

# Use of Sulfur Isotopes to Monitor Dissolved Sulfate Derived from a Fly Ash Emplacement Site, North-Central Colorado

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## INTRODUCTION

Beneficial use of coal fly ash for land applications or for large-scale structural fills is an attractive alternative to costly disposal, but such potentially widespread use of fly ash must be protective of human health and the environment. Of primary regulatory concern is the impact of soluble constituents of fly ash on the quality of surface water and ground water<sup>1,2</sup>. Typical safeguards at any site chosen for large-scale ash utilization (or disposal) include a network of wells installed to monitor changes in ground-water quality. Of particular interest are increases in total dissolved solids caused by dissolved major constituents of fly ash (Na, Ca, Mg, K, SO<sub>4</sub>, Cl) or increases in soluble trace constituents (As, Se, B, F, Cr, Mo) that may adversely impact human or ecosystem health. If dissolved concentrations are monitored as an indication of possible contamination, then it is critical to first establish the normal baseline range of dissolved concentrations at a site. Dissolved elements that are present at low baseline concentrations are potentially more sensitive to minor, perhaps non-hazardous, additions from fly ash leachate.

One water-quality parameter that could be incorporated in ground-water monitoring programs near fly ash emplacements is the S isotopic composition of dissolved sulfate. Successful use of this parameter requires that the S isotopic composition of sulfate in local ground water differs substantially from that of sulfate leached from fly ash. Large differences in isotopic composition are unlikely if an ash utilization/disposal site is in the immediate vicinity of isotopically-similar source coal at the producing mine, or is near large stockpiles of source coal and derivative fly ash at the utilizing power plant<sup>3</sup>. Isotopic contrasts are more likely, however, at sites of ash utilization/disposal that are far removed from the coal mine or power plant<sup>3,4</sup>. Differences in sulfur isotopic composition permit the use of relatively simple isotopic mass balance calculations to quantify contributions of sulfate from fly ash, even if local baseline concentrations of dissolved sulfate are high. Sulfur isotopic measurements of dissolved sulfate are easily incorporated in a monitoring plan because they are readily available from commercial laboratories at modest cost (<\$20/determination; C.A. Johnson, U.S. Geological Survey, oral commun., 2004).

This report illustrates the use of S-isotope measurements to monitor ash-derived sulfate in ground water near a prototype fly ash emplacement site in Colorado. The S-isotopic composition of sulfate in an upgradient "baseline" well and a network of downgradient

monitoring wells were measured and compared over time. Results indicate the rate of dispersion of ash-derived sulfate in local shallow ground water. Apparent contributions of ash-derived sulfate in some wells are also compared with a more traditional indicator of contamination that is based on increases in concentration of dissolved boron.

#### SITE DESCRIPTION AND SAMPLING

The study site is located approximately 50 km north of Denver, Colorado, in southwestern Weld County. The site is situated on a gravel terrace of Saint Vrain Creek, approximately 0.8 km north of the active stream channel and at the north edge of a pond formed during operations of an active gravel quarry (Fig. 1). Two small (15 m x 3 m x 3 m) east-west oriented trenches (Fig. 2) were filled with 400 tons of Class F fly ash in February 2002<sup>5</sup>. The ash was composed of approximately equal volumes of “Ca-ash” and “Na-ash” that contain sulfates formed during sequestration of SO<sub>2</sub> by lime spray injection and dry sorbant (trona) injection, respectively. The purpose of the emplacement was to provide a pilot-scale field demonstration of the utility of this fly ash mixture to serve as fill material under partial water-saturated conditions. The fly ash mixture was provided by Xcel Energy company and was specifically chosen on the basis of its previously documented low leachability and favorable pozzolanic properties<sup>6</sup>.



Figure 1. Aerial view of the fly ash emplacement site and surroundings in southwestern Weld County, Colorado

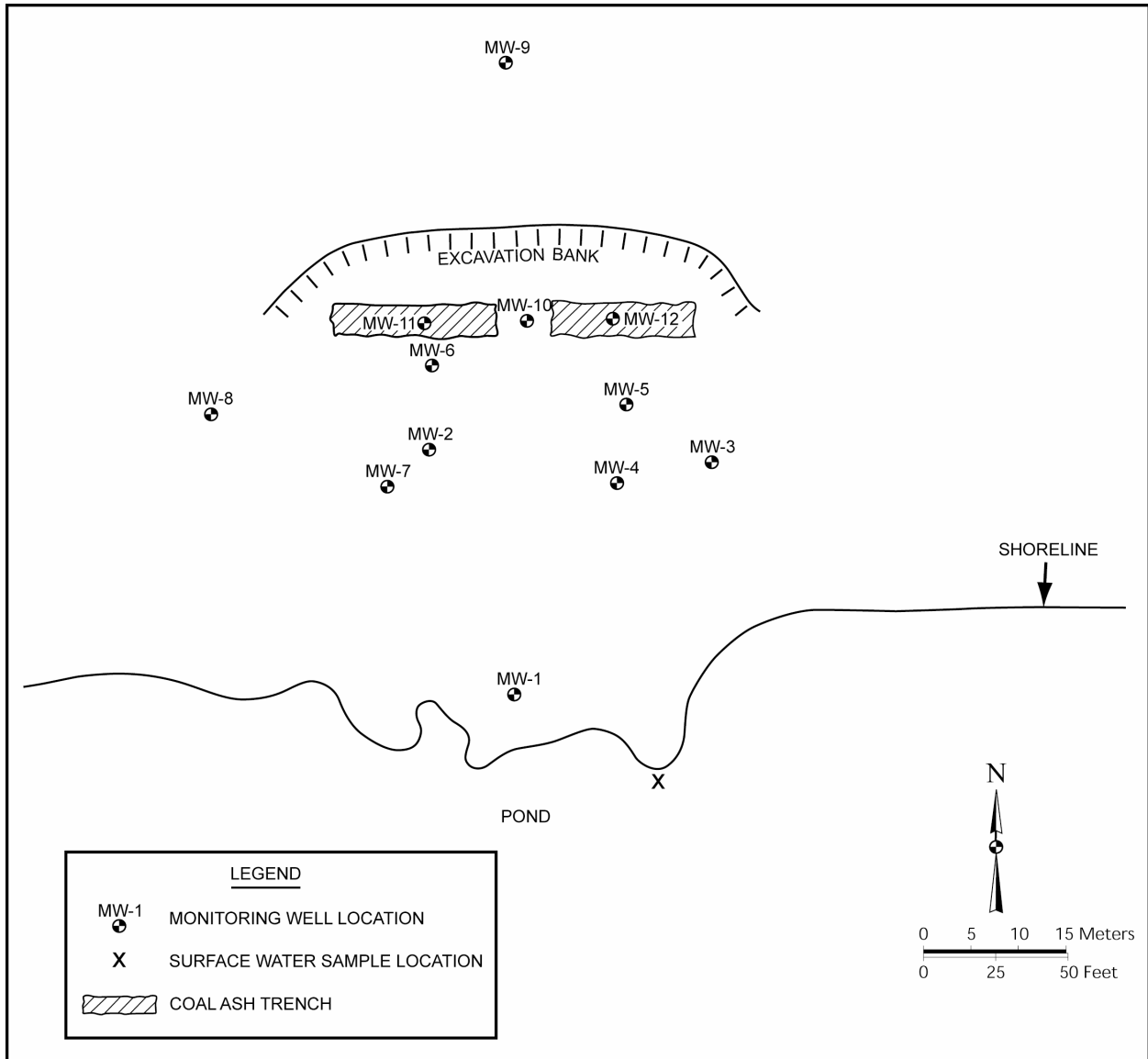


Figure 2. Locations of ground water monitoring wells at the fly ash emplacement site in southwestern Weld County, Colorado.

A network of nine monitoring wells (MW1-MW8, MW10), 2.5-4.5 m deep and located 0-38 m downgradient from the trenches, were supplemented by two wells within the trenches (MW11, MW12) and one upgradient well MW9 (Fig. 2). Depth to water varies from 0.5 to 4.0 m, and the average saturated thickness of the aquifer at the site is 1.7 m<sup>5</sup>. The aquifer is hosted within layers of relatively permeable sand, silty sand, and gravel. Wells generally penetrated no more than 0.5-1.0 m into the underlying relatively impermeable bedrock composed of marine Pierre Shale of Late Cretaceous age<sup>7</sup>. Ground-water flow at the site is from north to south towards the pond at an average rate of 0.8 m/day<sup>5</sup>. Wells were sampled periodically for a period of nine months after ash emplacement, and concentrations of dissolved major, minor, and trace constituents were tabulated. A smaller subset of water samples was selected for analysis of S-isotopic composition of dissolved sulfate. This subset was included because preliminary isotopic

analyses of water from the upgradient well (MW9, Fig.2) and of 1:1 (by weight) aqueous extracts of the fly ash indicated a potentially large (~10 per mil (‰)) isotopic contrast with respect to the  $\delta^{34}\text{S}$  of dissolved sulfate.

## METHODS

The sulfur isotopic composition of dissolved sulfate in water and aqueous extracts of fly ash was determined with a Micromass Optima mass spectrometer using a continuous flow method<sup>8</sup>. Dissolved sulfate was precipitated as barium sulfate by adding barium chloride to filtered solutions. The barium sulfates were combusted in an elemental analyzer to form  $\text{SO}_2$  gas that was introduced into the mass spectrometer. The sulfur isotopic composition is reported in terms of a  $\delta^{34}\text{S}$  value:

$$\delta^{34}\text{S} \text{ (in per mil, ‰)} = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000$$

R is the atomic  $^{34}\text{S}/^{32}\text{S}$  ratio and the standard is Cañon Diablo troilite (CDT). Reproducibility was  $\pm 0.2$  ‰. Our analysis of the National Bureau of Standards seawater sulfate standard #127 averaged 21.1 ‰ (n=7) compared to the most preferred value of 20.99 ‰<sup>9</sup>.

## RESULTS AND DISCUSSION

Local ground water sampled from upgradient well MW9 (Fig.2) has pH=7.0-7.5, sodium and sulfate as the major dissolved ions, and significant contributions of dissolved calcium and magnesium<sup>5</sup>. Dissolved sulfate in the well ranges from 1,000-1,200 mg/L, which exceeds the USEPA secondary drinking water standard of 250 mg/L, and is comparable to concentrations of 1,000-1,500 mg/L recorded in ash trench wells MW11 and MW12<sup>5</sup>. Such high natural concentrations of dissolved sulfate preclude the use of sulfate concentration as a sensitive indicator of contamination, but do not preclude the use of S isotopes for tracing ash-derived sulfate, provided that sufficient isotopic contrast exists.

The S isotopic composition of sulfate leached from six samples of fresh fly ash (Table 1) showed strongly positive values of  $\delta^{34}\text{S}$  of 6.1 to 12.9 ‰ (mean = 8.5). Positive  $\delta^{34}\text{S}$  values are typical for organic sulfur in low-sulfur (<1 wt.%) coals<sup>10</sup>. Low-sulfur Cretaceous coal from the Twentymile mine in northwestern Colorado<sup>11</sup> was combusted to produce the fly ash used in this study, and compositionally similar Cretaceous coal from northwestern Colorado exhibits positive values of  $\delta^{34}\text{S}$  in its organic-bound sulfur<sup>12</sup>. Apparently the S isotopic character of the low-sulfur source coal is mimicked in the soluble sulfate retained in the fly ash. In contrast, dissolved sulfate in seven samples of ground water from upgradient well MW9 had values of  $\delta^{34}\text{S}$  of -2.7 to -3.2 ‰ (Table 1). These negative values of  $\delta^{34}\text{S}$  typify a reservoir of sulfate that originated from pyritic sulfide within the marine Pierre Shale. The S isotopic character of this pyritic sulfide was determined during bacterially-mediated reduction of seawater sulfate<sup>13,14</sup>. Such a process strongly fractionates sulfur isotopes by favoring the lighter  $^{32}\text{S}$ , resulting in  $^{32}\text{S}$  enrichment and more negative  $\delta^{34}\text{S}$  values in the reduced sulfur<sup>15</sup>. Note that pyrite bearing, high-sulfur coals containing more bacteriogenic sulfides exhibit S-isotopic compositions of organic sulfur that are more variable and trending to lower  $\delta^{34}\text{S}$  values than in low-sulfur coals<sup>16,17,18</sup>.

Table 1.  $\delta^{34}\text{S}$  (‰) of soluble sulfate in original fly ash, and in water samples collected over time at the study site in Weld County, Colorado.

Ash emplaced 2/14/02. Well waters in **bold** have anomalous  $\delta^{34}\text{S}$  values compared to upgradient well MW9 and have  $>2.5$  mg/L dissolved B.

	11/09/01	2/22/02	3/11/02	3/18/02	4/15/02	5/13/02	8/13/02	11/12/02
<b>Monitoring Wells</b>								
MW9 24 m upgradient from trenches		-3.1	-3.0	-3.2	-2.9	-2.7	-2.7	-2.8
MW10 between trenches		-2.8	-2.9				-3.3	-3.4
MW11 west trench (bottoms in ash)		<b>1.4</b>	<b>4.6</b>	<b>5.2</b>	<b>6.3</b>	<b>4.8</b>	<b>4.1</b>	<b>2.2</b>
MW12 east trench (bottoms in shale)		-2.5	<b>0.6</b>	<b>3.9</b>	<b>-0.8</b>	-2.5	-2.2	-2.7
MW2 12 m below west trench	-2.6	-2.7	-2.9				-2.9	<b>-1.8</b>
MW3 12 m below east trench	-2.1	-2.8	-3.0				-3.3	-3.2
MW4 15 m below east trench		-2.8	-3.1				-3.2	-3.4
MW5 7.5 m below east trench		-2.8	<b>-1.6</b>	<b>-1.0</b>	<b>-1.0</b>	<b>-2.0</b>	-3.2	-3.4
MW6 2.5 m below west trench		-3.0	-2.9		-3.2	-3.3	<b>1.1</b>	<b>-0.6</b>
MW7 15 m below west trench		-2.8	-2.9				-3.2	-3.1
MW8 12 m below west trench		-2.7	-2.9				-2.9	-2.8
MW1 lakeshore 38 m below trenches	-2.4	-2.7	-2.6				-2.8	-2.8
<b>NBS127 standard</b>								
		21.1	21.2	21.0	21.2			21.1
		21.2		21.0				
<b>Original fly ash</b>								
Na-ash end member 1:1 aqueous leach		12.9						
Ca-ash end member 1:1 aqueous leach		6.1						
Mixed ash#1 (grab) 1:1 aqueous leach		7.8						
Mixed ash#2 (grab) 1:1 aqueous leach		7.4						
Mixed ash#3 (composite) 1:1 aqueous leach		8.6						
Mixed ash#4 (composite) 1:1 aqueous leach		8.4						

The majority of ground waters collected from the downgradient monitoring wells had  $\delta^{34}\text{S}$  values that were analytically indistinguishable, or only marginally different, from the upgradient well MW9, indicating little or no contamination from ash-derived sulfate during the period of sampling (Table 1). Important exceptions included waters collected from the two ash trench wells (MW11, MW12, Fig. 2). Waters from these two wells have  $\delta^{34}\text{S}$  values intermediate between fly ash extracts and local, shallow ground water. This result is expected, considering that pore water in the ash-filled trenches should contain dissolved sulfate from both these sources. Additional exceptions of greater interest include some water samples from downgradient wells MW5, MW6 and MW2. The S isotope data from these three wells indicate contributions of ash-derived sulfate that are spatially and temporally variable (Table 1). Data from MW5 indicates that the presence of ash-derived sulfate in a particular well may be short-lived and thus could represent passage of a pulse of sulfate released during initial wetting of fly ash by ground water. The time for ash-derived sulfate to reach a particular well (e.g., MW5 vs. MW6) is influenced by local differences in flow regime. Such differences are probably large in areas of relatively stagnant flow that lie immediately downgradient from ash-filled trenches of low hydraulic conductivity.

All well water samples that show an isotopic indication of some ash-derived sulfate also have concentrations of dissolved boron (B) that are high ( $>2.5$  mg/L; Table 2, Fig. 3), when compared to values of 0.3 to 2.4 mg/L B in other wells <sup>5</sup>.

Table 2 . Calculated mass fraction of fly ash-derived sulfate in selected monitoring wells at the fly ash emplacement site in southwestern Weld County, Colorado .

Well	Sampling date	B (mg/L)	$\delta^{34}\text{S}$ (‰)	Mass fraction of sulfate from ash ( $F_{\text{ash}}$ ) (based on S isotopes) <sup>1</sup>
MW 5	3/18/02	4.4	-1.0	0.19
	4/15/02	5.7	-1.0	0.17
MW 6	8/13/02	12.6	1.1	0.34
	11/12/02	9.6	-0.6	0.20
MW 2	11/12/02	4.9	-1.8	0.09
MW 12	3/11/02	14.3	0.6	0.31
	3/18/02	25.3	3.9	0.61
	4/15/02	7.4	-0.8	0.18
MW 11	3/11/02	34.5	4.6	0.66
	4/15/02	21.4	6.3	0.81
	8/13/02	16.9	4.1	0.61
	11/12/02	15.7	2.2	0.44

<sup>1</sup>Estimated errors of  $\pm 0.04$  for calculated  $F_{\text{ash}}$  are based on analytical errors of  $\pm 0.2\text{‰}$  for  $\delta^{34}\text{S}$ .

The initial very high B concentrations (15-35 mg/L) in water from the ash trench wells identifies B as a sensitive indicator of contamination at the study site<sup>5</sup>. The strong positive correlation ( $r=0.96$ ) between anomalous  $\delta^{34}\text{S}$  and dissolved B in all wells except MW11 (Fig. 3) confirms the utility of the S-isotopic measurements as another indicator of contamination. The samples from ash trench well MW11 show greater scatter about the best-fit correlation line (Fig. 3). One possible explanation is non-conservative behavior of dissolved B in the persistently highly alkaline (pH=9.4-11.9) waters from MW11. Under such pH conditions, the normally conservative, uncharged  $\text{B}(\text{OH})_3$  species is partially converted to a charged  $\text{BO}_2^-$  anion that is more subject to ion exchange reactions. Another possible cause of scatter is modification of sulfur isotope composition by bacterial sulfate reduction. This explanation is considered less likely because refractory organic matter in fresh fly ash tends not to be usable by bacteria<sup>1</sup>, and the consistent detection of dissolved oxygen and nitrate in MW11 and the other monitoring wells indicates sufficiently oxidizing conditions to inhibit sulfate reduction.

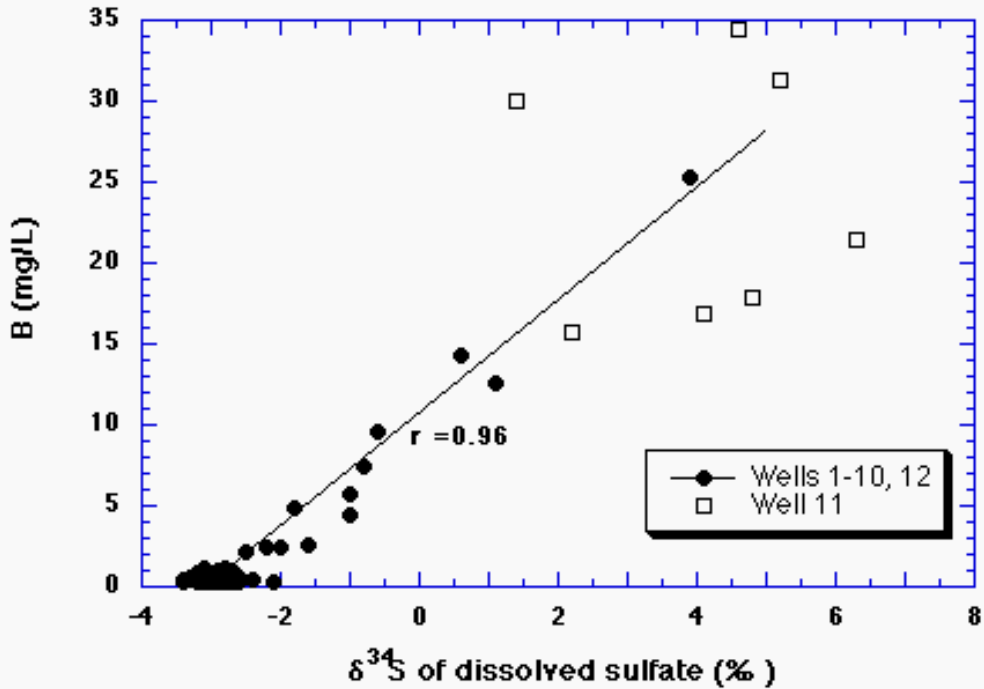


Figure 3. Relation between the sulfur isotopic composition of dissolved sulfate and the concentration of dissolved boron in groundwater monitoring wells at the fly ash emplacement site in southwestern Weld County, Colorado. The best-fit line and calculated correlation coefficient ( $r$ ) excludes data from well MW 11, shown as open squares.

For samples containing a mixture of sulfate derived from two sources such as ash leachate (ash) and local ground water (gw), the contribution from each source can be estimated based on isotopic mass balance. The operative equation is:

$$\delta^{34}\text{S}_{\text{mix}} = \delta^{34}\text{S}_{\text{ash}} (F_{\text{ash}}) + \delta^{34}\text{S}_{\text{gw}} (1-F_{\text{ash}}) \quad (1)$$

Where

$F_{\text{ash}}$  = mass fraction of sulfate contributed by ash leachate.

Equation (1) is rearranged to solve for  $F_{\text{ash}}$ . The total error in the calculated value of  $F_{\text{ash}}$  is based on analytical error in measurement of individual sulfur isotope values ( $\pm 0.2\%$ ), and error in the selection of appropriate sulfur isotopic values for the two sources (variable). The latter error is reduced if the range of isotopic composition of each source ( $\delta^{34}\text{S}_{\text{ash}}$ ,  $\delta^{34}\text{S}_{\text{gw}}$ ) is small, or if multiple determinations yield an average value with a small standard deviation. Sensitivity is increased as the isotopic contrast between the two sources increases. Accuracy is reduced if the assumption of conservative mixing of sulfate sources is compromised by bacterial sulfate

reduction that alters the isotopic composition of the samples. Once  $F_{\text{ash}}$  is determined, other simple equations are available to calculate, if desired, the volume percent of ash leachate in the mixture, and the concentration of  $\text{SO}_4$  in the ash leachate component<sup>19</sup>.

Sample calculations for some contaminated, B-rich water samples indicated that the mass fraction of ash-derived sulfate ( $F_{\text{ash}}$ ) in the total mass of dissolved sulfate ranged from 0.81 (81 percent) to as little as 0.09 (9 percent) (Table 2). The value chosen for  $\delta^{34}\text{S}$  of ash leachate was 8.5‰, the average of six determinations (Table 1). Values chosen for  $\delta^{34}\text{S}$  of ground water were the contemporaneous values recorded in upgradient well MW9 (Table 1). An analytical error of  $\pm 0.2\%$  for all measured  $\delta^{34}\text{S}$  values produces an error of approximately  $\pm 0.04$  (4 percent) in the calculated  $F_{\text{ash}}$  values. Thus, calculated  $F_{\text{ash}}$  values less than 10 percent are subject to greater relative error. As expected, the contribution of ash-derived sulfate is greatest in the ash trench wells MW11 and MW12. Ash-derived sulfate and boron concentrations decrease over time much more rapidly in MW12 than in MW11, indicating a more rapid approach to local ground water composition. The same behavior is noted for pH and concentrations of other dissolved constituents in MW12 (J. Adams, CGRS, written commun., 2002). A possible explanation is that ash trench well MW12 was completed in the underlying Pierre Shale whereas MW11 bottomed in the fly ash. In comparison to ash trench wells, monitoring wells more removed from the ash trench show less impact from ash-derived sulfate because of greater dilution by the large reservoir of ground-water sulfate.

## SUMMARY AND CONCLUSIONS

At sites where fly ash utilization or disposal is distant from the mine site or power plant it is possible to use sulfur isotopic measurements to detect and quantify ash-derived sulfate in local ground water. Three important requirements are (1) different S-isotopic composition of sulfate in fly ash leachate and local ground water, (2) sufficiently oxidizing conditions to inhibit bacterial sulfate reduction, and (3) conservative mixing of the two sulfate sources. If the S-isotopic compositions of two sulfate sources are sufficiently different, then simple calculations based on S-isotopic mass balance can provide estimates of their mixing proportions, even in the presence of significant baseline concentrations of dissolved sulfate. In this study, differences in  $\delta^{34}\text{S}$  of 10-12‰ permitted confident detection of as little as 10 percent of ash-derived sulfate in monitoring wells. Sulfur isotope analyses of dissolved sulfate are widely available at modest cost and can complement other indications of contamination such as elevated concentrations of dissolved B. Increased utilization of low-sulfur coals by power plants throughout the United States will increase the distribution of derivative fly ash exhibiting a typically positive  $\delta^{34}\text{S}$  composition. This isotopic signature can be used to good advantage for the estimation of environmental impacts associated with the use or disposal of coal fly ash.

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