High molybdenum in Wisconsin wells not from coal ash

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Example of molybdenum ore in rock matrix. Credit: Avner Vengosh, Duke University

When high levels of the trace element molybdenum (mah-LIB-den-um) were discovered in drinking-water wells in southeastern Wisconsin, the region's numerous coal ash disposal sites seemed to be a likely source of the contamination.

But some fine-grained detective work led by researchers from Duke University and The Ohio State University has revealed that the ponds, which contain the residues of coal burned in power plants, are not the source of the contamination.

It stems from natural sources instead.

"Based on tests using forensic isotopic 'fingerprinting' and age-dating techniques, our results offer independent evidence that coal ash is not the source of contamination in the water," said Avner Vengosh, professor of geochemistry and water quality at Duke's Nicholas School of the Environment.

"If this molybdenum-rich water had come from the leaching of coal ash, it would be relatively young, having been recharged into the region's groundwater aquifer from coal ash deposits on the surface only 20 or 30 years ago," Vengosh said. "Instead, our tests show it comes from deep underground and is more than 300 years old."

The tests also revealed that the contaminated water's isotopic fingerprint—its precise ratios of boron and strontium isotopes—did not match the isotopic fingerprints of coal combustion residuals.

These findings "de-link" the molybdenum from the coal ash disposal sites and instead suggest it is the result of natural processes occurring in the aquifer's rock matrix, said Jennifer S. Harkness, a postdoctoral researcher at Ohio State who led the study as part of her doctoral dissertation at Duke.

The researchers published their peer-reviewed paper this month in the journal *Environmental Science & Technology*.

Small quantities of molybdenum are essential to both animal and plant life, but people who ingest too much of it run the risk of problems that include anemia, joint pain and tremors.

Some of the wells tested in southeastern Wisconsin contained up to 149 micrograms of molybdenum per liter, slightly more than twice the safe drinking level standard of the World Health Organization, which is 70 micrograms per liter. The U.S. Environmental Protection Agency sets the limit even lower at 40 micrograms per liter.

To conduct the new study, Harkness and her colleagues used forensic tracers to determine the ratios of boron to strontium isotopes in each of the water samples. They also measured each sample's tritium and helium radioactive isotopes, which have constant decay rates and can be used to evaluate a sample's age, or "residence time" in groundwater. By integrating these two sets of findings, the scientists were able to piece together detailed information about the groundwater history, including when it first infiltrated the aquifer, and which types of rocks it had interacted with over time.

"This analysis revealed that the high-molybdenum water did not originate from coal ash deposits on the surface, but rather resulted from molybdenum-rich minerals in the aquifer matrix and environmental conditions in the deep aquifer that allowed for the release of this molybdenum into the groundwater," Harkness explained.

"What's unique about this research project is that it integrates two different methods—isotopic fingerprints and age-dating—into one study," she said.

Although the study focused on drinking water wells in Wisconsin, its findings are potentially applicable to other regions with similar geologies.

Thomas H. Darrah, associate professor of earth sciences at Ohio State, is Harkness's postdoctoral advisor at Ohio State and was a co-author of the new study.

More information: Jennifer S. Harkness et al, Naturally Occurring versus Anthropogenic Sources of Elevated Molybdenum in Groundwater: Evidence for Geogenic Contamination from Southeast Wisconsin, United States, *Environmental Science & Technology* (2017). DOI: 10.1021/acs.est.7b03716

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