with increasing depth at both reclaimed sites (Table 1) with the exception of water from well USGS-3A which contains anomalous dissolved oxygen concentrations greater than 1 mg/L. Isolated zones of ground water in the spoils could have different redox conditions but it is unlikely that oxygen could be present in ground water at the depth to which well USGS-3A is open (39 to 44 ft). Thus, the dissolved oxygen concentration measured in water from well USGS-3A probably is an artifact of well installation or possibly sample collection.

**Table 1.** Description of observation wells and dissolved chemicals in ground-water samples from mine spoils, east-central Texas, 1993–95

[Concentrations in milligrams per liter unless otherwise specified; ft, feet;  $\mu\text{S}/\text{cm}$ , microsiemens per centimeter at 25 degrees Celsius;  $^{\circ}\text{C}$ , degrees Celsius; --, nodata;  $\mu\text{g}/\text{L}$ , micrograms per liter; dpm/L, disintegrations per minute per liter; mmol/L, millimoles per liter]

Observation well (Fig. 1)	Date of sample	Total depth below land surface (ft)	Screened interval of well (ft)	Specific conductance ( $\mu\text{S}/\text{cm}$ )	Field pH (standard units)	Temperature ( $^{\circ}\text{C}$ )	Dissolved oxygen	Dissolved calcium	Dissolved magnesium	Dissolved sodium	Dissolved potassium	Bicarbonate	Dissolved sulfate	Dissolved chloride	Silica	Calculated dissolved solids
<b>Section A–A' (Fig. 1)</b>																
APM–30B	09–29–93	33	26–31	7,990	4.8	24.8	0.23	730	360	790	11.0	35	2,100	1,600	51	5,660
USGS–3B	06–08–95	20	15–20	5,310	4.2	21.3	.22	560	290	340	2.3	0	2,800	510	98	4,630
USGS–5A	06–08–95	20	15–20	9,210	5.7	22.3	.69	720	430	900	5.6	130	1,100	2,800	36	6,050
<b>Flowpath 1a</b>																
USGS–4A	06–08–95	44	39–44	2,920	6.2	21.8	--	52	77	270	4.8	340	330	400	7.0	1,310
USGS–3A	06–08–95	44	39–44	7,350	4.0	25.0	1.24	660	380	550	12.0	0	2,500	1,400	72	5,570
<b>Section B–B' (Fig. 1)</b>																
USGS–2A	06–07–95	40	35–40	4,030	6.1	25.0	.50	370	170	340	9.0	620	980	550	24	2,750
<b>Flowpath 2a</b>																
USGS–1B	06–07–95	40	35–40	950	6.2	22.6	--	31	13	150	1.8	270	73	110	38	550
APM–1A	06–07–95	43	35–40	3,430	6.2	22.5	1.04	260	100	330	8.1	470	690	500	35	2,160
<b>Flowpath 2b</b>																
USGS–1A	06–07–95	60	55–60	1,150	6.1	28.1	1.00	26	12	210	2.9	340	150	89	46	710
APM–1RD	06–07–95	60	52–57	4,260	5.7	28.0	.77	330	160	490	4.7	590	1,300	460	25	3,070
Observation well (Fig. 1)	Nitrate (as N)	Ammonium (as N)	Phosphate (as P)	Aluminum ( $\mu\text{g}/\text{L}$ )	Arsenic ( $\mu\text{g}/\text{L}$ )	Barium ( $\mu\text{g}/\text{L}$ )	Boron ( $\mu\text{g}/\text{L}$ )	Iron ( $\mu\text{g}/\text{L}$ )	Manganese ( $\mu\text{g}/\text{L}$ )	Zinc ( $\mu\text{g}/\text{L}$ )	Radium-226 (dpm/L)	Uranium-238 ( $\mu\text{g}/\text{L}$ )	$^{234}\text{U}/^{238}\text{U}$ activity ratio	Total organic carbon	Total inorganic carbon (mmol/L)	
<b>Section A–A' (Fig. 1)</b>																
APM–30B	0.07	9.7	0.01	540	19	200	1,500	160,000	9,800	1,900	--	0.23	1.05	18	11.78	
USGS–3B	.01	5.7	.03	4,130	5	100	2,100	18,200	12,400	<10	2.17	.20	2.17	19	.15	
USGS–5A	.01	.40	.02	20	3	100	110	16,000	12,000	30	1.85	--	1.24	14	7.47	
<b>Flowpath 1a</b>																
USGS–4A	.01	1.3	.01	<10	2	100	110	79,000	4,000	<10	1.12	.25	1.12	47	11.95	
USGS–3A	.01	6.2	.03	8,900	<1	100	1,200	31,000	13,000	500	2.56	.90	1.22	11	.22	
<b>Section B–B' (Fig. 1)</b>																
USGS–2A	.01	.60	.01	<10	5	100	460	30,000	6,200	10	1.23	.14	1.87	8	22.68	
<b>Flowpath 2a</b>																
USGS–1B	.02	.16	.04	<10	6	150	90	11,000	1,400	12	1.24	.17	1.24	8	9.19	
APM–1A	.02	.34	.05	100	2	100	200	23,000	4,600	10	1.36	--	--	4	15.74	
<b>Flowpath 2b</b>																
USGS–1A	.01	.04	.07	<10	5	62	70	2,000	800	<10	1.04	.52	1.11	3	12.76	
APM–1RD	.01	.65	.01	16	2	1,000	260	31,000	6,400	40	.80	6.3	1.26	7	35.63	

## **Major Ions and Hydrochemical Facies**

Major cation and anion data for water from the 10 wells completed in spoils are variable. Dissolved calcium, magnesium, and sodium concentrations range from 26 to 730 mg/L, 12 to 430 mg/L, and 150 to 900 mg/L, respectively (Table 1). Dissolved potassium and ammonium concentrations in the ground water range from 1.8 to 12 mg/L and 0.04 to 9.7 mg/L, respectively. Dissolved bicarbonate, sulfate, and chloride concentrations range from 0 to 620 mg/L, 73 to 2,800 mg/L, and 89 to 2,800 mg/L, respectively. Low pH and large amounts of dissolved sulfate are expected from pyrite oxidation in the mine spoils.

Major solutes in ground-water samples from wells along sections *A-A'* and *B-B'* show changes from wells upgradient to wells a few hundred feet downgradient. Hydrochemical facies (Back, 1961) of ground water in mine spoils vary from sodium sulfate to sodium calcium sulfate. Along section *A-A'*, the samples from upgradient wells principally are sodium and mixed-anion hydrochemical facies (Fig. 2) with relatively low dissolved solids concentration (1,310 mg/L from well USGS-4A (Fig. 3d)). Downgradient, the hydrochemical facies evolve to mixed-cation chloride sulfate facies, with some magnesium and bicarbonate, to mixed-cation, mixed-anion hydrochemical facies, with a maximum dissolved solids of 6,050 mg/L in water from well USGS-5A. From well USGS-3A to well APM-3OB and from well USGS-3B to well USGS-5A, dissolved sulfate concentrations decrease from 2,500 to 2,100 mg/L and 2,800 to 1,100 mg/L, respectively (Fig. 3c). The decrease in sulfate indicates the possibility of dilution or sulfate reduction. The increases in concentrations of dissolved sodium and chloride at wells APM-3OB and USGS-5A support dilution. At all wells, hydrogen sulfide odor was readily detected, indicating that sulfate reduction occurs in the mine-spoil aquifer; however, large amounts of sulfate reduction likely would not occur in ground water in the spoils.

Because of the proximity of the detention pond and the possibility that the gradient from the water table to the pond can reverse, the water sampled at wells APM-3OB and USGS-5A could represent spoil water mixed with more dilute pond water. Because this distinction between spoil water and pond water could not be determined and because chemical data of pond water were not available, these two wells were not considered in later mass-balance computations.

In ground water along section *B-B'*, hydrochemical facies evolve from sodium bicarbonate to mixed cation and mixed anion. The dissolved solids concentrations in wells along section *B-B'* (Fig. 4d) are generally lower than in wells along section *A-A'*, ranging

from 550 mg/L upgradient at well USGS-1B to 3,070 mg/L at well APM-1RD. Sulfate increased consistently in a downgradient direction in all wells sampled along section *B-B'* (Fig. 4c). Although chemical evolution is similar in flowpaths for both reclaimed areas, the differences in dissolved solids concentrations might result from changes that have occurred in handling of mine spoils and surface reclamation practices at each location. For example, pyrite content of spoils at section *A-A'* could be greater than at section *B-B'*.

## **Trace Elements**

Ground-water samples were analyzed for dissolved aluminum, arsenic, barium, boron, cadmium, chromium, copper, iron, lead, manganese, selenium, silver, zinc, radium-226, and uranium-238. Cadmium, chromium, copper, lead, selenium, and silver were not detected in any of the samples. Trace elements concentrations above laboratory detection limits are reported in Table 1 and discussed below:

**Aluminum.** Dissolved aluminum concentrations range from less than 10 to 8,900 micrograms per liter ( $\mu\text{g/L}$ ) (Table 1). The largest aluminum concentrations probably are caused by the high level of acidity in wells USGS-3A and USGS-3B (pH of 4.0 and 4.2, respectively). Where pH is greater than 6.0, aluminum concentrations usually are less than 20  $\mu\text{g/L}$ . The apparent relation between pH and aluminum concentration indicates that the acidity generated in the ground water enhances dissolution of amorphous aluminum, clay minerals, and aluminosilicates, which also is indicated by large silica ( $\text{SiO}_2$ ) concentrations—72 and 98 mg/L at wells USGS-3A and USGS-3B, respectively (Table 1).

**Arsenic.** Dissolved arsenic concentrations generally are low, ranging from less than 1 to 19  $\mu\text{g/L}$  in the water samples (Table 1). These concentrations indicate that arsenic is not present in appreciable amounts in samples of ground water from wells in spoil material along sections *A-A'* and *B-B'* and is not likely to be mobilized if present in the aquifer matrix under the existing geochemical conditions.

**Barium.** Dissolved barium concentrations range from 62 to 1,000  $\mu\text{g/L}$  in the water samples. Some barium might be present in spoil material as barium sulfate (barite), barium carbonate (witherite), or barium feldspar. Barium concentrations in water would be expected to be low because of the relatively low solubility of barite and the large amounts of sulfate in most of the ground water in the two reclaimed areas.

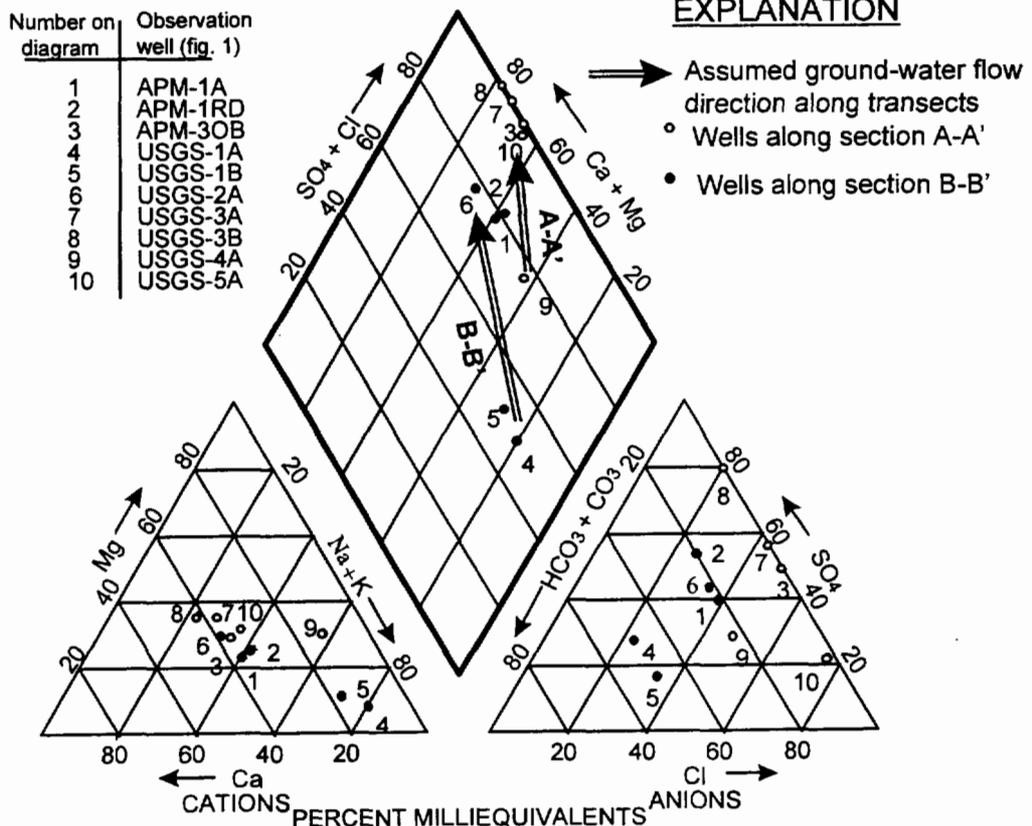
**Boron.** Dissolved boron concentrations range from 70 to 2,100  $\mu\text{g/L}$  in the water samples (Table 1). Although some boron could occur naturally in water in clay-rich

sedimentary aquifers, the largest boron concentrations occur in the samples having the lowest pH (wells APM-3OB, USGS-3B, and USGS-3A). This indicates that boron might be mobilized from aluminosilicate minerals that are undergoing acid dissolution.

**Iron and Manganese.** Concentrations of dissolved iron and manganese are high and range from 2,000 to 160,000  $\mu\text{g/L}$  and 800 to 13,000  $\mu\text{g/L}$ , respectively (Table 1). In water samples from wells in mine spoils along section A-A', concentrations of dissolved iron and manganese are higher than in water samples from wells along section B-B'. Concentrations of both solutes increase down-gradient along sections A-A' and B-B' (Figs. 3e, 3f, 4e, 4f). Increased concentrations of iron and manganese in ground water typically are caused by reducing conditions that mobilize the more soluble reduced  $\text{Fe}^{+2}$  and  $\text{Mn}^{+2}$  from less soluble  $\text{Fe}^{+3}$  and  $\text{Mn}^{+4}$  in mineral phases and amorphous coatings on grains. Because of the oxidation of pyrite in spoil material, iron can be released as  $\text{Fe}^{+2}$ , and the high acidity in water can enhance dissolution of other compounds of iron and manganese, resulting in mixed oxidation states of both elements in the aqueous phase.

**Zinc.** Dissolved zinc concentrations are highly variable, ranging from less than 10 to 1,900  $\mu\text{g/L}$ . In water samples along section A-A', dissolved zinc concentrations are highest; whereas in water samples along section B-B', the highest concentration is 40  $\mu\text{g/L}$  in water from well APM-1RD. This contrast in zinc concentrations between sections indicates either greater abundance of available zinc or geochemical conditions, such as lower pH, more favorable to mobilization of zinc in the older mine spoils along section A-A'.

**Radium-226 and Uranium-238.** Radium-226 and uranium-238 activities are relatively small in the water samples, ranging from 0.80 to 2.56 disintegrations per minute per liter (dpm/L) and 0.14 to 6.30  $\mu\text{g/L}$ , respectively (Table 1). Uranium increases with increasing depth along sections A-A' and B-B' (Figs. 3h, 4h). The activities of radium-226 are highest along section A-A', especially USGS-3A and USGS-3B where activities from samples are 2.56 and 2.17 dpm/L, respectively (Fig. 3g); which indicates that the higher acidity between sections A-A' and B-B' could affect the solubility of radium-226. Radium activities increase with increasing depth along section A-A' but decrease with increasing depth



**Figure 2.** Trilinear diagram of water analyses from observation wells in mine spoils, east-central Texas (well and section locations shown in Fig. 1).

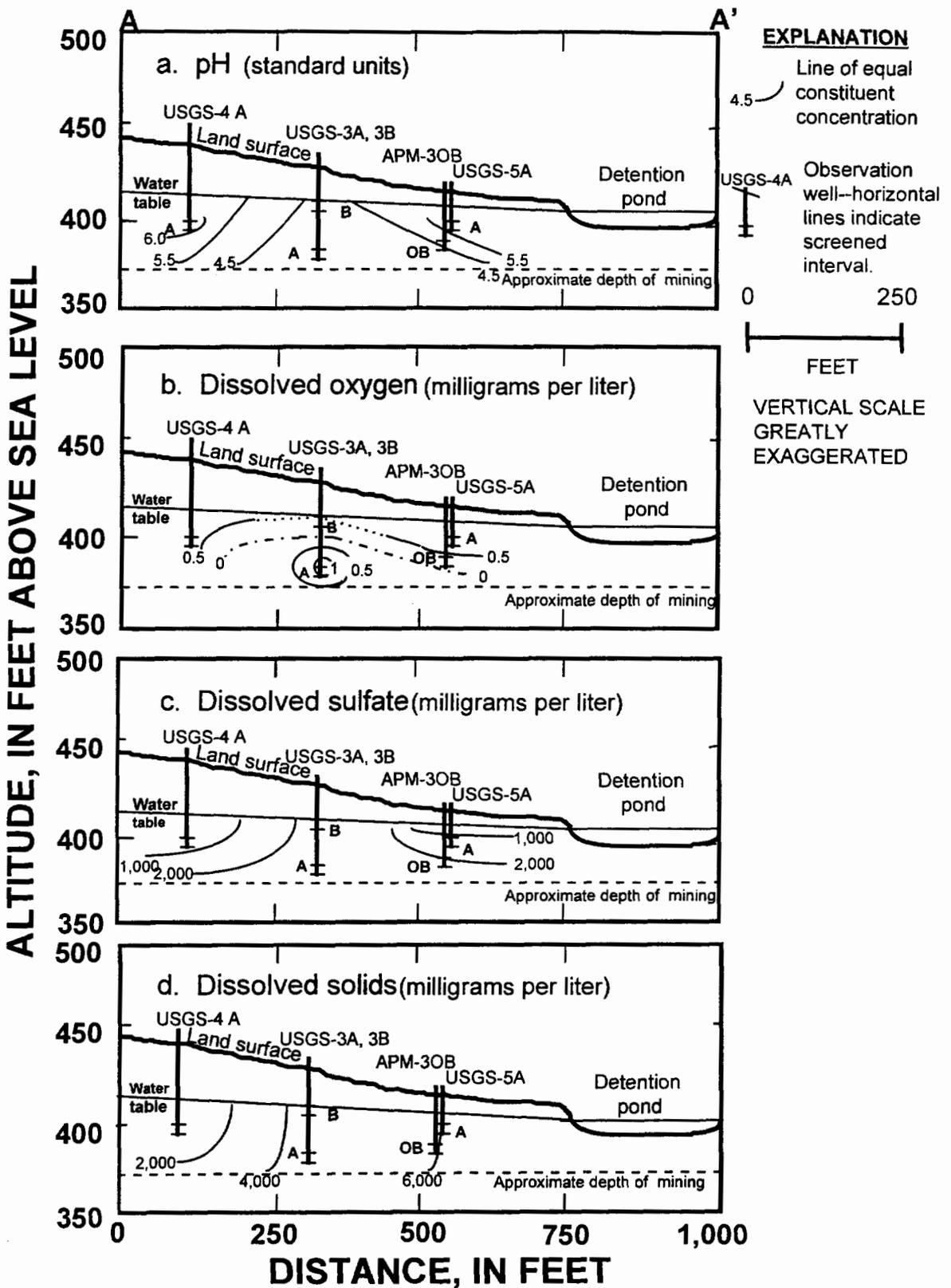


Figure 3. Section A-A' showing selected constituent concentrations in shallow ground water in mine spoils, east-central Texas (well and section locations shown in Fig. 1).

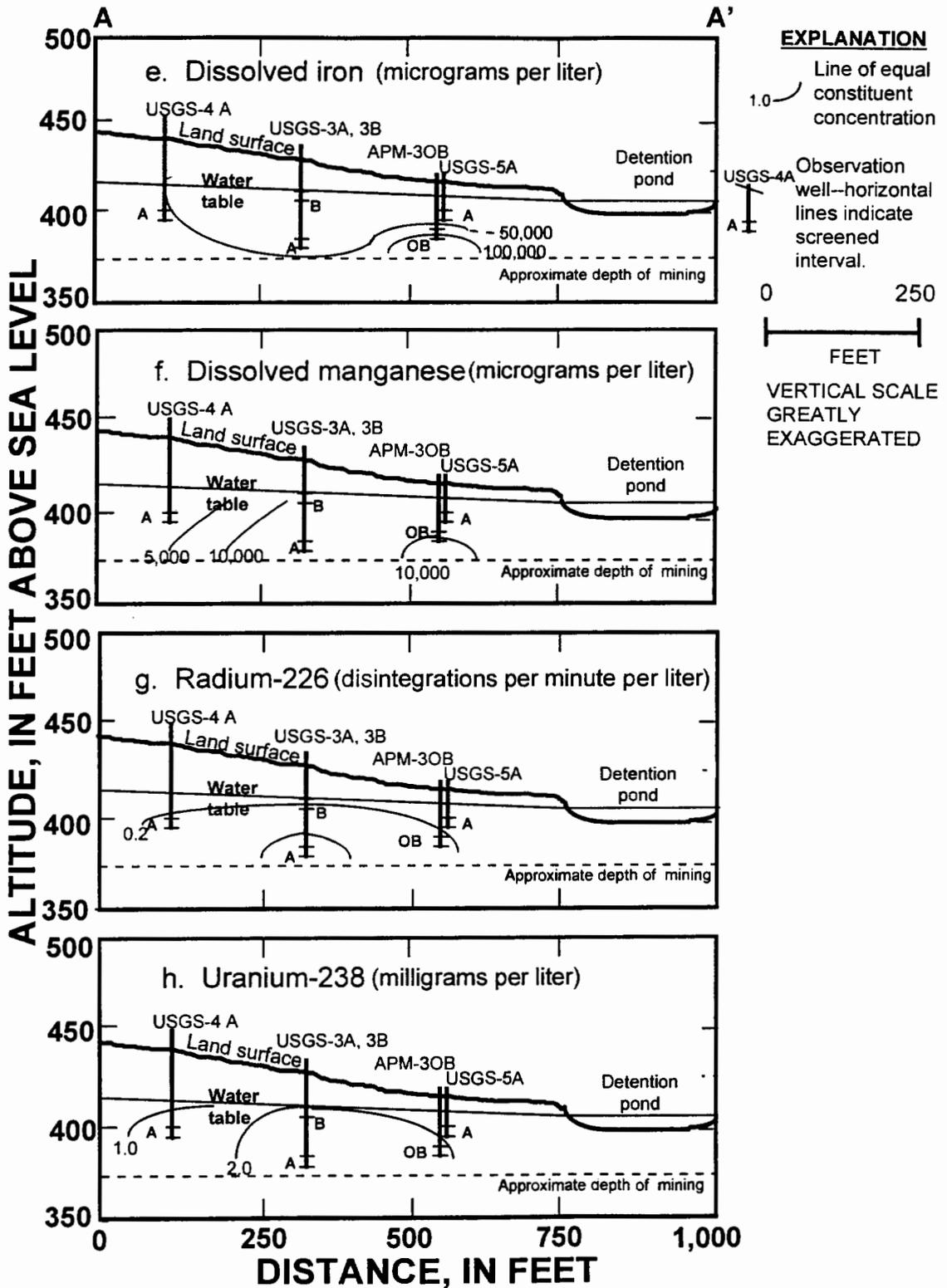
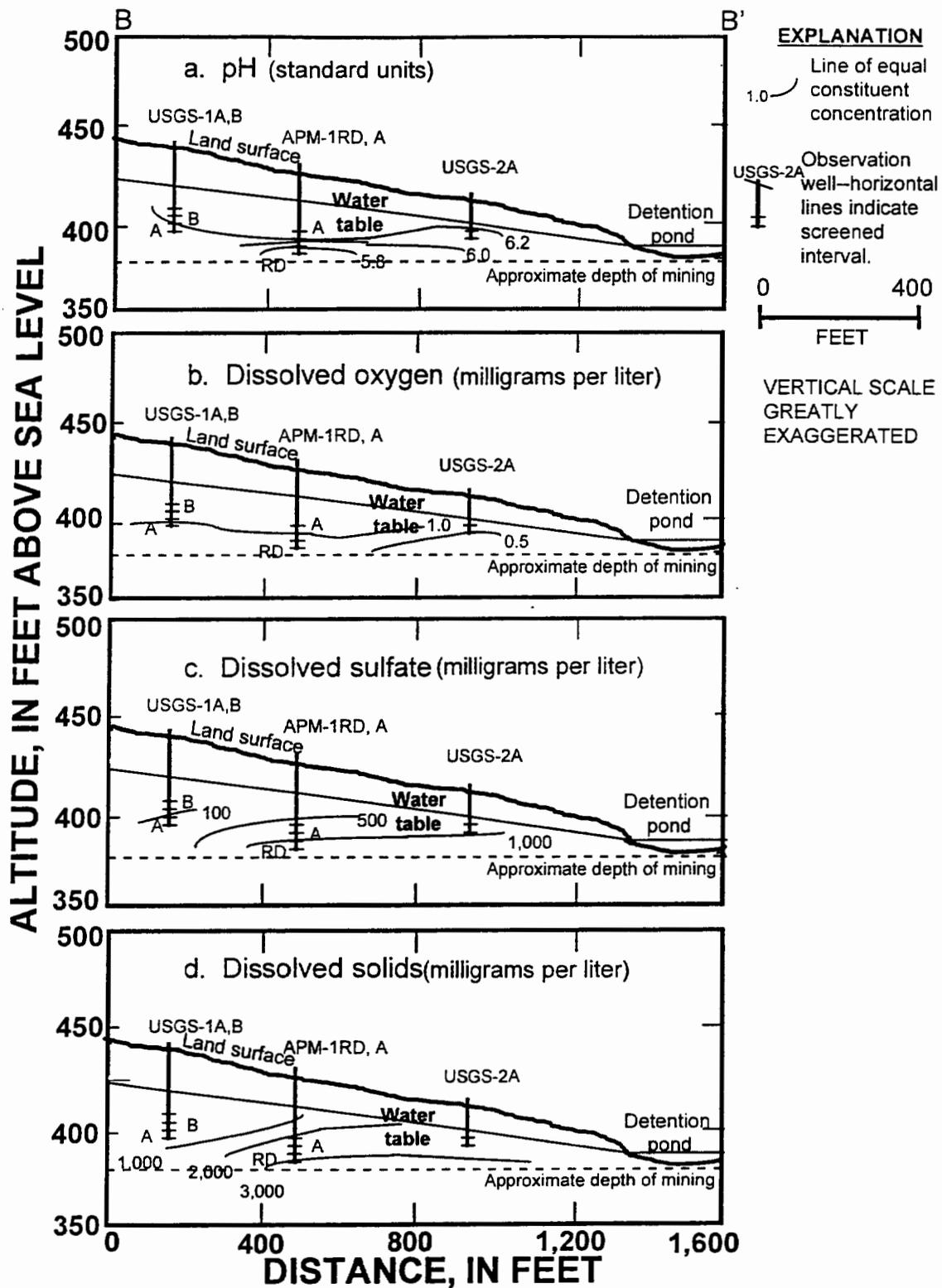


Figure 3. Continued.



**Figure 4.** Section B-B' showing selected constituent concentrations in shallow ground water in mine spoils, east-central Texas (well and section locations shown in Fig. 1).

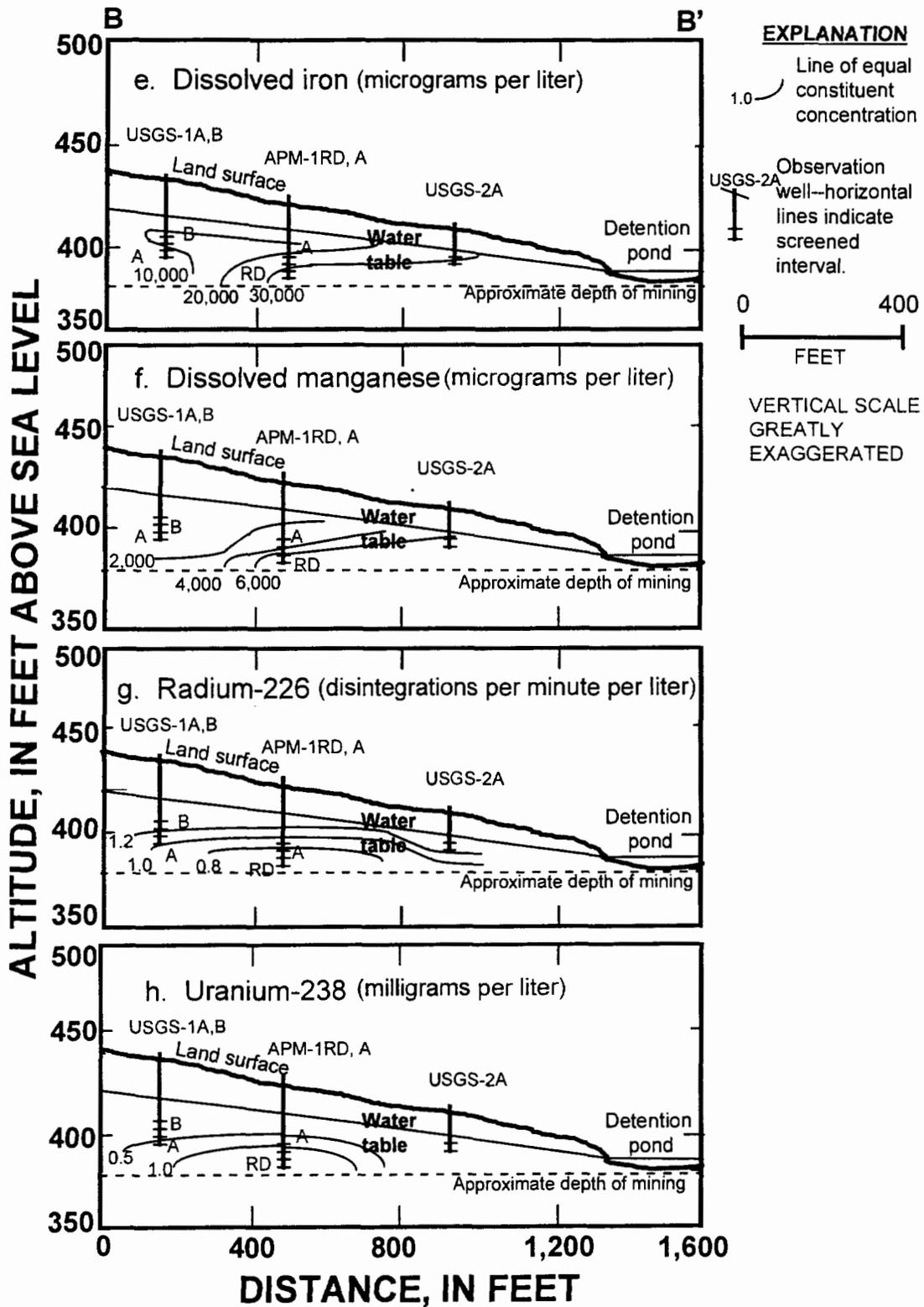


Figure 4. Continued.

**Table 2.** Saturation indices (log [ion activity product]/Kequilibrium (T)) for water samples from observation wells in the study area, east-central Texas, 1993–95

[-, undersaturation; near 0, saturation; +, oversaturation]

Observation well (Fig. 1)	Calcite CaCO <sub>3</sub>	Dolomite CaMg(CO <sub>3</sub> ) <sub>2</sub>	Gypsum CaSO <sub>4</sub> ·2H <sub>2</sub> O	Albite NaAlSi <sub>3</sub> O <sub>8</sub>	Kaolinite Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	Amorphous			Siderite FeCO <sub>3</sub>	Pyro-lu-site MnO <sub>2</sub>	Rhodo-chrosite MnCO <sub>3</sub>
						Alumina Al(OH) <sub>3</sub>	Silica SiO <sub>2</sub>	Iron hydroxide Fe(OH) <sub>3</sub>			
APM-1A	-0.47	-1.04	-0.64	0.55	7.27	-0.27	-0.5	3.59	-7.00	3.18	0.22
APM-1RD	-.73	-1.40	-.407	-1.50	4.37	-1.46	-.69	3.06	-6.50	1.84	-.02
APM-3OB	-2.50	-4.90	-.05	-1.90	3.80	-2.15	-.34	2.90	-6.90	.33	-1.90
USGS-1A	-1.39	-2.75	-1.90	-.54	5.13	-1.34	-.43	2.25	-7.90	1.94	-.50
USGS-1B	-1.36	-2.77	-2.10	-.58	5.40	-1.22	-.47	3.32	-7.40	2.83	-.26
USGS-2A	-.32	-.63	-.45	-1.50	3.90	-1.73	-.68	3.50	-6.60	2.75	.32
USGS-3A	-4.20	-8.40	-.04	-3.50	1.90	-3.25	-.19	1.20	-8.90	-.95	-3.50
USGS-3B	-4.40	-8.70	.01	-3.00	2.30	-3.25	-.03	1.47	-9.20	-.40	-3.50
USGS-4A	-1.20	-2.00	-1.48	-2.60	3.90	-1.25	-1.19	4.20	-6.50	3.2	.01
USGS-5A	-1.20	-2.40	-.34	-.72	4.80	-1.53	-.47	3.00	-7.70	2.53	-.54

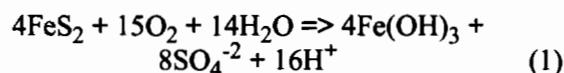
along section *B-B'* (Figs. 3g, 4g). Spoil material at the study site probably contains very small amounts of radium-226 and uranium-238, and geochemical conditions in the subsurface further contribute to the low concentrations of these elements in ground water (T.F. Kraemer, U.S. Geological Survey, oral commun., 1995). The low concentrations of these elements in the water samples limit meaningful interpretation of their transport along the flowpaths.

### Mineral-Water Interactions

Results of computations of the saturation index (SI) for water from the sampled wells are given in Table 2. In all well samples, calcite, dolomite, amorphous alumina, amorphous silica, and siderite are undersaturated, indicating that these solid phases, where present, can dissolve along ground-water flowpaths. Siderite was not detected in mineral analyses and is strongly undersaturated in water samples, indicating that it is not likely to be a controlling phase along these flowpaths. Amorphous iron hydroxide is oversaturated in all samples indicating that precipitation of this solid phase is likely along the flowpaths. Rhodochrosite was not detected in the bulk mineral analysis but is slightly oversaturated or near saturation in water from wells APM-1A, APM-1RD, USGS-2A, and USGS-4A. Rhodochrosite or impure calcite or siderite, where present, could provide a source of manganese to ground water. Oxides and hydroxides containing manganese,

such as manganite, also were considered as possible sources of manganese, but these are oversaturated in most of the water samples, except for samples from wells USGS-3A and USGS-3B. Manganese could come from manganite or other oxides of manganese by reduction but probably not dissolution. Gypsum SIs range from undersaturated in water from most wells to near saturation in water from wells APM-3OB, USGS-3A, and USGS-3B, indicating that, where present, gypsum can dissolve in ground water. Although gypsum was not detected in the bulk mineral analyses, it is present within some of the minor coal seams as a secondary mineral and can contribute calcium and sulfate to ground water.

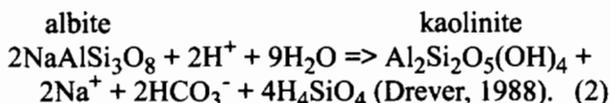
Mineral phases such as pyrite and röhmerite (FeIIFeIII(SO<sub>4</sub>)<sub>4</sub>·14H<sub>2</sub>O) are present in the spoils but were not tested for saturation because of insufficient data for computations. Pyrite oxidizes rapidly when mined sediment is exposed to air, releasing sulfate and acid to the aqueous phase (eqn. 1). However, in acidic weathering environments, intermediately oxidized iron sulfate compounds, such as röhmerite, can form instead of Fe(OH)<sub>3</sub> (Cravotta, 1994).



Solid iron hydroxide (Fe(OH)<sub>3</sub>) commonly forms as a product of pyrite oxidation. Pyrite and its oxidation products can be abundant locally in the reclaimed mine spoils and can oxidize and dissolve in recharge water and ground water, increasing dissolved

iron, dissolved sulfate, and acid. The acid can be neutralized by reaction with carbonate minerals, including calcite and dolomite, and aluminosilicate minerals such as illite and albite that are present in the mine spoils or added to soils.

Aluminosilicate phases considered in the speciation model were limited to albite, kaolinite, amorphous alumina, and amorphous silica. Albite is undersaturated in water from all wells except for well APM-1A, and kaolinite is oversaturated in water from all wells. This undersaturated/oversaturated combination indicates that the process of weathering (hydrolysis)—converting feldspars such as albite (eqn. 2) and orthoclase to kaolinite and releasing cations and silica—could occur in the mine spoil:



Amorphous alumina and amorphous silica are undersaturated in all the water samples, indicating that these solid phases could be dissolving from the mine spoils. Silica solubility, however, might be controlled by other polymorphs of silica such as chalcedony, giving rise to its possible precipitation from ground water.

### **Mass-Balance Modeling**

Although all 10 observation wells were sampled along the two assumed ground-water flowpaths, four of these wells were not used in flowpath modeling because of apparent mixing with other recharge water for which chemical data are not available. Three assumed flowpaths for the two sections provide sufficient information for geochemical mass balance and are defined as

#### **Section A-A'**

Flowpath FP1a: wells USGS-4A to USGS-3A;

#### **Section B-B'**

Flowpath FP2a: wells USGS-1B to APM-1A and

Flowpath FP2b: wells USGS-1A to APM-1RD.

Mass-balance models help define the net amount of dissolution and precipitation of selected minerals along an assumed flowpath between upgradient and downgradient wells. The ground-water flowpaths modeled were selected for their respective alignments with presumed ground-water-flow directions and for the observed water chemistry that indicates reaction with the aquifer matrix without mixing along the flowpaths.

The chemical data for the wells were analyzed for mineral equilibrium using a modified version of the aqueous speciation code WATEQF (Plummer and others, 1976) that is part of the NETPATH code (Plummer and others, 1994). The aqueous speciation code established the thermodynamic feasibility of dissolution and precipitation reactions in the mine spoils. The saturation state for a mineral or amorphous material is expressed as

$$\text{SI} = \log \text{IAP}/\text{K}(\text{T}), \quad (3)$$

where

IAP = ionic activity product determined by speciation model; and

K(T) = mineral or amorphous material equilibrium constant determined from thermodynamic data at the measured ground-water temperature (T), in kelvins.

In general, when SI is positive, the mineral or amorphous material is oversaturated, and precipitation is possible and dissolution is unlikely. When SI is zero, the mineral or amorphous material is saturated, and precipitation or dissolution is possible. When SI is negative, the mineral or amorphous material is undersaturated, and dissolution is possible and precipitation is unlikely.

Chemical evolution of the water along the three designated flowpaths was simulated using NETPATH. Results of mass-balance computations are shown in Table 3. Six plausible mass-balance models containing all of the pertinent mineral phases (Table 3) were produced for each of the three flowpaths (FP1a, FP2a, and FP2b) from more than 600 possible models tested. In general, halite, calcite, pyrite, and oxygen were reactants common to all the acceptable models, and amorphous iron hydroxide was a common product consistent with SIs for these minerals (Table 2). For the source of manganese, either manganese oxide (manganite) or manganese carbonate (rhodochrosite) was the reactant, although rhodochrosite was consistently undersaturated along all flowpaths in the speciation model and the more plausible phase controlling dissolved manganese concentration in the model.

Oxygen consumption was consistently large in the models (more than 40 millimoles per liter (mmol/L)), owing to pyrite oxidation (eqn. 2). However, such large amounts of oxygen exceed oxygen solubility and are not likely to diffuse into ground water. Thus, partially oxidized secondary sulfate phases, like r merite, that commonly form in mine spoils as a result of exposure of pyrite to atmospheric oxygen and moisture during mining operations could account for the large amounts of oxygen in the mass balance (Cravotta, 1994). Oxygen can react with pyrite to form minerals such as r merite before the spoils have been emplaced and rewetted. In

**Table 3.** Mass balance results from NETPATH for three ground-water flowpaths in the study area, east-central Texas

[Results in millimoles per liter; positive values indicate dissolution or ingassing; negative values indicate precipitation or outgassing; for exchange, + values indicate release of sodium from solid phase and - values indicate uptake of sodium into the solid phase; --, not used in a model]

Model	Halite NaCl	Calcite CaCO <sub>3</sub>	Dolomite CaMg(CO <sub>3</sub> ) <sub>2</sub>	Gypsum CaSO <sub>4</sub> ·2H <sub>2</sub> O	Mg/Na exchange	Ca/Na exchange	Albite NaAlSi <sub>3</sub> O <sub>8</sub>	Amorphous		Pyrite FeS <sub>2</sub>	Iron hydroxide Fe(OH) <sub>3</sub>	Pyro- lu- site	Rhodo- chrosite MnCO <sub>3</sub>	Lignite CH <sub>2</sub> O	Oxygen O <sub>2</sub>	Carbon dioxide CO <sub>2</sub>
								Alumina Al(OH) <sub>3</sub>	Silica SiO <sub>2</sub>							
<b>Flowpath 1a (Wells USGS-4A to USGS-3A)</b>																
1	25.5	8.61	7.97	--	-5.83	--	0.366	--	--	10.42	-11.2	0.18	--	--	42	-25.4
2	25.5	8.61	7.97	--	-5.83	--	.366	--	--	10.42	-11.2	--	0.18	--	42.1	-25.5
3	25.5	16.6	--	--	-13.8	--	16.3	--	-31.9	10.42	-11.2	.18	--	--	42	-17.4
4	25.5	16.6	--	--	-13.8	--	16.3	--	-31.9	10.42	-11.2	--	.18	--	42.1	-17.6
5	25.5	8.42	8.15	--	-5.65	--	--	0.36	1.09	10.42	-11.2	.18	--	--	42.1	-25.7
6	25.5	8.42	8.15	--	-5.65	--	--	.36	1.09	10.42	-11.2	--	.18	--	42.1	-25.7
<b>Flowpath 2a (Wells USGS-1B to APM-1A)</b>																
1	11.06	5.73	--	--	-3.59	--	3.98	--	-1.99	8.00	-3	.06	--	0.46	12.8	--
2	11.06	5.73	--	--	-3.59	--	3.98	--	-1.99	8.00	-3	--	.06	.4	12.8	--
3	11.06	2.22	1.99	1.53	-1.6	--	--	.003	-.05	2.46	-2.24	.06	.06	--	9.5	--
4	11.06	2.16	1.99	1.58	-1.6	--	--	.003	-.05	2.43	-2.21	--	.06	--	9.43	--
5	11.06	3.74	1.99	--	-1.6	--	--	.003	-.05	3.22	-3	.06	--	--	12.4	-1.53
6	11.06	2.16	1.99	--	-1.6	--	--	.003	-.05	3.21	-3	--	.06	--	12.4	-1.58
<b>Flowpath 2b (Wells USGS-1A to APM-1RD)</b>																
1	10.5	1.5	6.11	--	--	--	1.69	--	-3.74	6.01	-5.49	.1	--	9.44	31.6	--
2	10.5	1.5	6.11	--	--	--	1.69	--	-3.74	6.01	-5.49	--	.06	9.44	31.6	--
3	10.5	2.3	6.11	--	--	0.85	--	.0002	-.35	6.01	-5.49	.1	--	8.59	30.7	--
4	10.5	2.3	6.11	--	--	.85	--	.0002	-.35	6.01	-5.49	--	.1	8.59	30.7	--
5	10.5	.66	6.96	--	.85	--	--	.0002	-.35	6.01	-5.49	.1	--	8.59	30.7	--
6	10.5	.66	6.96	--	.85	--	--	.0002	-.35	6.01	-5.49	--	.1	8.59	30.7	--

both the unsaturated and saturated zones, the partially oxidized iron sulfate phases can dissolve and continue to oxidize, releasing sulfate, acidity ( $H^+$ ), and some iron into water. Although oxygen was measured in water from most of the wells (Table 1), hydrogen sulfide gas also was noticed in many of the same wells, indicating nonequilibrium or that the oxygen amounts could be artifacts of well installation or sample collection. Mass balance of hydrogen sulfide by sulfate reduction processes and sulfide minerals other than pyrite were not evaluated in the NETPATH models.

Feldspar hydrolysis (eqn. 2) is possible in the mine spoils, but excessively large amounts of feldspar were dissolved in the mass balance when this reaction was simulated. It is more likely that dissolution of amorphous alumina and silica from spoil material occurs, as shown in models 5 and 6 of FP1a (Table 3). This process is supported by column-leaching experiments described in the next section of this report. In the other flowpaths, FP2a and FP2b, silica could precipitate from solution, indicating that after initial leaching, silica concentrations likely are controlled by one or more polymorphs of silica such as quartz or chalcedony.

Oxidation of organic matter (coal residues) is substantial in models for FP2b. In the other flowpaths, oxidation of organic matter was not prominent. Along FP1a, loss of carbon dioxide was substantial in the models, indicating that large amounts of  $CO_2$  gas might be lost to the unsaturated zone from the aquifer along FP1a as a result of the low pH at the final well, USGS-3A. An alternative hypothesis is that  $CO_2$  could be lost as a result of outgassing during sample collection.

Other reactions simulated in NETPATH related gypsum dissolution and cation exchange reactions. Gypsum was only plausible as a reactant in models 3 and 4 of FP2a. Cation exchange generally is limited to sodium-for-magnesium exchange ( $Mg^{2+} + Na_2 - Ex \rightleftharpoons 2Na^+ + Mg - Ex$ ), except for FP2b where no exchange or small amounts of magnesium-for-sodium exchange occurred. Models 3 and 4 of FP2b indicate the possibility of a small amount of calcium-for-sodium exchange ( $Ca^{2+} + Na_2 - Ex \rightleftharpoons 2Na^+ + Ca - Ex$ ).

Although the differences in the models are small, the best mass-balance models (on the basis of relative amounts of mass transfer, phases simulated, and agreement with saturation states of the phases) for the three designated flowpaths are

FP1a—models 5 and 6,

FP2a—models 3 and 4, and

FP2b—models 5 and 6.

Owing to the small amounts of manganese, the mass transfer of pyrolusite or rhodochrosite in the models is relatively inconsequential compared to the amounts of mineral mass transfer occurring in the spoils; thus, the model pairs for each flowpath are nearly identical.

Substantial amounts of halite (sodium and chloride) are dissolved in every model. This indicates that sodium and chloride solutes are added to the aqueous phase from the mine spoils, probably from halite disseminated in the spoil material. The specific source of the sodium and chloride has not been identified, however.

### **Mobilization and Transport of Solutes from Column Experiment**

For the column experiment, all solute concentrations in water from the spoil leachate decreased throughout the period of leaching; under these conditions, the reaction rates of minerals could not be determined. Some minor changes in concentration gradients of certain elements did occur that might be attributed to channeling of the influent solution through the medium. In the leachate, dissolved oxygen was present in concentrations greater than 1.0 mg/L, and no sulfide odor was detected, indicating that sulfate reduction did not occur during the column experiment. Results of the column experiment are shown graphically in Figures 5–8.

### **Bromide Tracer**

In column experiments, a conservative tracer often is added to the leaching solution to determine breakthrough of the influent solution. Lithium bromide was added to the influent solution to produce approximately 10 mg/L dissolved bromide. The actual bromide concentration of the influent solution was measured at 9 mg/L. The bromide concentration was monitored to determine conservative breakthrough of the influent solution. A bromide concentration in the leachate of about 8 mg/L after about 2,000 minutes (min) (Fig. 5) indicates that, after about 9 pore volumes of the column, the breakthrough concentration of leachate was about 90 percent of the influent solution. The fact that the breakthrough concentration was less than that of the influent solution indicates that substantial dispersion was occurring in the column.

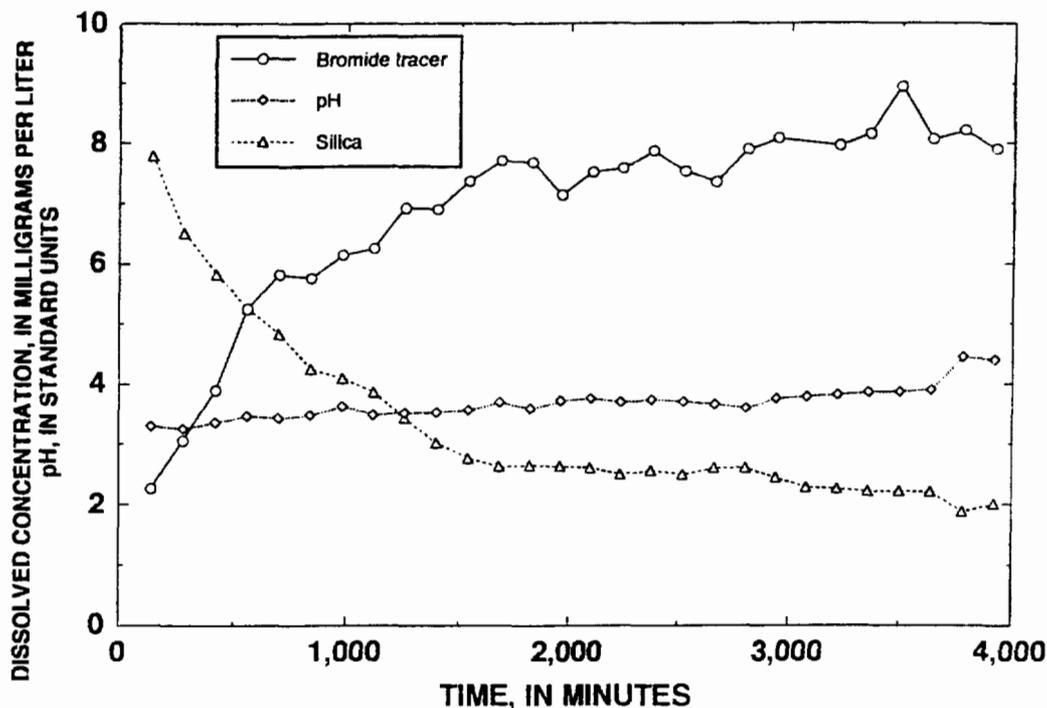


Figure 5. Relation of bromide tracer, pH, and dissolved silica concentrations with time in mine spoil leachate.

### pH and Silica

The pH of the influent solution was 4.5. The pH of the column experiment effluent outflow increased from 3.3 to 4.4 as the experiment progressed. This low initial column pH indicates that acidity is produced by the mine spoils but is leached out over time. Because of the low pH, large amounts of metals are likely to be mobilized in the aqueous phase. Silica concentrations decreased to just less than 3 mg/L at 1,500 min (Fig. 5), then decreased at a much slower rate for the remainder of the experiment. This indicates that soluble sources of silica are leached from the sediment quickly, and then dissolved silica approaches a steady-state concentration of about 2 mg/L, probably as a product of silicate and aluminosilicate hydrolysis reactions.

### Major Cations and Anions

Calcium, magnesium, sodium, and potassium cations in the leachate all decreased uniformly during the column experiment (Fig. 6), as did the anions sulfate, chloride, and nitrate (Fig. 7). Concentrations of the cations declined to low levels after 3,000 min (all less than 30 mg/L) and decreased only slightly afterwards. The

concentrations of the anions sulfate, chloride, and nitrate also decreased with time. Nitrate concentration declined to below the detection limit of 0.01 mg/L after 1,250 min. Dissolved sulfate decreased from 750 to 70 mg/L, showing little change after about 2,500 min.

### Trace Elements

Dissolved trace elements are divided into two groups for discussion—a low-concentration group consisting of barium, boron, chromium, cobalt, lead, and nickel (Fig. 8a) and a high-concentration group consisting of aluminum, iron, manganese, strontium, and zinc (Fig. 8b).

**Barium, Boron, Chromium, Cobalt, Lead, and Nickel.** Dissolved barium concentrations were relatively constant over the time of the column experiment, indicating low mobilization of barium in the aqueous phase. Barium concentrations of 140  $\mu\text{g/L}$  (Fig. 8a) were comparable to those of most flowpath sample data (about 100  $\mu\text{g/L}$ ) except for the sample at well APM-1RD (Table 1). Dissolved boron concentrations were relatively low, showing a small change from 240 to less than 100  $\mu\text{g/L}$  over the time of the column experiment (Fig. 8a). Boron showed several increases during the column experiment,

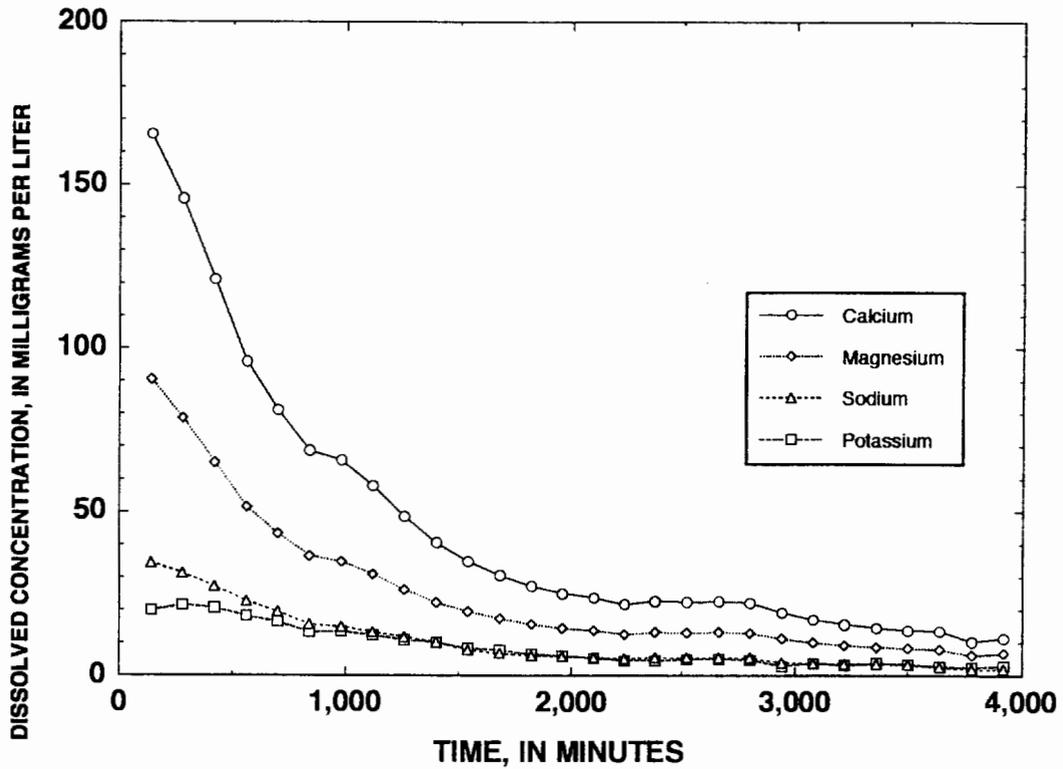


Figure 6. Relation of major dissolved cation concentrations with time in mine spoil leachate.

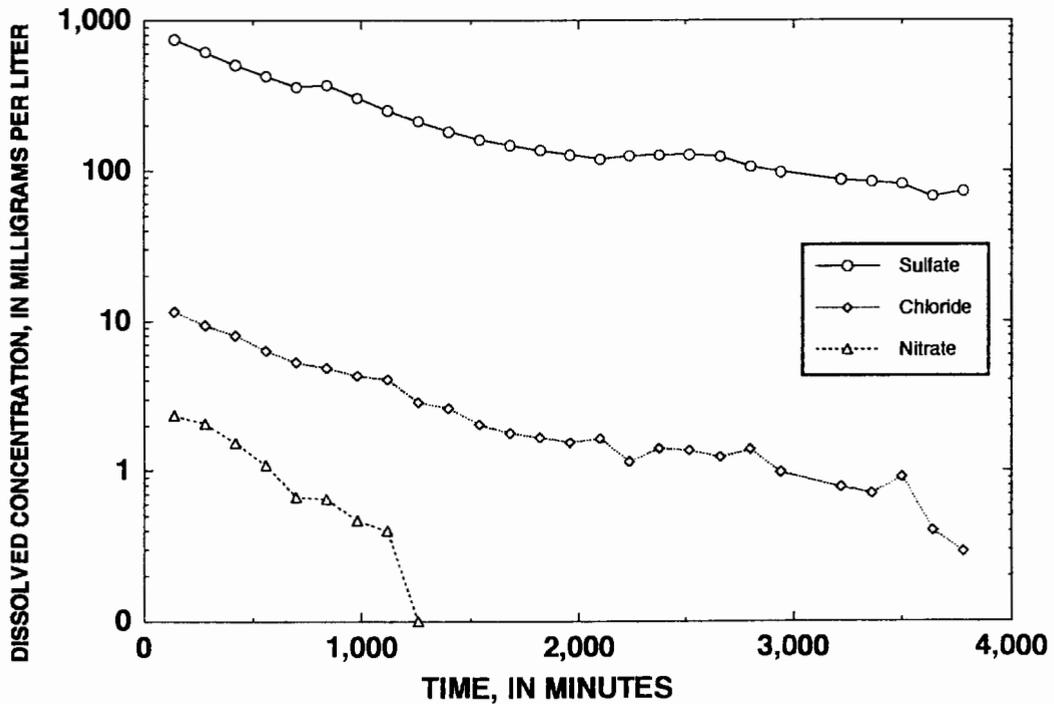


Figure 7. Relation of dissolved anion concentrations with time in mine spoil leachate.

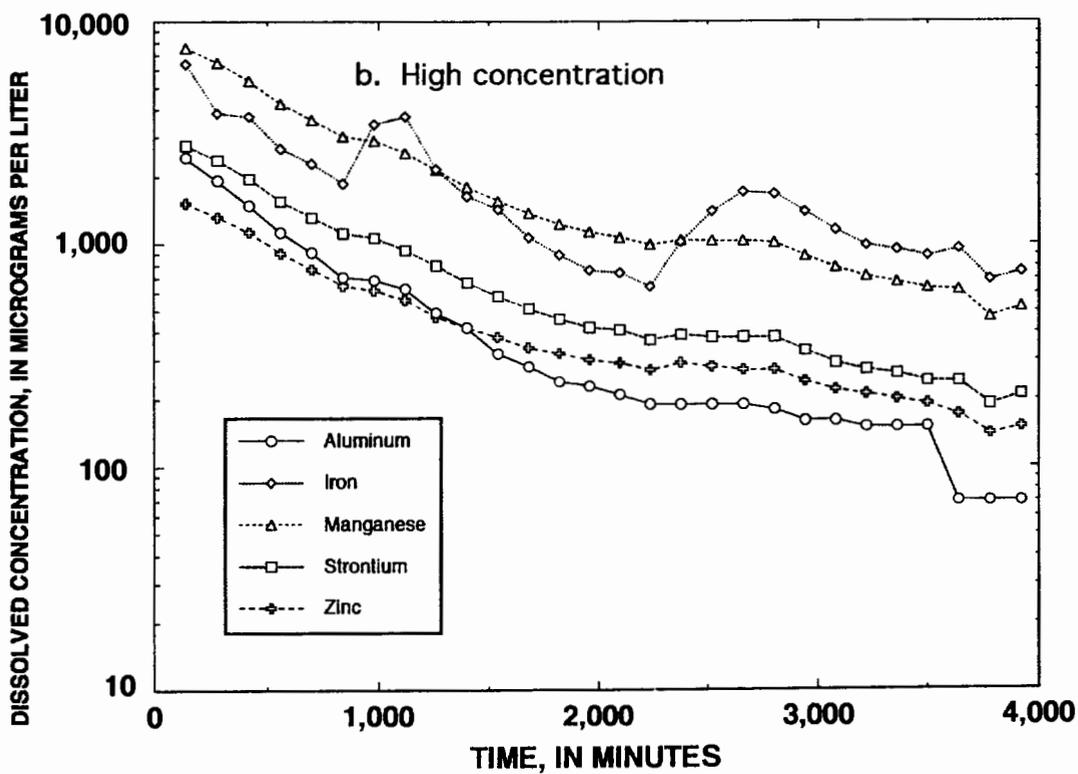
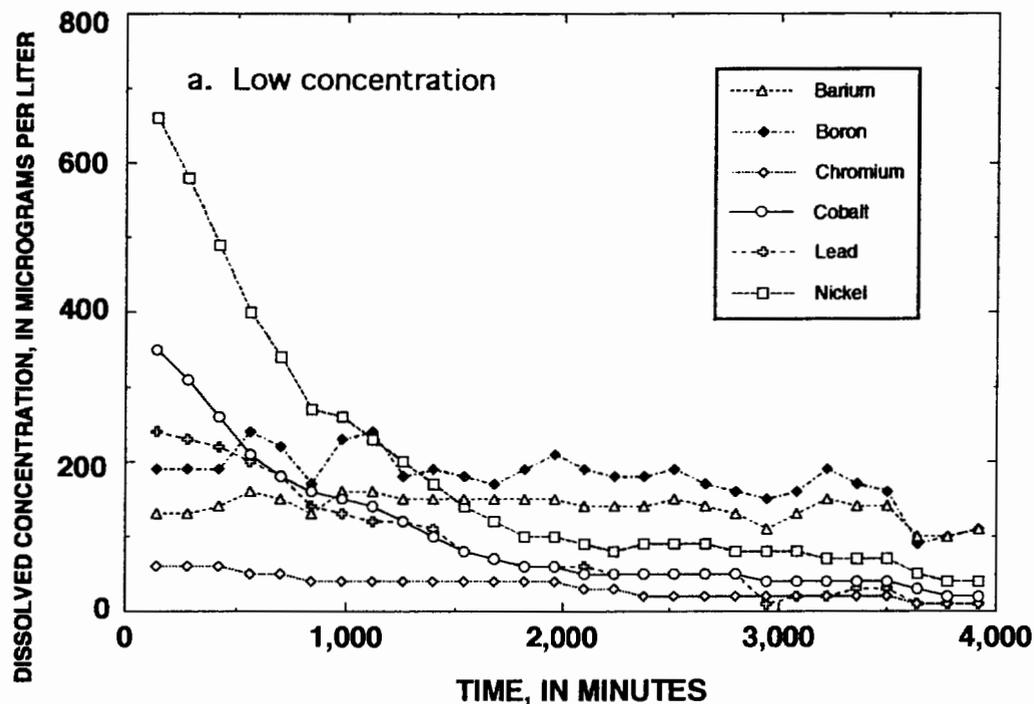


Figure 8. Relation of selected trace element concentrations with time in mine spoil leachate.

perhaps as some indication of the formation of preferential flow channels in the column by the influent solution or analytical variations. The source of boron was the mine spoils, however, and the increases also could indicate intermittent releases of boron from the spoils as minerals are dissolved.

Concentrations of dissolved chromium, cobalt, lead, and nickel decreased in leachate during the column experiment from 60 to 10  $\mu\text{g/L}$ , 350 to 20  $\mu\text{g/L}$ , 240 to 10  $\mu\text{g/L}$ , and 660 to 40  $\mu\text{g/L}$ , respectively (Fig. 8a). Concentrations of these elements were greater in the leachate than in the ground-water samples from the mine, indicating that geochemical conditions in the two spoils areas can inhibit the movement of some metals in ground water, probably as a result of the prolonged effects of reducing environments, the greater pH, and the presence of dissolved sulfide, which limits solubility of metal sulfides.

#### **Aluminum, Iron, Manganese, Strontium, and Zinc.**

Dissolved aluminum concentrations decreased from 2,440 to 70  $\mu\text{g/L}$  over the time of the column experiment, eventually becoming constant at about 70  $\mu\text{g/L}$  (Fig. 8b) after 3,500 min. The low pH initially contributed to the large aluminum concentrations, probably as a result of dissolution of the amorphous aluminum, amorphous aluminosilicates, and clays. The relatively constant aluminum concentration in the leachate achieved near the end of the column experiment probably was the result of chemical equilibrium of water with aluminosilicate minerals in the mine spoil material.

Dissolved iron concentrations ranged from 6,420 to 750  $\mu\text{g/L}$  near the end of the column experiment as a result of dissolution of ferric and ferrous iron solids in the spoil material. The leachate showed two anomalous increases of dissolved iron from about 2,000 and 650  $\mu\text{g/L}$ , possibly from formation of preferential flow channels in the column by the influent solution. The dissolved iron concentration became relatively constant near the end of the column experiment at about 700  $\mu\text{g/L}$  (Fig. 8b). Dissolved manganese concentrations also were large initially with concentrations ranging from 7,540 to 480  $\mu\text{g/L}$  over the time of the column experiment. Manganese decreased steadily, showing only minor inflections at the same times as the iron increases. Iron concentrations in the column leachate were less than those for ground-water samples from the reclaimed spoils (2,000 to 160,000  $\mu\text{g/L}$  (Table 1)), whereas manganese concentrations in the column leachate were comparable to those for ground water (800 to 13,000  $\mu\text{g/L}$  (Table 1)).

Dissolved strontium and zinc concentrations decreased from 2,760 to 190  $\mu\text{g/L}$  and 1,520 to 140  $\mu\text{g/L}$ , respectively, over the time of the column experiment. Decreases were relatively steady, with only slight inflections coinciding with the iron inflections previously

described. The range of dissolved zinc concentrations in the column experiment were comparable to the range of dissolved zinc concentrations in the ground-water samples (10 to 1,900  $\mu\text{g/L}$  (Table 1)).

## **Discussion**

The column experiment indicates that acidic conditions can form and cause the mobilization of common ions and trace elements upon rehydration of mine spoils. The acidic water is produced by the hydration and oxidation of pyrite, römmerite, and other sulfate minerals in the spoil material (Cravotta, 1994) although acidity was less in water from the two reclaimed areas than from the column experiment. Reclamation practices probably have helped to decrease acidity and promote development of reducing conditions in the subsurface (sulfate reduction), which limits acid production and the mobilization and transport of trace elements in the spoils at the mine site.

Bacterially mediated sulfate-reducing environments and the presence of dissolved sulfide in ground water in the mine spoils apparently have inhibited transport of several trace elements, including radium-226 and uranium-238, which were negligible in ground-water samples. As ground water flows through strongly reducing geochemical environments, hydrogen sulfide produced from bacterially mediated sulfate reduction can react with some metals to form insoluble metal sulfides, thus inhibiting transport and trapping the metals in the aquifer matrix.

Aluminum and silica are leached from the spoil material, as shown by the column experiment, indicating that solid phases containing these constituents are dissolving. Feldspar hydrolysis would yield relatively constant concentrations of aluminum and silica over the time of the column experiment. The decrease in concentration of aluminum and silica over time in the column experiment indicates that amorphous alumina and silica in the spoil material are the principal sources of aluminum and silica rather than feldspars, supporting conclusions of the mass-balance modeling.

Chemical data from ground water in the two reclaimed areas indicate that the highest acidity, the highest sulfate concentrations, and the highest iron concentrations are present in the deeper, downgradient parts of the spoil areas. The results are consistent with the movement of a "plume" of highly mineralized water formed upon rehydration of the spoils. Subsequent recharge water becomes less mineralized over time because the soluble solids are depleted. Water in the shallow upgradient parts of the flowpaths is less mineralized than water in the deeper downgradient parts; this less

mineralized water relates to the less mineralized leachate produced near the end of the column experiment.

The principal problems with water in mine spoils continue to be the large amounts of dissolved solids, dissolved iron, dissolved manganese, and low pH, which potentially can discharge to and degrade adjacent ground water and surface water. Exposure of spoils to air during mining enhances oxidation of pyrite and evaporation of interstitial fluids to form soluble, acid-enriched solids such as röhmerite. Rehydration after reclamation will mobilize solutes to produce acidity and high dissolved solids concentrations in initial spoil water. The effects could be lessened if spoil exposure to air was minimized.

### **Conclusions**

Ground-water samples from reclaimed land containing mine spoils in east-central Texas and leachate from a spoil-packed column indicate that large amounts of solutes are mobilized from the spoil material upon rehydration. Reclamation practices and intrinsic establishment of strongly reducing environments, such as sulfate reduction in ground water in coal mine spoils, appear to inhibit mobilization and transport of trace elements (possibly including radium-226 and uranium-238 although results are inconclusive) present in very small concentrations in the ground water from the reclaimed mine areas. Mass-balance models show that pyrite oxidation and dissolution of halite, carbonates, amorphous alumina, amorphous silica, and some gypsum are principal reactions occurring in reclaimed mine spoils. Sulfate reduction was apparent in the spoil material from detection of sulfide in ground water; however, the magnitude of sulfate reduction was apparently too small and not considered for mass balance. Increased dissolved solids concentrations (550 to 6,050 mg/L), large dissolved iron concentrations (2,000 to 160,000 µg/L), large dissolved manganese concentrations (800 to 13,000 µg/L), and low pH (4.0 to 6.2) in ground water from flowpaths in the two mine spoils reclamation areas are the primary water-quality concerns to be addressed in the design of reclamation practices.

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