SOUTHERN ENVIRONMENTAL LAW CENTER

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September 10, 2015

Via Email and U.S. Mail

Ms. Amy Axon, Hydrogeologist
Division of Waste Management
N.C. Department of Environment and Natural Resources
1646 Mail Service Center, Raleigh, NC 27699-1646
amy.axon@ncdenr.gov

Mr. Lance Norris, Public Works Director
Town of Chapel Hill
405 Martin Luther King Jr. Blvd.
Chapel Hill, NC 27514
lnorris@townofchapelhill.org

Dear Ms. Axon and Mr. Norris:

On behalf of Friends of Bolin Creek, the Southern Environmental Law Center submits the following comments on the Town of Chapel Hill ("Town") and Falcon Engineering's Revised Environmental Site Characterization Report, dated August 18, 2015 ("Report").[1] We urge DENR and the Town to avoid drawing premature conclusions from the single set of test results on which the Report is based. More sampling, covering a range of depths and locations, is needed to support any conclusions about the contamination. In addition, a recent Duke University study demonstrates the need to test for radioactive materials associated with coal ash.

Well Placement Concerns

The Report claims that the unpermitted coal ash dump on the Town's Police Department property "ha[s] not exceeded the groundwater standards down gradient of the landfill" and states that "NC DENR will likely consider the Town of Chapel Hill Police Department a low priority site." Report at 12. However, the Town has not documented the depth and direction of

[1] This appears to be at least the third revision since the original Site Characterization dated March 25, 2014; revisions dated June 18, 2015, and June 24, 2015 were deemed incomplete by DENR. *See* email chain attached as Attachment A. It is not clear from this record whether or not DENR's stated concerns regarding the purging/sampling protocol and hexavalent chromium testing method have been adequately addressed. *Id.*

groundwater flow at the site, so we do not know if the new wells are really located "down gradient of the landfill." In addition, the Report is based on only one round of sampling from two wells.

The Town has shifted the locations of the two new monitoring wells to the east compared to earlier sampling locations, and has increased the depth of the wells. It appears the earlier samples – which showed high levels of contamination – were taken from the very top of the water table and from locations more directly south of the fill. The two new wells are located further east, are deeper, and have 15-foot screens. Thus, it is not clear whether the difference between the July sampling results and prior reports showing high levels of contamination is due to the earlier wells having been developed improperly – or whether this difference is due to the new wells being located in areas less impacted by a plume of groundwater contamination.

The locations of the new wells cannot be evaluated adequately because the elevation and orientation of the water table at this site have not been documented. The Town cannot accurately state what the "down gradient" contaminant concentrations are without knowing whether the groundwater flow is toward the south, southeast, or southwest. We ask that DENR require the Town to obtain and provide information on the depth and direction of the groundwater flow at the site.

Based on the pre-fill topography of the site, it appears that the bulk of the contaminants may be migrating from the coal ash area toward the southwest. Therefore, we recommend that the Town install a new permanent well northwest of the current well MW-3A, to be located in the vicinity of former well MW-3. It should have a short screened interval (5-feet) that is set so it straddles the water table. This will help determine what pollutants may be migrating from the coal ash at the top of the water table. We ask that DENR require the installation of at least one additional monitoring well in the vicinity of former monitoring well MW-3.

Well Development Concerns

We believe the monitoring wells may have been improperly developed, which could interfere with an accurate assessment of the groundwater contamination at the site. High turbidity has been cited as a concern in several of the monitoring wells at the site, but such turbidity is common in groundwater that is impacted by coal ash. We recommend different well development techniques that we believe will achieve better results.

Well development requires stressing the well to get residual suspended solids out of the well and adjacent sand pack in order to prepare the well to give representative samples. The Report (p. 8) states that the current wells were developed by purging with a low-flow pump. By definition, low-flow pumping is designed ***not*** to stir up and remove particulates and is therefore inappropriate for well development.

Accordingly, we recommend and request that all monitoring wells be adequately prepared for sampling using pumping and/or surge blocks that will properly develop the wells, rather than low-flow purging.

After an additional well is installed in the vicinity of former well MW-3, all the wells should be properly developed and sampled again, including MW-1. This time, all wells should have both unfiltered and filtered samples collected. Collecting both filtered and unfiltered samples from all the monitoring wells will allow for a more complete picture of the nature and extent of the contamination.

Radioactivity Concerns

A recent study by Duke University scientists has showed that levels of naturally occurring radioactive materials in coal ash from all three major U.S. coal-producing basins are many times higher than the concentrations found in coal or soil. Nancy E. Lauer, *et al.*, "Naturally Occurring Radioactive Materials in Coals and Coal Combustion Residuals in the United States," Environmental Science and Technology, Sept. 2, 2015 (Attachment B). The paper notes that "[b]ecause of the elevated levels of radioactivity of CCRs [coal combustion residuals, *i.e.*, coal ash] compared to the background soil, the potential environmental impacts and human health risks associated with CCR disposal to the environment should be evaluated in future studies." Accordingly, we request that additional groundwater and soil samples be taken to test for the radioactive materials associated with coal ash that are identified in the Duke University study, including radium-226/228 and lead-210. It appears that prior groundwater monitoring and soil boring samples did not test for these materials. All future groundwater monitoring should include testing for these radioactive materials.

Infiltration and Drainage

Finally, the Phase 1 Environmental Site Assessment Report (dated July 18, 2013) included a photograph (Photo 4) of a water retention basin located south of the lower parking lot. If still present, the retention basin should be immediately eliminated and drainage redirected off of the ash-filled area. Retention of water on top of a filled area will increase infiltration into the subsurface and increase the potential for groundwater impacts.

Thank you for your consideration of these comments.

Sincerely,

Nicholas S. Torrey
Staff Attorney

Enclosure

cc: Qu Qi, DENR Inactive Hazardous Sites Branch, Central Unit Regional Supervisor
Friends of Bolin Creek Board Members

Attachment A

From:	Axon, Amy
To:	"Christopher Burkhardt"
Cc:	cbrooks@townofchapelhill.org; Qi, Qu
Subject:	RE: Attached: TOCHPD ESC Report
Date:	Monday, July 06, 2015 4:13:00 PM

Christopher:

Upon review of this report I continue to have questions regarding the procedures followed when collecting groundwater samples on May 26, 2015.

1. On the day of sample collection were the wells purged adequately to ensure that the groundwater pH, specific conductance and turbidity have stabilized as discussed in the EPA Groundwater Sampling Procedure document cited in our guidance document. This procedure can be found here: http://www.epa.gov/region4/sesd/fbqstp/Groundwater-Sampling.pdf. The field notes that you provided do not include and mention of the purging process during sampling. The notes do indicate very high turbidity levels in MW3a and MW4a, which causes concern. I would like to see ALL of the field readings and a description of the purging process.
2. During sample collection did you use a low flow pump or a bailer?

I also have a question about the sample results reported for Chromium. In your report, Table 1 and on the chain of custody, it appears that you analyzed for Hexavalent chromium. However, the lab report lists 6010c as the test method. Is method 6010c for total chromium or hexavalent chromium?

I look forward to your response.
Thanks,
Amy

From: Christopher Burkhardt [mailto:cburkhardt@falconengineers.com]
Sent: Wednesday, June 24, 2015 4:16 PM
To: Axon, Amy
Cc: cbrooks@townofchapelhill.org
Subject: Attached: TOCHPD ESC Report

Amy,

As a follow up to my earlier voicemail attached is the revised report.

I have added a copy of the field notes to the report, details about the well construction and development are included in section 2, I have reviewed Section 3.0, #1-16 of the Guidelines and revised the report as needed.

Please give me a call to discuss if you still have questions.

Christopher J. Burkhardt

Environmental Department Manager
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M 919-730-0064
cburkhardt@falconengineers.com
www.falconengineers.com

From: Axon, Amy [mailto:amy.axon@ncdenr.gov]
Sent: Monday, June 22, 2015 4:05 PM
To: Christopher Burkhardt; Jessica Hoglen
Cc: Curtis Brooks; Qi, Qu
Subject: RE: Attached: TOCHPD ESC Report

Hi Christopher:

I just did a quick review of the report and noticed that it is missing details about the well construction and development and the field notes that were taken during groundwater monitoring. Jessica and I had discussed the need to include field notes and details that had been left out of past reports. Please note the items listed in Section3.0, #1-16 of the Guidelines for Assessment and Cleanup document.

Once I get a complete Remedial Investigation Report I will complete me review.
Thanks
Amy

From: Christopher Burkhardt [mailto:cburkhardt@falconengineers.com]
Sent: Friday, June 19, 2015 3:49 PM
To: Axon, Amy
Cc: Curtis Brooks
Subject: Fwd: Attached: TOCHPD ESC Report

Good afternoon Amy,

I'm out of the office but I wanted to forward this report to you sooner rather than later.

Please find the revised Environmental Site Characterization Report for the Town of Chapel Hill Police Department attached to this email.

Thank you and have a great weekend!
-Christopher

Sent from my iPhone

Begin forwarded message:

From: "Christopher Burkhardt" <cburkhardt@falconengineers.com>
To: "cbrooks@townofchapelhill.org" <cbrooks@townofchapelhill.org>
Subject: Attached: TOCHPD ESC Report

Curtis,

Please find the revised ESC Report attached to this email.

Please let me know if you have any questions.

Thank you

Attachment B

Environmental Science & Technology

Article

pubs.acs.org/est

Naturally Occurring Radioactive Materials in Coals and Coal Combustion Residuals in the United States

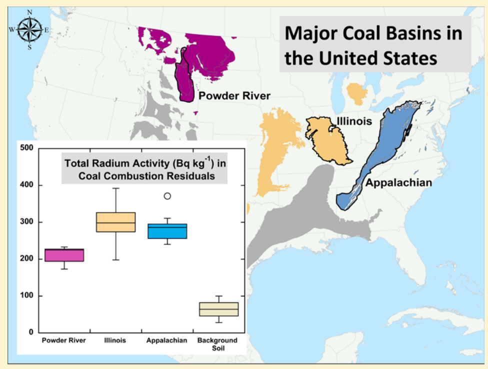
Nancy E. Lauer,[†] James C. Hower,[‡] Heileen Hsu-Kim,[§] Ross K. Taggart,[§] and Avner Vengosh*,[†]

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

[‡]Center for Applied Energy Research, University of Kentucky, Lexington, Kentucky 40511, United States

Supporting Information

ABSTRACT: The distribution and enrichment of naturally occurring radioactive materials (NORM) in coal combustion residuals (CCRs) from different coal source basins have not been fully characterized in the United States. Here we provide a systematic analysis of the occurrence of NORM (^{232}Th, ^{228}Ra, ^{238}U, ^{226}Ra, and ^{210}Pb) in coals and associated CCRs from the Illinois, Appalachian, and Powder River Basins. Illinois CCRs had the highest total Ra (^{228}Ra + ^{226}Ra = 297 ± 46 Bq/kg) and the lowest ^{228}Ra/^{226}Ra activity ratio (0.31 ± 0.09), followed by Appalachian CCRs (283 ± 34 Bq/kg; 0.67 ± 0.09), and Powder River CCRs (213 ± 21 Bq/kg; 0.79 ± 0.10). Total Ra and ^{228}Ra/^{226}Ra variations in CCRs correspond to the U and Th concentrations and ash contents of their feed coals, and we show that these relationships can be used to predict total NORM concentrations in CCRs. We observed differential NORM volatility during combustion that results in ^{210}Pb enrichment and ^{210}Pb/^{226}Ra ratios greater than 1 in most fly-ash samples. Overall, total NORM activities in CCRs are 7−10- and 3−5-fold higher than NORM activities in parent coals and average U.S. soil, respectively. This study lays the groundwork for future research related to the environmental and human health implications of CCR disposal and accidental release to the environment in the context of this elevated radioactivity.



■ INTRODUCTION

In spite of the rise of natural gas production, coal is still a major source for electricity production in the U.S. Long-term projection by the U.S. Energy Information Administration predicts that coal will continue as a major player in the U.S. electricity sector, up to 32% by 2040.[1] In 2013, 39% of the nation's electricity was generated from coal sources,[2] resulting in the production of 114 million tons of coal combustion residuals (CCRs)[3] that include fly ash, bottom ash, boiler slag, and flue-gas desulfurization (FGD) solids. Naturally occurring radioactive materials (NORM) are among the inorganic constituents that are present in coals and enriched in CCRs following the combustion of coal. The NORM in coal consist of primordial ^{238}U ($t_{1/2} = 4.5 \times 10^9$ years) and ^{232}Th ($t_{1/2} = 1.4 \times 10^{10}$ years) and their decay products, as well as ^{40}K ($t_{1/2} = 1.3 \times 10^9$ years). Previous studies have shown that NORM concentrations in CCRs can be as much as an order of magnitude greater than those of their feed coal sources[4,5] because of the elimination of carbon during combustion and coals commonly having ~10% ash content. Depending on the ash content of the feed coal, typical NORM concentrations in CCRs range from 3 to 10 times the concentrations in coal.[4−8] Consequently, the enrichment of NORM in CCRs raises potential human and environmental health concerns associated with the release of CCRs to the environment as either emission from smoke stacks, disposal to landfills, coal ash ponds, and abandoned mines, or spills.[9,10]

The radioactivity of coals and CCRs has been studied since the 1960s.[11,12] Because of their relatively long half-lives, the most commonly measured NORM in coals and CCRs are ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, ^{228}Ra, and ^{40}K.[4,13,14] It has been suggested that coal rank controls the NORM concentrations such that low-rank subbituminous coals, brown coals, and lignites are more effective at adsorbing metals during coalification and will therefore tend to have higher NORM concentrations compared to higher-rank bituminous coals.[15,16] Fly ash has been differentiated from bottom ash based on the enrichment of the volatile ^{210}Pb in fly ash and consequent depletion in bottom ash.[5,17] Similarly, studies have also shown ^{210}Pb, ^{238}U, and small ^{226}Ra variations in varying particle size fractions of fly ash.[4,5,16,18] Despite the long history of previous research on NORM in CCRs, very few studies have addressed the relationships of NORM concentrations and distribution in CCRs to the specific parent coal basins in the U.S. We hypothesize that the relationship between source coals and derived CCRs has important implications for understanding the major factors and processes that control the radioactivity of CCRs and for evaluating the potential human and environmental health risks

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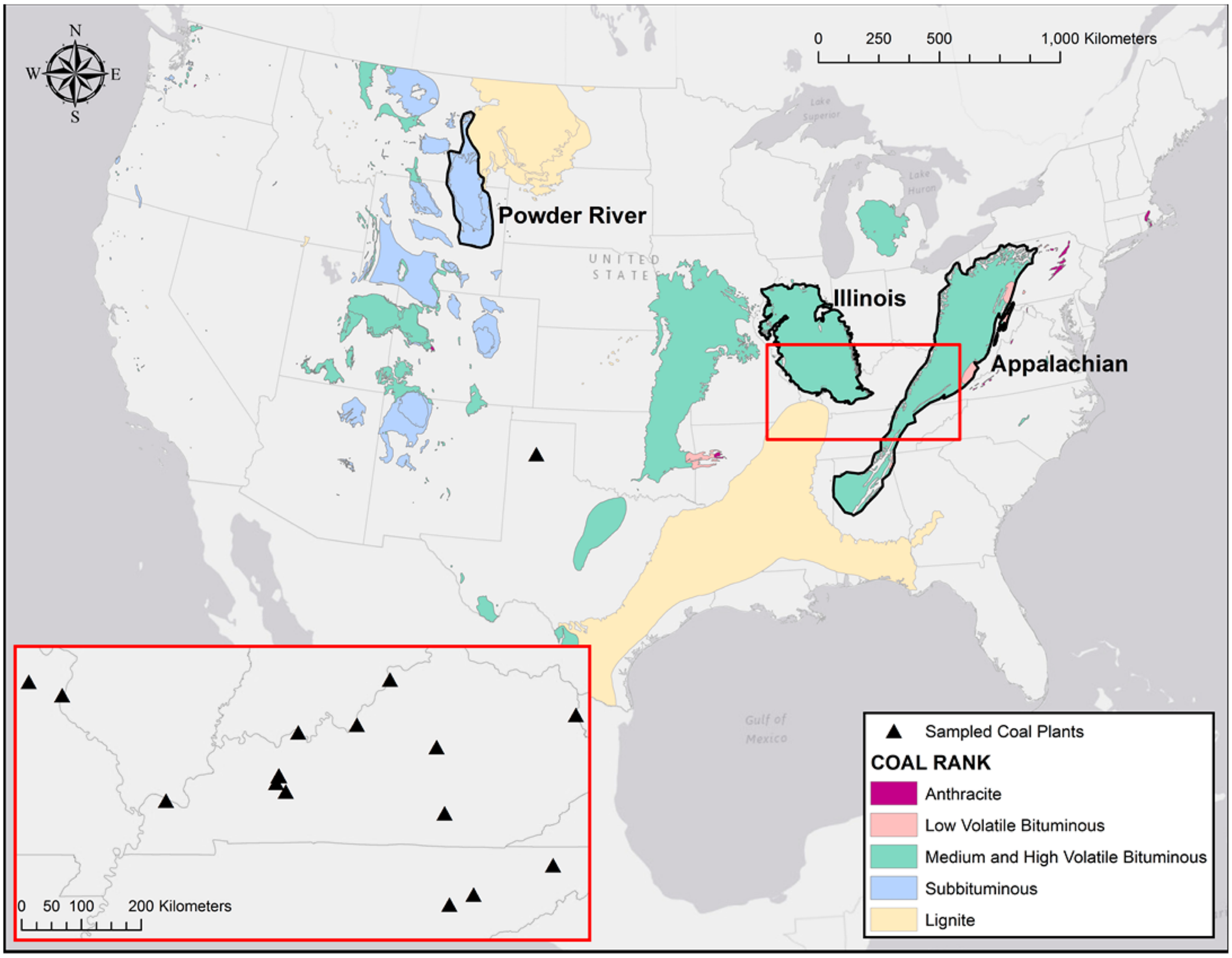

Figure 1. Map of major U.S. coal basins and locations of sampled coal power plants (shown primarily in a nested map). Coal basins are distinguished by coal rank. Coal basins investigated in this study include the Powder River, Illinois, and Appalachian Basins and are outlined with thick black lines. (Basemap source: Esri, DeLorme, HERE, MapmyIndia.)

associated with coal combustion and disposal of CCRs to the environment.

The objectives of this study are to provide systematic data of NORM concentrations and ratios in CCRs originating from the three major coal-producing basins in the U.S., the Appalachian, Illinois, and Powder River Basins (Figure 1), which produced 25%, 13%, and 41%, respectively, of the total U.S. coal (in 2013),[19] and to address the potential implications associated with the disposal and accidental release of CCRs to the environment. We measured ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, and ^{228}Ra in coals and CCRs from the Appalachian, Illinois, and Powder River Basins, and characterized the ^{228}Ra/^{226}Ra, Th/U, and ^{210}Pb/^{226}Ra ratios as well as the total Ra activity (^{228}Ra + ^{226}Ra). Assuming radioactive secular equilibrium (i.e., the activity of the parent is equal to the activity of the progeny radionuclides) within the U and Th decay chains, at least through ^{226}Ra and ^{228}Ra in both coals and CCRs,[4,11,20,21] the ^{228}Ra and ^{226}Ra activities and activity ratios in CCRs should reflect the original U and Th concentrations and ratios in the feed coals. Differential volatilization of certain elements during coal combustion could result in different activity ratios in CCRs compared to source coals. Accordingly, we hypothesize that CCRs would have NORM concentrations and ratios based on the original U and Th concentrations and the chemical characteristics of the feed coals.

MATERIALS AND METHODS

Sample Collection from Coal-Fired Power Plants. Coal (n = 11) and fly-ash [mechanical, baghouse, and electrostatic precipitator (ESP); n = 54] samples were collected dry from coal-fired power plants (n = 16) in the U.S. between 2007 and 2013 (Figure 1). While CCRs can refer to all byproducts produced during coal combustion (fly ash, bottom ash, boiler slag, and FGD solids), for the purpose of this study, CCRs will only refer to those fly-ash fractions mentioned above. Because coal-fired power plants will often burn feed coal blends from multiple coal basins, careful attention was paid to collect CCR samples specifically from plants burning feed coal from only one known coal basin at the time of sampling. When possible, fly-ash samples were collected from individual rows of the ESP.

Radionuclide Analysis. ^{238}U ($t_{1/2}$ = 4.5 × 10^9 years), ^{226}Ra ($t_{1/2}$ = 1600 years), ^{210}Pb ($t_{1/2}$ = 22 years), and ^{228}Ra ($t_{1/2}$ = 5.8 years) were measured in coals and CCRs at the Laboratory for Environmental Analysis of RadioNuclides (LEARN) at Duke University. Coal and CCR samples (~30 g) were homogenized and packed in clear snap-lid Petri-style dishes of uniform geometry (6.5 cm diameter and 2 cm height), which were then sealed with electrical tape and coated in wax to prevent the escape of radon gas. Packaged samples incubated for at least 27 days, or ~7 half-lives of ^{222}Rn ($t_{1/2}$ = 3.8 days), in order for ^{226}Ra to reach secular equilibrium with its short-lived progeny, ^{214}Pb ($t_{1/2}$= 26.9 minutes) and ^{214}Bi ($t_{1/2}$ = 19.7 minutes), and for ^{228}Ra to reach secular equilibrium with its immediate daughter, ^{228}Ac ($t_{1/2}$ = 6.15 hours). Following incubation, samples were measured on a Canberra DSA2000 broad-energy-germanium γ detector surrounded by Pb shielding for at least 80000 seconds in order to minimize the statistical counting error. Confidence intervals for all radionuclides were mainly less than ±5% (1σ) in CCR samples and less than ±10% (1σ) in coal samples with only a few exceptions for ^{238}U and ^{210}Pb in lower activity samples (Tables S2−S4). Energy efficiencies for ^{238}U, ^{226}Ra, ^{228}Ra, and ^{210}Pb were determined using CCRMP U/Th ore reference material (DL-1a) packaged, sealed, and incubated in the same geometry as the unknown samples. Replicate analyses of different standards yield 2σ of 4% for ^{226}Ra and 16% for ^{228}Ra.[22]

^{238}U was analyzed through the ^{234}Th (63 keV) peak, ^{226}Ra was analyzed through the ^{214}Pb (351 keV) peak, ^{228}Ra was analyzed through the ^{228}Ac (911 keV) peak, and ^{210}Pb was analyzed directly through its 47 keV peak. Activities were calculated manually by summing peak counts, subtracting corresponding background counts, and correcting for detector efficiency at that peak. We corrected for the decay of unsupported ^{210}Pb during the time between sampling and analysis. Because ^{210}Pb decays at a relatively low energy of 47 keV, we also corrected for self-adsorption of ^{210}Pb γ emissions by the sample itself using a ^{210}Pb point source by methods described in Cutshall et al.[23] ^{232}Th ($t_{1/2}$ = 1.4 × 10^{10} years) and ^{238}U were measured by inductively coupled plasma mass spectrometry (Agilent 7700x) after heated digestion with nitric and hydrofluoric acids in a subset of CCR samples. The accuracy was assessed using the National Institute of Standards and Technology standard reference material (SRM) for fly ash, SRM 1633c (see details in the Supporting Information). Finally, data were compared and statistics were summarized using analysis of variance techniques.

■ RESULTS AND DISCUSSION

NORM Activities and Ratios in CCRs from U.S. Coal Basins. Mean activities and ranges for ^{238}U, ^{226}Ra, ^{210}Pb, ^{232}Th, and ^{228}Ra, along with Th/U, ^{228}Ra/^{226}Ra, ^{210}Pb/^{226}Ra, ^{226}Ra/^{238}U, and ^{228}Ra/^{232}Th activity ratios in coals and CCRs from the Appalachian, Illinois, and Powder River Basins are presented in Table 1 and Figure 2. Coals from the Illinois Basin had the highest total Ra activity (n = 5; ^{228}Ra + ^{226}Ra = 39 ± 8 Bq/kg) with the lowest ^{228}Ra/^{226}Ra activity ratio (0.28 ± 0.11), followed by coals from the Appalachian Basin (n = 3; 37 ± 2 Bq/kg; 0.61 ± 0.10) and the Powder River Basin (n = 3; 28 ± 12 Bq/kg; 1.07 ± 0.36) (Table 1). NORM concentrations in CCRs mimic this trend; CCRs derived from Illinois Basin coals have the highest total Ra activity (n = 28; 297 ± 46 Bq/kg) with the lowest ^{228}Ra/^{226}Ra ratio (0.31 ± 0.09), followed by CCRs from the Appalachian Basin (n = 14; 283 ± 34 Bq/kg; 0.67 ± 0.09) and the Powder River Basin (n = 12; 213 ± 21 Bq/kg; 0.79 ± 0.10) (Table 1 and Figures 2 and 3). The mean total Ra activity of Powder River Basin CCRs was statistically different from the mean total Ra activities of the Illinois and Appalachian Basin CCRs (p < 0.01). The mean total Ra activities of the Appalachian and Illinois Basin CCRs were not statistically different from each other. The mean ^{228}Ra/^{226}Ra activity ratios

Table 1. Mean and Range Values of Radionuclide Activities (in Bq/kg) and Activity Ratios in U.S. Coals and CCRs

sample type	n[a]	^{232}Th	^{228}Ra	^{238}U	^{226}Ra	^{210}Pb	Th/U	^{228}Ra / ^{226}Ra	^{210}Pb / ^{226}Ra	^{226}Ra/ ^{238}U	^{228}Ra/ ^{232}Th
Appalachian											
coal	3		14 (12−15)	20 (18−21)	23 (21−25)	21 (17−23)		0.61 (0.49−0.68)	0.93 (0.83−1.03)	1.18 (1.07−1.38)	
CCRs	14	112 (79−131)	113 (88−139)	171 (131−248)	170 (133−232)	193 (111−324)	0.69 (0.38−0.99)	0.67 (0.56−0.80)	1.12 (0.75−1.64)	1.01 (0.80−1.18)	1.01 (0.87−1.19)
Illinois											
coal	5		8 (6−13)	30 (23−43)	31 (22−42)	27 (22−37)		0.28 (0.14−0.41)	0.88 (0.74−1.00)	1.02 (0.94−1.10)	
CCRs	28	67 (49−81)	68 (53−94)	228 (135−341)	230 (142−325)	284 (81−483)	0.32 (0.20−0.53)	0.31 (0.20−0.52)	1.25 (0.30−2.07)	1.01 (0.75−1.25)	1.04 (0.87−1.25)
Powder River											
coal	3		14 (11−19)	12 (6−21)	14 (7−23)	12 (6−19)		1.07 (0.79−1.48)	0.83 (0.81−0.86)	1.24 (1.12−1.38)	
CCRs	12	86 (80−96)	93 (80−110)	114 (85−142)	120 (93−139)	131 (70−184)	0.76 (0.57−1.02)	0.79 (0.64−0.95)	1.08 (0.64−1.37)	1.07 (0.95−1.22)	1.02 (0.91−1.17)

[a]The number of samples (n) contributing to the average values is accurate for all radionuclides and ratios excluding ^{232}Th and ratios including ^{232}Th. Because only a subset of samples were measured for ^{232}Th, values provided in the table for ^{232}Th, Th/U, and ^{228}Ra/^{232}Th are an average of n = 7 Powder River Basin CCRs, n = 20 Illinois Basin CCRs, and n = 12 Appalachian Basin CCRs.

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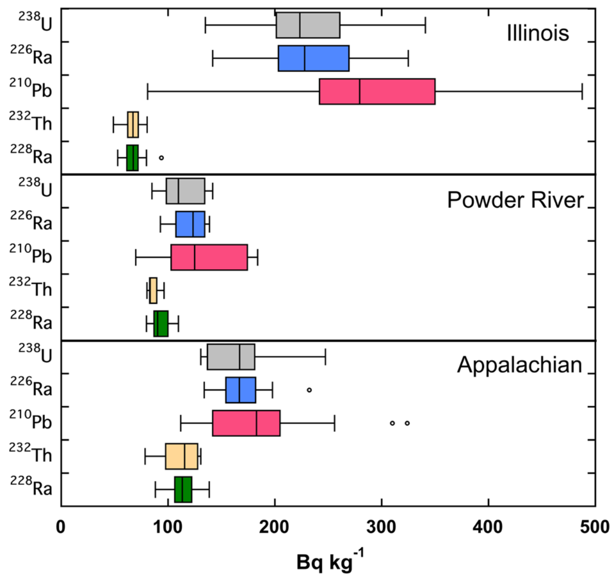

Figure 2. Boxplots of the ^{238}U (gray), ^{226}Ra (blue), ^{210}Pb (pink), ^{232}Th (tan), and ^{228}Ra (green) activities (Bq/kg) in CCRs originating from Illinois, Powder River, and Appalachian Basin coals. ^{238}U and ^{226}Ra as well as ^{232}Th and ^{228}Ra appear to be in secular equilibrium in CCRs, while ^{210}Pb activities are higher because of the volatizaliation of Pb during combustion.

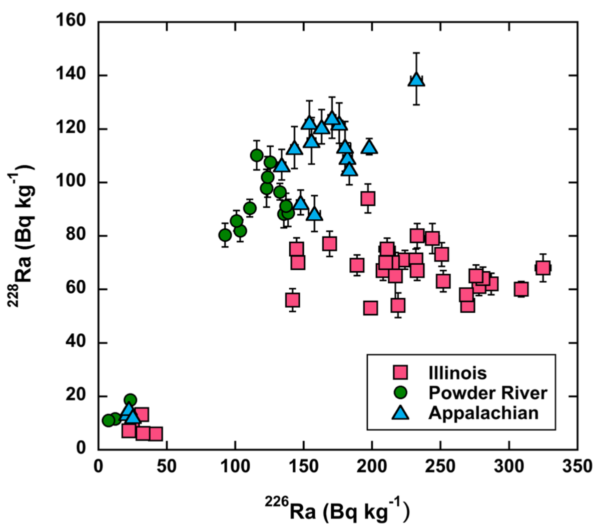

Figure 3. ^{228}Ra versus ^{226}Ra in U.S. coals and CCRs from the Illinois (pink squares), Powder River (green circles), and Appalachian (blue triangles) Basins. Error bars represent 95% confidence intervals, which do not extend past the marker boundaries in some samples.

of CCRs originating from all three coal basins were significantly different ($p < 0.01$). The ^{228}Ra/^{226}Ra ratios reported in this study are consistent with the ^{228}Ra/^{226}Ra ratios in coals and CCRs reported in previous studies (Table 2).[12,13,24,25]

Our data show that total Ra activities are ~7−10 times higher in U.S. CCRs compared to coals, with the highest activities in CCRs originating from Illinois and Appalachian coals and the lowest in CCRs generated from Powder River coals. This 7−10-fold enrichment is expected from the elimination of carbon during combustion from coals containing 10−15% ash content, which is typical for low-ash U.S. coals. In coals and CCRs from all three basins, ^{226}Ra, which is part of the U decay series, is generally higher than ^{228}Ra, which is part of the Th decay series (Figures 2 and 3). This observation indicates that variations in the total Ra activities and ratios are mainly controlled by variations in ^{226}Ra, which, in turn, reflects the original concentration of ^{238}U in the feed coal. Figure 4 shows the established relationship between ^{226}Ra in CCRs and ^{238}U in the source coals using data from this study as well as data from different countries reported in previous studies.[4−8] The data show that ^{226}Ra in CCRs correlates linearly with ^{238}U in the original feed coals, and high-ash coals (~30−40% ash) produce CCRs with relatively lower NORM concentrations compared to low-ash coals (~10−15% ash). These correlations indicate

Table 2. Average ^{228}Ra/^{226}Ra and Th/U Activity Ratios in Coals and CCRs Reported in the Present and Previous Studies

sample type	^{228}Ra/^{226}Ra	Th/U	study
Appalachian			
coal	0.61		this study
CCRs	0.67	0.69	this study
ESP fly ash	0.64		Eisenbud and Petrow[12]
coal		0.92	Swanson[24]
coal		0.54	Beck et al.[13]
Illinois			
coal	0.28		this study
CCRs	0.31	0.32	this study
coal		0.31	Klein et al.[25]
inlet fly ash		0.22	Klein et al.[25]
coal		0.38	Swanson[24]
coal		0.25	Beck et al.[13]
Powder River			
coal	1.07		this study
CCRs	0.79	0.76	this study
coal	0.83		Coles et al.[4]
ESP fly ash	0.77		Coles et al.[4]
coal		1.13	Swanson[24]

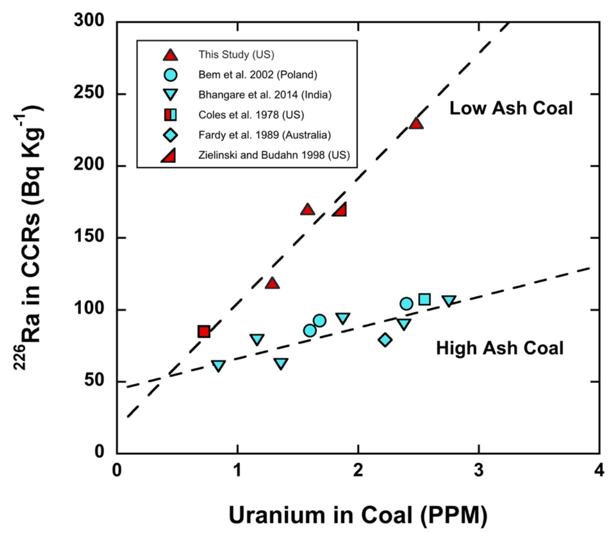

Figure 4. ^{226}Ra in CCRs (Bq/kg) versus U in parent coals (ppm) from this and previous studies. Note the distinction between low- and high-ash coals that results in respectively higher and lower ^{226}Ra activities in residual CCRs. These relationships provide a useful tool for the universal prediction of ^{226}Ra in CCRs based on the U and ash contents in the parent coals. Best-fit lines can be represented by $y = 82.8x + 23.2$ for low-ash coals and $y = 21.6x + 46.3$ for high-ash coals.

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that the original ^{238}U and the ash contents of the feed coals are the two predominant factors that control the ^{226}Ra activity in the produced CCRs. This relationship is important for a universal prediction of ^{226}Ra activities in fly ash produced from different types of coals worldwide. Coals with relatively higher ^{238}U concentrations would generate CCRs with relatively higher ^{226}Ra activities that will follow the linear relationships established in Figure 4. In the same manner, we predict that the ^{228}Ra activity in CCRs is directly correlated with the ash content and the original ^{232}Th in the feed coals.

Despite the enrichment and redistribution of radionuclides in the combustion process, during which coal is converted to ash, the ^{228}Ra/^{226}Ra activity ratios in CCRs reflect the ratios of their corresponding feed coal sources and are distinguishable among different coal basins (Table 1 and Figure 3). These distinct ^{228}Ra/^{226}Ra activity ratios in CCRs are also consistent with the Th/U activity ratios in CCRs reported in this study (Table 1 and Figure S4) and the Th/U activity ratios in coals and CCRs reported in previous studies (Table 2). These observations, combined with the observation that concentration enrichments match what would be predicted simply from the loss of organic matter during combustion, indicate that Ra, U, and Th are largely retained in CCRs during the combustion process. We can also infer that radioactive secular equilibrium, a condition in which the activity of a parent nuclide is equal to the activity of all progeny nuclides, likely exists in the U and Th decay chains in CCRs at least through ^{226}Ra and ^{228}Ra, respectively. ^{228}Ra/^{232}Th and ^{226}Ra/^{238}U activity ratios of ~1 provide further evidence for this finding (Table 1 and Figures S6 and S7).

On the basis of the results of this study and the principles of radioactive secular equilibrium, the total radioactivity in CCRs (from the U and Th decay chains) can be estimated by knowing either the original ^{238}U and ^{232}Th concentrations and ash contents in the feed coal or by knowing the ^{238}U and ^{232}Th (or ^{226}Ra and ^{228}Ra) concentrations in the CCRs. In such cases, the following assumptions would have to be made relating to the behavior of radionuclides in the U and Th decay series during combustion: (1) other long-lived isotopes of U (^{234}U) and Th (^{230}Th, ^{228}Th) are largely retained in CCRs following coal combustion, analogous to what we observed for ^{238}U and ^{232}Th; (2) ^{224}Ra is also retained in CCRs, analogous to what is observed for ^{228}Ra and ^{226}Ra; (3) ^{222}Rn (half-life = 3.8 days), which is lost during coal combustion because of its gaseous nature, reestablishes radioactive equilibrium with its immediate parent, ^{226}Ra, within ~27 days via in-growth, and there is minimum further radon emanation, which is consistent with previous radon emanation studies;[26,27] (4) other shorter-lived daughter products also quickly reestablish radioactive equilibrium with their parent radionuclide via in-growth and decay. In conclusion, radionuclides in the U and Th decay series in CCRs older than 27 days may be approximately in radioactive secular equilibrium with the exception of certain radionuclides that become volatile during combustion.

Differential Volatilization of NORM during the Combustion Process. The long half-lives of ^{238}U and ^{232}Th of 10^9 and 10^{10} years, respectively, and the age of U.S. coals suggest that the U and Th decay series in U.S. coals are likely in secular equilibrium. Previous studies have confirmed that the decay products in the U and Th decay series are in secular equilibrium in coals but not in CCRs because of the different volatile properties of the radionuclides, especially ^{210}Pb.[4,5] The high temperature at which coal is burned promotes the volatilization of Pb and thus fractionation of ^{210}Pb, resulting in its depletion in residual bottom ash and enrichment in finer-grained fly ash. Consequently, ^{210}Pb is not usually in secular equilibrium with its preceding nuclides (^{226}Ra and ^{238}U) in fly ash, despite being in secular equilibrium with its preceding nuclides in coals (Table 1 and Figure 2). This nuclide fractionation during coal combustion has been reported by Coles et al.,[4] who distinguished group I elements (nonvolatile and nonenriched in fly ash) from group II elements (enriched because of differential volatilization). In this study, we find that fly-ash samples collected from individual ESP rows with increasing distance from the furnace have increasing ^{210}Pb activities and ^{210}Pb/^{226}Ra ratios, up to activity ratios of ~2 (Table 1 and Figure S2). Each additional sequential ESP row is responsible for collecting finer-grained ash that escaped the previous row, and later rows are positioned further from the furnace, where they are collecting relatively cooler-temperature and finer-grained ash. This observation indicates that the preferential capture of ^{210}Pb at relatively lower temperatures causes fractionation and consequential enrichment of ^{210}Pb in progressively finer-grained coal ash (with greater surface area to mass ratios). Although this study did not quantify the retention of ^{210}Pb to specific grain sizes, the observed pattern indicates that relatively finer fly-ash particles would likely have the highest ^{210}Pb activities.

^{210}Pb's relatively long 22-year half-life compared to its daughter products (e.g., ^{210}Po, $t_{1/2}$ = 138 days) suggests that a new secular equilibrium between ^{210}Pb and its progeny, including ^{210}Po, may be established after approximately 7 half-lives of ^{210}Po, or approximately 2.5 years, via in-growth. We therefore expect that ^{210}Po will also be further enriched in fly ash because of both the enrichment of its grandparent ^{210}Pb and subsequent decay, as well as the known volatilization of ^{210}Po itself during combustion.[18] The enrichment of ^{210}Pb and ^{210}Po effectively breaks the secular equilibrium in the U decay chain in CCRs, and their enrichment in finer-grained ash should be taken into consideration in dose assessments related to CCR radioactivity and estimations of total NORM in CCRs. When the U and Th decay nuclides are in secular equilibrium, the total α activity is 8 times the ^{226}Ra activity and 6 times the ^{228}Ra activity and ranges from 1200 to 3100 Bq/kg in CCRs. However, the enrichment of ^{210}Pb (and subsequent decay) and ^{210}Po would increase the total α activity in relatively finer fly-ash particles.

Previous studies were not conclusive with respect to the behavior of Ra during combustion processes.[4,16,28] Previous studies have suggested that ^{226}Ra can become volatile during combustion while ^{228}Ra does not because of the differences in the modes of occurrence of U and Th in coals.[4,17] U in coal is bound to both the organic and mineral phases and is commonly found as uraninite (UO_2) in the coal matrix, while Th is almost exclusively associated with the ash mineral matrix, commonly in monazite and zircon minerals.[29] Our data show a general trend of decreasing ^{228}Ra/^{226}Ra activity ratios with increasing ESP row (Figure S3). However, these slight variations are within the range of the 95% confidence intervals, and thus our data do not support the concept of ^{228}Ra/^{226}Ra fractionation due to volatilization of ^{226}Ra. Additionally, our data show that the ^{228}Ra/^{226}Ra activity ratios in CCRs reflect the ^{228}Ra/^{226}Ra activity ratios in their corresponding feed coals (Table 1 and Figure 2), further suggesting that ^{226}Ra is not substantially enriched in CCRs with increasing distance from the furnace.

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Environmental and Human Health Implications. The average ^{226}Ra concentration in soil worldwide is approximately 32 Bq/kg and commonly ranges from 25 to 50 Bq/kg.[30] Assuming that the average ^{228}Ra/^{226}Ra activity ratio in soil is 1.2 (the average continental crust Th/U activity ratio = ∼1.2),[30] the average total Ra activity in soil can be estimated to be ∼70 Bq/kg. Therefore, the data from this study indicate that the total NORM in U.S. CCRs (from U and Th decay chains) is ∼3−5 times greater than those in background soil. In addition to total Ra, the ^{228}Ra/^{226}Ra ratios are also distinguishable from a representative background soil. CCRs originating from Illinois coals have the highest ^{226}Ra activities and lowest ^{228}Ra/^{226}Ra activity ratios (0.3), which are distinctive from the representative background soil ratio of ∼1.2. CCRs originating from Appalachian and Powder River coals have higher ^{228}Ra/^{226}Ra ratios (0.7 and 0.8), which are closer to, yet still typically lower than, the expected ^{228}Ra/^{226}Ra ratio of the background soil. Delineation of CCRs in the environment may therefore be possible by identifying not only the elevated levels of NORM but also distinct ^{228}Ra/^{226}Ra activity ratios. For example, the 2008 TVA coal ash spill in Kingston, TN, caused contamination of river sediments and soil that exhibited elevated NORM and ^{228}Ra/^{226}Ra ratios of ∼0.7, which was different from the local background soil ratio of ∼1.[9]

Because of the elevated levels of radioactivity of CCRs compared to the background soil, the potential environmental impacts and human health risks associated with CCR disposal to the environment should be evaluated in future studies. With the near elimination of the fugitive emission through installation of efficient ESPs and other particulate emission control devices, the radiation dose due to direct emission of CCRs from smoke stacks has been found to be within background levels.[12,31] However, in countries where particulate emission control devices are not regulated or enforced, fugitive power-plant particulate emissions in addition to resuspension of fine CCR particles from landfills might pose additional human health risks due to inhalation that are not yet well understood. On the basis of the correlations demonstrated in Figure 4, U and ash contents in coals could be used to estimate ^{226}Ra activities in produced CCRs (Table 3) and to predict the NORM concentrations in air upon CCRs' fugitive emission to the atmosphere. Additionally, CCR disposal to surface impoundments raises concerns about the potential leaching of Ra from CCRs and leaking of the effluents to underlying groundwater from unlined coal ash ponds and/or discharge to surface water.[32] As far as we are aware, the NORM activity has not been monitored in surface impoundment effluents or in landfill leachates and, thus, the risks related to possibly elevated NORM in CCR-contaminated waters are largely unknown.

Overall, our study shows that the combustion of coal causes an enrichment of NORM in CCRs that correlates with the U and Th concentrations and ash content of the parent coals. Coals and corresponding CCRs have distinct ^{228}Ra/^{226}Ra activity ratios and total Ra activities that are characteristic of the source basin of the feed coals and also distinguishable from the background soil. Volatilization of Pb results in further enrichment of ^{210}Pb and its progeny nuclides in fine fly-ash particles, resulting in a breakage in secular equilibrium and overall higher radioactivity in finer-grained fly ash. We show that CCRs in the U.S. have total Ra activities typically 7−10 times the activities of coal and 3−5 times the activities of average U.S. soil. The results of this study serve to better quantify radionuclide concentrations and ratios in CCRs from the major U.S. coal basins and lay the groundwork for future research related to the human and environmental health impacts of coal combustion in the context of CCR radioactivity. Specifically, the results of this study are important for the future estimation of radionuclide concentrations in inhaled air containing suspended CCR particulates, calculation of inhalation doses to high-risk populations such as power-plant workers, and evaluation of radionuclide dissolution/adsorption and mobility in the environment near coal ash disposal ponds.

Table 3. Relationship between U in Coal and Potential ^{226}Ra Concentration in Air, Based on Correlations between Feed Coals and Associated CCRs Shown in Figure 4

	U in coal (ppm)	^{226}Ra in CCRs (Bq/kg)	^{226}Ra per μg CCR in m^3 air (μBq/μg·m^3)
low-ash coal	1	106	0.11
($[^{226}Ra]_{CCR,Bq/kg} = 82.8[U]_{coal,ppm} + 23.2$	2	189	0.19
$[^{226}Ra]_{CCR,Bq/kg} = 6.7[U]_{coal,Bq/kg} + 23.2$)	3	272	0.27
	4	354	0.35
	5	437	0.44
	6	520	0.52
	7	603	0.60
	8	686	0.69
	9	769	0.77
	10	851	0.85
high-ash coal	1	68	0.07
($[^{226}Ra]_{CCR,Bq/kg} = 21.6[U]_{coal,ppm} + 46.3$	2	89	0.09
$[^{226}Ra]_{CCR,Bq/kg} = 1.8[U]_{coal,Bq/kg} + 46.3$)	3	111	0.11
	4	133	0.13
	5	154	0.15
	6	176	0.18
	7	198	0.20
	8	219	0.22
	9	241	0.24
	10	262	0.26

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b01978.

Further information on the analytical techniques along with seven figures and four tables (PDF)

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Notes

The authors declare no competing financial interest.

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