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Lithium isotope fingerprints in coal and coal combustion residuals from the United States.

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Abstract

Coal is a major energy source worldwide and is a large fraction of the total energy production in the US. The disposal of coal combustion residuals (CCRs) into landfills and surface impoundments present an environmental challenge given the high levels of toxic metals in CCRs that are highly mobile into the aquatic phase. Here we present the lithium isotope composition of coals and CCRs originated from several U.S. basins. $\delta^7\text{Li}$ values in CCR leachates from the Appalachian Basin, the Illinois Basin and the Powder River Basin vary from -7‰ to +12.8‰, with an average of $\pm 1.6 \pm 5.0$ ‰. CCR's from the Powder River Basin had a higher $\delta^7\text{Li}$ of 7.6 ± 5.4 ‰ compared to the Appalachian and Illinois Basins ($+0.3 \pm 6.6$ ‰ and -0.1 ± 1.3 ‰, respectively). Effluents from six coal ash ponds in North Carolina show a similar range in lithium isotopes ($\delta^7\text{Li} = -6.2$ to $+8.7$ ‰) suggesting limited lithium isotope fractionation during storage in surface impoundment. We show that lithium isotopes, particularly when coupled with boron isotopes, could distinguish CCR contaminants from oil and gas wastewater, including conventional produced waters and hydraulic fracturing fluids.

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1. Introduction

In spite of the rise of unconventional energy resources, coal is still a major energy source and consists about 37% of the total energy production in the US.¹ Both surface (i.e., mountaintop) and subsurface coal mining results in water quality degradation due to the formation of metal-rich acid mine drainage and alkaline effluents that enhance selenium mobilization, respectively.^{2,3} The unregulated disposal of coal combustion residues also generates water contamination.⁴⁻⁶ In some areas, such as WV, the legacy of coal mining and conventional oil and gas exploration coexist with recent unconventional shale gas drilling.

Isotopes are useful tracers of contamination in groundwater because they are sensitive to mixing of small (<1%) of contaminated fluids into freshwater. In addition, multi-isotope systems have been applied to distinguish between different source waters. In particular, boron, strontium, and sulfur isotopes have been successfully applied in attempts to delineate coal related contamination in the environment.^{7,8} Lithium isotopes, especially when combined with boron or strontium isotopes, could be a powerful tool to delineate coal ash contamination in areas impacted by other industries, including oil and gas activity.

This study aims to characterize the lithium isotope variations of coal and coal combustion residuals (CCRs), as well as the isotope signature of effluents originated from coal ash ponds in North Carolina. In order to evaluate the efficacy of lithium isotopes as a potential tracer for CCR contamination, we combined boron and lithium isotopes to show that the lithium and boron isotope signatures of CCRs are distinct from other contamination sources such as oil and gas wastewaters and also different from the composition of most natural waters.

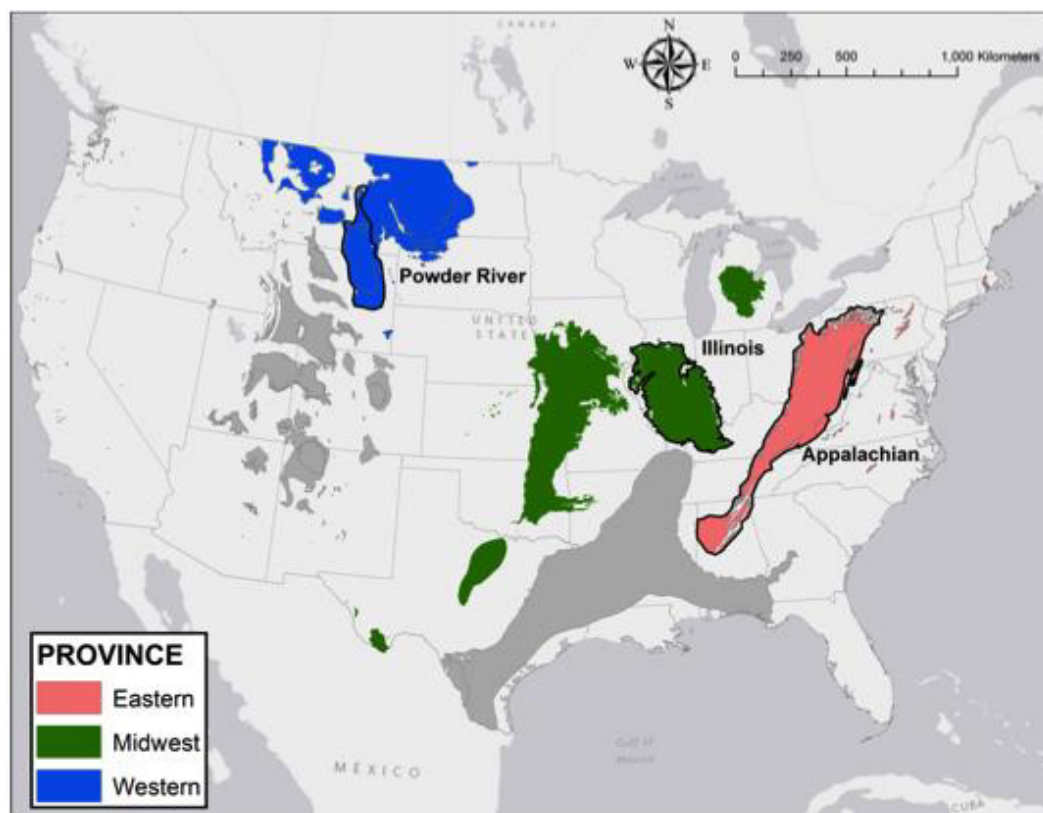


Figure 1. Map of major coal U.S. coal basins. The color of each basin corresponds to the region (Eastern, Midwestern or Western). Sources basins for the coal analysed this in this study are outlined in black.

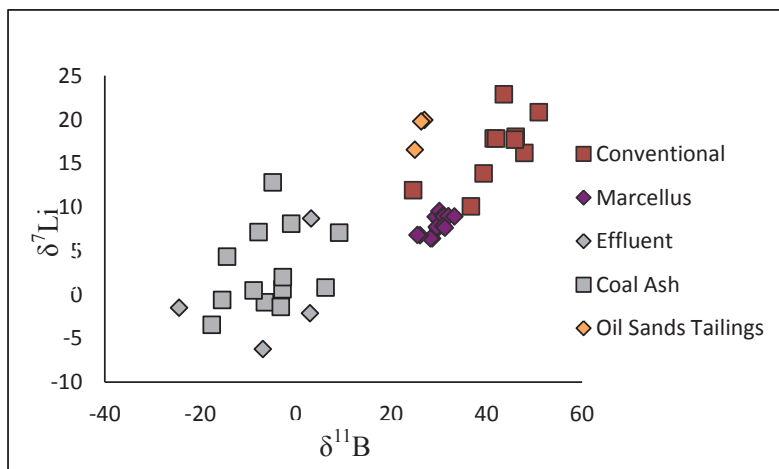
2. Methods

Coal and fly ash samples were collected from coal-fired power and steam plants burning coals from the Appalachian, Illinois, and Powder River Basins in the U.S. (Figure 1). CCR samples were provided by Tennessee Valley Authority (coal plants John Sevier, Bull Run, and Kingston), Duke University Steam Plant, and Jim Hower of the University of Kentucky. Effluents samples from outfalls of coal ash effluent were collected from Hyco Lake, Mayo Lake, Lake Norman, Mountain Island Lake, Lake Wylie, Dan River and the French Broad River in North Carolina.

Coal and coal combustion residuals were leached with DI water and analyzed for inorganic chemistry and isotopes according to EPA Method 1316. Lithium isotopes were measured by using the Neptune MC-ICP-MS in BRGM, France. $^7\text{Li}/^6\text{Li}$ ratios were normalized to the L-SVEC standard solution (NIST SRM 8545)⁹ and presented as $\delta^7\text{Li}$. Long-term replicate measurements of NIST SRM 8545 standard yielded a precision of 0.5‰.

3. Results

Lithium isotopes were measured in leaching solutions extracted from CCRs and coals originated from the Appalachian Basin, Illinois Basin, and Powder River Basin. The $\delta^7\text{Li}$ values vary from -7 to +12.8‰, with an average of +1.6‰ for all CCRs effluents. CCRs from the Powder River Basin (n=3) had elevated $\delta^7\text{Li}$ (mean = +7.6±5.4‰) relative to the Appalachian (n=7) and the Illinois Basins (n=7) (+0.3‰± 6.6 and -0.1‰±1.2,



The integration of lithium and boron isotopes⁷ provides a unique tool for distinguishing CCR contaminants

Figure 3. Boron and lithium isotopes for coal and coal combustion residual leachates and effluents compared to other fossil fuel-associated waters. Coal products and the resulting discharged effluents are isotopically distinct from oil and gas related waters, which makes boron and lithium isotopes useful tools to fingerprint fossil fuel contaminations sources. Boron values of CCRs and coal from Ruhl et al. (2014)⁷ and isotopes values for Marcellus FF and conventional PW from Warner et al. (2013).¹⁰

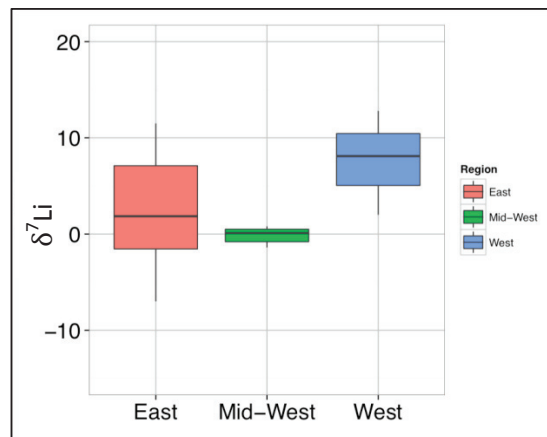


Figure 2. Range of lithium isotope ratios for coal ash from different regions in the U.S. Box plot represents the median (bold line), the top and bottom of the box present the first and third quartiles, respectively and the whiskers represent the maximum and minimum values. Coal ash from the west basin has elevated $\delta^7\text{Li}$ (mean = 7.6‰, n=3) compared to the Mid-West (mean=-0.1‰, n=7) and East (mean = 0.3‰, n=7) basins. Total range of lithium isotopes is -

respectively; Fig. 1). Leaching of unprocessed coals (n=3) from the Appalachian Basin yielded a mean $\delta^7\text{Li}$ of +6.0±6.1‰. In addition, effluents were collected from six coal ash ponds in North Carolina that store CCRs from coal plants burning Appalachian coals. The effluents showed a $\delta^7\text{Li}$ range of -6.2 to +8.7‰, which is similar to the CCR leaching results and suggesting a limited isotope fractionation of lithium during storage in surface impoundments.

from oil and gas wastewater, including conventional produced waters and hydraulic fracturing flowback fluids. Both coals and CCRs have lower $\delta^7\text{Li}$

and $\delta^{11}\text{B}$ values compared to oil and gas wastewaters¹⁰ as well as oil sands process-affected water (Figure 2).

4. Conclusions

Both experimental leaching and field data reveal that coals and CCRs are characterized by a distinctive lithium isotope signature, which could be useful for tracing contaminated waters in the environment. The relatively low $\delta^7\text{Li}$ values in coals and CCRs are associated with also low $\delta^{11}\text{B}$, which together could be applied to evaluate and quantify contributions of effluents from coal ponds in receiving waters. The multi-isotope approach is particularly useful when distinguishing between more than two sources. Coal ash ponds and coal mining are often located in areas where other fossil fuel developments are taking place. For example, the rapid rise of hydraulic fracturing in the Marcellus Basin has raised concerns about impact on water quality in areas near shale gas development. Given the long legacy of contamination from subsurface and surface mining in some areas there is a need for a robust tool for distinguishing between old and new contamination. Isotope fingerprints of different fossil fuel-impacted water sources could be a valuable tool for delineating these different sources and determining their differential impact on water resources.

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