

Occurrence of Metals and Leaching characteristics of Coal Ash from Punta Catalina in Dominican Republic

Zhen Wang, Avner Vengosh

Nicholas School of the Environment, Duke University, Durham, North Carolina, USA

Abstract

This report provides the results of investigation of the occurrence of trace metals and in a coal ash sample we received from the Punta Catalina power station, also known as the Hatillo power station, is a 752-megawatt (MW) coal-fired power plant in Punta Catalina-Hatillo, Azua, Dominican Republic. We conducted systematic leaching experiments of the coal ash sample following the United States Environmental Protection Agency's (U.S. EPA) integrated leaching evaluation system, known as Leaching Environmental Assessment Framework (LEAF). The concentrations of toxic elements such as arsenic (As), selenium (Se), molybdenum (Mo), antimony (Sb), and thallium (Tl) in the investigated coal ash sample are significantly higher than those in common soil. A comparison of the bulk concentrations of elements to a U.S. fly ash sample sourced from the Appalachian Basin coals shows that most of the elements in the coal ash from Punta Catalina have lower concentrations (except calcium and boron), most likely reflecting mix-sources of fly ash and bottom ash, as evidenced also by the coarser particles size of the coal ash sample. The relatively lower concentration of trace elements in the coal ash is also reflected by the results of the LEAF leaching experiments that show overall lower concentrations of elements in the leachates as compared to concentrations in the leachates generate from the U.S. fly ash. Nonetheless, the concentrations of certain toxic heavy metals in the leachates, including molybdenum, selenium, lithium, thallium, barium, and lead, exceed some of the drinking water and ecological thresholds values of the World Health Organization (WHO), the U.S. EPA Maximum Drinking Water Level (MCL), and the U.S. EPA National Recommended Aquatic Life Criteria for chronic exposure (CCC). Therefore, uncontrolled management and release of the coal ash from Punta Catalina plant to the environment and water resources poses high environmental and human health risks.

1. Introduction

The United States Environmental Protection Agency's (U.S. EPA) integrated leaching evaluation system, known as Leaching Environmental Assessment Framework (LEAF), consists of four leaching methods designed to provide a description of the release of inorganic constituents of potential concern (COPCs) for a wide range of solid materials. Two of these

methods were performed on the coal ash sample from Dominican Republic to assess trace element leaching under a range of pH values (LEAF Method 1313) and liquid-to-solid ratios (LEAF Method 1316). The data are presented below with the comparison to a fly ash sample from a coal power plant in the United States. We received a single coal ash sample from Punta Catalina power station in Dominican Republic, collected by Enrique de León (National Committee for the Fight Against Climate Change, CNLCC and Institute of Lawyers for the Protection of the Environment, INSAPROMA).

2. Methods

LEAF Method 1316 is an equilibrium-based leaching test intended to evaluate a range of liquid-to-solid ratios (US EPA, 2017a). Six high density polyethylene (HDPE) bottles were prepared for each ash sample, including five bottles with liquid to solid (L/S) ratios of 0.5, 1, 2, 5, and 10 (mL/g-dry), and one method blank containing only 20 mL deionized (DI) water. These were shaken on a New Brunswick Scientific C1 Platform Shaker at 180 rpm for 24 h at room temperature.

LEAF Method 1313 is designed to evaluate the partitioning of constituents between liquid and solid phases at or near equilibrium conditions over a wide range of pH values (US EPA, 2017b). In the current study, extraction fluids with target pH values ranging from 2 to 13 (i.e. 2, 3, 4, 5.5, 7, 9, 10.5, 12, 12.6) were prepared through titration of 0.01M HNO₃ and 0.01M NaOH solutions. Nine HDPE bottles were prepared for each ash sample, plus three additional bottles for a DI blank, a NaOH solution blank, and a HNO₃ solution blank. Pre-weighed ash samples were mixed with extraction fluid at a L/S ratio of 10:1 (mL/g-dry) in HDPE bottles and then shaken on a New Brunswick Scientific C1 Platform Shaker at 180 rpm for 24 h at room temperature.

For both methods, leachates were extracted using 5-mL metal-free syringes equipped with 0.45- μ m syringe filter units and then stored in acid-washed HDPE bottles. pH values were measured with a pre-calibrated YSI pH probe immediately after the extraction. For the leachates from the LEAF Method 1313, a 5-mL aliquot was taken for the measurement of hexavalent chromium (Cr(VI)) via an anion exchange chromatography on a Thermo Scientific Dionex IonPac AS7 column (4 mm \times 250 mm) according to EPA Method 218.6 (Environmental Monitoring Systems Laboratory, 1996). The rest of the extracted leachates were further acidified with HNO₃

to pH < 2 for storage prior to trace element analysis on a Thermo Fisher X-Series II inductively coupled plasma mass spectrometer (ICP-MS). The method detection limit (MDL) for each analyzed trace element was calculated by the mean determined concentration plus three times the standard deviation of a set of method blanks (US EPA, 2016). The MDLs for all the analyzed trace elements are listed in Table 1. It should be noted that the elemental concentrations that are below the corresponding MDL were substituted with a positive value just below the MDL to make plotting possible (Appendix data table). For reference, the U.S. EPA maximum contaminant level (MCL) in drinking water (US EPA, 2015a), the U.S. EPA criterion continuous concentration (CCC) for freshwater aquatic life (US EPA, 2015b), and the World Health Organization (WHO) guideline values (GLV) for drinking water quality (WHO, 2008) are also listed in Table 1. In addition to leaching experiments, the coal ash sample was subjected to full digestion in a hydrofluoric acid (HF) and nitric acid (HNO₃) mixture, from which the bulk chemistry (major and trace elements) was determined on ICP-MS.(Wang et al., 2020) The QA/QC was achieved by measuring a coal fly ash standard, SRM 1633c, from National Institute of Standards and Technology (NIST).

Table 1. Method detection limit (MDL), U.S. EPA maximum contaminant level (MCL) in drinking water, U.S. EPA criterion continuous concentration (CCC) for freshwater aquatic life, and WHO guideline value for drinking water for the analyzed trace elements (in µg/L). * CCC for Cr(VI).

Elements	Li	B	V	Cr	Mn	Co	Ni	Cu	Zn	As
MDL	0.000	2.542	0.055	0.374	0.329	0.017	0.131	3.705	3.948	0.011
USEPA MCL				100				1300		10
WHO GLV		500		50	400		20	2000		10
USEPA CCC				11*			52		120	150
Elements	Se	Rb	Sr	Mo	Cd	Sb	Ba	Tl	Pb	
MDL	0.021	0.032	0.011	0.000	0.000	0.011	0.344	0.000	0.137	
USEPA MCL	50				5	6	2000	2	15	
WHO GLV	10			70	3	20	700		10	
USEPA CCC					0.72				3.2	

3. Results

3.1. Bulk metals in coal ash

The bulk chemistry data of the coal ash sample (DO) from Punta Catalina power station are presented in the Appendix data table. As shown in Figure 1, most of the trace elements analyzed in the DO coal ash sample are depleted relative to the U.S. fly ash sample sourced from

the Appalachian Basin coals (BRFA), except for calcium and boron, which are relatively enriched in the DO coal ash. The lower metals concentrations in the DO sample could reflect possible mixture of bottom ash and fly ash in the sample, which is also reflected by a relatively larger particle size of the DO coal ash sample as compared to common fly ash. A comparison of the bulk concentrations of metals in DO coal ash sample to the average values of metals in North Carolina soils (Figure 2) show systematic relative enrichment of some of the toxic elements, particularly As, Se, Sr, Mo, and Tl (Figure 2).

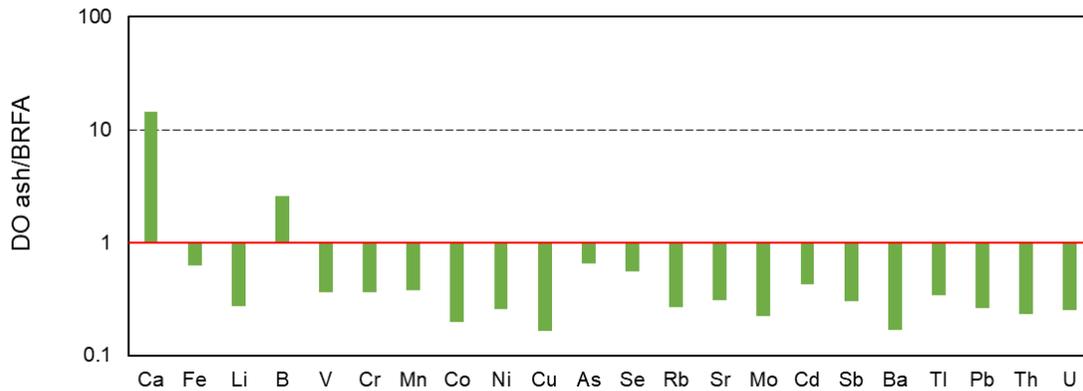


Figure 1. Comparison of bulk concentrations of trace elements in the DO coal ash sample with the U.S. fly ash sample.

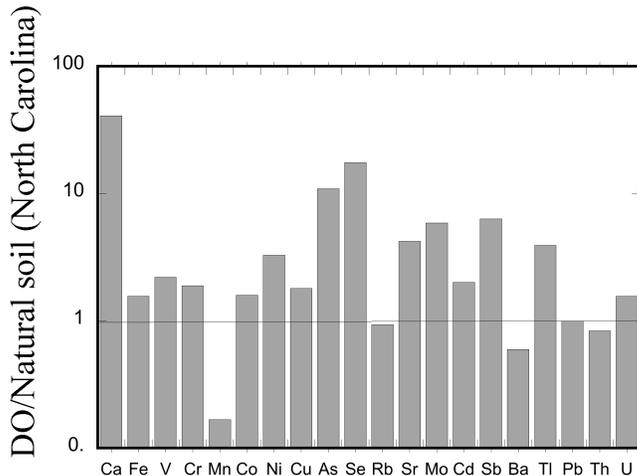


Figure 2. Comparison of bulk concentrations of trace elements in the DO coal ash sample with the average values of metals in North Carolina Soils.

3.2. *Leaching characteristics as a function of L/S ratio (LEAF Method 1316)*

The final pH values of the extracted leachates for the DO coal ash sample as well as the U.S. fly ash sample over the entire liquid to solid (L/S) range are shown in Figure 3. The post-leaching pH values of the DO ash are relatively stable, higher than that of BRFA. Given the “natural pH” of coal ash is generally defined as the final pH when the ash is extracted with DI water at a L/S ratio of 10 mL/g (Kosson et al., 2010), the DO ash sample is classified as alkaline ash.

Despite slight variations, all the elements plotted in Figure 3 exhibit an overall similar leaching behavior over the range of liquid-to-solid (L/S) ratios between 0.5 and 10 mL/g. The concentrations of trace elements (i.e., Sb, Mo, Se, Cu, As, V, and Cr) in the leachates of the DO ash are relatively stable as the L/S ratio increases, and are lower than that of BRFA, which correspond to the relatively depletion of these elements in the bulk coal ash as compared to the U.S. fly ash (Figure 1).

Unlike the relatively stable trend for the elements shown in Figure 3, the elements plotted in Figure 4 exhibit some variations over the entire L/S range. The concentrations of Mn and Ni have the highest concentration at L/S ratio of 0.5, which decrease to the level of MDL at L/S ratios of 0.5, 2, and 5, and then see an increase at L/S ratio of 10. The other elements, including Li, Tl, Ba, Pb, Rb, and Sr, display a notable decreasing trend as the L/S ratio increases, reflecting the “dilution effect”. As compared to the respective screening levels recommended by the U.S. EPA and WHO listed in Table 1, the data show Tl, Ba, and Pb concentrations in the leachates exceed at least one of the drinking water (WHO or MCL) and ecological screening levels (Figure 4).

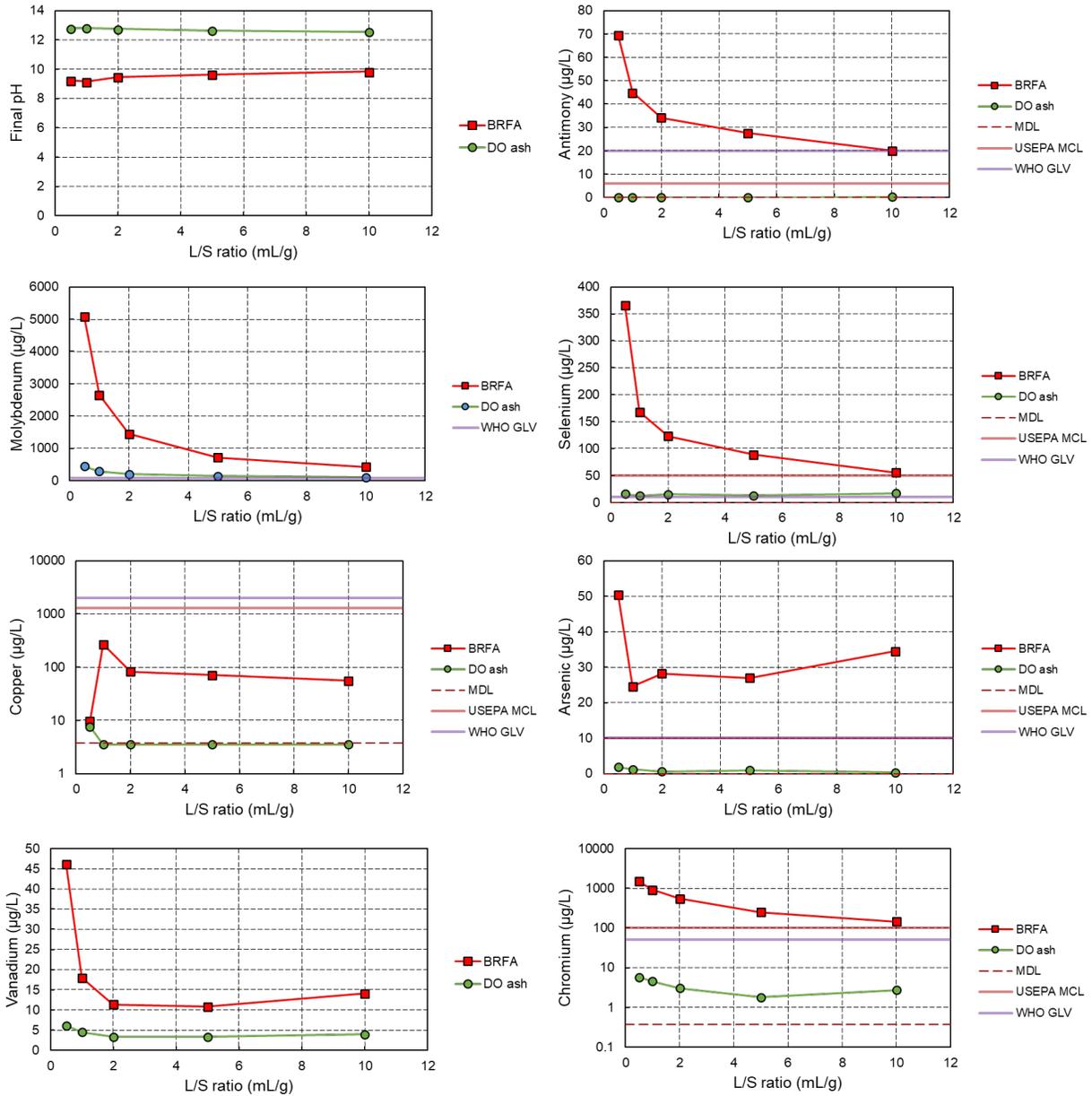


Figure 3. Final pH values and concentrations ($\mu\text{g/L}$) of selected elements in the leachates over a range of liquid-to-solid (L/S) ratios under the LEAF Method 1316. MDL, U.S. EPA MCL, WHO GLV, and U.S. EPA CCC are plotted where available (Table 1).

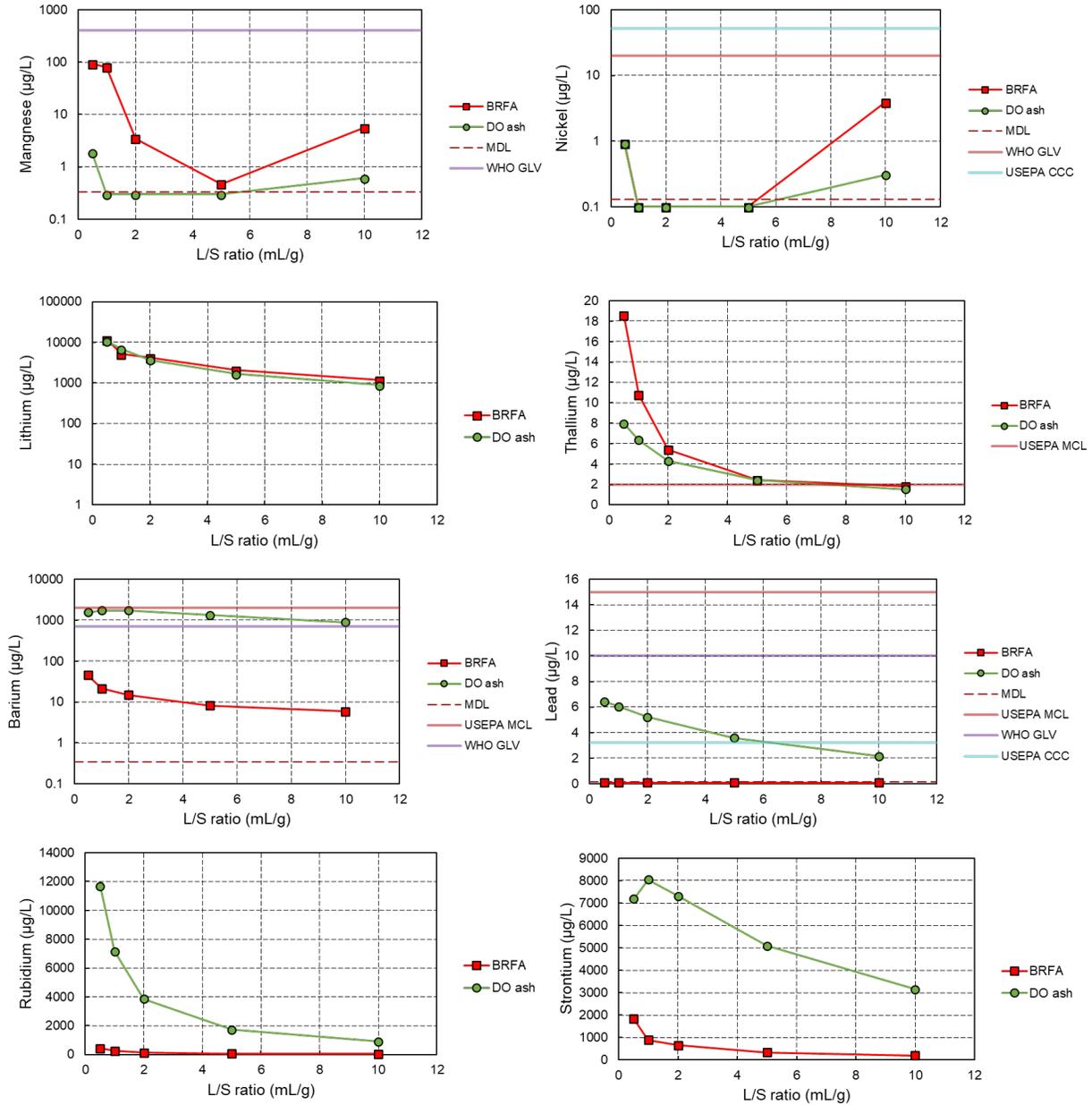


Figure 4. Concentrations (µg/L) of selected elements in the leachates over a range of liquid-to-solid (L/S) ratios under the LEAF Method 1316. MDL, U.S. EPA MCL, WHO GLV, and U.S. EPA CCC are plotted where available (Table 2).

3.3. Leaching characteristics as a function of pH value (LEAF Method 1313)

The final pH values of the extracted leachates for the DO ash sample as well as the U.S. fly ash sample BRFA over the entire initial leaching pH range are shown in Figure 5. The final pH of the leachate is a function of the natural pH of the ash sample and the initial leaching pH of the

extraction liquid added to it (US EPA, 2017b; Zhao et al., 2020). The natural pH of coal ash controls its buffering capacity. The final pH values of the DO ash leachates are relatively stable over the entire range of initial pH, reflecting a strong buffering capacity that drags the leachate pH up to their own natural pH (determined by DI water leaching at L/S ratio of 10 mL/g) (Figure 3), even with the initial leaching pH being very acid, as low as 2.

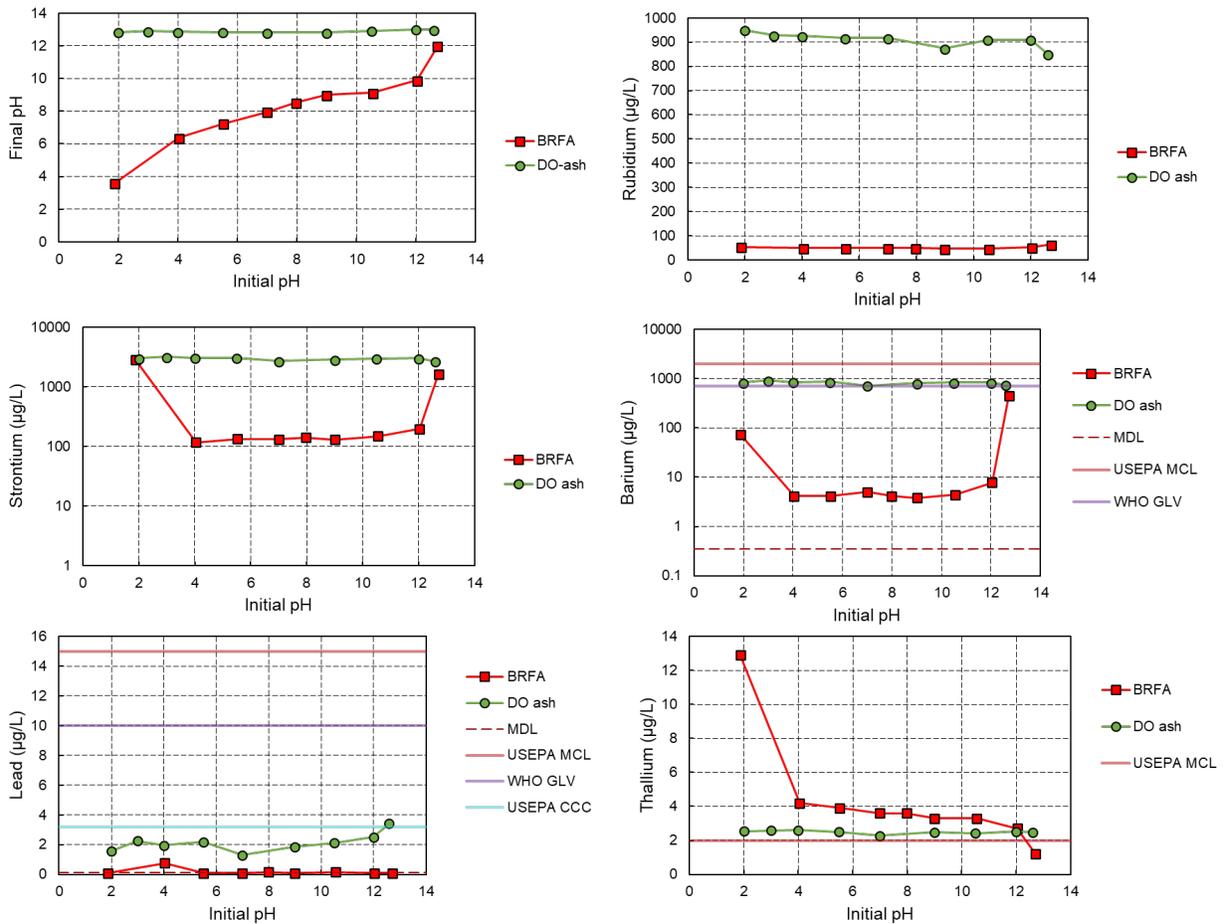


Figure 5. Final pH values and concentrations (µg/L) of selected elements in the leachates over a range of initial leaching pH values under the LEAF Method 1313. MDL, U.S. EPA MCL, WHO GLV, and U.S. EPA CCC are plotted where available (Table 2).

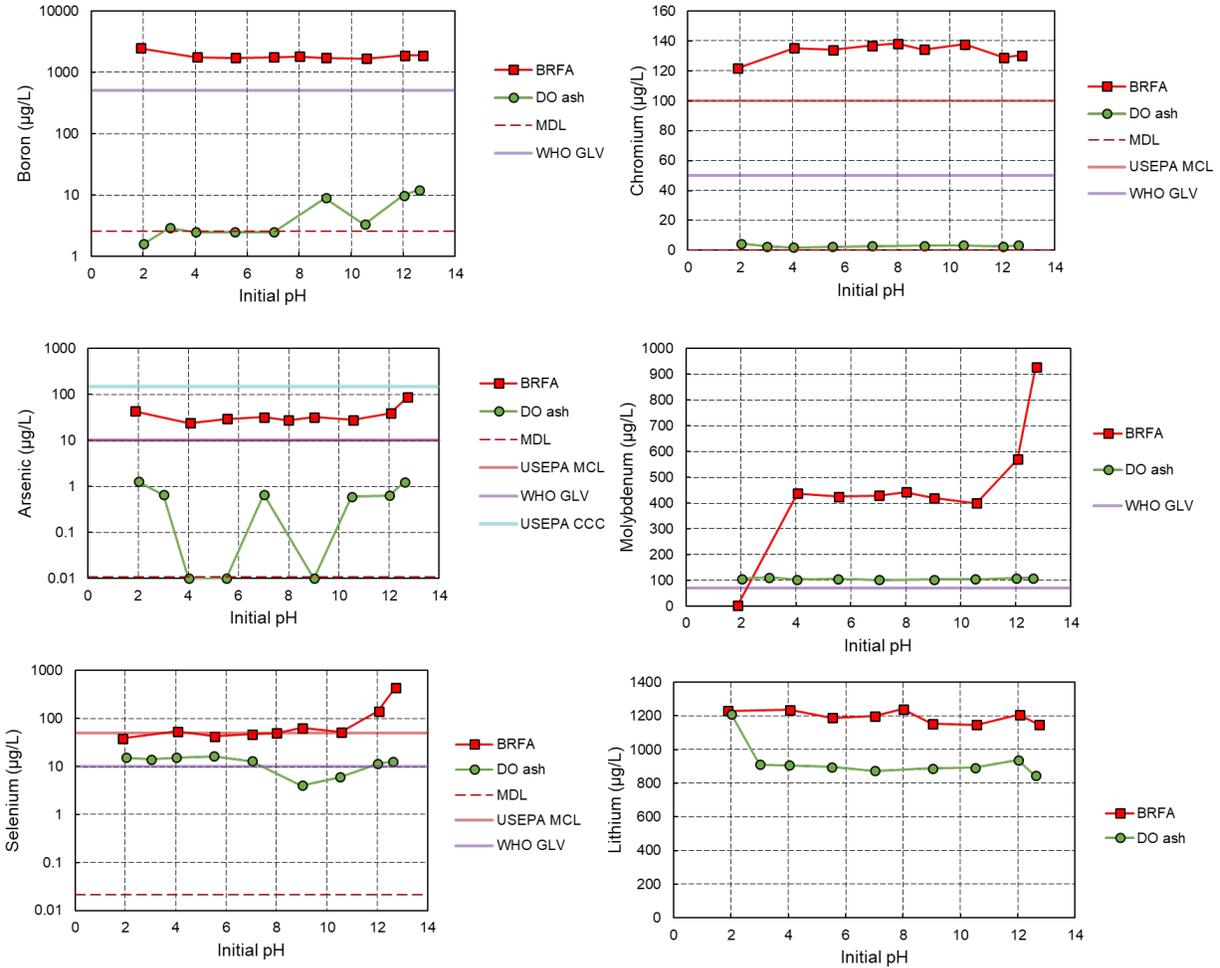


Figure 6. Concentrations ($\mu\text{g/L}$) of selected elements in the leachates over a range of initial leaching pH values under the LEAF Method 1313. MDL, U.S. EPA MCL, WHO GLV, and U.S. EPA CCC are plotted where available (Table 2).

Corresponding to the stable pH in the leachates, the concentrations of most of the elements in the leachates over the entire pH range are also stable (Figures 5 and 6). The concentrations of Rb, Sr, and Ba in the DO ash leachates are higher than that of the U.S. fly ash BRFA, while the rest of elements are generally lower in the DO ash leachates than that in the BRFA leachates (Figures 5 and 6). In comparison to the respective screening levels recommended by the U.S. EPA and WHO listed in Table 1, Ba, Tl, Mo, and Se concentrations in the DO ash leachates exceed the screening levels, whereas the rest of elements have lower concentrations than the screening levels.

4. Conclusions

By conducting the U.S. EPA LEAF leaching experiments on a single coal ash sample from the Punta Catalina power station in Dominican Republic, the current study presents a systematic characterization and evaluation of the occurrence of metals and leaching characteristics of a suite of trace elements under various pH conditions and liquid to solid ratios, as compared with the one U.S. fly ash samples. The concentrations of toxic elements such as As, Se, Mo, Sb, and Tl in the investigated coal ash sample are significantly higher than those in common soil as we compared the new data to the average metal concentration of North Carolina soils. The data show relatively lower concentration of metals in the coal ash sample as compared to the U.S. fly ash and therefore, the majority of trace elements exhibit different leaching trends for the DO ash than the U.S fly ash over the range of initial leaching pH values and L/S ratios. Nonetheless, the concentrations of certain toxic heavy metals in the leachates including Mo, Se, Li, Tl, Ba, and Pb exceed some of the drinking water and ecological thresholds values of the World Health Organization (WHO), the U.S. EPA Maximum Drinking Water Level (MCL), and the U.S. EPA National Recommended Aquatic Life Criteria for chronic exposure (CCC). Therefore, uncontrolled management and release of the coal ash from Punta Catalina plant to the environment and water resources poses high environmental and human health risks.

References

- Environmental Monitoring Systems Laboratory, 1996. DETERMINATION OF DISSOLVED HEXAVALENT CHROMIUM IN DRINKING WATER, GROUNDWATER, AND INDUSTRIAL WASTEWATER EFFLUENTS BY ION CHROMATOGRAPHY, in: *Methods for the Determination of Metals in Environmental Samples*. Elsevier, pp. 290–304. <https://doi.org/10.1016/B978-0-8155-1398-8.50016-1>
- Izquierdo, M., Querol, X., 2012. Leaching behaviour of elements from coal combustion fly ash: An overview. *International Journal of Coal Geology, Minerals and Trace Elements in Coal* 94, 54–66. <https://doi.org/10.1016/j.coal.2011.10.006>
- Kosson, D.S., Garrabrants, A., Sanchez, F., Kariher, P., Thorneloe, S., Helms, G., 2010. Use of a Leaching Assessment Framework for Evaluation of the Impacts of Coal Type and Facility Configuration on Beneficial Use Scenarios for Coal Combustion Residues.
- US EPA, O., 2017a. SW-846 Test Method 1316: Liquid-Solid Partitioning as a Function of Liquid-to-Solid Ratio in Solid Materials Using a Parallel Batch Procedure [WWW Document]. US EPA. URL <https://www.epa.gov/hw-sw846/sw-846-test-method-1316-liquid-solid-partitioning-function-liquid-solid-ratio-solid> (accessed 10.4.20).
- US EPA, O., 2017b. SW-846 Test Method 1313: Liquid-Solid Partitioning as a Function of Extract pH Using a Parallel Batch Extraction Procedure [WWW Document]. US EPA. URL

- <https://www.epa.gov/hw-sw846/sw-846-test-method-1313-liquid-solid-partitioning-function-extract-ph-using-parallel-batch> (accessed 8.16.20).
- US EPA, O., 2016. Definition and Procedure for the Determination of the Method Detection Limit, Revision 2 [WWW Document]. US EPA. URL <https://www.epa.gov/cwa-methods/method-detection-limit-frequent-questions> (accessed 10.4.20).
- US EPA, O., 2015a. National Primary Drinking Water Regulations [WWW Document]. US EPA. URL <https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations> (accessed 9.29.20).
- US EPA, O., 2015b. National Recommended Water Quality Criteria - Aquatic Life Criteria Table [WWW Document]. US EPA. URL <https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table> (accessed 10.4.20).
- Wang, Z., Coyte, R.M., Dwyer, G.S., Ruhl, L.S., Hsu-Kim, H., Hower, J.C., Vengosh, A., 2020. Distinction of strontium isotope ratios between water-soluble and bulk coal fly ash from the United States. *International Journal of Coal Geology* 222, 103464. <https://doi.org/10.1016/j.coal.2020.103464>
- WHO (Ed.), 2008. Guidelines for drinking-water quality, 3rd ed. ed. World Health Organization, Geneva.
- Zhao, L., Dai, S., Finkelman, R.B., French, D., Graham, I.T., Yang, Y., Li, J., Yang, P., 2020. Leaching behavior of trace elements from fly ashes of five Chinese coal power plants. *International Journal of Coal Geology* 219, 103381. <https://doi.org/10.1016/j.coal.2019.103381>