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Legacy of Coal Combustion: Widespread Contamination of Lake Sediments and Implications for Chronic Risks to Aquatic Ecosystems

Zhen Wang, Ellen A. Cowan, Keith C. Seramur, Gary S. Dwyer, Jessie C. Wilson, Randall Karcher, Stefanie Brachfeld, and Avner Vengosh*

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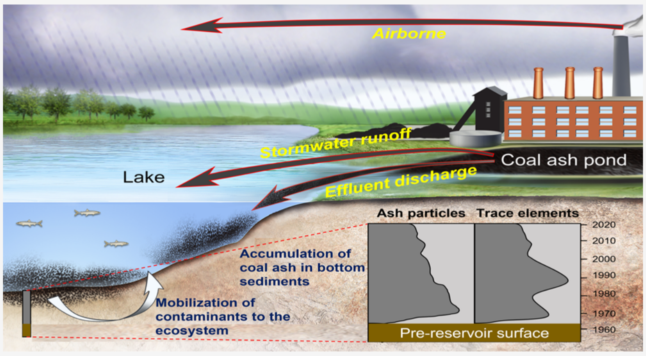
ABSTRACT: Elevated concentrations of toxic elements in coal ash pose human and ecological health risks upon release to the environment. Despite wide public concerns about water quality and human health risks from catastrophic coal ash spills and chronic leaking of coal ash ponds, coal ash disposal has only been partially regulated, and its impacts on aquatic sediment quality and ecological health have been overlooked. Here, we present a multiproxy approach of morphologic, magnetic, geochemical, and Sr isotopic analyses, revealing unmonitored coal ash releases over the past 40 to 70 years preserved in the sediment records of five freshwater lakes adjacent to coal-fired power plants across North Carolina. We detected significant sediment contamination and potential chronic ecological risks posed by the occurrence of hundreds of thousands of tons of coal ash solids mainly resulting from high-magnitude stormwater runoff/flooding and direct effluent discharge from coal ash disposal sites. The proximity of hundreds of disposal sites to natural waterways across the U.S. implies that such contamination is likely prevalent nationwide and expected to worsen with climate change.



KEYWORDS: *coal ash, lacustrine sediment, multiproxy tracing, aquatic ecosystems*

1. INTRODUCTION

Coal combustion residuals (CCRs, or coal ash) are generated from burning coal for electricity and one of the largest industrial solid waste streams in the U.S.,[1] representing a major anthropogenic impact on the environment. While a fraction of this coal ash is currently recycled for beneficial reuse, a significant amount (~50%) is disposed of in wet surface impoundments (i.e., coal ash ponds) and dry landfills,[1] many of which are adjacent to natural waterways used for turbine cooling in coal-fired power plants.[2] Micrometer-sized coal ash particles contain elevated concentrations of hazardous metals and metalloids (e.g., Pb, Cr, Cd, Hg, As, Se, and Mo) that are easily leached into aquatic systems. For this reason, the release of coal ash to the environment, whether intentional or incidental, has raised serious public concerns about the potential risks posed to human and ecological health.[3−11] Although coal is being replaced by natural gas for power generation, environmental challenges posed by the accumulation of coal ash and its inadequate disposal over decades of coal combustion continue to persist.[12]

Lacustrine sediments are natural repositories for trace elements and, thus, serve as an important geologic archive for preserving the anthropogenic impacts over time.[13] Under this paradigm, bottom sediments in lakes and/or reservoirs adjacent to coal-fired power plants and coal ash disposal sites can record both chronic and acute impacts of coal combustion. For example, previous studies have shown that sediments in Lake Erie (USA),[14] Lake Wabamun and Grand Lake (Canada),[15,16] and Lake Macquarie (Australia)[17] contained elevated levels of As, Se, Co, Tl, Sb, Cd, etc., most likely derived from nearby coal ash disposal sites. The southeastern U.S., in particular, has witnessed several catastrophic failures of disposal units resulting in large-scale coal ash releases into aquatic systems in 2008 and 2014[3−5,7,10,11] and a spill triggered by hurricane flooding in 2018.[9] Systematic monitoring of coal ash impacts was seriously lacking until the first national regulations on safe disposal of coal ash were finalized by the U.S. Environmental Protection Agency (U.S. EPA) in 2015.[12,18] While this "Coal Ash Rule" requires monitoring of water resources specifically,[18] the influences of coal ash particles on the quality of aquatic sediment and the potential ecological risks have been largely overlooked. The paucity of data on this front has consequently limited our understanding

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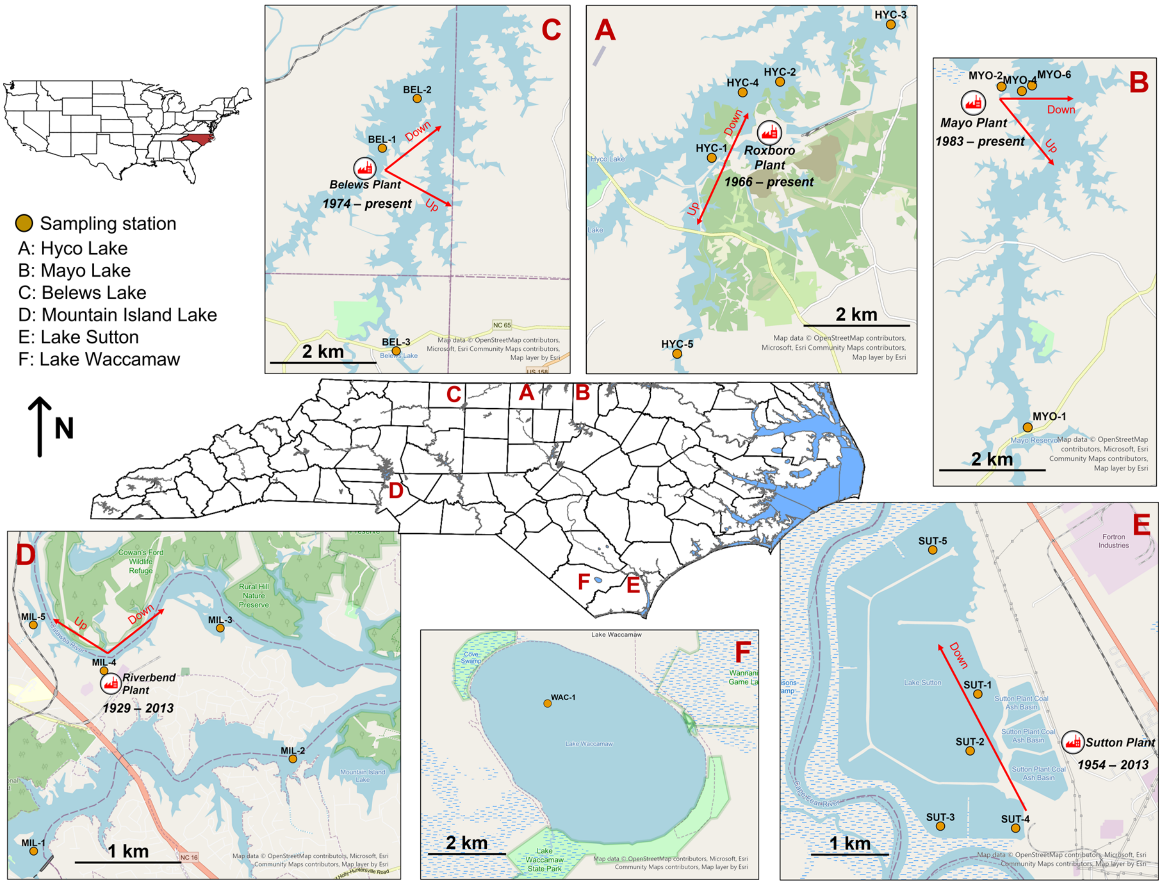

Figure 1. Map of sediment sampling stations in freshwater lakes adjacent to coal-fired power plants across North Carolina. Lake Waccamaw is a natural lake sampled as a reference for Lake Sutton. Up and down arrows denote upstream and downstream relative to the coal ash pond, respectively. Sediment cores retrieved from the downstream station were selected for chronological analysis (i.e., HYC-1, HYC-2, MYO-6, BEL-2, MIL-3, and SUT-3). Analyzed upstream cores are HYC-5, MYO-1, BEL-3, and MIL-5.

of the magnitude of coal ash contamination in aquatic ecosystems.

This study aims to fill the data gap by assessing both the spatial and temporal occurrences of coal ash within bottom sediments deposited over the history of five freshwater lakes distributed across the Piedmont and Coastal Plain of North Carolina (Figure 1). To this end, we adopt a holistic approach including optical and scanning electron microscopy, magnetic properties, trace element geochemistry, and strontium (Sr) isotope measurements. These lakes are man-made reservoirs, constructed primarily as a source of cooling water for the adjacent coal-fired power plants (Supporting Information (SI) Table S1). They are surrounded by public parklands and high-value private residential properties and are important recreational and economic resources (i.e., fishing and boating) for nearby urban and suburban communities. Mountain Island Lake, in particular, is also used as a drinking water source for hundreds of thousands of residents around Charlotte, NC.[19,20] Water contamination from discharge of coal ash effluents[8] and their impacts on aquatic organisms[21−23] have been previously reported for a few of these lakes. Here, we hypothesize that bottom sediments of these lakes may preserve the legacy of undocumented historic coal ash releases from the associated coal-fired power plants.

2. MATERIALS AND METHODS

2.1. Sample Collection and Processing. Field sampling campaigns were launched between July 2020 and August 2021 to five reservoirs, namely, Hyco Lake, Mayo Lake, Belews Lake, Mountain Island Lake, and Lake Sutton (Figure 1 and SI Table S1). A natural lake (Lake Waccamaw) in Columbus County, NC was also sampled as a reference for Lake Sutton.[9,23] Sediment cores were retrieved from the depocenter of each lake using a gravity corer with a stainless-steel core nose and a plastic liner. Upon retrieval, sediment cores were maintained in a vertical orientation when returned to the laboratory and stored in a refrigerator at 4 °C prior to processing. Grab samples were collected at the sediment−water interface down to a depth of 10 cm using a stainless-steel Ekman box corer. Sediment cores were sliced at 1 cm intervals, oven-dried at 40 °C, and ground using a ceramic mortar and pestle to pass through a 200-mesh stainless-steel sieve for subsequent chronological, microscopic, chemical, and isotopic analyses. Separate sediment cores were sliced at 5 cm intervals for porewater extraction using a centrifuge. Extracted porewater samples were all filtered using a 0.45 μm metal-free syringe filter and then acidified with HNO_3 for chemical analysis.

2.2. Analytical Methods. Sediment chronology was achieved by measuring the activities of ^{226}Ra, ^{210}Pb, and ^{137}Cs on a Canberra broad-energy germanium gamma detector (HPGe) at Duke University. Each measurement lasted for >168,000 s in order to minimize the uncertainty associated

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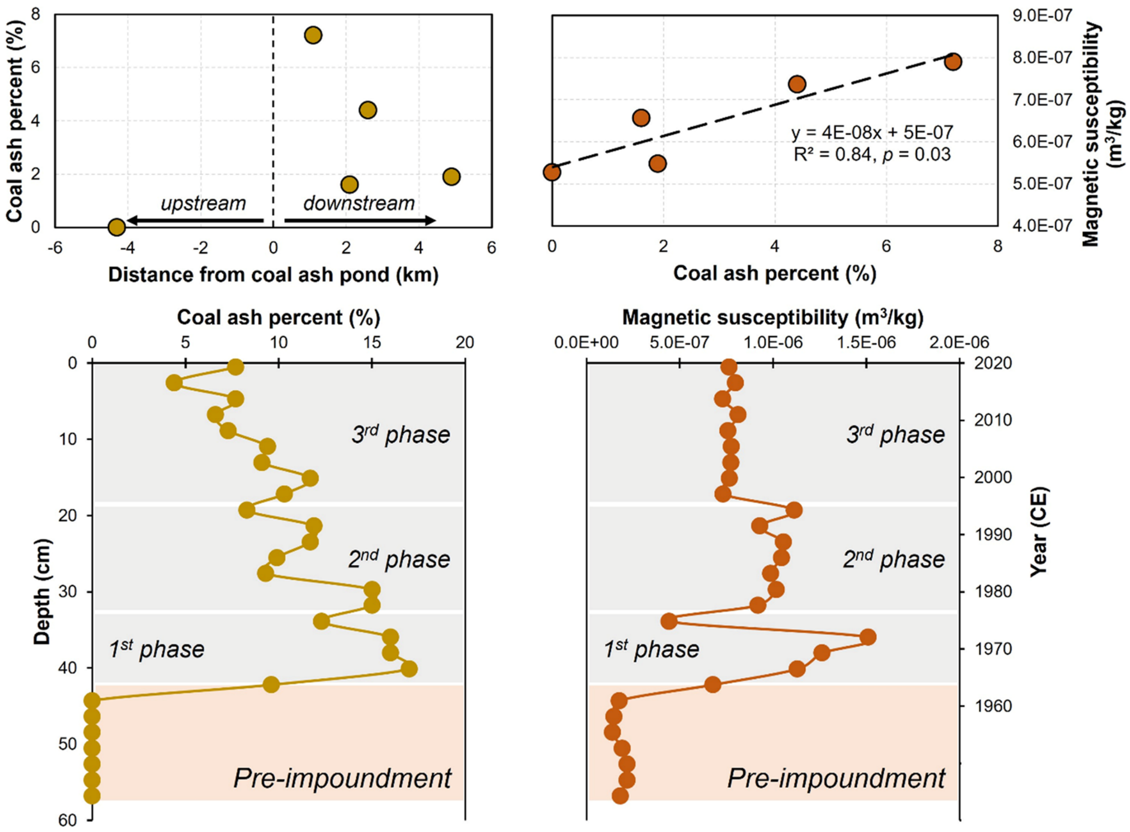


Figure 2. Physical characteristics (i.e., coal ash count and magnetic susceptibility) of coal ash in sediments of Hyco Lake. Coal ash percent in surface sediments versus the distance from the coal ash pond (upper left). Coal ash percent in surface sediments versus low-field magnetic susceptibility (upper right). Downcore profiles of the coal ash percent (lower left) and magnetic susceptibility (lower right) in the core HYC-1 retrieved from Hyco Station 1.

with photon counting statistics. Sample preparation and radionuclide measurements have been described in a previous study.[24] Details regarding the age-depth model and the sedimentation rate are elaborated in SI Text S1.

The morphology and percent of coal ash particles present in the sectioned sediment samples were identified and determined at a 500× magnification using a Leica DMLP polarizing microscope equipped with a Swift model F automated point counter at Appalachian State University. Details of sample preparation, counting procedures, and method reproducibility are presented in SI Text S2. The mass-normalized low-field magnetic susceptibility (χ_{LF}, m^3/kg) was measured on an MFK2A Kappabridge using an applied field of 200 A/m and a frequency of 976 Hz at Montclair State University. Freeze-dried bulk sediment was packed into size 4 gelatin capsules, and the mass was recorded.

Major and trace elements were measured on a Thermo Fisher X-Series II inductively coupled plasma-mass spectrometer (ICP-MS) at Duke University, using the sample digestion method described elsewhere.[9] The accuracy and precision were assessed by measuring the U.S. Geological Survey (USGS) Cody Shale standard SCo-1 ($n = 22$) and the National Institute of Standards and Technology (NIST) Montana II soil standard 2711a ($n = 14$) (SI Dataset S3). Aliquots of digested solution were taken for the measurement of $^{87}Sr/^{86}Sr$ ratios on a Triton thermal ionization mass spectrometer (TIMS) at Duke University.[25] Over the course of analysis, the mean $^{87}Sr/^{86}Sr$ value from repeated measurements of the NIST SRM 987 was 0.710256 ± 0.000006 (1SD, $n = 120$).

2.3. Calculations and Statistics. The enrichment factor (EF) was calculated using the equation below:

$$\mathrm{EF} = ([\mathrm{X}]/[\mathrm{Al}]\mathrm{sample})/([\mathrm{X}]/[\mathrm{Al}]\mathrm{background}) \quad (1)$$

where [X] is the concentration of a metal or metalloid and [Al] is the concentration of Al, which has been routinely used as a reference element as it is conservative and a major constituent of clay minerals.[26,27] Additional details on the EF are in SI Text S3. The risk quotient (RQ) was calculated as a first-order assessment tool for ecological risk by dividing the concentration of a metal(loid) contaminant in the sediment by its corresponding sediment quality guideline value.[28]

Nonparametric analyses, including Spearman's rank correlation and the Mann−Whitney test, were performed in R (v 4.1.1).[29] Rho (ρ) represents the correlation coefficient, and statistical significance is based on the p value ($p < 0.01$ for the 99% confidence interval and $p < 0.05$ for the 95% confidence interval).

3. RESULTS AND DISCUSSION

3.1. Chronology of Sediment Cores. The unsupported ^{210}Pb (i.e., $^{210}Pb_{ex}$) activity variations with depth in six sediment cores (i.e., HYC-1, HYC-2, MYO-6, BEL-2, MIL-3, and SUT-3; Figure 1) exhibited a downcore decay profile (SI Figures S1 and S2), providing the basis for calculating the sediment ages, using the constant flux constant sedimentation (CFCS) model (SI Figure S3 and Dataset S1).[30,31] The ^{210}Pb-dating results were independently verified by both the man-made radionuclide ^{137}Cs with a distinctive activity peak in ca.

1964 from nuclear weapon testing fallout[31] and/or via the depth of sediment lithology changes, marking the transition from the preimpoundment surface to lacustrine sediments. Cores were dated back to ~1964 for HYC-1 and HYC-2, ~1981 for MYO-6, ~1971 for BEL-2, ~1957 for MIL-3, and ~1972 for SUT-3 (SI Figure S3 and Dataset S1). Additional details on the chronology and sedimentation rate are described in SI Text S1.

3.2. Morphological and Magnetic Evidence for Coal Ash Contamination in Lake Sediments. Due to high-temperature combustion, coal ash is mainly composed of inorganic particles with distinctive spherical and amorphous morphologies,[32−35] which are identified using optical microscopy and easily distinguished from naturally occurring sediment (SI Figures S4 and S5). We detected coal ash particles in nearly all of the surface sediments (up to 10 cm deep) from all five lakes, ranging from 0.7 to 17.8% of the total sediment particles. Among all five lakes, the highest percentage was found in the surface sediment from Mayo Station 2 (MYO-2), located downstream from a coal ash pond. Relatively lower percentages of coal ash were detected in the upstream surface sediments from Mayo Lake and Belews Lake (SI Figure S6). Conversely, the one upstream surface sediment (MIL-5) in Mountain Island Lake, located within 2 km of the coal ash pond, had a coal ash percent comparable to the two nearest downstream surface sediments (MIL-3 and MIL-4). The coal ash percent in surface sediments of Lake Sutton did not exhibit a trend with the distance from the coal ash pond (SI Figure S6).

The total coal ash percent in the lacustrine sediments of Hyco Lake cores HYC-1 and HYC-2 ranged between 4.4 and 17% and from 2 to 12.7%, respectively. In contrast, no ash particles were present below the depth of the preimpoundment surface (Figure 2 and SI Dataset S2). In Mayo Lake, the total ash in the lacustrine interval of the core MYO-6 (i.e., upper 13 cm) varied between 2.7 and 9.7%. Interestingly, coal ash particles were also counted (4.7−9.7%) below the preimpoundment surface (>13 cm deep), indicating that coal ash was present in the stream drainage basin before the construction of Mayo Lake and the operation of Mayo Plant in the early 1980s (SI Dataset S2). Scanning electron photomicrographs (SEM) show that coal ash particles in the preimpoundment interval were morphologically distinctive from those in the lacustrine sediments, with the former being coarse amorphous particles with a minor fraction of spheres and the latter composed of a mix of small spheres with amorphous particles (SI Text S4 and Figure S7). In the Belews Lake core BEL-2, the total percent of ash was in the range of 1.3 and 5.7%, lower than that in the Mountain Island Lake core MIL-3 (1−10.7%) and the Lake Sutton core SUT-3 (2.3−8.3%). The presence of coal ash throughout the core from Lake Sutton suggests that coal ash has been released to the lake continuously ever since its construction in 1972 and continuing after 2013, when coal was replaced with natural gas at the Sutton Plant (SI Dataset S2 and Table S1). Similarly, continuous coal ash release was recorded in Mountain Island Lake sediments from the base to the top of the core (MIL-3), despite the retirement of Riverbend Steam Station in 2013 (SI Dataset S2 and Table S1). Compared to the downstream cores, a lower percentage yet consistent amount of coal ash was also detected in the upstream cores (i.e., HYC-5, MYO-1, and MIL-5) (SI Dataset S2), reflecting the ubiquitous presence of coal ash.

Low-field magnetic susceptibility (χ_{LF}) measured in sediments was found to be positively correlated with the total counted coal ash percent (e.g., $R^2 = 0.84$, $p = 0.03$ for Hyco Lake surface sediments; Figure 2). This is consistent with previous findings that coal ash is distinguishable from natural watershed sediments due to the presence of magnetite and maghemite ferrospheres.[10,11,36,37] The downcore profiles of the coal ash percent and magnetic susceptibility in the core HYC-1 were largely consistent ($R^2 = 0.76$, $p = 1.6 \times 10^{-9}$; Figure 2). Similarly, positive correlations between the coal ash percent and magnetic susceptibility were also observed for surface sediments and sediment cores from the other lakes (SI Dataset S2 and Figure S8). However, watershed and bedrock geology with high rock magnetism (e.g., diabase dikes) could contribute naturally magnetic minerals to lake sediments that may render the magnetic signal of coal ash less sensitive,[11] particularly when the coal ash content is relatively low.

Three phases of coal ash release can be identified throughout the history of Hyco Lake (Figure 2), corresponding to the changes of environmental regulations and coal ash disposal. The first phase was between 1960s and 1970s when the strongest physical signal (i.e., the ash count and magnetism) of coal ash was detected in the sediments. This was prior to the enactment of the Clean Air Act (CAA).[38] Coal ash detected in sediments during this period was mainly characterized by coarse amorphous particles with strong magnetism (SI Figure S9), likely indicating that finer spherical particles with weak magnetism may have been emitted to the atmosphere rather than being stored near the plant. The second phase was from late 1970s to mid-1990s, during which the amount of coal ash decreased. This is likely due to the storage of coal ash in ponds near the plants in accordance with the requirements of the CAA. Coal ash found in sediment during this period had smaller spherical morphologies with lower magnetic susceptibility (SI Figure S9) due to the dilution by more weakly magnetic ash morphologies. The third phase was from mid-1990s to the present when coal ash releases decreased (Figure 2), which can be attributed to the change in coal ash disposal from wet surface impoundments to dry landfills.[22]

3.3. Trace Element and Strontium Isotopic Evidence for Coal Ash Contamination in Lake Sediments. Trace element compositions of lacustrine sediments were significantly different from those of preimpoundment intervals ($p < 0.01$) for cores HYC-1, HYC-2, MYO-6, BEL-2, and SUT-3 and for the core MIL-3 between the post-1957 and pre-1957 intervals (SI Dataset S3 and Figures S10−S15). Arsenic, Se, Mo, Cd, Sb, and Tl, which we designated as Group 1, exhibited negative correlations with Al and Fe along the cores ($p < 0.001$ for all except for As and Se). The Group 1 elements have been shown to be distinctively enriched in coal ash relative to naturally occurring sediments and soils,[39−43] and thus, their synchronous enrichment within the cores reflects coal ash input. In contrast, the variations of V, Cr, Co, Ni, Cu, Zn, Pb, Th, and U, designated as Group 2, were positively correlated with those of Al and Fe within the core ($p < 0.05$), largely reflecting their correspondence to the natural fluctuations in the clay content of sediments.[44] Copper and Zn in cores HYC-1 and HYC-2, V and Pb in the core BEL-2, and Cu in the core SUT-3, however, exhibited different profiles from Al and Fe, likely suggesting their input from anthropogenic sources other than coal ash (SI Figures S10−S15).

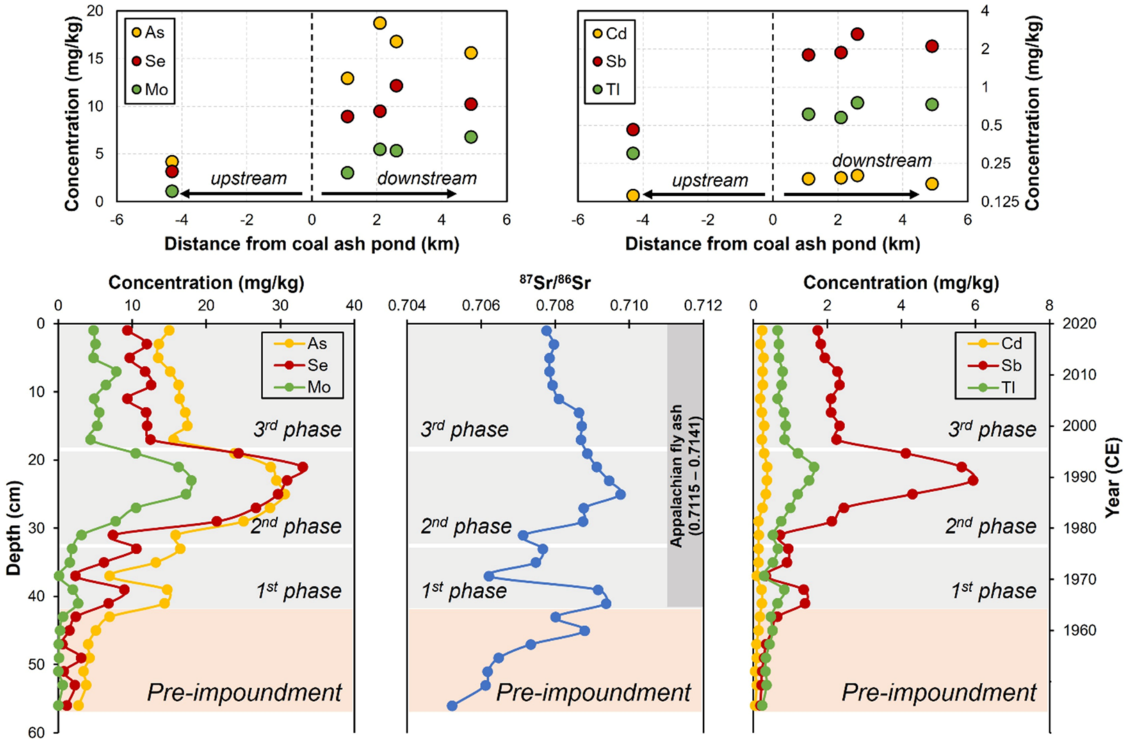


Figure 3. Chemical characteristics (i.e., trace elements and Sr isotopes) of coal ash in sediments of Hyco Lake. Concentrations of the Group 1 elements in surface sediments relative to the distance from the coal ash pond (upper panel). Downcore profiles of the concentration of the Group 1 elements and $^{87}Sr/^{86}Sr$ ratios in the sediment core HYC-1 retrieved from Hyco Station 1 (lower panel).

The surface sediments showed a spatial trend where downstream sediments had higher trace element concentrations, particularly for the Group 1 elements, than the corresponding upstream sediments (e.g., Figure 3 and SI Figure S16 for Hyco Lake). Similar trends were also observed for the surface sediments collected from Mayo Lake, Belews Lake, and Mountain Island Lake, except that many of the Group 2 elements in the upstream sediment in Belews Lake were higher than in the two downstream sediments (SI Figures S17−S19). In Lake Sutton, the concentrations of trace elements were higher with an increasing distance from the coal ash pond for the Sutton Plant, and all the trace element concentrations in the surface sediments were significantly higher than the respective concentrations in the surface sediment collected from Lake Waccamaw, except for Cd, Zn, and Pb (SI Figure S20).

Enrichment factors (EFs) were calculated for each core based on eq 1 by referring to the upstream sediments (SI Text S3). Consistent among all five lakes, the Group 1 elements had higher median EFs compared to the Group 2 elements in most of the cores (SI Dataset S4). Extremely high Cu (median EF = 30.8) was observed in the core SUT-3, likely associated with the historic use of copper sulfate for treating algal blooms at Sutton Lake.[45] The cumulative EFs of the Group 1 elements (i.e., EF1_cum) and Group 2 elements (i.e., EF2_cum) are shown in SI Dataset S4 and Figure S21. The EF1_cum in HYC-1 and HYC-2 ranged from 7.5 to 31 and from 7.3 to 48, respectively. While the highest coal ash percentage and the strongest magnetic susceptibility were identified in Hyco Lake during the first phase (i.e., 1960s to 1970s) (Figure 2 and SI Figure S9), the strongest chemical signal (i.e., the highest EF1_cum) was observed in sediments deposited during the second phase, between late 1970s and mid-1990s. Following the switch of disposal from coal ash ponds to dry landfills in early 1990s,[22] the trace element enrichment notably decreased and yet continued to show contamination up to the present (Figure 3 and SI Figure S21).

As shown in SI Dataset S4 and Figure S21, enrichment of both groups of trace elements in the core MYO-6 peaked between 2005 and 2006, corresponding to documented pollution in Mayo Lake during that time.[22] The EF1_cum ranged between 11 and 51 in the core BEL-2 and peaked between the 1970s and mid-1980s. Belews Lake experienced severe Se contamination from discharge of coal ash effluents prior to 1986, after which the plant changed from wet surface impoundment to dry landfills.[22,46,47] In the core MIL-3, sediments deposited since 1957 showed a significantly higher EF1_cum than earlier sediments, which chronologically corresponds to the construction of coal ash basin for the nearby coal-fired power plant in 1957.[48] In Sutton Lake, the EF1_cum of sediments in the core SUT-3 was between 13 and 120, reflecting a constant enrichment of the Group 1 elements from the beginning of the lake impoundment in 1972 to the present. While the upstream cores were used as a reference for the EF calculation, they still showed much larger variations of the Group 1 elements (e.g., the CV% of Sb was up to 90% in the core BEL-3), significantly greater than those of Al and Fe and most of the Group 2 elements (SI Dataset S3), implying that the impact of coal ash in these lakes is pervasive. This is consistent with the detection of coal ash particles in these upstream cores (SI Dataset S2).

The $^{87}Sr/^{86}Sr$ variations in the bulk sediments of the core HYC-1 largely corresponded to the variations of the Group 1 elements along the core (Figure 3). Coal-fired power plants in North Carolina dominantly burn coals sourced from the Appalachian Coal Basin.[8] Correspondingly, a clear mixing

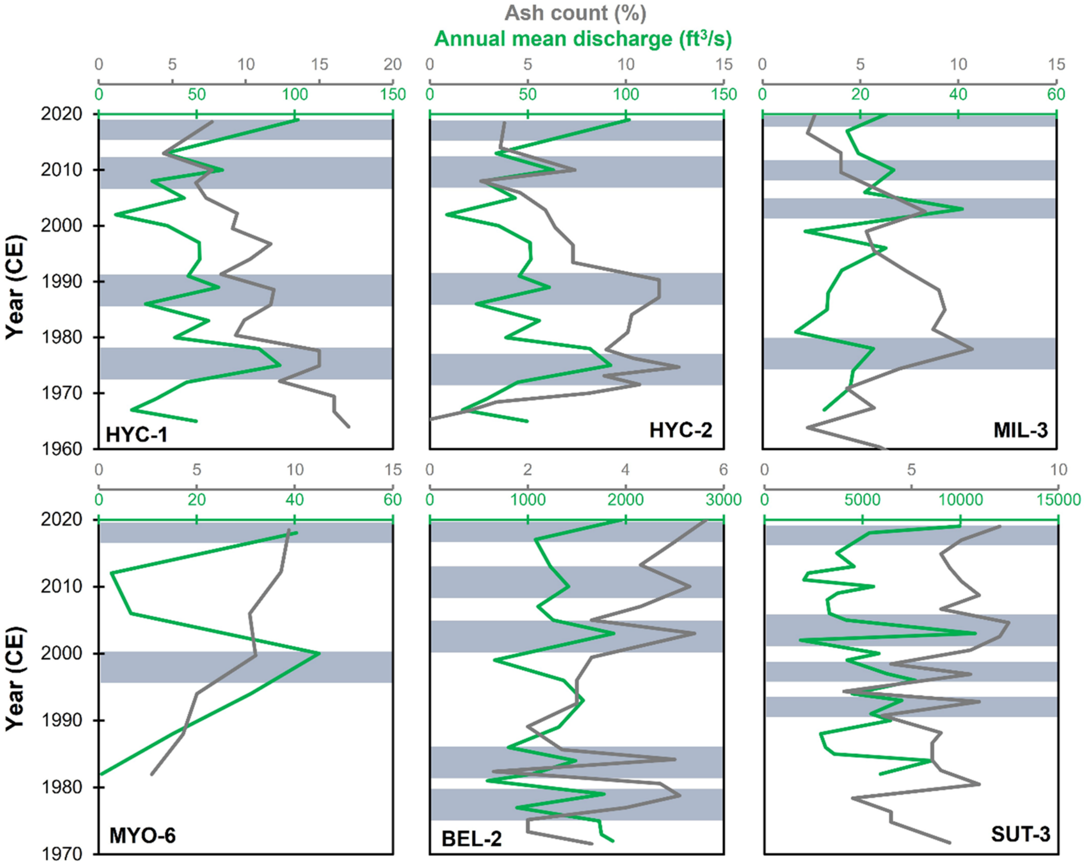


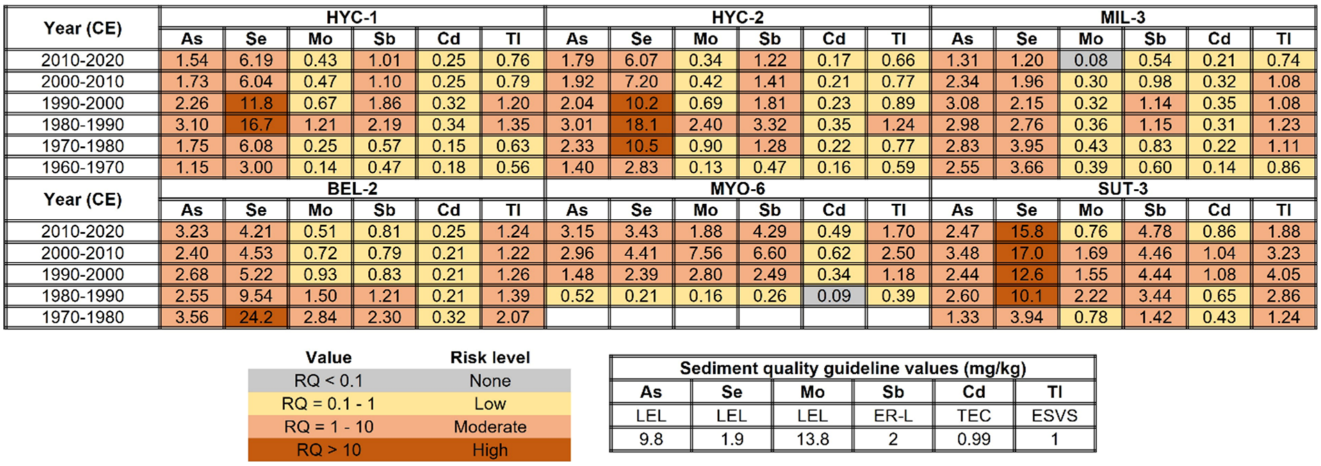
Figure 4. Comparison of the coal ash content (%) and annual mean discharge (cubic feet per second) recorded at USGS gaging stations near each lake. The gaging station number is 02077200 for Hyco, 02077670 for Mayo, 02071000 for Belews, 02142900 for Mountain Island, and 02105769 for Sutton. HYC-1 and HYC-2 denote Hyco Station 1 and Hyco Station 2, respectively. MYO-6 denotes Mayo Station 6, BEL-2 is Belews Station 2, MIL-3 is Mountain Island Lake Station 3, and SUT-3 is Lake Sutton Station 3.

relationship was observed between the more radiogenic (i.e., higher $^{87}Sr/^{86}Sr$ ratios) Appalachian fly ash (0.7115−0.7141)[25] and the less radiogenic reference sediments (i.e., 0.7095 for Hyco Lake and 0.7102 for Mayo Lake). In contrast, the $^{87}Sr/^{86}Sr$ ratio of the reference sediment in Belews Lake was 0.7246, much higher than that of Appalachian fly ash.[25] Consistently, the lowest $^{87}Sr/^{86}Sr$ ratios found in sediments deposited between 1970s and 1980s in the core BEL-2 of Belews Lake were associated with the peak of trace element enrichment (SI Dataset S3 and Figure S22). The $^{87}Sr/^{86}Sr$ ratios of the core SUT-3 were encompassed by the range of Appalachian fly ash (SI Figure S22), which confirms that coal ash contamination in Lake Sutton sediments occurs across the entire lake and throughout the lake history. In Mountain Island Lake, the $^{87}Sr/^{86}Sr$ ratios in the more recently deposited sediment interval (i.e., since 2010) of the core MIL-3 fell within the compositional range of Appalachian fly ash, despite that the trace element enrichment was lower than the sediments deposited between 1970s and 2000s, whose $^{87}Sr/^{86}Sr$ ratios were much higher than the Appalachian coal fly ash (SI Figure S22), implying the use of a different source of coal during this period.

3.4. Mechanisms for Coal Ash Release into Lake Sediments.

Coal ash is known to have an inherent compositional and morphological heterogeneity.[33,49] Volatile elements (i.e., Group 1 elements and Pb) are selectively enriched in fly ash relative to bottom ash.[50] Furthermore, small spheres crystallized from vaporizing and condensing phases during combustion tend to enrich volatile elements, as opposed to amorphous particles derived from direct decomposition and recrystallization of coal minerals.[32,50] We conducted experimental mixing between bulk fly ash and fresh sediment (see details in SI Text S5) that demonstrated that the presence of coal ash in sediments is determined equally by its physical and chemical signals (SI Tables S2 and S3). This contrasts with the field data of this study, where the storage of coal ash in ponds caused a reduction of its physical occurrence in the sediments (Figure 2), whereas the chemical signals became more pronounced (Figure 3), which suggests different mechanisms for coal ash release.

By comparing the mean annual stream discharge records from the USGS database on waterflow levels in each of the lakes over the operating period of the nearby coal-fired power plants,[51] we show that during periods of high average streamflow and thus high precipitation, a relatively high percentage of coal ash was correspondingly observed in the lake sediments (Figure 4). This indicates that stormwater runoff could have entrained ash particles from the storage ponds, particularly those located on floodplains, thus transporting coal ash solids directly into lakes. Extreme weather events such as hurricanes can cause massive coal ash releases via this pathway, as demonstrated by the spill in Lake Sutton after the landfall of category 4 hurricane Florence in 2018.[9] Thus, the episodic spills associated with stormwater runoff and/or flooding of ash storage ponds during intense rainfall events could be one of the mechanisms to account for the



Year (CE)	HYC-1						HYC-2						MIL-3					
	As	Se	Mo	Sb	Cd	Tl	As	Se	Mo	Sb	Cd	Tl	As	Se	Mo	Sb	Cd	Tl
2010-2020	1.54	6.19	0.43	1.01	0.25	0.76	1.79	6.07	0.34	1.22	0.17	0.66	1.31	1.20	0.08	0.54	0.21	0.74
2000-2010	1.73	6.04	0.47	1.10	0.25	0.79	1.92	7.20	0.42	1.41	0.21	0.77	2.34	1.96	0.30	0.98	0.32	1.08
1990-2000	2.26	11.8	0.67	1.86	0.32	1.20	2.04	10.2	0.69	1.81	0.23	0.89	3.08	2.15	0.32	1.14	0.35	1.08
1980-1990	3.10	16.7	1.21	2.19	0.34	1.35	3.01	18.1	2.40	3.32	0.35	1.24	2.98	2.76	0.36	1.15	0.31	1.23
1970-1980	1.75	6.08	0.25	0.57	0.15	0.63	2.33	10.5	0.90	1.28	0.22	0.77	2.83	3.95	0.43	0.83	0.22	1.11
1960-1970	1.15	3.00	0.14	0.47	0.18	0.56	1.40	2.83	0.13	0.47	0.16	0.59	2.55	3.66	0.39	0.60	0.14	0.86

Year (CE)	BEL-2						MYO-6						SUT-3					
	As	Se	Mo	Sb	Cd	Tl	As	Se	Mo	Sb	Cd	Tl	As	Se	Mo	Sb	Cd	Tl
2010-2020	3.23	4.21	0.51	0.81	0.25	1.24	3.15	3.43	1.88	4.29	0.49	1.70	2.47	15.8	0.76	4.78	0.86	1.88
2000-2010	2.40	4.53	0.72	0.79	0.21	1.22	2.96	4.41	7.56	6.60	0.62	2.50	3.48	17.0	1.69	4.46	1.04	3.23
1990-2000	2.68	5.22	0.93	0.83	0.21	1.26	1.48	2.39	2.80	2.49	0.34	1.18	2.44	12.6	1.55	4.44	1.08	4.05
1980-1990	2.55	9.54	1.50	1.21	0.21	1.39	0.52	0.21	0.16	0.26	0.09	0.39	2.60	10.1	2.22	3.44	0.65	2.86
1970-1980	3.56	24.2	2.84	2.30	0.32	2.07							1.33	3.94	0.78	1.42	0.43	1.24

Value	Risk level
RQ < 0.1	None
RQ = 0.1 - 1	Low
RQ = 1 - 10	Moderate
RQ > 10	High

Sediment quality guideline values (mg/kg)					
As	Se	Mo	Sb	Cd	Tl
LEL	LEL	LEL	ER-L	TEC	ESVS
9.8	1.9	13.8	2	0.99	1

Figure 5. Heat map of the decadal average risk quotient (RQ) values for the Group 1 elements in the six dated sediment cores from all five lakes. LEL denotes the lowest effect level, TEC denotes the threshold effect concentration, ER-L denotes effects range low, and ESVS denotes the ecological screening value for soil, all of which are in mg/kg and represent the contaminant concentrations below which no adverse ecological effects are expected.

occurrence of coal ash in the lake sediments. This is reasonable as North Carolina is vulnerable to hurricanes whose impacts can be long-lasting. Given that the probability for extreme weather events and urban flooding is predicted to increase due to intensifying global warming and climate change,[52] it is likely that coal ash disposal units, particularly those on floodplains, will experience more frequent intense flooding, which will result in increasing releases of coal ash and associated contaminants in the future.

The second mechanism for coal ash release is the continuous direct discharge of coal ash effluents from storage ponds. The accumulation of contaminants from coal ash effluents in lake bottom sediment was suggested to be via adsorption onto suspended matter in the lake water column, which could be subsequently mobilized to the aqueous phase during periods of thermal water stratification and reducing conditions.[8] However, this could hardly explain the significant enrichment of trace elements in the sediments (Figure 3). Therefore, it is likely that fine-grained particles that are highly enriched in the Group 1 elements are directly transported in effluents released from coal ash ponds and discharged directly into the adjacent lake. A previous study has shown that lightweight cenospheres were floating in ash ponds that contributed to the total suspended solids and total trace element concentrations in the effluents.[53] This could explain the presence of coal ash in sediments also during low stream discharge periods (Figure 4). The National Pollution Discharge Elimination System (NPDES) Program established by the Clean Water Act (CWA) permitted effluent discharge as part of regular coal-fired power plant operation,[54] which could result in a chronic contribution of coal ash solids to lake sediments.

The third probable mechanism is the (re)deposition of airborne ash particles in the lake watershed, which later are transported and accumulated in the lake sediments. Fugitive emission of coal ash particles from coal-fired power plants and associated coal ash disposal sites has been shown to be responsible for the presence of coal ash in the surrounding soils.[39,55,56] Thus, it is likely that some of the coal ash particles observed in the lake sediments are of airborne origin, deposited within the watershed, and then redeposited to the lake over time.[36] Our observations of the presence of a low percentage of coal ash particles in the upstream sediments may indicate their airborne origin given that they are located relatively far from the coal-fired power plant. However, the chemical signals were generally low compared to the downstream sediments that were much influenced by the first two mechanisms. It is also possible that coal ash present in the preimpoundment intervals of the Mayo Lake core MYO-6 was derived from land application of coal ash used as soil amendments prior to the construction of the lake.[57] Overall, our data show that while the percent of coal ash was mostly low (<10% of the total sediment volume), the enrichment of toxic trace elements within sediment was much more prominent, implying that the contamination caused by even a small percent of coal ash could be impactful and would result in elevated concentrations of toxic elements in the sediments.

3.5. Chronic Ecological Risks to Aquatic Ecosystems.

The chemical composition of lake sediments plays an important role in the overall ecological health of sediment-dwelling organisms (e.g., benthic invertebrates), which could further influence the health of fish and wildlife that feed on them and the overall aquatic ecosystem.[58] We used the freshwater sediment quality guideline values (i.e., the lowest effect level, LEL and threshold effect concentration, TEC, based on availability) for As, Se, Mo, Sb, Cd, V, Cr, Ni, Cu, Zn, and Pb and the ecological screening value in soil for Tl (SI Table S4).[58−60] Figure 5 illustrates the heat map of the mean decadal RQs for the Group 1 elements, which we have shown are highly enriched in the sediments of all five lakes. Arsenic, Se, Sb, Mo, and Tl appeared to pose greater long-term ecological risks than Cd throughout most of the lake history. Due to the persistent nature of these contaminants in the environment, As and Se were above the moderate risk level (i.e., 1 < RQ < 10) in all five lakes, as were Mo, Sb, and Tl for Mayo Lake, Sb and Tl for Lake Sutton, and Tl for Belews Lake. The highest chronic ecological risk (RQ > 10) was posed by Se in Hyco Lake between 1970 and 1990, in Lake Sutton from 1980 until the present, and in Belews Lake prior to 1980 (Figure 5). These three lakes were documented as having severe Se contamination and fish poisoning both historically and recently.[21,22,47,61] Additionally, V, Cr, Ni, and Cu all seem to pose moderate long-term risks with the RQ between 1 and 10 in the lake sediments throughout the history of the lakes (SI Figure S23).

Contaminants that are soluble in water are even of greater concern due to their higher bioavailability.[62] The ecological risks of trace elements in sediment porewater were assessed by referring to the U.S. EPA chronic criterion concentration (CCC) values for freshwater aquatic life for As, Se, Cd, Ni, Cu, Zn, and Pb,[63] the Canadian Environmental Quality Guidelines (CEQGs) for the protection of freshwater aquatic life for Mo and Tl,[64] and the toxicity reference value (TRV) for Sb[60] (SI Table S5). The core SUT-5 had the highest trace element concentrations in the extracted porewater among all five lake cores, while core BEL-2 porewater had the highest concentrations of Se and Mo (SI Dataset S5). For the Group 1 elements, core SUT-5 porewater had Cd exceeding its respective CCC value (0.72 μg/L) by up to four times and Tl above its CEQG value of 0.8 μg/L by up to 10-fold, whereas no exceeding concentration was observed for Se, Mo, Sb, and As relative to their CCC values, except for porewater extracted at depths of 25−30 cm having an As concentration up to ∼200 μg/L (SI Figure S24). Given that all the contaminant criteria were determined by toxicity assessment with the presence of a single contaminant, the co-occurrence of multiple contaminants as shown in this study (e.g., Cd, Tl, Ni, Zn, and Cu in SUT-5; SI Figure S25) likely implies higher collective ecological risks, even with below-threshold concentrations of the individual contaminants.

The mobilization of oxyanion elements (i.e., As, Se, Mo, and Sb) from the hosting sediments to porewater was different from that of cationic elements (i.e., Ni, Cu, Zn, and Pb) (SI Figures S24−S29). A clear downward diffusion and migration were observed for oxyanion elements (i.e., As, Mo, and Sb) along the core, as evidenced by their broader peaks in porewater compared to the sharp peaks within sediments (SI Figures S24−S29). The occurrence of these oxyanions in porewater is consistent with their higher leachability under anoxic conditions,[65−68] which prevail in these lakes,[8] inferring a greater bioavailable potential. In addition, the higher toxicity of soluble species such as As(III)[40,65] and Sb(III)[43,69] under anoxic conditions could pose greater risks to aquatic organisms. While Se, Cd, and Zn tend to be less mobile under reducing conditions,[68,70,71] they also exhibited some mobilization into the aquatic phase (SI Figures S24−S29), likely due to their high concentrations in the hosting sediments. By dividing the concentration of contaminants in porewater by that in hosting sediment (i.e., the potential release coefficient, PRC), we show that the PRC of As was largely one order of magnitude higher than that of Se (SI Figures S24−S29), corresponding to their differential leachability under anoxic conditions.[68,71] Overall, our data indicate that although coal ash is buried in the bottom sediments, toxic trace elements are mobilized into ambient porewater and thus can become available for biological uptake.

4. BROADER ENVIRONMENTAL IMPLICATIONS

While previous research has evaluated the environmental impacts of contaminants derived from the discharge of coal ash effluents[8] and leaking of coal ash ponds,[6,12] this study shows that coal ash solids have been continuously released into nearby lakes that are used for recreational activities and even as a drinking water source. North Carolina has 14 coal-fired power plants (both active and retired) and over 30 coal ash impoundments,[72] which means that the presence of coal ash solids in aquatic sediments is likely ubiquitous across the state. Based on the mean coal ash percent within sediment cores, mean sediment density, and mean sediment thickness, we made a first-order estimate of the mass of coal ash present in the bottom sediment within the depocenter of each lake. The highest amount of coal ash was estimated for Hyco Lake (0.15−0.22 Mt), followed by Mountain Island Lake (0.14−0.21 Mt), Belews Lake (0.10−0.15 Mt), Mayo Lake (0.08−0.12 Mt), and Lake Sutton (0.05−0.07 Mt) (see details in SI Table S6). Further constraints on this estimate can be achieved by a more systemic core sampling to better represent the shape of the lake depocenter.[73] With the exception of Lake Sutton, these lakes are open systems and hydrologically connected to the downstream riverine systems. Thus, it is likely that small spherical ash particles were spread beyond the local lacustrine systems and further to the downstream riverine systems (i.e., via flow releases through dams).

There are hundreds of coal ash ponds and landfills across the U.S. (SI Figure S30), and many of them are located near natural waterways.[2] Given that these coal ash disposal units are known to constantly discharge coal ash effluents into adjacent public waterways[2] and are vulnerable to high stream flow and/or flooding if located on floodplains, the unmonitored historic releases of coal ash as shown in this study for North Carolina are likely to occur nationwide. The magnitude of coal ash contamination in lake sediments decreased upon the switch from coal ash ponds to dry landfills[22] as shown in Belews Lake and Hyco Lake (SI Figure S21), likely associated with the reduction of direct effluent discharges. Nonetheless, considering the increasing trend of extreme precipitation due to anthropogenic climate change,[52] the possibility of coal ash spills induced by stormwater flooding is likely to increase.

Moreover, the mobilization of coal ash contaminants in anoxic lake sediments suggests that buried coal ash in landfill sites could be chemically mobile and has the potential to release contaminants. Although these landfills are typically capped with geosynthetic materials with low permeability and contoured to prevent infiltration of surface water, many are located in low lying areas that extend beneath the water table and therefore continue to contaminate the underlying groundwater systems.[12] Similarly, the closed coal ash ponds with the cover of vegetation and geosynthetic materials are also posing risks. The redox conditions in these closed systems would likely induce mobilization of oxyanion contaminants such as As, Mo, and Sb into the porewater and thus contaminate the underlying groundwater. This assessment is in agreement with a recent study showing the mobilization of As and Se in a closed surface impoundment and selective release of As relative to limited Se mobilization under anoxic conditions.[68]

Overall, the findings of this study highlight the legacy of inadequate coal ash storage, its vulnerability to extreme weather conditions, and its chronic risks to aquatic ecosystems. The specific ecological impacts on aquatic biota of these lakes warrant a detailed evaluation. While this study focuses on North Carolina, we assert that the magnitude of sediment contamination by coal ash and its consequential ecological risks are much more prevalent than previously realized, suggesting a problem of a national or global scale. Therefore, future studies should investigate the occurrences of coal ash contaminants in similar aquatic systems in other regions of the U.S. and in countries heavily dependent on coal such as China and India.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c04717.

Supporting texts, figures, tables, with additional details on the experiments, methods, and characterization data (PDF)

(Dataset S1) Age-depth models of dated sediment cores from each of the five lakes (XLSX)

(Dataset S2) Results of the coal ash count and magnetic susceptibility of sediment cores and surface sediments (XLSX)

(Dataset S3) Results of elemental concentrations and $^{87}Sr/^{86}Sr$ ratios in sediment cores and surface sediments (XLSX)

(Dataset S4) Results of the enrichment factor (EF) and the risk quotient (RQ) of trace elements in sediment cores and surface sediments (XLSX)

(Dataset S5) Results of trace element concentrations in porewater and sediments (XLSX)

■ AUTHOR INFORMATION

Corresponding Author

Avner Vengosh − *Nicholas School of the Environment, Duke University, Durham, North Carolina 27708, United States*; orcid.org/0000-0001-8928-0157; Email: vengosh@duke.edu

Authors

Zhen Wang − *Nicholas School of the Environment, Duke University, Durham, North Carolina 27708, United States*

Ellen A. Cowan − *Department of Geological and Environmental Sciences, Appalachian State University, Boone, North Carolina 28608, United States*

Keith C. Seramur − *Department of Geological and Environmental Sciences, Appalachian State University, Boone, North Carolina 28608, United States*

Gary S. Dwyer − *Nicholas School of the Environment, Duke University, Durham, North Carolina 27708, United States*

Jessie C. Wilson − *Department of Geological and Environmental Sciences, Appalachian State University, Boone, North Carolina 28608, United States*

Randall Karcher − *Department of Geological and Environmental Sciences, Appalachian State University, Boone, North Carolina 28608, United States*

Stefanie Brachfeld − *Earth and Environmental Studies, Montclair State University, Montclair, New Jersey 07043, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.est.2c04717

Notes

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