

Evidence for Coal Ash Ponds Leaking in the Southeastern United States

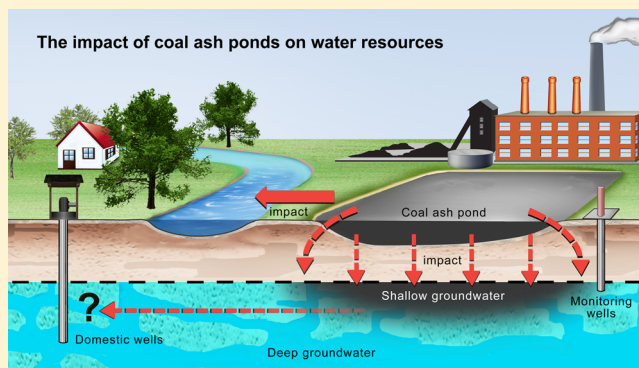
Jennifer S. Harkness,[†] Barry Sulkin,[‡] and Avner Vengosh^{*,†}

[†]Division of Earth and Ocean Sciences, Nicholas School of the Environment, Duke University, Durham, North Carolina 27708, United States

[‡]Environmental Consultant, Nashville, Tennessee, 37218, United States

S Supporting Information

ABSTRACT: Coal combustion residuals (CCRs), the largest industrial waste in the United States, are mainly stored in surface impoundments and landfills. Here, we examine the geochemistry of seeps and surface water from seven sites and shallow groundwater from 15 sites in five states (Tennessee, Kentucky, Georgia, Virginia, and North Carolina) to evaluate possible leaking from coal ash ponds. The assessment for groundwater impacts at the 14 sites in North Carolina was based on state-archived monitoring well data. Boron and strontium exceeded background values of 100 and 150 $\mu\text{g/L}$, respectively, at all sites, and the high concentrations were associated with low $\delta^{11}\text{B}$ (-9‰ to $+8\text{‰}$) and radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7070 to 0.7120) isotopic fingerprints that are characteristic of coal ash at all but one site. Concentrations of CCR contaminants, including SO_4 , Ca, Mn, Fe, Se, As, Mo, and V above background levels, were also identified at all sites, but contamination levels above drinking water and ecological standards were observed in 10 out of 24 samples of impacted surface water. Out of 165 monitoring wells, 65 were impacted with high B levels and 49 had high CCR-contaminant levels. Distinct isotope fingerprints, combined with elevated levels of CCR tracers, provide strong evidence for the leaking of coal ash ponds to adjacent surface water and shallow groundwater. Given the large number of coal ash impoundments throughout the United States, the systematic evidence for leaking of coal ash ponds shown in this study highlights potential environmental risks from unlined coal ash ponds.



INTRODUCTION

The United States annually generates about 110 million tons of coal combustion residuals (CCRs),¹ which include fly ash, bottom ash, boiler slag, and flue gas desulfurization (FGD) byproducts.^{1,2} About 56% of CCRs are deposited in surface impoundments and landfills.¹ Recent CCR spills from the Tennessee Valley Authority (TVA) in Kingston, TN^{3–6} and Duke Energy in Eden, NC,^{7,8} combined with findings of contaminants in effluents discharged from coal ash ponds,^{9–11} have increased public awareness of the environmental and human health risks of CCR storage and disposal. National regulations by the U.S. Environmental Protection Agency (USEPA) permit the discharge of CCR effluents through outfalls regulated by the National Pollutant Discharge Elimination System (NPDES), but the leaking of unlined ponds is prohibited.¹

The EPA CCR Management Rule has documented reports of 40 confirmed and 113 potential damage cases due to storage and disposal of CCRs.¹ A total of 60% of the damage cases are groundwater or surface water contamination due to the leaking of surface impoundments.¹ Many of these cases report concentrations of As, Se, and B, among others, that exceed EPA standards for drinking water, aquatic-life exposure, and health advisory standards.¹ In the scientific literature, seeping of coal

ash pond water to surface water and groundwater has been documented over the last 30 years. Meyer et al. (1979) found that seepages from a coal ash pond in Indiana Dunes National Lakeshore, IN raised groundwater levels 10–15 feet.¹² Coutant et al. (1978) reported iron- and sulfate-rich seepages from the TVA Bull Run Steam Plant that were enriched even compared to the main pond overflow control releases,¹³ and Brodie et al. (1989) reported iron- and manganese-rich seepages as the TVA Widows Creek, Kingston, and Colbert steam plants.¹⁴ However, there are no studies that assess systematic leaking from ponds at a regional scale.

CCR effluents are enriched in a large number of elements, many of which are toxic.^{9–11,15–18} An extensive literature review of the leaching behavior of elements from coal ash by Izquierdo et al. (2012) identified oxyanionic-forming species (i.e., As, B, Cr, Mo, Sb, Se, and V) as highly leachable from coal ash and controlled by pH and Ca/SO_4 ratios in the coal ash.¹⁸ Ruhl et al. (2012) identified enrichment of these oxyanion

Received: April 7, 2016

Revised: May 26, 2016

Accepted: May 27, 2016

Published: June 10, 2016

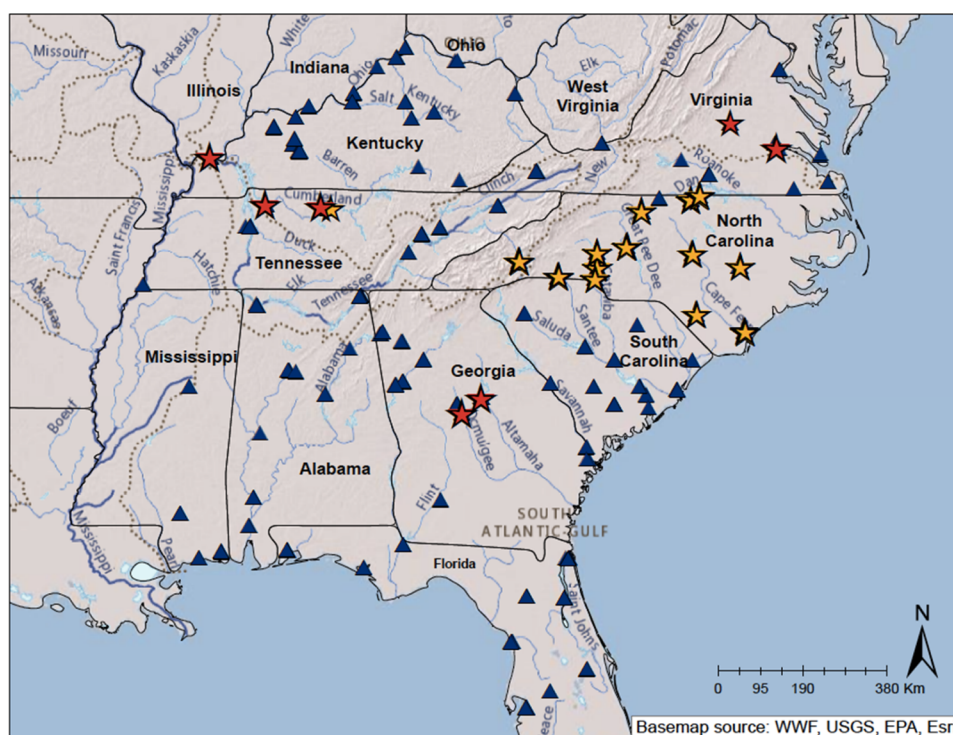


Figure 1. Locations of coal ash ponds in the southeastern United States (blue triangles).³³ Most sites have multiple ash ponds that are indicated by a single triangle. Red stars mark sites that were assessed for leaking to surface water, and the orange stars mark sites assessed for migration of impacted water to shallow (<30 m) groundwater.

species, along with Ca, Mg, Sr, Li, F, Cl, Br, SO_4 , and Tl in effluents discharging from coal ash ponds to lakes in North Carolina.⁹ The presence of these elements can be indicative of CCR-impacted water; however, studies have shown that certain elements (i.e., SO_4 , As, and Se) can be differentially leached from CCRs or modified by redox and acidity conditions, making them poor tracers for delineating CCR-impacted water in the environment.^{19–21} Isotopic systems, however, have been identified as superior tracers of CCR–water interactions and the mixing of CCR-impacted water with natural waters.^{22,23}

B, Sr, Li, and Mo isotopes have been suggested as potential tracers to delineate coal and CCR impacts in the environment.^{22,24–27} Previous studies have found that coals and coal ash leachates have distinctive B and Sr isotope ratios^{17,22,23,28} and the mobilization of both B and Sr from CCRs does not induce isotope fractionation; thus, the B and Sr isotopic ratios of impacted water will reflect the CCR composition.²² Although B and Sr mobilization from CCRs is pH-dependent²² and may have different leaching kinetics,^{14,19} they are highly soluble in water and not affected by redox processes. Davidson and Bassett (1993) measured $\delta^{11}\text{B}$ values ranging from -19.2‰ to $+15.8\text{‰}$ in four fly ash samples and emphasized the increased sensitivity of isotopic tracers relative to using elemental concentrations alone.²³ Brubaker et al. (2013) and Spivak-Birndorff et al. (2012) reported elevated Sr concentrations and distinctively high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7107 to 0.7150) in leachates from different types of CCRs, compared to average crustal rocks and soils.^{17,28} Ruhl et al. (2014) examined the $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{11}\text{B}$ values of CCRs from 14 plants covering three coal basins in the United States and found ranges consistent with those from the previous studies (-17.6 to $+6.3\text{‰}$ and 0.70975 to 0.71251, respectively).²² However, the addition of Sr-rich lime (CaO) or CaCO_3 as part of the desulfurization

(FGD) process can modify the Sr isotope ratios of the original coals, resulting in lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in CCRs. In addition, blending coal from different sources could generate CCRs with different compositions.^{9,22}

B and Sr have also been tested as tracers of CCR-impacted water in field studies. Ruhl et al. (2014) found that boron isotopes were reliable tracers for detecting the CCR impact from the TVA Kingston spill, as well as effluents discharged from ash ponds in North Carolina and Tennessee.²² In contrast, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of background water were similar to those of CCRs in some cases.²² As a result, the use of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as a tracer is site-dependent, highlighting the value of using a two-isotope system. Similar results for groundwater impacted by CCRs were obtained by Buska et al. (2004), with high B (15 700 to 24 000 $\mu\text{g/L}$) and distinct $\delta^{11}\text{B}$ values (0.1 to 6.6 ‰) relative to other anthropogenic impacts (i.e., municipal wastewater) in four samples.²⁷ It should be noted that the B and Sr isotope ratios in groundwater can be affected by water–rock interactions, and the original isotopic signatures of the contaminations source can be modified to reflect the composition of the host aquifer rocks, particularly in clay-rich media.^{30,31}

Here, we integrated the geochemistry of dissolved inorganic constituents and isotopic ($\delta^{11}\text{B}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) tracers to identify CCR-impacted water in seeps and surface water near coal ash ponds at seven sites, as well as the migration of impacted water to shallow groundwater monitoring wells at 15 sites (Figure 1). We hypothesize that the combined B and Sr elemental and isotopic fingerprints of CCRs can be distinguished from background water, as well as other potential sources, and can be used as proxies to delineate migration of CCR contaminants into adjacent surface water and groundwater. We also hypothesize that high concentrations of other dissolved inorganic trace elements (e.g., As and Se) will also be

present in waters that have been impacted, yet their concentrations would vary with environmental conditions. We therefore distinguish “impacted water” with geochemical indicators for CCRs but without elevated concentrations of other constituents from “contaminated water” that has both geochemical indicators for CCR migration and concentrations of dissolved metals or metalloids that exceed national drinking water or ecological exposure standards. Given the large numbers of coal ash ponds across the country, this study aims to implement new tools to evaluate the potential leaking of unlined CCR impoundments in the United States.

MATERIALS AND METHODS

Site Selection and Sample Collection. This study is based on (1) new data generated from sampling campaigns in Tennessee, Georgia, Virginia, and Kentucky, and (2) archived groundwater data reported by the North Carolina Department of Environmental Quality (NC-DEQ).³² A total of 39 surface water and seep samples were collected during the summer and fall of 2015 at the TVA Cumberland (site TN1) and Gallatin (TN2) plants in Tennessee, the TVA Shawnee plant in Kentucky (KY1), the Georgia Power Arkwright (GA1) and Branch (GA2) plants in Georgia, and the Dominion Chesterfield (VA1) and Bremono (VA2) plants in Virginia. Sample sites were selected on the basis of access, and no a priori knowledge of contamination due to leaking or accidental releases was available. All sites contain coal ash storage impoundments that are unlined.³³ TN2 was the only site at which we were allowed access to the monitoring wells by the utility, and shallow groundwater samples from nine monitoring wells (TNMW) were collected in July and September 2015 (Figure S8 and Table S1). Water chemistry data for 156 shallow groundwater monitoring wells located near coal ash ponds at 14 coal-fired power plants in NC was obtained from the NC DEQ database for groundwater samples collected and analyzed between 2010 and 2015 (Figure S9 and Table S2).³² To the best of our knowledge, this data set encompasses all monitoring wells at all coal ash ponds in North Carolina, although not all wells were reported at every time point. Maps and descriptions of samples are available in the [Supporting Information](#).

Background water values were determined on the basis of several different sources. At sites TN1, TN2, GA2, VA2, and KY1, upstream water or seeps or small streams away from the ponds were sampled to establish the baseline water quality onsite and are labeled in the maps in the [Supporting Information](#). Concentrations in reference samples from GA2 and VA2 were provided from previous testing but were not analyzed directly in this study. Background wells designated by the utility were included in the shallow groundwater monitoring wells at some sites, including those directly sampled in this study and reported on the NC-DEQ web site. In addition, values for background surface water and groundwater were obtained from previously published studies and unpublished data sets to establish regional baseline values.^{4,9,22,29,34,35}

Chemical and Isotope Analysis. A total of 48 samples were collected from seven sites and analyzed for major and trace elements as well as boron and strontium isotopes ($\delta^{11}\text{B}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) at Duke University. All data collected as part of the study are presented here, and no sites or individual samples were omitted. Chloride and sulfate anions were measured by ion chromatography on a Dionex IC DX-2100, major cations by direct current plasma optical emission spectrometry (DCP-OES),

and trace elements by VG PlasmaQuad-3 inductively coupled plasma mass spectrometer (ICP-MS). The DCP and ICP-MS instruments were calibrated to the National Institute of Standards and Technology 1643e standard, which was used at varying concentrations before, after, and throughout sample runs. Internal standards of In, Th, and Bi were spiked into all samples prior to measurement on the ICP-MS. The detection limit of the ICP-MS of each element was determined by dividing three times the standard deviation of repeated blank measurements by the slope of the external standard.⁹

Strontium and boron isotopes were analyzed by thermal ionization mass spectrometry (TIMS) on a ThermoFisher Triton at the Duke University TIMS lab. $^{11}\text{B}/^{10}\text{B}$ ratios were measured as BO_2^- ions in negative mode, normalized to NIST NBS SRM-951,³⁶ and presented in $\delta^{11}\text{B}$ notation following an oxidation step using 10% Optima hydrogen peroxide to remove organic interferences. Long-term replicate measurements ($n = 60$) of the NBS SRM-951 standard yielded a precision of 0.6‰. Strontium from water samples was preconcentrated by evaporation in HEPA filtered clean hood and redigested in 0.6 mL of 3.5N Optima HNO_3 from which strontium was separated using Eichrom Sr-specific ion-exchange resin. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were collected in positive mode on the TIMS, and external reproducibility was comparable to standard NIST987 (0.710265 ± 0.000006).

Statistical Analysis. All concentrations are reported to the instrumental precision of ± 0.1 mg/L for major elements and ± 0.1 $\mu\text{g/L}$ for trace elements. B isotopes are measured to the tenth place ($\pm 0.1\text{‰}$), and Sr isotope ratios are measured to the fifth decimal place (± 0.00001). All statistical analyses (Pearson correlations, analysis of variance, and ANOVA) were done using R v3.2.0 (The R Foundation). All inorganic chemical data were log-transformed to normalize the data except the B and Sr isotope ratios and pH, which were normally distributed. Any sample that was measured as a 0 or nondetect was assigned a value that was $1/3$ of the detection limit to prevent loss of data during the log-transformation. All correlations are reported as the Pearson product-moment correlation coefficient, Pearson's r . An r value of 0 indicates no correlation, +1 is a total positive correlation, and -1 is a total negative correlation. A p value of <0.05 indicates a slope that is significantly distinct from the 0 slope at a 95% confidence limit. One-way ANOVA was used to determine if the mean values between different water types (seeps and surface water or tested and background) were statistically different at a 95% confidence limit ($p < 0.05$).

RESULTS AND DISCUSSION

Background Characterization of Surface Water and Seeps. B concentrations ranged from 26.0 to 85.6 $\mu\text{g/L}$ in background samples, and Sr concentrations ranged from 25.2 to 152.9 $\mu\text{g/L}$. Ruhl et al. (2012) reported B concentrations from 5.8 to 26.7 $\mu\text{g/L}$ in the Clinch and Emory rivers upstream of the Kingston spill in Tennessee, Sr concentrations of 21 to 122.8 $\mu\text{g/L}$ in Tennessee rivers, and 16 to 153.8 $\mu\text{g/L}$ in North Carolina rivers.^{4,9,22} A 5-year USGS study reported a B range of 1 to 66 $\mu\text{g/L}$ in 68 surface waters from Tennessee and 6 to 120 $\mu\text{g/L}$ in 91 surface waters from the southeast United States.²⁹ On the basis of these values, we established B and Sr concentrations threshold values for background surface waters of 100 and 150 $\mu\text{g/L}$, respectively.

$\delta^{11}\text{B}$ was measurable in four background samples, with values of 0.4 to 15.9‰ (Table 1). Ruhl et al. (2014) reported $\delta^{11}\text{B}$

Table 1. Chemical Data for All Surface Samples from the Seven Sites and Shallow Groundwater at TN2^a

Sample ID	B (μg/L)	δ ¹¹ B (‰)	Sr (μg/L)	⁸⁷ Sr/ ⁸⁶ Sr	pH	Cl (mg/L)	SO ₄ (mg/L)	Mg (mg/L)	Ca (mg/L)	As (μg/L)	Cd (μg/L)	Cr (μg/L)	Fe (μg/L)	Mn (μg/L)	Mo (μg/L)	Ni (μg/L)	Pb (μg/L)	Se (μg/L)	V (μg/L)	Zn (μg/L)
TN1-BG-1	51.1	15.9	152.9	0.70855	7.98	5.7	6.4	4.4	52.6	0.5	n.d. ^b	0.4	155.1	72.7	0.2	1.1	n.d.	n.d.	0.9	0.8
TN1-Seep-1	40621.3	14.8	1521.6	0.71199	5.50	51.6	196.9	15.5	766.2	1.8	1.5 [^]	4.2	1635.1 [^]	14666	48.5	56.8	0.4	10.8 [^]	8.4	37.4
TN1-Seep-2	12867.0	30.0	520.2	0.71013	4.00	52.9	89.6	33.3	425.9	1.5	1.5 [^]	n.d.	2067.5 [^]	68314	1.7	67.7	n.d.	6.4 [^]	3.5	62.7
TN1-Seep-3	4315.0	7.6	1129.4	0.70856	7.88	11.2	41.0	40.1	210.4	2.1	n.d.	0.6	640.1	1444.0	11.9	4.3	n.d.	0.8	3.9	4.4
TN1-SW-1	139.4		157.1			8.3	9.4	5.1	55.0	0.8	n.d.	0.6	152.3	57.7	1.1	3.2	n.d.	0.7	1.6	3.3
TN1-SW-2	100.0	16.3	157.4	0.70876	7.23	8.0	9.1	5.2	55.5	0.7	n.d.	0.5	156.4	64.9	0.6	1.8	n.d.	0.3	1.3	1.7
TN1-SW-3	117.0	16.0	158.5	0.70870	7.23	7.4	7.8	5.0	55.8	0.8	n.d.	0.4	171.3	76.1	0.5	1.2	n.d.	0.6	1.2	1.2
TN1-Lagoon-1	3310.2	16.4	636.8	0.70957	7.43	12.7	64.5	21.8	204.5	0.9	n.d.	2.4	631.9	252.6	20.4	3.4	n.d.	0.2	1.5	3.3
TN1-Lagoon-2	3162.3	15.7	625.3	0.70960	7.52	8.0	38.5	21.1	202.3	0.8	0.1	1.6	644.0	784.1	21.3	3.4	n.d.	1.1	1.8	2.7
TN1-NPDES	26.5		129.5	0.70970	7.48	6.4	23.3	5.6	35.7	0.5	n.d.	0.3	107.4	7.6	0.3	1.2	n.d.	n.d.	0.8	2.1
VA1-BG-1	85.6	0.4	139.4	0.71077		43.0	50.4	5.7	34.7	0.9	n.d.	0.4	73.0	5.6	1.9	1.7	n.d.	0.8	1.7	1.3
VA1-SW-1	375.3	-5.1	944.5	0.71014		41.6	102.3	11.7	63.0	3.2	n.d.	n.d.	1967.4 [^]	1493.4	4.2	7.7	n.d.	n.d.	0.9	1.2
VA1-SW-2	685.8	-1.0	620.9	0.71113		80.8	77.9	13.2	76.8	17.4 [*]	0.1	1.3	229.1	1281.2	10.1	2.4	0.1	7.2 [^]	3.4	8.0
KY1-BG-1	25.8	5.9	154.0	0.71066		36.6	36.1	7.8	23.8	0.7	n.d.	0.3	75.4	30.8	0.6	1.3	0.1	0.7	1.3	3.3
KY1-SW-1	644.3	3.1	199.0	0.71058		28.6	55.7	7.0	33.8	0.5	n.d.	0.3	83.2	148.9	10.7	1.8	n.d.	0.4	1.1	58.7
VA2-BG-1	26.0		25.2			4.8	1.4	1.7	3.2	0.8		n.d.	588.0	16.7	n.d.	0.6		n.d.	n.d.	n.d.
VA2-SW-1	178.1	-1.2	390.2	0.71083		10.2	30.5	7.9	25.1	45.4 [*]	0.1	0.2	75.2	29.9	35.3	1.3	n.d.	1.2	47.2	0.9
VA2-SW-2	6.7	-0.5	37.5			4.6	1.7	5.6	4.5	0.3	n.d.	n.d.	180.8	90.8	n.d.	0.5	0.1	0.3	0.4	2.4
VA2-SW-3	54.6		131.0			19.7	0.7	5.2	25.4	10.7 [*]	n.d.	1.7	41.6	7900.0	0.7	18.1		0.9	8.9	26.5
TN2-BG-1	44.9	10.0	89.5	0.70972	8.54	1.6	7.8	4.2	53.0	1.0	n.d.	0.2	187.9	22.2	1.0	1.4	0.1	n.d.	0.8	21.2
TN2-Seeps-1	8734.0	6.7	1008.6		7.88	1.0	30.2	8.0	124.4	0.7	0.1	n.d.	364.5	3968.8	0.1	2.0	0.2	n.d.	0.4	3.3
TN2-Seeps-2	5907.3	7.7	372.9	0.70985	6.94	2.4	56.2	5.3	95.2	3.7	n.d.	n.d.	21744 [^]	10447	0.8	1.6	n.d.	n.d.	0.3	1.4
TN2-Seeps-3	489.2	-3.5	205.2	0.71168	6.17	0.9	84.4	7.6	58.7	0.3	n.d.	n.d.	14704 [^]	4021.8	0.1	9.9	n.d.	n.d.	n.d.	8.5
TN2-Seeps-4	31.4	13.9	317.8	0.71066	7.86	0.4	6.7	19.1	138.0	0.7	n.d.	1.1	863.5	3354.6	n.d.	4.78	n.d.	0.4	0.1	1.5
TN2-SW-1	72.1	8.1	102.9	0.71056	7.35	4.5	23.1	5.2	25.3	0.4	n.d.	0.1	69.6	43.2	0.3	0.6	n.d.	n.d.	0.7	0.6
TN2-NPDES	245.6	-0.5	412.9	0.71187	7.16	5.4	44.0	6.0	41.5	5.1	n.d.	3.8	113.7	13.7	6.1	1.2	n.d.	15.1 [^]	30.6	1.3
GAI-Dam-1	1866.5	-3.2	121.3	0.70792		6.6	35.5	18.1	23.5	0.1	n.d.	n.d.	38.2		0.2	0.4	n.d.	n.d.	1.1	2.1
GAI-SW-1	1643.1	-9.2	166.4	0.70697		5.6	88.0	22.7	44.2	n.d.	n.d.	n.d.	39.4	404.0	9.9	1.6	n.d.	n.d.	2.2	4.3
GA2-BG-1	50.0							2.2	5.6	0.1	n.d.	n.d.	900.0	46.0	n.d.		n.d.	n.d.	2.5	
GA2-BG-2	50.0				7.52		3.4	0.8	1.5	1.1	n.d.	9.0	10900 [^]	67.2	n.d.		4.1 [^]	n.d.	24.6	
GA2-Dam-1	2100.8	-8.3	554.0	0.71118		3.9	427.3	16.8	124.3	0.5	n.d.	n.d.	240.4	2493.2	0.2	1.2	n.d.	n.d.	0.2	20.2
GA2-Seep-1	2479.3	1.7	231.8	0.70915	7.26	6.7	548.2	63.4	123.3	0.3	n.d.	3.1	206.9	671.2	0.6	n.d.	n.d.	0.6	1.1	12.0
GA2-Seep-2	2255.5	-3.4	531.1	0.70824	7.40	6.9	579.0	76.5	101.2	0.3	n.d.	1.7	432.7	909.8	0.5	n.d.	n.d.	0.3	0.6	10.6
GA2-Seep-3	2413.0	-2.1	417.3	0.71053	6.69	7.6	681.0	64.3	146.1	0.5	n.d.	1.3	770.4	724.9	0.3	n.d.	n.d.	n.d.	0.5	11.2
GA2-SW-1	770.5	-4.6	167.5	0.70980		7.6	501.6	21.2	42.5	0.1	n.d.	n.d.	26.2	708.5	3.0	1.0	n.d.	n.d.	0.7	2.0
GA2-SW-2	1268.9	-0.8	532.8	0.70777		7.2	418.3	31.3	84.4	0.1	n.d.	n.d.	9.1	3475.4	0.1	2.4	n.d.	n.d.	0.4	4.4

Table 1. continued

Sample ID	B ($\mu\text{g/L}$)	$\delta^{11}\text{B}$ (‰)	Sr ($\mu\text{g/L}$)	$^{87}\text{Sr}/^{86}\text{Sr}$	pH	Cl (mg/L)	SO_4 (mg/L)	Mg (mg/L)	Ca (mg/L)	As ($\mu\text{g/L}$)	Cd ($\mu\text{g/L}$)	Cr ($\mu\text{g/L}$)	Fe ($\mu\text{g/L}$)	Mn ($\mu\text{g/L}$)	Mo ($\mu\text{g/L}$)	Ni ($\mu\text{g/L}$)	Pb ($\mu\text{g/L}$)	Se ($\mu\text{g/L}$)	V ($\mu\text{g/L}$)	Zn ($\mu\text{g/L}$)
GA2-SW-3	1711.6	3.2	349.2	0.70970		6.7	445.4	46.9	74.3	0.1	n.d.	n.d.	9.0	3386.7	0.5	5.6	n.d.	n.d.	0.3	4.8
GA2-SW-4	1960.2	-5.1	577.1	0.71089		8.1	446.9	25.6	119.7	0.1	n.d.	n.d.	135.3	3496.1	0.1	1.1	n.d.	n.d.	0.2	3.2
GA2-SW-5	1879.3	-9.9	1132.0	0.71143	6.74	4.1	200.8	19.5	102.0	131.0*	n.d.	0.5	123.2	8948.7	62.3	n.d.	n.d.	0.5	1.0	74.2
GA2-SW-6	1115.5		605.0	0.71152	7.20	7.4	265.8	20.9	48.7	0.1	n.d.	n.d.	300.3	1030.2	n.d.	n.d.	n.d.	n.d.	0.2	4.6
TN-WM22	20.2	17.7	83.3	0.70877		4.9	2.7	5.4	69.7	n.d.	n.d.	1.0	154.2	2.3	0.3	1.1	n.d.	0.2	0.7	3.5
TN-MW25	15.3	8.0	259.0	0.70872		34.5	27.7	26.9	101.1	n.d.	n.d.	2.3	401.6	47.7	n.d.	2.1	n.d.	2.3	0.9	1.3
TN-NRS20	5347.7	-0.2	1136.5	0.71180		2.3	1078.5	26.9	371.4	0.6	0.1	n.d.	24834*	11500	5.0	29.8	0.1	0.1	0.3	34.1
TN-NRS27	4617.5	1.5	1048.7	0.71106		2.3	770.8	25.5	307.5	n.d.	n.d.	n.d.	463.9	664.2	4.6	3.5	n.d.	n.d.	n.d.	6.0
TN-NRS19R	3930.9	2.8	1195.9	0.71269		1.7	2239.5	29.0	437.5	0.4	10.6*	n.d.	178602*	33617	n.d.	228.4*	3.2*	7.7*	11.9	630.1*
TN-NRS26	6249.0	0.0	979.0	0.71135		0.1	774.3	24.4	326.1	0.4	n.d.	1.2	11811*	6815.9	12.1	7.5	n.d.	0.8	0.1	1.9
TN-MW17	1494.1	8.8	612.6	0.70922		1.4	246.6	26.5	145.1	n.d.	n.d.	0.2	528.5	8.0	2.6	2.4	n.d.	n.d.	0.2	2.8
TN-MW23	341.0	6.1	225.2	0.70981		9.7	198.3	7.4	193.8	n.d.	n.d.	0.9	784.3	25.4	n.d.	3.1	n.d.	1.1	n.d.	2.0
TN-MW24	70.6	13.1	234.8	0.70910		1.4	254.0	10.6	264.8	n.d.	n.d.	1.8	1057.1*	16.3	2.0	4.8	n.d.	2.0	n.d.	1.7

*Concentrations in background samples are shown in bold for each site. Samples exceeding the EPA maximum contaminant level (MCL)³⁹ are indicated by *, and samples above the ecological threshold of the criterion continuous concentration (CCC)⁴⁰ are indicated by ^. The MCL is the drinking water regulation,³⁹ and CCC is the National Recommended Water Quality Criteria for Aquatic Life.⁴⁰

^Concentrations below the instrumental detection limit are denoted by n.d. Empty entries indicated no analysis for that sample.

values of 9.6‰ and 10.2‰ in the Emory and Clinch rivers, respectively.²² $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in some background waters were less radiogenic than values found in coal ash leachates (e.g., TN1 upstream = 0.70855), while other background waters had $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that were similar to those of coal ash leachates (VA1 upstream = 0.71077, TN2 reference seep = 0.71066, and KY1 upstream = 0.71066). Variations of $^{87}\text{Sr}/^{86}\text{Sr}$ in surface water across the region are common, as shown in Ruhl et al. (2014), with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging from 0.7117 to 0.7124 in Tennessee rivers and from 0.7125 to 0.7170 in North Carolina lakes.²² Overall, it is clear that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in background waters are not always distinct from coal ash leachates. For this reason, a two-isotope system approach is used for the subsequent analyses. Levels of other dissolved inorganic constituents in background water are summarized in Table 1.

Tracing CCRs in Surface Water. We focus first on the variations in B and Sr geochemistry as tracers to identify CCR-impacted water in the environment. B and Sr concentrations in the tested samples ranged from 6.7 to 40 621.3 $\mu\text{g/L}$ and 37.5 to 1521.6 $\mu\text{g/L}$, respectively, and the mean values were statistically higher using a one-way ANOVA test (mean = 3046.3 $\mu\text{g/L}$, $p < 0.05$, and mean = 450.5 $\mu\text{g/L}$, $p < 0.05$) compared to the background samples (51.3 and 101.7 $\mu\text{g/L}$, respectively). B and Sr concentrations exceeding background values were found at all seven sites (Figure 2 and Table 1) and consisted of nine seeps, 14 surface water samples, and one NPDES outfall out of the 34 total surface samples collected. B and Sr concentrations were correlated across all sites ($r = 0.77$, $p < 0.05$; Figure 3). Our analysis shows that the highest concentrations of B and Sr were observed in the seep samples ($p < 0.05$ for both), while the surface water samples had lower concentrations, likely due to dilution by background water and rain runoff (Figure S10). Seeps at the TN1 site had the highest concentrations, up to 406- and 10-fold higher than regional background levels, although background seeps were not directly sampled at this site for comparison. B and Sr were positively correlated to Cl in samples collected at TN1 ($r = 0.84$, $p < 0.05$ and $r = 0.68$, $p < 0.05$, respectively).

Boron isotope ratios yielded a $\delta^{11}\text{B}$ range of -9.2‰ to +30.0‰ (Figure 2). At all sites except TN1, the seeps and surface waters with B > 100 $\mu\text{g/L}$ were associated with $\delta^{11}\text{B} < 8.1$ ‰ (Figure S10 and Table 1), which are lower than values typical for surface waters in the region (9.6‰ to 13.9‰) and within the range expected for leaching of coal ash (-17.6‰ to +6.3‰).²² The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in pond effluents ranged from 0.7070 to 0.7120 (Figure 2), with a general increase of $^{87}\text{Sr}/^{86}\text{Sr}$ with Sr concentrations toward isotopic ratios found in U.S. coal ash (e.g., Appalachian, ~0.7124; central United States, ~0.712; and Powder River Basin, ~0.7122)²² in all but one site (GA1) (Figures 2 and S10). A pair of the seeps and the lagoon water from the TN1 site had higher $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7096 to 0.7120) compared to the upstream value (0.70855; Table 1).

The high B and Sr concentrations and the distinctive B and Sr isotope variations in the seeps and surface water most likely reflect (1) the mixing of CCR leachates with the source water in the pond; (2) the mixing of outfall effluents and seeps with background water; and (3) interactions with clay minerals during the migration of effluents through the pond walls. At sites TN2, GA2, VA1, VA2, and KY1, the high B and Sr concentrations, along with distinctly low $\delta^{11}\text{B}$ values, are strong evidence for the discharge of coal ash pond water to local surface water. Similar to the results from Ruhl et al. (2014),²² the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were not always distinct from background

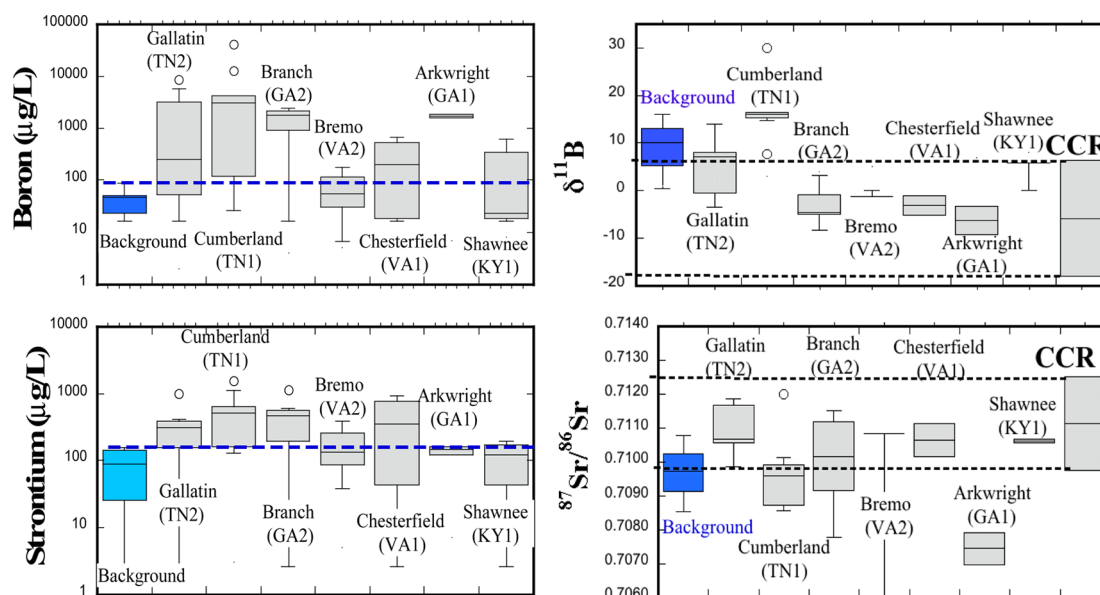


Figure 2. Boxplots of B and Sr concentrations and their isotope ratios in samples collected from all seven sites assessed for leaking to surface waters, including background surface water ($n = 6$), Gallatin (TN2; $n = 6$), Cumberland (TN1; $n = 9$), Branch (GA2; $n = 10$), Brema (VA2; $n = 3$), Chesterfield (VA1; $n = 2$), Arkwright (GA1; $n = 2$), and Shawnee (KY1; $n = 2$). Background concentrations and ratios are highlighted in blue and signified by the blue dotted lines. The range of B and Sr isotope values reported for CCR leachates in previous studies are included, labeled as CCR, and signified by the black dotted lines.^{17,22–24,28}

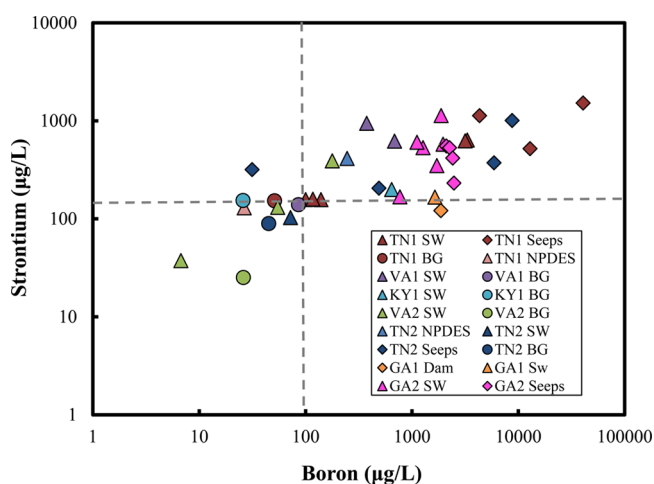


Figure 3. Strontium vs boron concentrations (log-normalized) in seeps (diamonds), surface water (triangles), and background water (circles) at all seven sites. The data show a linear correlation ($r = 0.77$, $p < 0.05$) between Sr and B concentrations. Site-specific background concentrations all fall within the lower left quadrant, below the B and Sr background concentration limits (100 and 150 $\mu\text{g/L}$, respectively; marked by the gray dotted line). The majority of seeps and surface water fall in the upper right quadrant, above background concentrations. The positive correlation between B and Sr in samples exceeding background concentrations suggests that the elevated values are driven by the same source (i.e., coal ash pond leakage).

ratios, even when the Sr concentrations were significantly higher. One exception is at TN1, where $\delta^{11}\text{B}$ values in the seeps were anomalously high (up to 30‰) relative to the typical $\delta^{11}\text{B}$ range in CCRs (Table 1 and Figure 2).²² However, the B and Sr concentrations were the highest measured in any sample. The extremely high B concentrations (250- to 800-fold enrichment) relative to the upstream water (<50 $\mu\text{g/L}$) at TN1 cannot be explained by the evaporation of natural waters

because the same enrichment was not observed for other conservative elements such as Cl (9-fold enrichment; Table S1).

The relatively high $\delta^{11}\text{B}$ could be explained by interaction with clay minerals during the migration of the effluents in the sediments that compose the coal ash pond walls and modification of the B isotope ratios. Boron adsorption to the clay minerals favors the lighter ^{10}B , and the fractionation produces ^{11}B enrichment in the residual effluents.³⁰ However, this mechanism is unlikely given the extremely high B concentration (40 mg/L) in the seep water. Alternatively, the desorption of B from clay minerals could generate a solution with high B content. In such a scenario, a typical exchangeable B from marine clays (i.e., shale) has $\delta^{11}\text{B}$ of $\sim 15\text{‰}$, so the exchangeable sites on the clay minerals must have equilibrated with a brine with $\delta^{11}\text{B} > 50\text{‰}$ to generate exchangeable B with $\delta^{11}\text{B}$ of $\sim 30\text{‰}$.³⁷ However, even desorption from shale or brine interactions is unlikely to result in a B concentration of 40 mg/L. A more in-depth study at this site is needed to further evaluate the factors that control the B isotope variations and possible link to the Chattanooga Shale that is exposed in this area.³⁸ Overall, only at the TN1 site do we observe seeps with relatively high $\delta^{11}\text{B}$ that is not consistent with the CCR isotope composition. In contrast to B, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the seeps and surface water at the TN1 site were consistent with ratios expected for CCRs and were distinctly higher than the ratio in the upstream sample.

Although most sites reflect leaking of effluents from active coal ash ponds, two of the sites we investigated contained retired or closed ash-disposal areas. At the GA1 site, discharge from below the dam at a retired pond and downstream surface water were characterized by high B (1867 and 1643 $\mu\text{g/L}$, respectively) with negative $\delta^{11}\text{B}$ values (-3.2 and -9.2‰ ; Table 1 and Figure 2) that suggests there is still CCR effluents leaking from the ponds after closure of the plant 13 years ago.³³ At the TN2 site, surface water in a cove near a closed disposal area (non-registered site) had high B (489.2 $\mu\text{g/L}$) with low $\delta^{11}\text{B}$ (-3.5‰) and high Sr (205.2 $\mu\text{g/L}$), compared to the

background water (44.9 to 89.5 $\mu\text{g/L}$, respectively; Table 1). These examples show that the closure or disuse of coal ash impoundments does not necessarily eliminated leaking of the CCR-impacted pond water to the surrounding environment.

Geochemistry of Contaminants in CCR Effluents. We identified two geochemical types of CCR-impacted water. The first (Type A) had significantly higher Cl (>10 mg/L, $p < 0.05$) with lower SO_4/Cl molar ratios ($p < 0.05$) found at the TN1, VA1, VA2, and KY1 sites (Figure S11). The second type (Type B) found at the TN2, GA1, and GA2 sites had significantly lower Cl (<10 mg/L, $p < 0.05$) and higher SO_4/Cl molar ratios ($p < 0.05$) (Figure S12; Table 1). One-way ANOVA tests found that As, Mo, and V concentrations were significantly higher in Type A waters ($p < 0.05$) (Table 1). B and Sr concentrations in Type A samples were positively correlated with Cl ($r = 0.49$, $p = 0.05$ and $r = 0.55$, $p = 0.05$; Figure S11). As, Se, and Mo were also positively correlated with Cl ($r = 0.39$, $p < 0.05$; $r = 0.68$, $p < 0.05$; and $r = 0.50$, $p < 0.05$; respectively).

Concentrations of As or Se exceeding background values were measured in all Type A seeps and surface water (up to 57-fold for As and 300-fold for Se) except at KY1, while both elements were enriched in nine of the 14 samples. Enrichments for all elements are shown in Table S1. In contrast, Type B waters had significantly lower concentrations of As, Se, and Mo. As and Se were only elevated compared to background in Type B waters at the NPDES outfall at TN2 (7-fold and 39-fold, respectively; Table S1). TN2-Seep-2 and GA2-SW-5 had 5-fold and 10-fold As enrichment, respectively. Concentrations of trace elements exceeding drinking-water standards (EPA maximum contaminant level)³⁹ and aquatic-life criteria (EPA criterion continuous concentration)⁴⁰ were observed in 29% of the investigated surface water samples (six Type A samples and four Type B samples) and are indicated in Table 1.

The high Cl in Type A water relative to an excess of SO_4 in the Type B water is likely due to differences in coal source, contributions from FGD residues, or differences in redox conditions. The linear correlations between trace elements (B, Sr, As, Se, and Mo) and Cl in the Type A water indicate that evaporation processes lead to the enrichment of these elements in the pond water and subsequent enrichment of contaminants in the CCR-impacted surface waters. A total of five of the Type A samples had As and Se concentration above the drinking-water and ecological standards (>5 and >10 $\mu\text{g/L}$, respectively) and are thus defined as contaminated water.

The two sites from the closed coal ash ponds had Type B waters, and no elevated concentrations of trace metals were identified in the seeps (TN2) or surface water (GA1) at these sites. The significantly lower concentrations of CCR contaminants in Type B waters could reflect different processes in the coal ash ponds (e.g., lack of evaporation, reducing environment) or different CCR sources. The relatively higher SO_4 in Type B water infers FGD contribution, from which trace-metal mobilization could be limited relative to leaching from fly ash.

Field studies of the TVA spill and laboratory microcosm experiments found that pH and redox conditions will influence the mobilization of elements from CCRs in the environment.^{4,20,21} Field pH was limited to only three sites (TN1, TN2, and GA2) and ranged from pH 4 to 8.5. Mobilization of Fe, Mn, B, and SO_4 were observed in water with pH < 7 (Figure S13). Under low pH (<7), Fe and Mn occur as mobile phases (Fe^{2+} and Mn^{2+}) but will precipitate as oxides ($\text{Fe}(\text{OH})_2$ and $\text{Mn}(\text{OH})_2$) at higher pH, which explains the lower concentrations in more basic water (Figure S13). B speciation is also controlled

by acidity, with the noncharged species, boric acid ($\text{B}(\text{OH})_3$), predominant at lower pH relative to the charged borate ion ($\text{B}(\text{OH})_4^-$) ($\text{pK}_a = 9.2$).³⁷ The borate ion is more likely to coprecipitate into secondary phases, and therefore, dissolved B concentrations are lower at high pH (Figure S13). Batch leaching experiments found that As and Se release is minimized between pH 4.5 to 7 but increases in more acidic and basic conditions.^{4,20,21} However, Se and As concentrations are also influenced by redox conditions due to higher absorption affinity for oxidized arsenate, As(V), while under reducing conditions, the reduced arsenite (As(III)) is more mobile, and the reduced selenite (Se(IV)) or elemental Se^0 is more insoluble than the oxidized selenate (Se(VI)). Redox was not measured in the field during this study, so we cannot relate the variations in As and Se concentrations to redox conditions. The most important take-away from this is that leaking of pond water does not necessarily always lead to significant contamination by toxic trace elements and that environmental impacts need to be considered on a case-by-case basis.

Shallow Groundwater Underlying the Gallatin Coal Ash Pond in Tennessee. Data from seven monitoring wells at the TN2 site were compared to two background wells (MW-22 and MW-25) (Figure S8). MW-22 is located away from the coal ash ponds, with mean B and Sr concentrations of 20 ± 20 and 80 ± 3 $\mu\text{g/L}$, $\delta^{11}\text{B} = 17.7 \pm 1.1\text{‰}$, and $^{87}\text{Sr}/^{86}\text{Sr} = 0.70877$, which represents baseline groundwater in the shallower alluvium aquifer (Table 1). MW-25 reflects background groundwater in the deeper carbonate aquifer and had B and Sr concentrations of 15.3 and 260 $\mu\text{g/L}$, respectively, with $\delta^{11}\text{B} = 8.0 \pm 0.5\text{‰}$ and $^{87}\text{Sr}/^{86}\text{Sr} = 0.70872$ (Table 1).

B concentrations in the monitoring wells ranged from 70.6 to 6249.0 $\mu\text{g/L}$ and $\delta^{11}\text{B}$ values range from -0.2‰ to $+13\text{‰}$, with an inverse correlation between B concentration and $\delta^{11}\text{B}$ ($r = -0.91$, $p < 0.05$; Figure 4). Sr concentrations ranged from 225.2 to 1195.9 $\mu\text{g/L}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios increased with Sr concentrations from a ratio of 0.70922 to 0.7118 ($r = 0.84$, $p < 0.05$; Figure 4). The three wells around the active ash pond (TN-MW17, 23, and 24) were all screened into the alluvium aquifer and had B concentrations that ranged from 70.6 to 1491.1 $\mu\text{g/L}$ and Sr concentrations that ranged from 225.2 to 612.6, which all exceeded the concentrations found in the alluvium background well. The $\delta^{11}\text{B}$ values ranged from 6.1 to 13.1 ‰ and were all depleted compared to TN-MW22. TN-MW24 had the lowest B concentration and the highest $\delta^{11}\text{B}$ value relative to the values expected for CCRs. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.70922 to 0.70981 were all more radiogenic than TN-MW22. The groundwater had relatively low concentrations of dissolved metals and metalloids (Al, V, As, Se, and Mo) that did not exceed values in the background well.

Wells near the non-registered site (NRS), a retired ash-disposal area, had higher B (3930.9 to 6249.0 $\mu\text{g/L}$) and Sr concentrations (979.0 to 1195.9 $\mu\text{g/L}$) compared to wells near the active ash ponds, with $\delta^{11}\text{B}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the range of CCR leachates (-0.2 to $+2.8\text{‰}$ and 0.71106 to 0.71269, respectively). The deepest wells (NRS-26 and 27), which were screened into the bedrock near the NRS site, had B and Sr concentrations that exceeded the background carbonate aquifer well TN-MW25 by up to 400- and 4-fold, respectively (Table 1). The $\delta^{11}\text{B}$ values of 1.5 and 0.1 ‰ in the two wells were distinctly lower than the isotope values in the carbonate aquifer background well ($8.0 \pm 0.5\text{‰}$), and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.71106 and 0.71135) were higher compared to the background well (0.70872). The shallow groundwater near the NRS

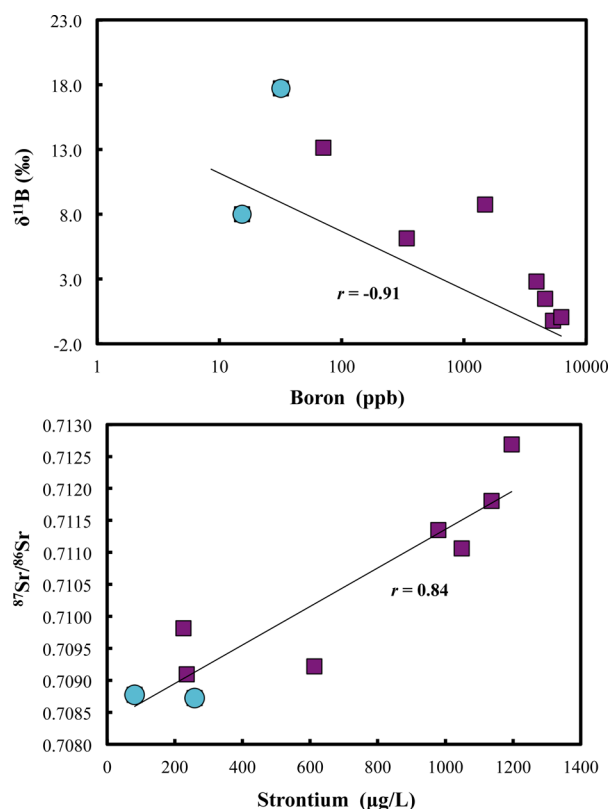


Figure 4. Linear correlations between (A) B and $\delta^{11}\text{B}$ values and (B) Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the nine shallow groundwater wells at the TN2 site. Blue circles are the values in the designated background wells, and purple squares represent the impacted wells. Shallow groundwater wells with higher boron concentrations had lower $\delta^{11}\text{B}$ values ($r = -0.90$, $p < 0.05$) toward the values found in CCRs (a range of -20% to $+8\%$),^{22–24} and wells with higher Sr concentrations had higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ($r = 0.84$, $p < 0.05$) toward the values found in CCRs (a range of 0.7095 to 0.7130).^{17,22,28} The strong linear correlations support migration of water from the coal ash ponds as the source of high B and Sr levels and mixing with regional groundwater.

pond had high SO_4 (2240 mg/L) and Ca (~ 900 mg/L), with a high correlation of Ca to SO_4 ($r = 0.97$, $p < 0.05$; molar ratio of ~ 1 ; Figure S15) and low Cl, similar to the Type B water. The highest concentrations of dissolved metals and metalloids (Mn, V, Se, As, and Mo; Table 1) were found in the wells near the NRS site. National drinking water and aquatic life criteria threshold values were exceeded for Cd, Fe, Ni, Pb, Se, and Zn in the NRS-19R well, which is a shallower alluvium aquifer well (Figure 2 and Table 1).

CCR impacts to the shallow groundwater under the TN2 site is supported by the strong relationships between B and Sr and their respective isotope ratios, with $\delta^{11}\text{B}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that were distinctly different than the background wells. However, there is no evidence for contamination from toxic trace elements in all but one well. The large differences between the shallow groundwater found around the active ash pond and those from the NRS site most likely reflect the differences between migration of coal ash pond water that has been diluted in the large impoundment compared to the NRS site. It could also reflect differences in the coal type that was stored historically in the NRS site compared to the sources of the relatively recent coal ash in the active pond.

The high B and Sr concentrations with low $\delta^{11}\text{B}$ values and high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the carbonate wells NRS-26 and NRS-27 compared to the background carbonate well MW-25 suggests migration of impacted water from the old disposal site to the deeper fractured carbonate aquifer underlying the TN2 site. However, no contamination from trace metals and metalloids was observed in the carbonate wells. More extensive sampling of regional aquifers around the coal ash ponds, coupled with a detailed hydrogeological analysis, is needed to determine if contamination from the ash pond is affecting local drinking water aquifers. The data presented in this study includes only two samples from the carbonate aquifer, which is not sufficient to determine any large-scale impact.

Shallow Groundwater Underlying Coal Ash Ponds in North Carolina. Archived water chemistry data from 156 wells monitoring groundwater underlying all 14 coal ash ponds in North Carolina (a total of 1830 water samples collected between 2010 and 2015)³² was analyzed to evaluate the possible leaking of coal ash ponds to local groundwater (Table S3). This data set includes concentrations of Cl, SO_4 , As, B, Fe, Mn, Se, Ni, Al, Cr, Cu, Zn, and TDS. No isotope data was available, so the assessment was based on concentrations alone. Background concentrations were determined from (1) a Duke University data set of 231 private drinking water wells from the central (Piedmont) area of North Carolina with B concentrations ranging from undetected to 100 $\mu\text{g/L}$ (mean = 20 $\mu\text{g/L}$) in groundwater,^{34,35} and (2) background groundwater wells designated at each site by Duke Energy and included in the archived data set³² that all had values of <100 $\mu\text{g/L}$ (the analytical detection limit used by the state agency is 50 $\mu\text{g/L}$), which are consistent with average values of regional groundwater in North Carolina. B concentrations greater than background values were detected in 58 of the 156 monitoring wells (37%; Figure 5). Groundwater underlying the Asheville, Sutton, Buck, Lee, Cape Fear, and Marshall coal plants had B levels greater than 1000 $\mu\text{g/L}$, with the groundwater underlying the Lee coal plant having the highest concentrations (up to 5000 $\mu\text{g/L}$). Similar to the patterns observed in the impacted surface water, groundwater with Cl and moderate SO_4 levels (Sutton, Mayo, Lee, and Weatherspoon) had high concentrations of metals and metalloids, while groundwater with high SO_4 concentrations (Roxboro, Asheville, Cape Fear, Buck, Marshall, and Dan River) had lower concentrations (Figure 5 and Table S3).

Analysis of the data reveals that most of the impacted groundwater with low SO_4 had relatively high concentrations of Ni, Al, Mn, Cr, Cu, Zn, Se, and As contents (Figure 5 and Table S3). Out of the 58 impacted monitoring wells, 48 (85%, 30% of the total wells) had concentrations that exceeded EPA water standards. Conspicuously high levels of As (up to 665 $\mu\text{g/L}$) were reported from well CMW-6 in the Lee coal plant in Wayne County that was also associated with the highest B levels (mean = 3400 $\mu\text{g/L}$; Figure 5). As, in particular, was negatively associated with SO_4 and was only present in high concentrations in the low- SO_4 water (Figure 5). The low SO_4 in groundwater may be an indicator of redox conditions, in which sulfate is reduced, and arsenic, in the form of the arsenite (As III) species, has higher mobility in groundwater. Se, however, was elevated in both high- and low- SO_4 water types (Figure 5). Similar to observations in the surface samples, high concentrations of B were not always associated with detectable levels of other CCR-related contaminants, and thus, some wells

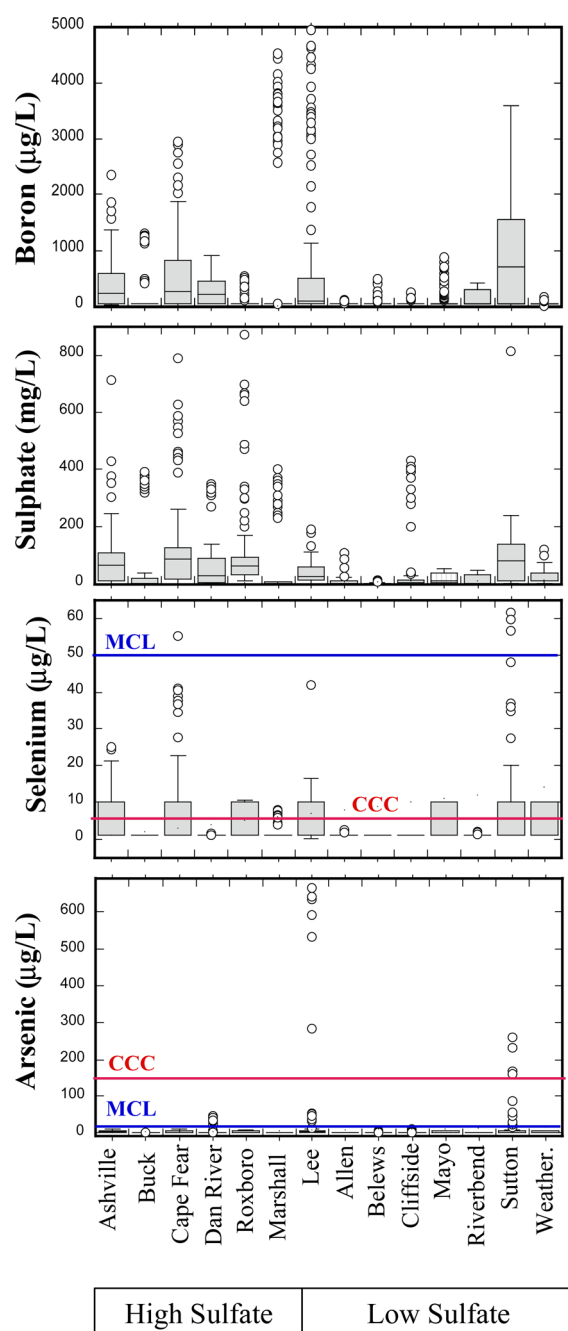


Figure 5. Boxplots for (A) boron, (B) sulfate, (C) selenium, and (D) arsenic in groundwater from the shallow monitoring wells in North Carolina.³⁵ Data were separated into high- and low-sulfate water types. The blue line represents the EPA Maximum Contaminant Level (10 ppb for As and 50 ppb for Se),³⁹ and the pink line represents the EPA Criterion Continuous Concentration (150 ppb for As and 5 ppb for Se).⁴⁰

were impacted by CCR effluents (high B but low trace elements) while others were also contaminated.

Overall, the data presented in this study for 22 sites in the southeastern United States show evidence for the surface or subsurface leaking of coal ash ponds and, in some cases, the contamination of nearby water sources. Our data show that B, and sometime Sr isotopes can be used to identify leaking of coal ash ponds, but a CCR geochemical signature is not always associated with contamination from other CCR contaminants. Thus, the coal sources, as well as geochemical variations in the ponds and the ambient environment (pH and redox state)

cause variations in concentrations of toxic elements and therefore differential water quality impacts. The current CCR management rules do not specify a preference for the removal of solid CCRs during closure of ponds.¹ We presented evidence that the closure of coal ash ponds does not necessarily eliminate the leaking of impacted water from coal ash ponds to the environment. With over 500 coal ash ponds in the southeastern United States,³³ the results presented in this study suggest significant releases of coal ash impacted water to the environment. The magnitude and long-term environmental effects of leaking coal ash ponds are not fully understood, and future studies should further evaluate the overall impact of the coal ash environmental legacy in the United States and other parts of the world where coal ash is disposed to unlined surface impoundments. Future studies should also focus on monitoring the water quality in drinking water wells near coal ash ponds to determine whether contaminated groundwater has further migrated from the shallow aquifers underlying coal ash ponds to the regional aquifers and the associated risks to human health in these areas.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b01727.

Figures showing locations of potentially contaminated samples and groundwater-monitoring wells, locations and boron concentrations of groundwater monitoring wells, B and Sr relationships, SO_4 –Cl ratios in Types A and B water, B versus Cl for Type A waters, negative relationships between pH and compounds in seeps and surface water, and Ca versus SO_4 for the wells around the non-registered site. Tables showing descriptions of shallow groundwater monitoring wells, enrichment factors for dissolved constituents, and data reported by the North Carolina Department of Environmental Quality for shallow groundwater wells. (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: vengosh@duke.edu; phone: 919-681-8050; fax: 919-684-5833.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge funding from the Southern Environmental Law Center. We thank and acknowledge Mark Quarles and Jen Hilburn for their assistance in the field; Gary Dwyer, Nancy Lauer, Rachel Coyte, and Jon Karr for their assistance with laboratory work and chemical analyses; and Andrew J. Kondash for his assistance with the data analysis and statistics. We thank the five anonymous reviewers who greatly helped to improve the quality of the early versions of this manuscript.

■ REFERENCES

- (1) *Hazardous and Solid Waste Management System; Disposal of Coal Combustion Residuals From Electric Utilities: Final Rule*; United States Environmental Protection Agency: Washington, DC, 2015; pp 21301–21501.
- (2) Punshon, T.; Seaman, J. C.; Sajwan, K. S., The production and use of coal combustion products. In *Chemistry of Trace Elements in Fly Ash*; Springer: 2003; pp 1–11.

- (3) Ruhl, L.; Vengosh, A.; Dwyer, G. S.; Hsu-Kim, H.; Deonarine, A.; Bergin, M.; Kravchenko, J. Survey of the potential environmental and health impacts in the immediate aftermath of the coal ash spill in Kingston, Tennessee. *Environ. Sci. Technol.* **2009**, *43* (16), 6326–6333.
- (4) Ruhl, L.; Vengosh, A.; Dwyer, G. S.; Hsu-Kim, H.; Deonarine, A. Environmental impacts of the coal ash spill in Kingston, Tennessee: an 18-month survey. *Environ. Sci. Technol.* **2010**, *44* (24), 9272–9278.
- (5) Liu, Y.-T.; Chen, T.-Y.; Mackee, W. G.; Ruhl, L.; Vengosh, A.; Hsu-Kim, H. Selenium speciation in coal ash spilled at the Tennessee Valley Authority Kingston site. *Environ. Sci. Technol.* **2013**, *47* (24), 14001–14009.
- (6) Deonarine, A.; Bartov, G.; Johnson, T. M.; Ruhl, L.; Vengosh, A.; Hsu-Kim, H. Environmental impacts of the Tennessee Valley Authority Kingston coal ash spill. 2. Effect of coal ash on methylmercury in historically contaminated river sediments. *Environ. Sci. Technol.* **2013**, *47* (4), 2100–2108.
- (7) Yang, Y.; Colman, B. P.; Bernhardt, E. S.; Hochella, M. F. Importance of a Nanoscience Approach in the Understanding of Major Aqueous Contamination Scenarios: Case Study from a Recent Coal Ash Spill. *Environ. Sci. Technol.* **2015**, *49* (6), 3375–3382.
- (8) Lemly, A. D. Damage cost of the Dan River coal ash spill. *Environ. Pollut.* **2015**, *197*, 55–61.
- (9) Ruhl, L.; Vengosh, A.; Dwyer, G. S.; Hsu-Kim, H.; Schwartz, G.; Romanski, A.; Smith, S. D. The impact of coal combustion residue effluent on water resources: a North Carolina example. *Environ. Sci. Technol.* **2012**, *46* (21), 12226–12233.
- (10) Alberts, J. J.; Newman, M. C.; Evans, D. W. Seasonal variations of trace elements in dissolved and suspended loads for coal ash ponds and pond effluents. *Water, Air, Soil Pollut.* **1985**, *26* (2), 111–128.
- (11) Dreesen, D. R.; Gladney, E. S.; Owens, J. W.; Perkins, B. L.; Wienke, C. L.; Wangen, L. E. Comparison of levels of trace elements extracted from fly ash and levels found in effluent waters from a coal-fired power plant. *Environ. Sci. Technol.* **1977**, *11* (10), 1017–1019.
- (12) Meyer, W.; Tucci, P. *Effects of Seepage from Fly-Ash Settling Ponds and Construction Dewatering on Ground-Water Levels in the Cowles Unit, Indiana Dunes National Lakeshore, Indiana. Water-Resources Investigations (Final)*; USGS: Reston, VA, 1976–77; Pages: 103.
- (13) Coutant, C. C.; Wasserman, C. S.; Chung, M. S.; Rubin, D. B.; Manning, M. Chemistry and biological hazard of a coal ash seepage stream. *J. - Water Pollut. Control Fed.* **1978**, 747–753.
- (14) Brodie, G. A.; Hammer, D. A.; Tomljanovich, D. A. *Constructed Wetlands for Treatment of an Ash Pond Seepage*; Lewis Publishers: Boca Raton, FL, 1989; 211–220.
- (15) Chapelle, F. H. A proposed model for predicting trace metal composition of fly-ash leachates. *Environ. Geol.* **1980**, *3* (3), 117–122.
- (16) Theis, T. L.; Richter, R. O. Chemical speciation of heavy metals in power plant ash pond leachate. *Environ. Sci. Technol.* **1979**, *13* (2), 219–224.
- (17) Brubaker, T. M.; Stewart, B. W.; Capo, R. C.; Schroeder, K. T.; Chapman, E. C.; Spivak-Birndorf, L. J.; Vesper, D. J.; Cardone, C. R.; Rohar, P. C. Coal fly ash interaction with environmental fluids: Geochemical and strontium isotope results from combined column and batch leaching experiments. *Appl. Geochem.* **2013**, *32*, 184–194.
- (18) Izquierdo, M.; Querol, X. Leaching behaviour of elements from coal combustion fly ash: an overview. *Int. J. Coal Geol.* **2012**, *94*, 54–66.
- (19) Theis, T. L.; Wirth, J. L. Sorptive behavior of trace metals on fly ash in aqueous systems. *Environ. Sci. Technol.* **1977**, *11* (12), 1096–1100.
- (20) Schwartz, G. E.; Rivera, N.; Lee, S.-W.; Harrington, J. M.; Hower, J. C.; Levine, K. E.; Vengosh, A.; Hsu-Kim, H. Leaching potential and redox transformations of arsenic and selenium in sediment microcosms with fly ash. *Appl. Geochem.* **2016**, *67*, 177–185.
- (21) Wang, T.; Wang, J.; Tang, Y.; Shi, H.; Ladwig, K. Leaching Characteristics of Arsenic and Selenium from Coal Fly Ash: Role of Calcium. *Energy Fuels* **2009**, *23* (6), 2959–2966.
- (22) Ruhl, L. S.; Dwyer, G. S.; Hsu-Kim, H.; Hower, J. C.; Vengosh, A. Boron and strontium isotopic characterization of coal combustion residuals: validation of new environmental tracers. *Environ. Sci. Technol.* **2014**, *48* (24), 14790–14798.
- (23) Davidson, G. R.; Bassett, R. L. Application of boron isotopes for identifying contaminants such as fly ash leachate in groundwater. *Environ. Sci. Technol.* **1993**, *27* (1), 172–176.
- (24) Williams, L. B.; Hervig, R. L. Boron isotope composition of coals: a potential tracer of organic contaminated fluids. *Appl. Geochem.* **2004**, *19* (10), 1625–1636.
- (25) Harkness, J. S.; Ruhl, L. S.; Millot, R.; Kloppman, W.; Hower, J. C.; Hsu-Kim, H.; Vengosh, A. Lithium Isotope Fingerprints in Coal and Coal Combustion Residuals from the United States. *Procedia Earth Planet. Sci.* **2015**, *13*, 134–137.
- (26) Chappaz, A.; Lyons, T. W.; Gordon, G. W.; Anbar, A. D. Isotopic fingerprints of anthropogenic molybdenum in lake sediments. *Environ. Sci. Technol.* **2012**, *46* (20), 10934–10940.
- (27) Buszka, P. M.; Fitzpatrick, J. A.; Watson, L. R.; Kay, R. T. *Evaluation of Ground-Water and Boron Sources by Use of Boron Stable-Isotope Ratios, Tritium, and Selected Water-Chemistry Constituents near Beverly Shores, Northwestern Indiana, 2004*; Geological Survey (US): Reston, VA, 2007; 2328–0328.
- (28) Spivak-Birndorf, L. J.; Stewart, B. W.; Capo, R. C.; Chapman, E. C.; Schroeder, K. T.; Brubaker, T. M. Strontium isotope study of coal utilization by-products interacting with environmental waters. *J. environ. Qual.* **2012**, *41* (1), 144–154.
- (29) Butterwick, L.; de Oude, N.; Raymond, K. Safety assessment of boron in aquatic and terrestrial environments. *Ecotoxicol. Environ. Saf.* **1989**, *17* (3), 339–371.
- (30) Vengosh, A. Salinization and Saline Environments. In: Sherwood Lollar, B. (ed.), *Environmental geochemistry, Treatise in Geochemistry Second*; Holland, H. D., Turekian, K. T., Executive Eds., Elsevier Science: Oxford, England, 2013; Volume 11, pp 325–378.
- (31) Vengosh, A.; Lindberg, T. T.; Merola, B. R.; Ruhl, L.; Warner, N. R.; White, A.; Dwyer, G. S.; Di Giulio, R. T. Isotopic imprints of mountaintop mining contaminants. *Environ. Sci. Technol.* **2013**, *47* (17), 10041–10048.
- (32) North Carolina Department of Environmental Quality. Groundwater Monitoring Data for Coal Ash Ponds, 2015; <http://deq.nc.gov/about/divisions/water-resources/water-resources-hot-topics/dwr-coal-ash-regulation/groundwater-monitoring-data-for-duke-energy-coal-ash-facilities> (accessed June 4, 2016).
- (33) Southern Alliance for Clean Energy. Southeast Coal Ash Waste 2015; <http://www.southeastcoalash.org/> (accessed November 2015).
- (34) Vinson, D. S.; Vengosh, A.; Hirschfeld, D.; Dwyer, G. S. Relationships between radium and radon occurrence and hydro-chemistry in fresh groundwater from fractured crystalline rocks, North Carolina (USA). *Chem. Geol.* **2009**, *260* (3), 159–171.
- (35) Merola, R. B. Arsenic Exposure from groundwater in Union County, North Carolina. *School of the Environment*; Duke University: Durham, NC, 2009.
- (36) Dwyer, G. S.; Vengosh, A. Alternative Filament Loading Solution for Accurate Analysis of Boron Isotopes by Negative Thermal Ionization Mass Spectrometry. In *American Geophysical Union Meeting*, San Francisco, CA; December 15–19, 2008; AGU: Washington, D.C., 2008.
- (37) Spivack, A. J.; Palmer, M. R.; Edmond, J. M. The sedimentary cycle of the boron isotopes. *Geochim. Cosmochim. Acta* **1987**, *51* (7), 1939–1949.
- (38) Vine, J. D. *Element Distribution in Some Paleozoic Black Shales and Associated Rocks*. Geological Survey Bulletin 1214-G; US Government Printing Office: Washington, D.C., 1969.
- (39) United States Environmental Protection Agency. Table of Regulated Drinking Water Contaminants 2016; <https://www.epa.gov/your-drinking-water/table-regulated-drinking-water-contaminants> (accessed November 2015).
- (40) United States Environmental Protection Agency. National Recommended Water Quality Criteria: Aquatic Life Criteria Table 2016; <http://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table> (accessed November 2015).