Performance and Risks of Acid Mine Drainage Neutralization with Fly Ash from India and the United States

By

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Executive Summary

Acid mine drainage (AMD) and coal ash disposal can affect the quality of surface and groundwater near mines and disposal sites. Water contamination from AMD is a major cause of environmental and water quality degradation in regions of coal mining in India and the United States. Coal ash contains heavy metals that can be mobilized into water and thus contaminate surface water and groundwater through leaking of coal ash ponds and landfills. Given that AMD is acidic, while coal ash is often alkaline, and both can pose environmental and human health risks, this study examines the possible use of coal ash as a medium for neutralizing the acidity of AMD.

The study aims to evaluate if interaction of AMD with coal ash would reduce the negative environmental impact of AMD. Fly ash samples from six locations in India and from the three major coal basins in the United States were used for neutralization experiments. Synthetic AMD was created in the lab to mimic the average pH and chemistry of AMD in India and the US. Through systematic laboratory experiments reacting fly ash with AMD at different liquid to solid ratios, I show that some types of calcium-rich fly ash can effectively neutralize AMD, with removal of some contaminants, but mobilization of other toxic elements from the fly ash into the neutralized AMD. The results show that fly ash samples from the US, which have higher calcium content, were more effective at neutralization than samples from India.

Concentration of toxic elements in the final leachate after neutralization was compared with human health and ecological standards from the US, India, and World Health Organization to identify potential environmental impacts of this method of AMD neutralization. While neutralization was achieved in many samples, the data show certain contaminants were retained in the AMD and others were mobilized from the fly ash samples from India and the US. Generally, the Indian fly ash samples that were able to reach a final pH within the neutral pH range (6.5-9) resulted in lower concentrations of toxic elements than fly ash samples from the US that reached the neutral pH range. These experimental results have implications for possible alternative technologies for AMD remediation in India, as well as coal ash disposal and management in the United States.

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1. Introduction

Mining and coal combustion have led to degradation of surface and groundwater worldwide. Coal remains the world's largest single source of electricity worldwide (WCA, 2020), and therefore effective methods to prevent water contamination from coal mining and combustion are necessary. Acid mine drainage (AMD) is formed in active and abandoned mine sites when pyrite (an iron sulfide mineral) is oxidized with the infiltration of meteoric water, which leads to the formation of sulfuric acid and dissolved iron in AMD. This acidic water causes the leaching of heavy metals from rocks. Water contaminated with AMD can become toxic for aquatic life, altering habitat through the precipitation of metals, and is often unsafe for domestic, agricultural, and industrial uses (Skousen et al., 2019).

In India, where coal is the most abundant energy source, coal mining and AMD have caused large ecological damage in areas near the coal mines and reduced the availability of clean water for domestic uses (Chabukdhara and Singh, 2016). While coal mining has caused environmental degradation, it has also led to economic development (Tiwary, 2001). The growing economy and population in India are expected to further increase demand for electricity, and therefore, expected to increase coal production and utilization (Chabukdhara and Singh, 2016).

Previous studies have examined the impact of AMD on human and ecological health in India, finding water and sediment contaminated with toxic metals, low pH and high sulfate effluents, reduction of clean water availability, and chronic health conditions in residents living near coal mines (Chabukdhara and Singh, 2016; Dutta et al., 2020; Rinchin et al., 2017; Sahoo et al., 2016; Sangita and Prasad, 2010; Singh and Sinha, 1992; Swer and Singh, 2003; Swer and Singh, 2004; Tiwary, 2001). Many studies have focused on the northeast region of India due to the abundant coal deposits and low pH of AMD in the region. In northeastern India, AMD is contaminating drinking water resources (Chabukdhara and Singh, 2016), and therefore, the Indian Ministry of Coal is looking for a solution. For example, in the Jaintia Hills district of Meghalaya, AMD with a pH between 2-3, high levels of sulfate, iron, and heavy metals is impacting local water sources and causing a major drinking water quality issue (Swer and Singh, 2003). Furthermore, low pH and water quality impairments in the region have led to biodiversity loss, including a fish kills in the Lukha River (Chabukdhara and Singh, 2016; Swer and Singh, 2003). A survey of 600 people living within 5km of coal mines in Ramgarh, India, where toxic metals were also found in the environment, revealed that residents near coal mines were twice as likely to have upper respiratory diseases, and three to four times as likely to have eye, skin, and hair diseases (Rinchin et al., 2017).

While issues of AMD are more widespread and have a greater impact on local communities in India, the United States is also facing environmental degradation from AMD. Although coal mining is declining in the United States, issues of AMD continue to affect the environment due to the persistent nature of AMD pollution (Sangita and Prasad, 2010; Skousen et al., 2000). In the US, AMD pollutes over 20,000 km of streams (Skousen et al., 2019), and the US Environmental Protection Agency (EPA) considers the ecological risks from AMD to be "second only to global warming and ozone depletion" (Acharya and Kharel, 2020). A study in Lee County, VA, where coal mining has occurred since the 1800s, found pH levels in surrounding surface waters ranging from 2.73 to 5.2, with high metal concentrations throughout the watershed, leading to low benthic macroinvertebrate numbers in areas impacted by the low pH water (Cherry et al., 2001). Gammons et al. (2010) studied the Great Falls-Lewistown Coal Field in central Montana, one of the few coal basins in the west with AMD runoff issues, and found that the pH ranged from 3.1 to 3.5, with high sulfate concentrations and the presence of iron, aluminum, zinc, nickel, manganese, cobalt, copper and cadmium in the AMD.

Coal ash is one of the largest sources of industrial solid waste in the United States, with over 100 million tons produced each year (US EPA, 2015a). While some coal ash is put to beneficial use, about ~60% of the annual produced coal ash is often stored in impoundments and landfills adjacent to waterways (Vengosh et al., 2019). Coal ash contains high concentrations of heavy metals that tend to be leached out upon interaction with water. Research in the US has shown surface water and groundwater contamination by leaking of coal ash ponds throughout the southeast (Harkness et al., 2016; Vengosh et al., 2019). Major coals ash spills have occurred in Kingston, Tennessee (Cowan et al., 2013; Cowan et al., 2015; Ruhl et al., 2009; Ruhl et al., 2010; Ruhl et al., 2014) and along the Dan River, North Carolina (Cowan et al., 2017; Shin et al., 2017; Yang et al., 2015). In India, fly ash generation has been increasing and is currently at about 200 million tons of fly ash generated each year. While some fly ash goes to beneficial use, the rest must be disposed of in a safe manner and is available for AMD neutralization (Yousuf et al., 2020).

While both AMD and coal ash can damage the environment and pose human health risks, this study examines the possible use of coal ash as a medium to neutralize the acidity of AMD. Previous studies have shown that some fly ashes tend to produce high pH effluent upon interaction with water, and therefore, fly ash can potentially be used as a medium to neutralize low-pH AMD (Gitari et al., 2006; Gitari et al., 2010). Previous studies have also indicated that the composition of fly ash and AMD influences the efficacy and sustainability of AMD neutralization by fly ash (Gitari et al., 2006; Qureshi et al., 2016). Therefore, it is critical to examine the fly ash and AMD of the specific region in order to evaluate the potential use of fly ash for AMD neutralization.

In the United States, mines throughout all the major coal basins have already begun placing coal combustions wastes in active and abandoned coal mines (Skousen et al., 2012; Ziemkiewicz & Knox, 2006). Studies on areas where high-pH coal ash has been used for mine reclamation through soil amendments, pit lake filling, sealing pit floor, grouting and capping, generally show an increase in pH, but varying results with respect to the impact on water and soil quality (Skousen et al., 2012). In Clinton County, PA the reclamation of a 15-ha surface coal mine included grouting and capping using fly ash. Through groundwater monitoring in 42 wells, it was found that grouting has led to increase in pH and reduction of pollutant loads (Skousen et al., 2012). A National Academy of Sciences study, has found that there was insufficient water quality data near coal mines where coal ash was disposed, and therefore could not determine if coal combustion residue (CCR) placement in coal mines might result in improvement, or degradation of water quality (National Academy of Sciences, 2006). Due to lack of sufficient research, specifically focused on contamination from CRR placed in mine sites in the US, this master's project evaluates the ability of different fly ash samples, derived from coals originating from the major coal basins in the United States, to neutralized AMD.

The objectives of this study are to determine the performance and risks of using different types of fly ash from India and the United States as an alternative medium used to neutralize the acidity of AMD from different regions in India and the United States. The study design includes investigation of the required AMD to fly ash liquid to solid (L/S) ratios for successful neutralization of AMD, and examination of the water quality consequences upon interaction of AMD with fly ash. Controlled lab experiments in which fly ash from different coal plants in India and the US were mixed with synthetic AMD for 24 hours at different L/S ratios were conducted. pH was measured throughout the experiments and trace element variations in the leachates generated from these experiments were analyzed. The study investigates the relationships between fly ash chemistry and neutralization potential, aiming to develop a framework for understanding the neutralization potential of the different types of fly ash in India and the US. The study also examines the performance and risk of using fly ash as a medium for neutralization by evaluating the concentration of trace elements in the leachate generated from the AMD-fly ash reaction experiments in comparison to human health and ecological standards.

2. Literature Review

Previous studies have examined the neutralization capacity of different fly ashes and the leaching potential of major and trace elements upon interaction of AMD with fly ash (Dutta et al., 2009; Gitari et al., 2006; Kim, 1999; Pérez-López et al., 2007; Qureshi et al., 2016; Ziemkiewicz & Knox, 2006). These studies have shown that the mineralogical and chemical compositions of the fly ash control its buffering capacity and the neutralization potential upon interaction with AMD. Additionally, it was found that the ratios of AMD to fly ash and reaction duration are important factors that control the performance of fly ash as a medium for neuralization. Previous studies have also shown general improvement in the quality of the treated AMD, with pH shifting from acidic towards neutral pH in the treated water (Backstrom and Sartz, 2011; Gitari 2006; Jia, 2014; Prasad and Mortimer, 2011; Perez-Lopez, 2007, 2009).

There are multiple ways in which fly ash can reduce the toxicity of AMD, including neutralization, bacterial inhibition, and pyrite encapsulation to prevent contact with oxidizing agents (Bulusu et al., 2007; Kim, 1999; Pérez-López et al., 2007), but most experiments have focused on the neutralization potential. Column leaching studies and batch titrations have been used to examine the leachability of elements in different pH ranges, as fly ash is mixed with AMD (Bäckström & Sartz, 2011; Gitari et al., 2008; Kim, 1999; Pérez-López et al., 2007; Qureshi et al., 2016). Some studies have utilized collected fly ash generally from coal power plants with simulated AMD developed in the lab, or actual samples of AMD from the field. The results of the lab experiments have shown general improvement in the quality of mine drainage through neutralization or encapsulation, but leaching of trace elements from fly ash still occurred

(Bäckström & Sartz, 2011; Gitari et al., 2008; Kim, 1999; Pérez-López et al., 2007; Qureshi et al., 2016).

Prasad and Mortimer (2011) converted fresh fly ash from power plants in India to zeolites, which were used to treat AMD from the United Kingdom. Their results indicated that the raw fly ash was not effective at removing metals, except Pb, from mine waters but rather resulted in the leaching of metals from the fly ash to mine water. The greater surface area of the zeolite proved to be more effective at removing trace metals from acid mine water, especially when a larger amount of zeolite were added into the mixture (Prasad & Mortimer, 2011).

Gitari et al (2006) examined the optimal ratios and contact time to maximize removal of contaminants when using coal fly ashes to neutralize AMD in South Africa. Both fly ash and AMD (pH 2.39 – 2.92) were collected in the field prior to conducting batch neutralization in the lab with a contact time between 120 and 360 minutes. They determined that the fly ash to AMD ratio, contact time, and chemical composition of the AMD would control the removal of contaminants from AMD and the final solution composition (Gitari et al., 2006). Additionally, their conclusions highlight a high removal of major and trace elements from two AMD samples, which was directly linked to the amount of fly ash used and the final pH (Gitari et al., 2006).

The leaching of elements from fly ash from West Bengal, India was studied by Dutta et al. (2009) to determine its potential for back-filling of abandoned mines. They conducted batch leaching with solutions with a wide range of pH values, at different L/S ratios and contact times. The fly ash samples had differed in alkalinity because of the concentrations and mobility of Ca, Na, and K, which influenced the change in pH throughout the experiments. Their experiments have shown that toxic heavy metals were considerably mobilized from fly ash under acidic conditions, but with much less mobility when final pH values reached neutral or alkaline conditions (Dutta et al., 2009).

A comparison of lab and field studies in West Virginia, where fly ash has been used to treat AMD was conducted by Ziemkiewicz & Knox (2006). This study has showen that the variations of multiple chemical parameters in the leachates, including pH, acidity, Al, As, Fe, and Mn were successfully predicted in the lab experiments, while others water quality parameters such as conductivity, sulfate, Ca, Pb, and Cr were not (Ziemkiewicz & Knox, 2006). This information is valuable to understand the extent that lab studies can predict the results of fly ash and AMD interaction in the field.

In addition to using fly ash, AMD has been treated with active "conventional" treatments, such as limestone and lime (Prasad & Mortimer, 2011), as well as passive treatments such as utilizing solid residue produced by active treatment (Gitari et al., 2008) and biological metal removal (Cheong et al., 1998). Active treatments utilize CaO, $CaCO_3$, NaOH, Na_2CO_3, $Ca(OH)_2$, NH_3 to neutralize AMD and have been shown to cause metals to precipitate out (Acharya and Kharel, 2020; RoyChowdhury et al., 2015). While NaOH and Na_2CO_3 have high neutralization efficiency, they are expensive chemicals, whereas CaO, $Ca(OH)_2$, and NH_3, are more cost effective, but require intensive monitoring and storage, and can present human health issues (Acharya and Kharel, 2020). Passive treatments, which are more applicable for abandoned mines, include wetlands, vertical flow systems, and limestone drains, channels, ponds, sand beds, and diversion wells (Acharya and Kharel, 2020). Passive treatments often provide less control over the outcomes and a high cost of waste disposal, but require less maintenance and lower operating costs (RoyChowdhury et al., 2015; Acharya and Kharel, 2020). Whereas active treatments require continuous maintenance and expensive chemicals, but they are efficient and don't require extra space (RoyChowdhury et al., 2015). Efficacy of treatment methods will differ based on site-specific characteristics (Acharya and Kharel, 2020; RoyChowdhury et al., 2015) and therefore no treatment method can be deemed the most effective for all mines. Kalin et al., (2005) compared active and passive methods and found that passive systems have the potential to have the least negative environmental impacts because conventional liming treatments produces secondary waste with high concentrations of metals (Kalin et al., 2005). Based on challenges with both active and passive treatment of AMD, as well as fly ash disposal, fly ash for treatment of AMD has the potential to provide a more cost effective and efficient method for the treatment of the two different wastes, fly ash and AMD, through one treatment process.

3. Methods

3.1 Materials

Fly ash samples from 6 different locations in India (n=6) and 3 different basins in the United States (n= 7) were used for the neutralization experiments (Table 1).

Table 1. Source and location for fly ash samples used in leaching experiments.

Name	Type	Power Plant	Location
India 1	Fly Ash	Local brick plant	Namchik-Namphuk, Arunachal Pradesh, India
India 2	Fly Ash	Chandrapur Super Thermal Power Station	Chandrapur, Maharastra, India
India 3	Fly Ash	Satpura Thermal Power Station	Betul, Madhya Pradesh, India
India 4	Fly Ash	Koradi Thermal Power Station	Nagpur, Maharashtra, India
India 5	Fly Ash	Vindhyachal Super Thermal Power Station	Singrauli, Madhya Pradesh, India
India 6	Fly Ash	Local brick plant	West Daranggiri, Meghalaya, India
Appalachia 1	Fly Ash	E.W. Brown	Kentucky, United States
Appalachia 2	Fly Ash	Big Sandy	Kentucky, United States
Appalachia 3	Fly Ash	TVA Bull Run Fossil Plant	Tennessee, United States
Illinois 1	Fly Ash	Trimble	Kentucky, United States
Illinois 2	Fly Ash	E.W. Brown	Kentucky, United States
Illinois 3	Fly Ash	Trimble	Kentucky, United States
Powder River	Fly Ash	Meramec	Missouri, United States

Synthetic AMD solution was created in the lab to mimic the average pH and chemistry of an AMD sample from Gorbi, India (Table 2). Synthetic AMD for the different coal basins in the US was generated in the lab based on literature data on average pH and chemistry of AMD from each of the basins (Table 3, Cravotta, 2008a,b; Behum et al., 2011; Gammons et al., 2010). Literature with other synthetic AMD recipes was also reviewed (Coetser et al., 2006; Kondash et al., 2013). pH and chemistry data of AMD from Illinois (Behum et al., 2011) were similar to those of the AMD sample from Gorbi, India and therefore the same AMD solution was used for both Illinois and India leaching experiments (Table 2). Gammons et al., (2010) have found that chemistry of AMD in the west is similar to that documented in Pennsylvania (Cravotta, 2008a), but the average pH is lower. Therefore, the same synthetic AMD chemistry was used for the Powder River and Appalachia leaching experiments, but the pH was adjusted for each basin using sulfuric acid to lower the pH and sodium hydroxide to raise the pH (Table 4). The synthetic AMD used for the India fly ash experiments mimics the composition of the actual

AMD sample from Gorbi, India. The synthetic AMD for Appalachia, Illinois, and Powder River Basin were developed based on literature data on the composition of AMD from these regions.

Table 2. ICP-MS and IC Data for the AMD sample from Gorbi, India. All units are ppb (µg/L).

Sample	pH	Li	B	Na	Mg	Al	K	Ca	V	Cr
Gorbi AMD	2.4	180	1.34	43400	82100	111513	3000	236000	0.57	31.2
		V	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**
Gorbi AMD	2.4	0.57	31.2	8833	22481	1534	2564	61.2	7356	12.6
		Se	**Rb**	**Sr**	**Mo**	**Ag**	**Cd**	**Sb**	**Ba**	**Tl**
Gorbi AMD	2.4	168	30.4	949	*bdl*	*bdl*	6.33	*bdl*	*bdl*	8.22
		Pb	**Th**	**U**	**F**	**Cl**	**NO3**	**SO4**	**NH4**	
Gorbi AMD	2.4	29.9	7.36	10.4	3400	8100	8400	1830000	5240	

Table 3. 50th percentile of AMD discharges from 140 abandoned coal mines in Pennsylvania, 1999 (Cravotta III, 2008). Data were used to develop synthetic AMD. All units are ppb (µg/L).

Sample	pH	Al	B	Br	Ca	Cl	Co	Fe	Li
Appalachia AMD 50th %	5.2	1250	44	36	88000	7300	58	32000	69
		Mg	**Mn**	**K**	**Si**	**Na**	**Sr**	**SO4**	
Appalachia AMD 50th %	5.2	38000	2350	2800	7900	15000	720	520000	

Table 4. Recipe for each synthetic AMD. The same synthetic AMD was used for India and Illinois because the chemistry of natural AMD from the two regions are similar. The same AMD at different pH values was used for Appalachia and Powder River. Sulfuric acid or sodium hydroxide were added until desired pH was achieved.

India/Illinois

	g/L
NaCl	0.11
FeSo4X7H20	0.061
Al2(SO4)3	0.707
MgSO4xH20	0.407
CaSO4x2H2O	0.802
MnSO4	0.024
Sulfuric Acid	

Appalachia Low

	g/L
NaCl	0.0190
FeSo4X7H20	0.1593
CaSO4x2H2O	0.3780
MgSO4xH20	0.2163
Na2SO4	0.0232
Sulfuric Acid	

Appalachia High

	g/L
NaCl	0.0190
FeSo4X7H20	0.1593
CaSO4x2H2O	0.3780
MgSO4xH20	0.2163
Na2SO4	0.0232
Sodium Hydroxide	

3.2 Experimental Design

Batch neutralization experiments were carried out at room temperature for 24 hours in acid washed 60ml bottles. The experimental design was based on the EPA LEAF method 1316 (US EPA, 2017); 20 mL of synthetic AMD was mixed with fly ash at L/S ratios of 3:1, 5:1, 10:1, and 20:1. Bottles of AMD and fly ash mixture were shaken on a New Brunswick Scientific C1 Platform Shaker at 180 rpm for 24 hours at room temperature. pH was measured at 1, 3, 6, 9, 12, and 24 hours after the beginning of the experiment using a pre-calibrated pH probe. Following 24 hours, leachate was extracted and separated from the coal ash using a 30-mL metal-free syringe with 0.45-µm filters and stored in acid-washed HDPE bottles (Vengosh et al., 2019). Final pH of the extracted leachate was measured, and then samples were acidified with nitric acid to pH <2 and stored at 4 °C refrigerator until the ICP-MS and cation IC analysis. Aliquots of leachate samples were also taken for anion and chromium IC analyses

3.3 Analytical Methods

Anions were measured by ion chromatography (IC) on a Dionex IC DX-2100 instrument; major cations were measured by cation IC and trace elements by a Thermo Fisher X-Series II inductively coupled plasma mass spectrometer (ICP-MS). The ICP-MS instruments were calibrated to the National Institute of Standards and Technology 1643e standard. The detection limit of ICP-MS for each element was determined by dividing 3 times the standard deviation of repeated blank measurements by the slope of the external standard (Vengosh et al., 2016).

Final pH was plotted over 24 hours to determine which samples reached circumneutral. For our results, we defined circumneutral as pH = 6.5-9 based on EPA aquatic life and drinking water standards (US EPA, 2015b; US EPA, 2015c) and examined samples within and slightly outside the range to account for error in pH readings (i.e., pH analytical error of ±1 unit). Bulk chemistry data of each fly ash sample was compared with final pH value to determine which elements in the fly ash influence neutralization potential. Spearman correlation was used to calculate correlation (rho) and p-value because data were not normally distributed. Final concentrations of elements in samples that reached a pH > 6.2 were analyzed in comparison to final pH and concentrations in initial AMD. The US EPA sets human health (US EPA, 2015b) and ecological standards (US EPA, 2015c) for toxic elements, the Bureau of Indian Standards sets drinking water specifications (BIS, 2012) and the World Health Organization (WHO, 2017) sets guidelines values (GLV) for drinking water quality, which were compared with the results from each leaching experiment to determine the impact on people and the environment (Table 5).

Table 5. US EPA maximum contaminant level (MCL) in drinking water, US EPA criterion continuous concentration (CCC) for freshwater aquatic life, India drinking water specification 2nd revision (BIS), and WHO 4th edition guideline value (WHO) for drinking water for the analyzed trace elements (in µg/L).

Elements	*B*	*Cr*	*Mg*	*Al*	*Mn*	*Ni*	*Cu*	*Zn*	*As*	*Ca*
US EPA MCL		100					1300		10	
WHO GLV 4th	2400	50				70	2000		10	
BIS	500	50	30000	30	100	20	50	5000	10	75000
US EPA CCC		11 (Cr(VI))				52		120	150	
Elements	**Fe**	***Se***	***Mo***	***Cd***	***Sb***	***Ba***	***Tl***	***Pb***	**U**	
US EPA MCL		50		5	6	2000	2	15		
WHO GLV 4th		40		3	20	700		10	30 P	
BIS	300	10	70	3		700		10		
US EPA CCC	1000			0.72				2.5		

4. Results

4.1 Neutralization Capacity of Fly Ash

Several fly ash samples evaluated in this study successfully neutralized AMD during the 24 hour reaction time, whereas other samples did not, despite low L/S ratios of AMD to fly ash. Though experiments were conducted for 24hrs, the majority of pH change occurred within the first hour (Fig 1). The AMD to fly ash ratio (L/S ratio) seems to affect the neutralization potential for multiple of the Indian ashes, but had less of an effect on the US fly ash samples. Overall, fly ash samples from India were less effective at neutralization than those from the US (Fig 2; Fig 3). Only 2 Indian fly ash-AMD mixtures successfully reached pH > 6.5, at the 3:1 L/S ratio, and no Indian fly ash samples reached neutral pH at the 10:1 L/S ratio (Fig 2).

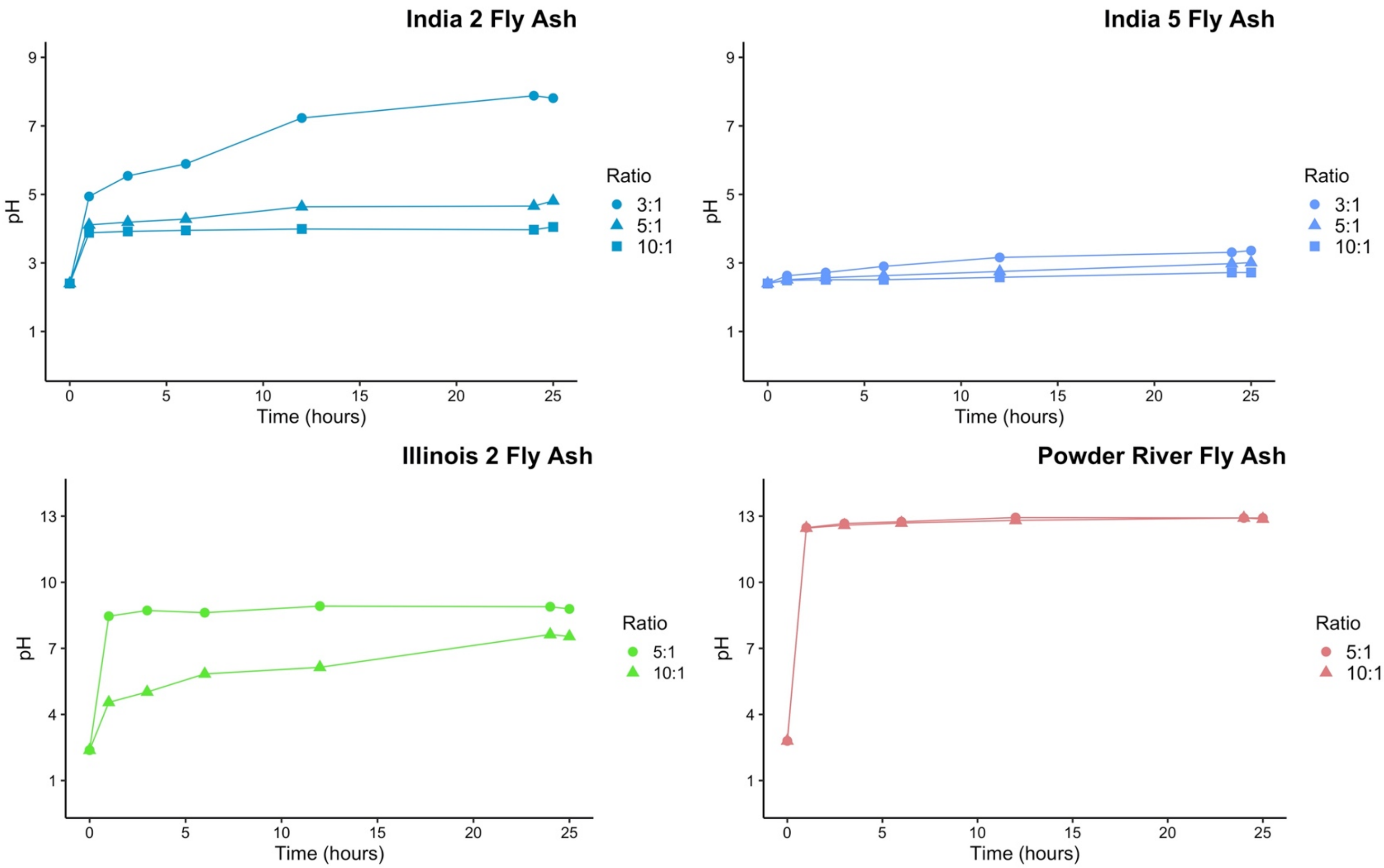


Figure 1. pH over time with mixtures of synthetic AMD and fly ash from India and the United States at different L/S ratios.

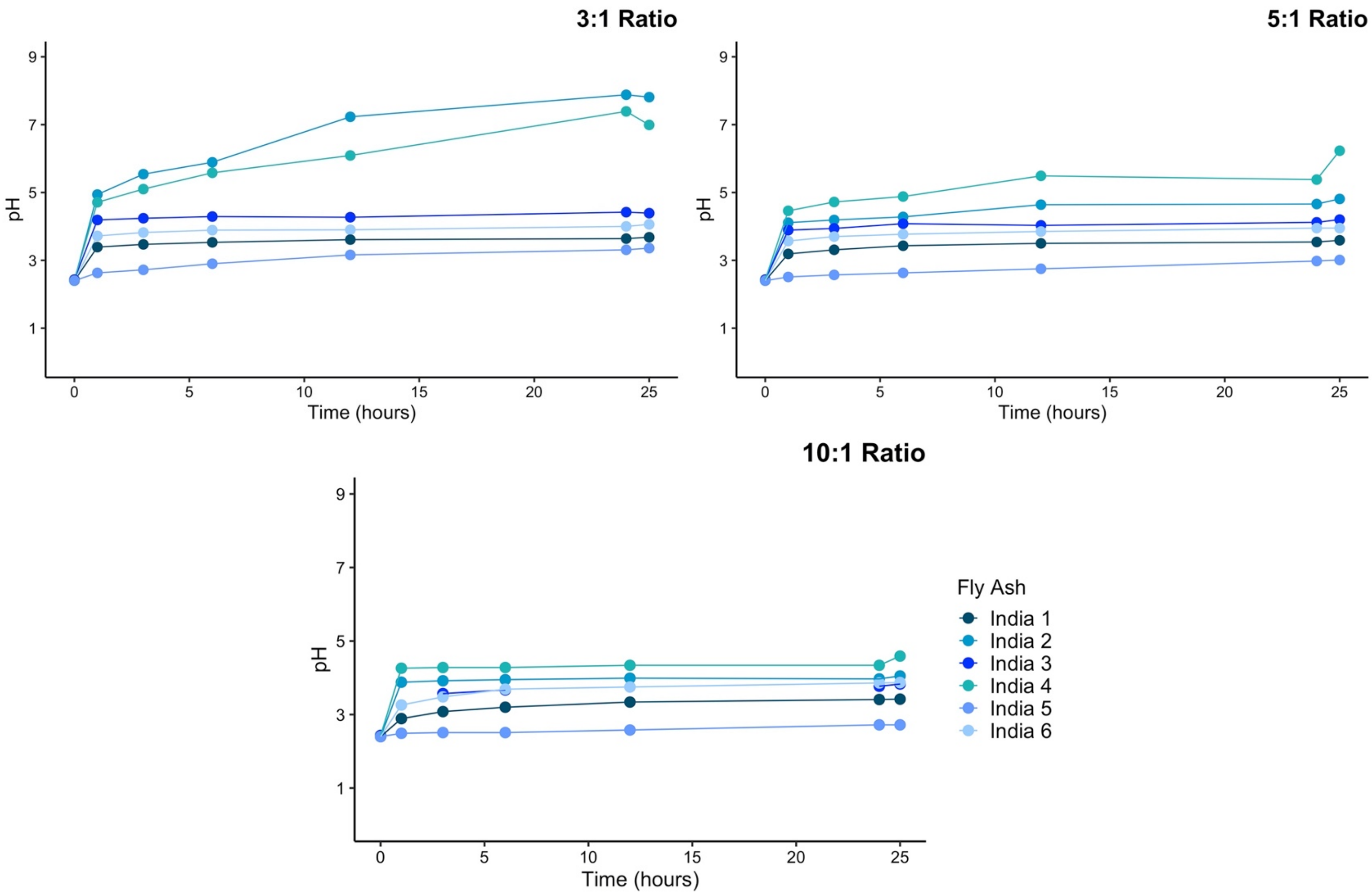


Figure 2. pH of India fly ashes mixed with synthetic India AMD over time and at different L/S ratios.

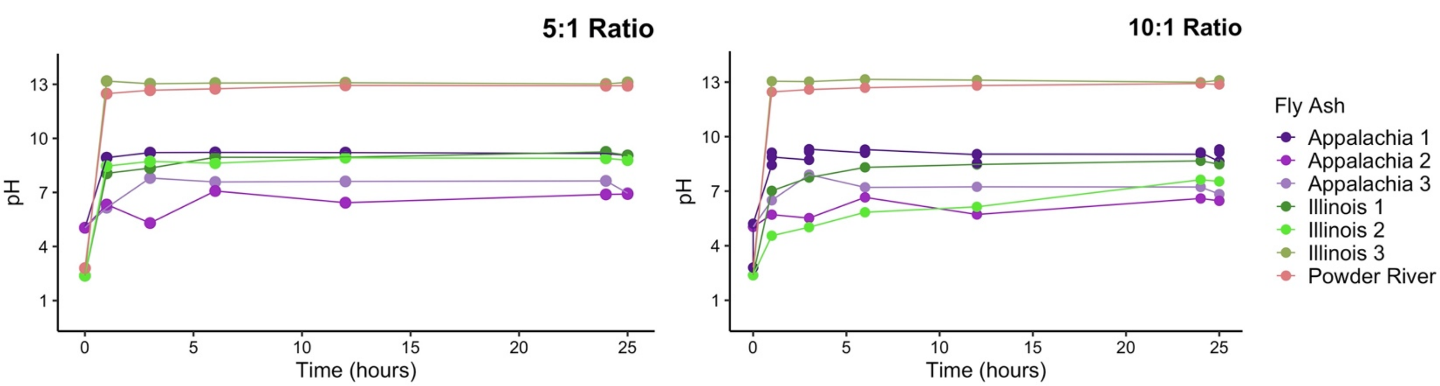


Figure 3. pH of fly ash from three different basins in the United States mixed with synthetic AMD over time and at different L/S ratios.

The chemical composition of the fly ash was found to be an important factor for the neutralization capacity of AMD by fly ash. The results of AMD-fly ash interaction of six fly ash samples from India and seven samples from the US show a significant (p-values< 0.001; Table 6) correlation between magnesium and calcium in the fly ash solids and final pH of the leachates (Table 7; Table 9). High concentrations of calcium in fly ash was associated with higher final pH, regardless of the initial pH of the AMD (Fig 4). At Ca concentration of ~9,000 mg/kg samples started to reach a neutral pH at the 10:1 L/S ratio, but the two India fly ash samples with Ca content slightly above that concentration were unable to neutralize the AMD. The only two Indian fly ash samples that successfully neutralized AMD were India 2 and India 4, which had the highest Ca concentrations of the six India fly ash samples.

Table 6. Spearman correlation coefficient and p-value for correlation between concentration of magnesium and calcium in the solid fly ash and final pH value of leachate. Correlation was calculated in samples with a 10:1 L/S ratio.

	Final pH	
Element	Correlation Coefficient (rho)	p-value
Mg	0.85	0.0004354
Ca	0.83	0.0007779

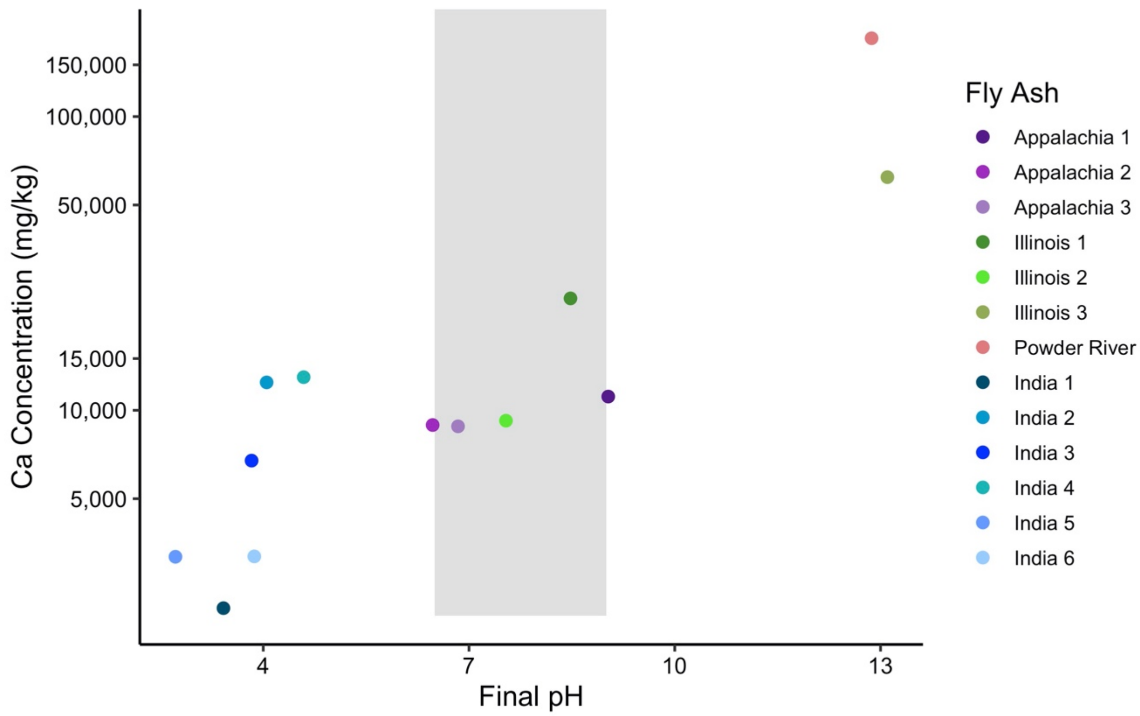


Figure 4. Concentration of calcium in fly ash compared with final pH of leachate at a L/S ratio of 10:1. Gray box indicates circumneutral pH range from 6.5-9.

4.2 Enrichment of Trace Elements in the Leachates

4.2.1 INDIA

Analysis of major and trace elements in leachate was conducted on samples that reached a pH > 6.2 upon interaction with the Indian fly ash. Enrichment and depletion of both major and trace elements relative to the initial synthetic AMD solution occurred during the interaction of the India fly ash samples with the synthetic AMD (Table 7). Aluminum and sodium were depleted during the interaction, while magnesium, and calcium became relatively enriched in the leachates (Fig 5). Manganese was depleted for all samples that reached neutral pH, except India 4 fly ash at the 5:1 ratio, which had the lowest pH value of the samples analyzed (pH = 6.23). The synthetic AMD had low trace element concentrations, and therefore most of the trace elements in the leachates were enriched due to mobilization upon interaction with the fly ash (Table 7). Iron was the only trace element that was depleted in all of the samples (Fig 6). Lead was also depleted in the two India 4 fly ash samples at a 3:1 and 5:1 L/S ratio, but was slightly enriched in the India 2 sample (Fig 6).

Table 7. Final concentration of major (ppm) and trace elements (ppb) after India fly ash and AMD leaching experiments. All experiments ran for 24 hours.

Major Elements (ppm)

Fly Ash	AMD	Ratio	Initial pH	Final pH	Na	Mg	Al	Ca	Mn
India 4	India	3:1	2.4	6.99	40.0	70.1	1.18	742	3.62
India 4	India	5:1	2.4	6.23	42.9	67.4	1.87	649	11.2
India 2	India	3:1	2.4	7.81	44.4	49.7	2.02	619	2.67
AMD	India		2.4	2.4	43.8	44.5	99.4	229	8.64

Trace Elements (ppb)

Fly Ash	AMD	Ratio	Initial pH	Final pH	Li	B	V	Cr	Fe	Co	Ni	Cu	Zn	As
India 4	India	3:1	2.4	6.99	1269	5062	20.0	53.3	< 216	4.84	9.08	3.03	0.00	2.42
India 4	India	5:1	2.4	6.23	865	4737	9.71	< 13.4	5186	48.5	169	6.07	72.2	2.43
India 2	India	3:1	2.4	7.81	523	4821	61.4	24.8	< 221	0.62	< 5.61	10.5	71.3	4.96
AMD	India		2.4	2.4	*bdl*	*bdl*	*bdl*	*bdl*	22533	0.62	*bdl*	*bdl*	*bdl*	0.62
					Se	**Rb**	**Sr**	**Mo**	**Cd**	**Sb**	**Ba**	**Tl**	**Pb**	**U**
India 4	India	3:1	2.4	6.99	35.7	< 11.5	270	442	0.61	5.45	19.4	< 0.04	7.27	< 0.03
India 4	India	5:1	2.4	6.23	10.3	13.4	828	100	3.64	4.25	31.0	0.61	7.89	< 0.03
India 2	India	3:1	2.4	7.81	17.4	15.5	1383	448	1.24	6.82	44.6	< 0.04	11.2	2.48
AMD	India		2.4	2.4	*bdl*	*bdl*	*bdl*	*bdl*	*bdl*	*bdl*	*bdl*	*bdl*	8.68	0.62

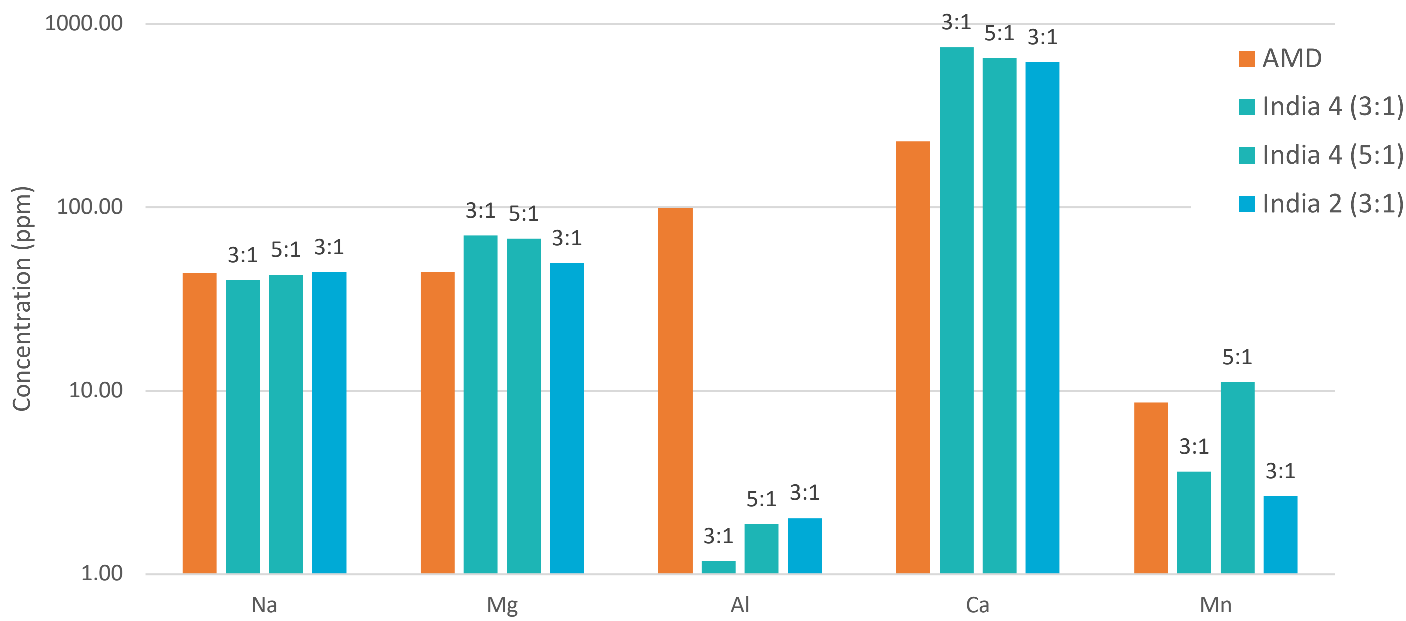


Figure 5. Initial and final concentration of major elements in synthetic AMD and leachate after 24hr leaching with two different fly ashes from India at different L/S ratios.

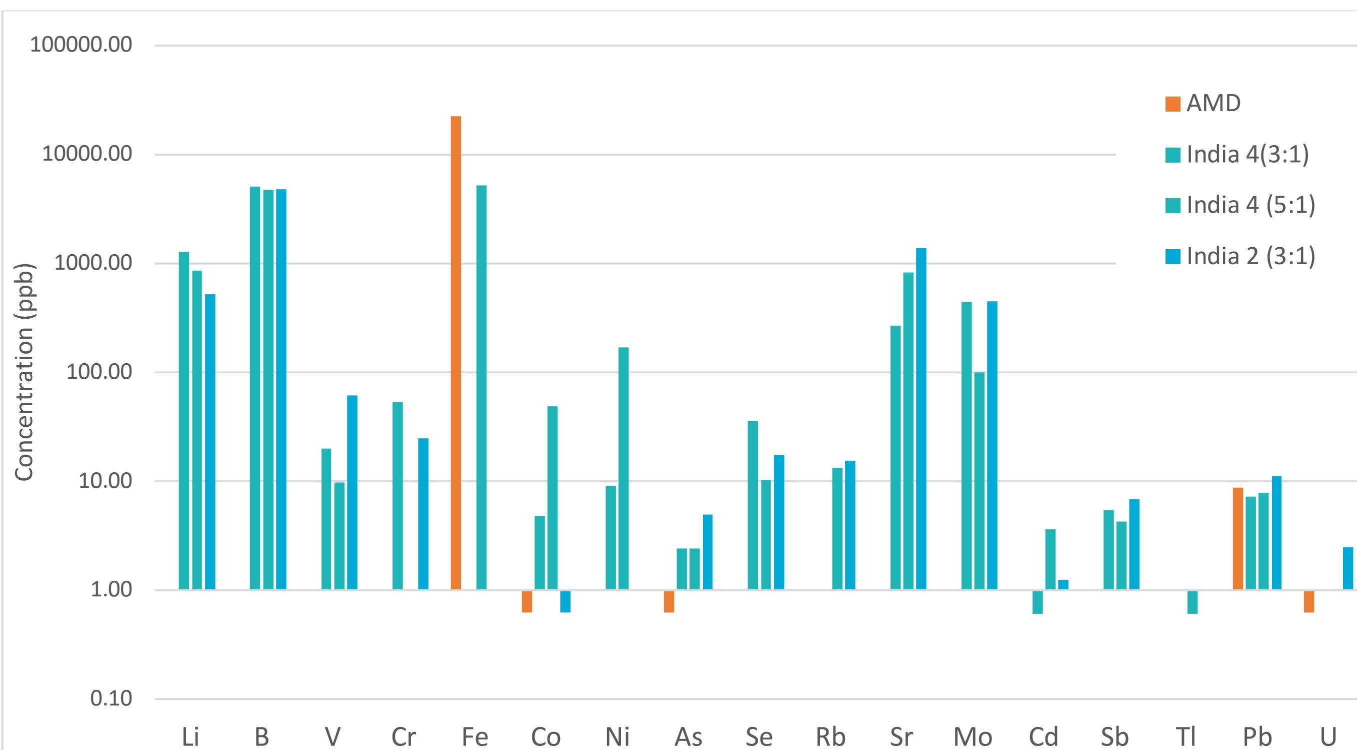


Figure 6. Initial and final concentration of trace elements in synthetic AMD and leachate after 24hr leaching with two different fly ashes from India at different L/S ratios (3:1, 5:1 from left to right).

Figure 7 shows the enrichment ratios (i.e the ratios of elements in the AMD relative to leachate) of the elements that were present in both the synthetic AMD and the final leachate. Values below 1 indicate that the element was removed from the AMD through neutralization with fly ash, while values above 1 indicate that the element was enriched upon interaction and mobilization from the fly ash (Fig 7; Table 8). Based on chemistry data from the actual AMD sample from India (Table 2), we determined the expected concentrations of different elements if this process was to be implemented in the field. We evaluated how much of each element was added through interaction with the synthetic AMD and added it to the concentration of each element measured in the AMD sample from Gorbi, India (Table 9). The values were compared with health and ecological standards (BIS 2012, EPA, 2015b; EPA, 2015c; WHO, 2017) to determine if they would have harmful impacts on the ecosystem and human health (Table 5).

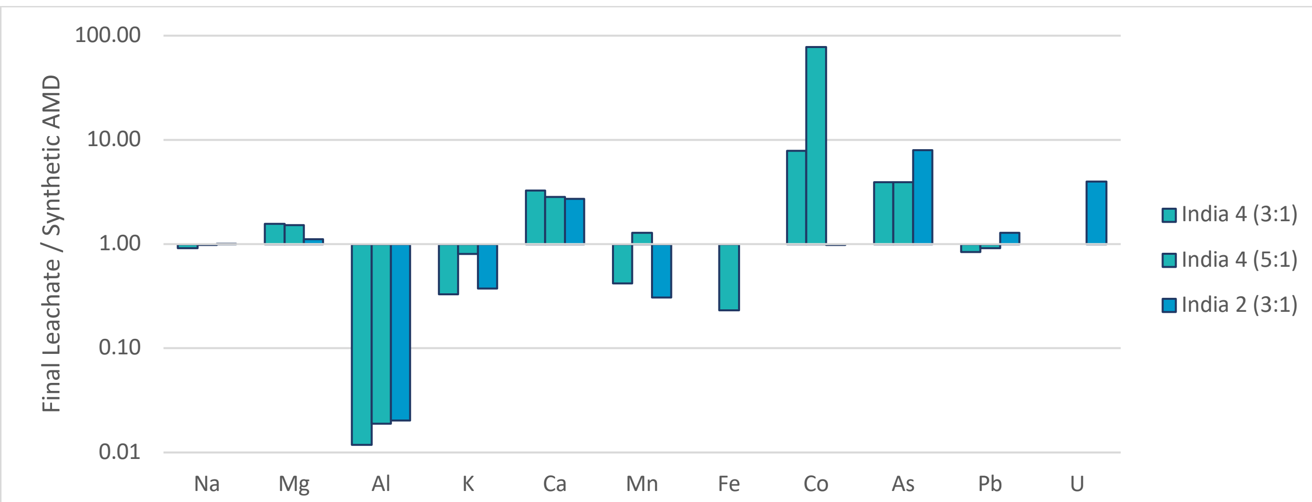


Figure 7. Enrichment of major and trace elements in leachate samples that reached a pH > 6.2 after 24hr leaching with two different fly ashes from India at different L/S ratios (3:1, 5:1 from left to right).

Table 8. Enrichment ratios of major and trace elements in leachate samples that reached a pH > 6.2 after 24hr leaching with two different fly ashes from India at different L/S ratios.

Fly Ash	AMD	Ratio	Initial pH	Final pH	Na	Mg	Al	K	Ca	Mn	Fe	Co	As	Pb	U
India 4	India	3:1	2.43	6.99	0.91	1.57	0.01	0.33	3.25	0.42	N/A	7.81	3.91	0.84	N/A
India 4	India	5:1	2.43	6.23	0.98	1.51	0.02	0.80	2.84	1.29	0.23	78.3	3.91	0.91	N/A
India 2	India	3:1	2.4	7.81	1.01	1.12	0.02	0.37	2.70	0.31	N/A	1.00	8.00	1.29	4.00

Table 9. Expected concentration of leachate when fly ash samples are mixed with natural AMD. Concentrations are calculated by adding the concentration of each element that was added to the synthetic AMD upon interaction with the fly ash to the original element concentrations in natural AMD. Negative numbers indicate more of the element was removed through interaction of fly ash and synthetic AMD than was originally present in the Gorbi, India AMD sample. All concentrations are ppb.

Fly Ash	Ratio	Initial pH	Final pH	Li	B	Na	Mg	Al	K	Ca	V	Cr
India 4	3:1	2.4	6.99	1397	5063	11632	88270	13294	-9959	719685	20.6	84.5
India 4	5:1	2.4	6.23	993	4738	14544	85617	13990	-1355	626485	10.3	31.2
India 2	3:1	2.4	7.81	652	4823	16138	67935	14140	-9177	595773	61.9	56.0
				Mn	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**As**	**Se**	**Pb**
India 4	3:1	2.4	6.99	3813	-52.4	1538	2573	61.2	7356	14.4	203	28.5
India 4	5:1	2.4	6.23	11355	5133	1582	2733	61.2	7356	14.4	178	29.1
India 2	3:1	2.4	7.81	2863	-52.4	1534	2564	61.2	7356	17.0	185	32.4
				Rb	**Sr**	**Mo**	**Ag**	**Cd**	**Sb**	**Ba**	**Tl**	**U**
India 4	3:1	2.4	6.99	30.5	1219	442	0.61	6.94	5.45	0.00	8.22	9.81
India 4	5:1	2.4	6.23	43.8	1778	100	2.43	9.97	4.25	0.00	8.82	9.81
India 2	3:1	2.4	7.81	45.9	2332	448	0.00	7.57	6.82	0.00	8.22	12.3

Figures 8 and 9 show the relationship between final pH (after 24 hour reaction) and concentration of major and trace elements. While calcium concentration in leachate increased with final pH, aluminum concentration decreased with pH (Fig 8). Lithium, boron, and antimony also showed clear increases with increased final pH, while iron levels decreased (Fig 9).

Arsenic concentrations were above human health and ecological standards at lower pH values, but in leachates that reached neutralization, arsenic concentrations were below all threshold values. Likewise, concentrations of antimony, thallium, zinc, copper, selenium and barium were not detected and/or below drinking water and ecological standards in most leachates at neutral pH. Lead and cadmium concentrations exceeded WHO drinking water standards, but were below EPA's drinking water standards. Most lead, chromium and cadmium concentrations were under the drinking water standards, but exceeded ecological standards (Fig 9). Many of the samples were above the Bureau of Indian Standards limits. Overall, the leaching experiments show that the successful neutralization of AMD with Ca-rich Indian coal ash would decrease concentrations of elements like calcium, iron, and aluminum in the effluents while the concentrations of toxic elements (e.g., arsenic) that leach out from the fly ash would, in most cases (except boron), remain below the EPA and WHO drinking water and ecological standards.

Major Elements

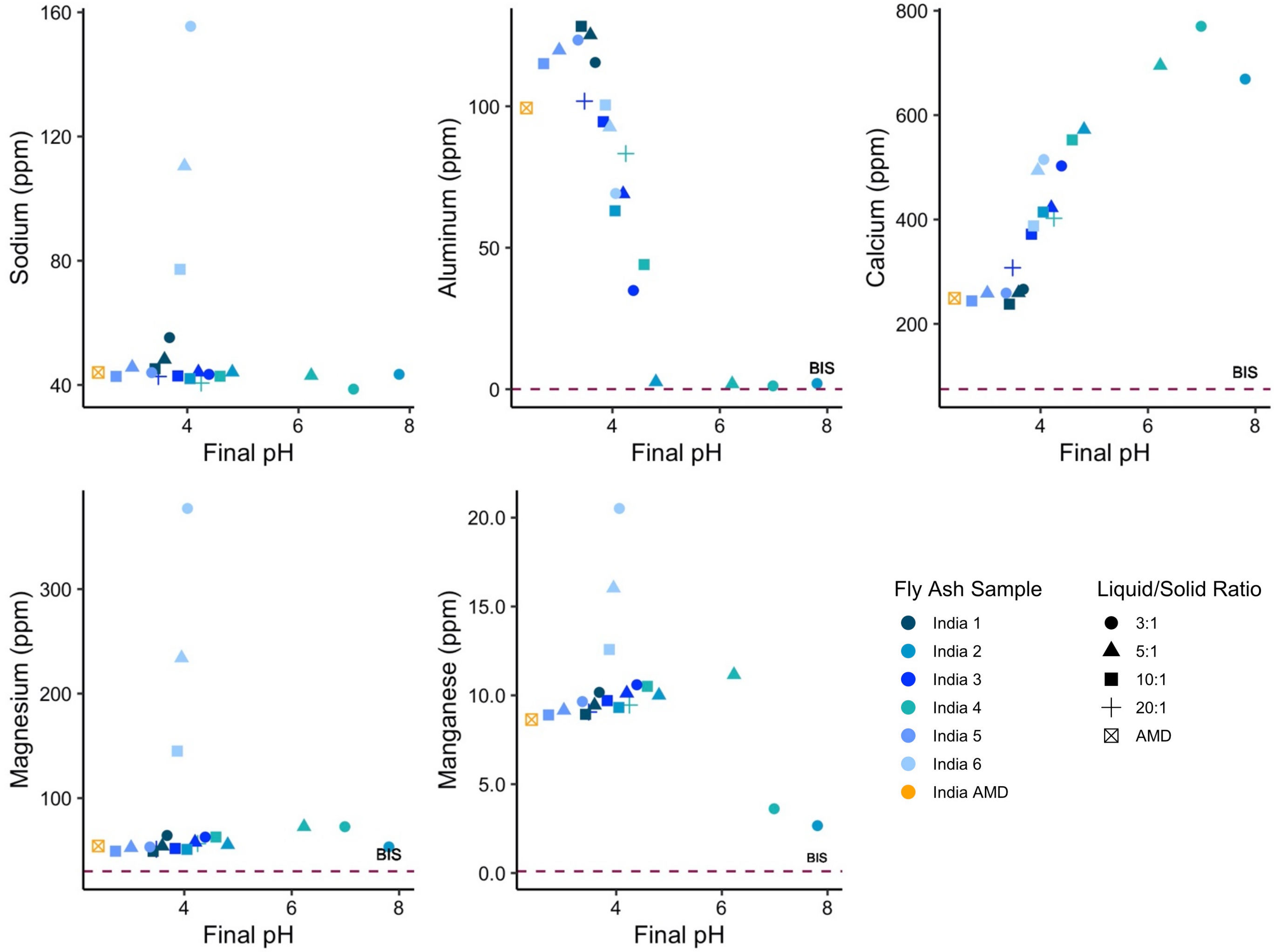
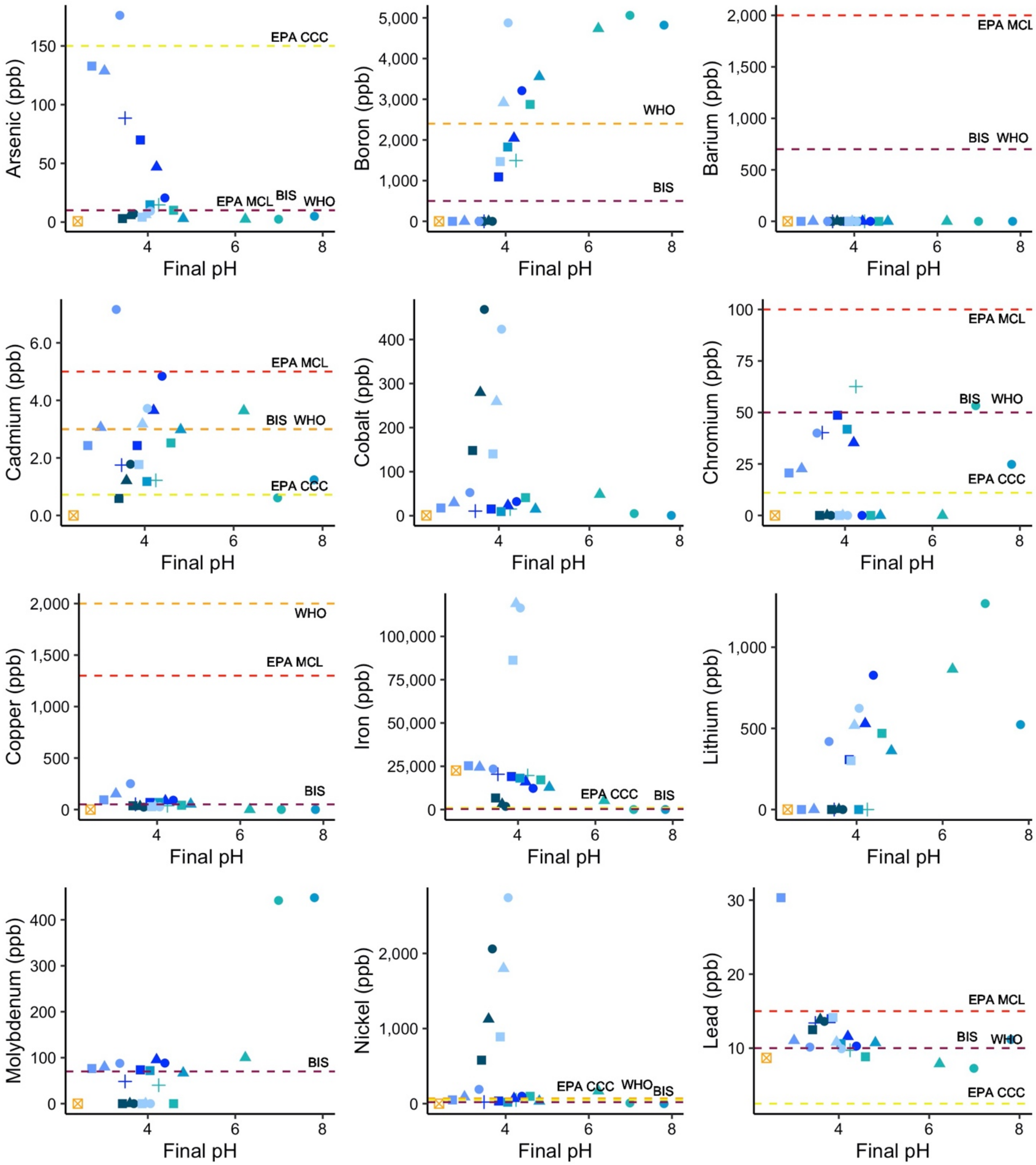


Figure 8. Final concentration of major elements in comparison with final pH for each fly ash sample at different L/S ratios. The colors represent the different fly ash samples and the shapes represent different L/S ratios. Original concentration of each element in AMD is shown by the orange square. WHO guideline value, Bureau of Indian Standards, EPA MCL, and EPA CCC are shown by dotted line when applicable.

Trace Elements



Trace Elements

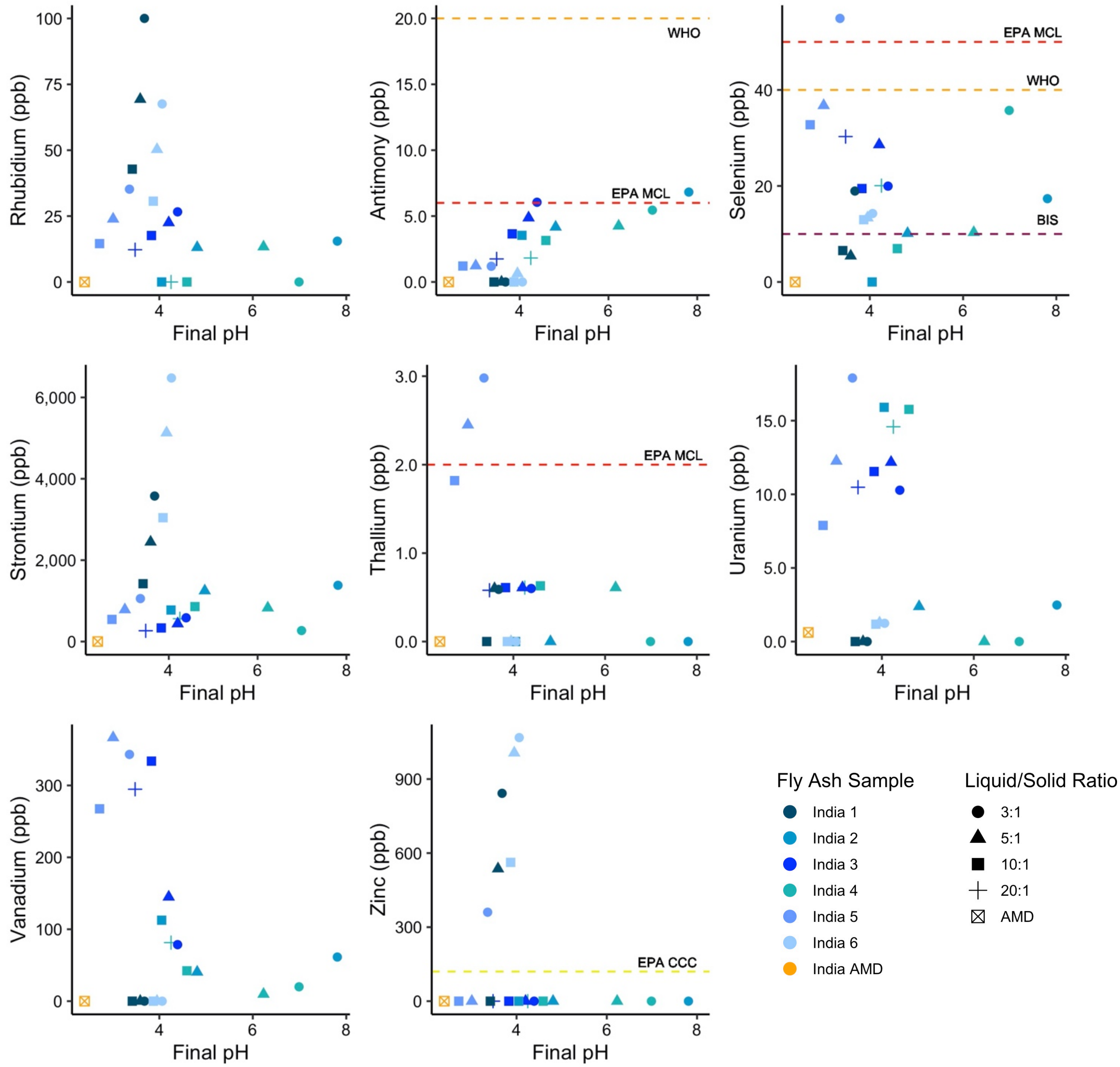


Figure 9. Final concentration of trace elements in comparison with final pH for each fly ash sample at different L/S ratios. The colors represent the different fly ash samples and the shapes represent different L/S ratios. Original concentration of each element in AMD is shown by the orange square. WHO guideline value, Bureau of Indian Standards, EPA MCL, and EPA CCC are shown by dotted line when applicable.

4.2.2 UNITED STATES

All of the fly ash samples from the three different basins in the US, Appalachia, Illinois, and Powder River, reached pH ≥ 6.5 upon interaction with AMD with pH range from 2.4 to 5.2 at L/S ratios of 5:1 and 10:1. Appalachia 1 fly ash successfully neutralized synthetic AMD samples with a starting pH of both 2.8 and 5 at a 10:1 L/S ratio, resulting in the same final pH value. Major elements such as sodium and calcium were enriched across experiments with fly ash from all three US basins (Table 10; Fig. 10). Magnesium concentrations decreased upon AMD interaction with fly ash from the Powder River coal and one of the fly ashes from the Illinois Basin (Illinois 3) , which reached the highest final pH values of 12.92 and 13.11 respectively (Fig 10). Manganese concentrations decreased during interaction with fly ash from the Appalachian and Illinois coals (Fig 10). All three synthetic AMD solutions used in the experiments started with high concentrations of iron that was depleted to below the detection limit after interaction with all of the US fly ash samples (Fig. 11). Cobalt concentrations decreased through reactions with Appalachia fly ash samples, while many other trace elements were enriched. Lead concentrations decreased in all the Illinois samples and cobalt was depleted in all samples except Illinois 2 at a 10:1 ratio (Fig. 11). Other trace elements such as boron, chromium, strontium, arsenic, and uranium were enriched in the leachates after 24 hours of AMD interaction with the US fly ash (Fig. 11). In contrast, the Powder River samples had very low concentrations of trace elements present after the 24 hour interaction. Lithium, barium, boron, rubidium, and strontium were the only elements that became enriched in the effluents following the interaction with Powder River fly ash (Fig. 11).

Table 10. Final concentration of major (ppm) and trace elements (ppb) after US fly ash and AMD leaching experiments. All experiments ran for 24 hours.

Major Elements (ppm)

Fly Ash	AMD	Ratio	Initial pH	Final pH	Na	Mg	Al	Ca	Mn
Appalachia 3	App High	5:1	5.04	6.96	39.3	40.9	< 0.165	288	0.01
Appalachia 3	App High	10:1	5.04	6.84	28.6	32.0	< 0.162	195	0.02
Appalachia 1	App High	5:1	5.04	9.05	36.7	27.5	3.7	402	< 0.0028
Appalachia 1	App High	10:1	5.04	8.63	27.7	24.9	2.4	262	< 0.0029
Appalachia 1	App Low	10:1	2.8	9.3	24.6	28.0	1.0	277	< 0.0029
Appalachia 1	App High	10:1	5.21	9.15	27.7	24.6	2.4	257	< 0.0028
Appalachia 2	App High	5:1	5.04	6.91	19.7	27.1	< 0.164	477	0.64
Appalachia 2	App High	10:1	5.04	6.47	18.9	24.0	< 0.164	272	0.39
App High AMD			5.04	5.04	17.9	20.1	0.00	82	0.02
Illinois 3	India	5:1	2.38	13.11	199	< 0.0279	< 0.163	1169.	< 0.00284
Illinois 3	India	10:1	2.38	13.1	127	< 0.0284	< 0.166	1265	< 0.00289
Illinois 1	India	5:1	2.38	9.05	90.4	53.2	4.38	612	0.26
Illinois 1	India	10:1	2.38	8.48	65.0	51.4	1.18	588	1.13
Illinois 2	India	5:1	2.38	8.79	113	42.6	2.22	571	0.18
Illinois 2	India	10:1	2.38	7.54	81.0	58.1	< 0.164	640	8.48
India AMD			2.38	2.38	43.8	44.5	99.4	229	8.64
Powder River	App Low	5:1	2.8	12.92	256	< 0.0275	21.9	18.4	1027
Powder River	App Low	10:1	2.8	12.87	106	< 0.0216	13.4	8.95	638
App Low AMD			2.8	2.8	14.3	21.1	0.00	83.7	0.00

Trace Elements (ppb)

Fly Ash	AMD	Ratio	Initial pH	Final pH	Li	B	V	Cr	Fe	Co	Ni	Cu	Zn	As
Appalachia 3	App High	5:1	5.04	6.96	2722	5999	16.5	97.3	< 210	0.59	7.67	< 20.7	< 332	36.6
Appalachia 3	App High	10:1	5.04	6.84	1432	3270	12.2	40.1	< 207	1.16	10.5	< 19.7	< 316	20.9
Appalachia 1	App High	5:1	5.04	9.05	1513	7534	29.2	98.1	< 208	< 0.14	< 5.28	< 19.4	< 311	161
Appalachia 1	App High	10:1	5.04	8.63	847	4324	21.2	44.8	< 210	< 0.14	< 5.34	< 19.5	< 313	145
Appalachia 1	App Low	10:1	2.8	9.3	841	4427	17	33.4	< 209	< 0.14	< 5.3	< 19.7	< 316	96.1
Appalachia 1	App High	10:1	5.21	9.15	841	4295	21.1	56.2	< 209	< 0.14	< 5.3	< 19.6	< 314	138
Appalachia 2	App High	5:1	5.04	6.91	1698	2263	< 7.62	< 13	< 210	60.1	320	< 19.5	8304	1.77

Appalachia 2	App High	10:1	5.04	6.47	1018	1334	< 7.58	< 13	< 209	44.6	239	< 19.7	8087	1.17
App High AMD			5.04	5.04	70.7	*bdl*	*bdl*	*bdl*	26988	4.75	*bdl*	*bdl*	*bdl*	*bdl*
Illinois 3	India	5:1	2.38	13.11	1106	16094	55.5	245	< 208	< 0.14	< 5.29	< 19.5	< 313	9.34
Illinois 3	India	10:1	2.38	13.1	649	8259	65.9	131	< 213	< 0.14	< 5.37	< 19.8	< 318	16.0
Illinois 1	India	5:1	2.38	9.05	1037	65520	149	389	< 212	< 0.14	< 5.38	< 19.8	< 319	39.8
Illinois 1	India	10:1	2.38	8.48	721	37980	90.4	181	< 208	< 0.14	< 5.28	< 19.5	< 313	23.9
Illinois 2	India	5:1	2.38	8.79	300	31816	< 7.7	22	< 212	< 0.14	< 5.39	< 19.9	< 319	17.9
Illinois 2	India	10:1	2.38	7.54	772	21739	< 7.58	< 12.9	< 209	25.78	225.5	< 19.6	< 314	2.93
India AMD			2.38	2.38	*bdl*	*bdl*	*bdl*	*bdl*	22533	0.62	*bdl*	*bdl*	*bdl*	0.62
Powder River	App Low	5:1	2.8	12.92	296	5056	< 7.43	< 12.6	< 205	< 0.14	< 5.2	< 19.2	< 308	< 0.56
Powder River	App Low	10:1	2.8	12.87	154	3034	< 5.83	< 9.92	< 161	< 0.11	< 4.09	< 15	< 242	< 0.44
App Low AMD			2.8	2.8	52.3	*bdl*	*bdl*	0.59	33385	*bdl*	*bdl*	*bdl*	*bdl*	*bdl*

Fly Ash	**AMD**	**Ratio**	**Initial pH**	**Final pH**	**Se**	**Rb**	**Sr**	**Mo**	**Cd**	**Sb**	**Ba**	**Tl**	**Pb**	**U**
Appalachia 3	App High	5:1	5.04	6.96	93.2	82.6	123	1242	1.77	47.2	< 207	5.31	< 0.58	0.59
Appalachia 3	App High	10:1	5.04	6.84	56.3	50.5	< 97.8	629	0.58	29.6	< 203	4.65	< 0.58	< 0.03
Appalachia 1	App High	5:1	5.04	9.05	197	28.6	4108	820	0.58	21.0	< 204	1.75	< 0.58	5.84
Appalachia 1	App High	10:1	5.04	8.63	94.3	20.6	2800	433	< 0.15	15.3	< 206	1.77	< 0.58	5.31
Appalachia 1	App Low	10:1	2.8	9.3	101	21.7	2971	383	< 0.15	14.1	< 205	1.76	< 0.58	8.20
Appalachia 1	App High	10:1	5.21	9.15	132	19.9	2815	416	< 0.15	14.6	< 205	1.76	< 0.58	5.27
Appalachia 2	App High	5:1	5.04	6.91	21.8	33.6	397	< 37.46	12.4	5.30	< 206	10.0	< 0.58	< 0.03
Appalachia 2	App High	10:1	5.04	6.47	22.9	25.2	253	< 37.30	8.21	7.04	< 205	8.21	< 0.58	< 0.03
App High AMD			5.04	5.04	*bdl*	*bdl*	36.2	*bdl*	*bdl*	*bdl*	7.72	*bdl*	*bdl*	*bdl*
Illinois 3	India	5:1	2.38	13.11	117	197	1882	7381	6.42	< 0.21	258	44.4	1.75	3.50
Illinois 3	India	10:1	2.38	13.1	50	113	1212	3874	2.97	< 0.22	< 208	36.8	1.19	4.16
Illinois 1	India	5:1	2.38	9.05	218	78.5	1022	3085	2.97	44.0	< 208	27.4	< 0.59	38.1
Illinois 1	India	10:1	2.38	8.48	139	38.5	839	1772	1.75	31.5	< 204	16.9	< 0.58	39.7
Illinois 2	India	5:1	2.38	8.79	42.9	121	122	1840	1.79	15.5	< 209	4.17	< 0.59	0.60
Illinois 2	India	10:1	2.38	7.54	27	101	411	73.2	74.4	7.62	< 205	21.7	< 0.58	< 0.03
India AMD			2.38	2.38	*bdl*	*bdl*	*bdl*	*bdl*	*bdl*	*bdl*	*bdl*	*bdl*	8.68	0.62
Powder River	App Low	5:1	2.8	12.92	< 3.55	64.9	123422	< 36.5	< 0.15	< 0.21	42971	< 0.04	< 0.57	< 0.03
Powder River	App Low	10:1	2.8	12.87	< 2.79	27.1	63437	< 28.7	< 0.12	< 0.16	25140	< 0.03	< 0.45	< 0.03
App Low AMD			2.8	2.8	*bdl*	*bdl*	25.0	*bdl*	*bdl*	*bdl*	*bdl*	*bdl*	*bdl*	*bdl*

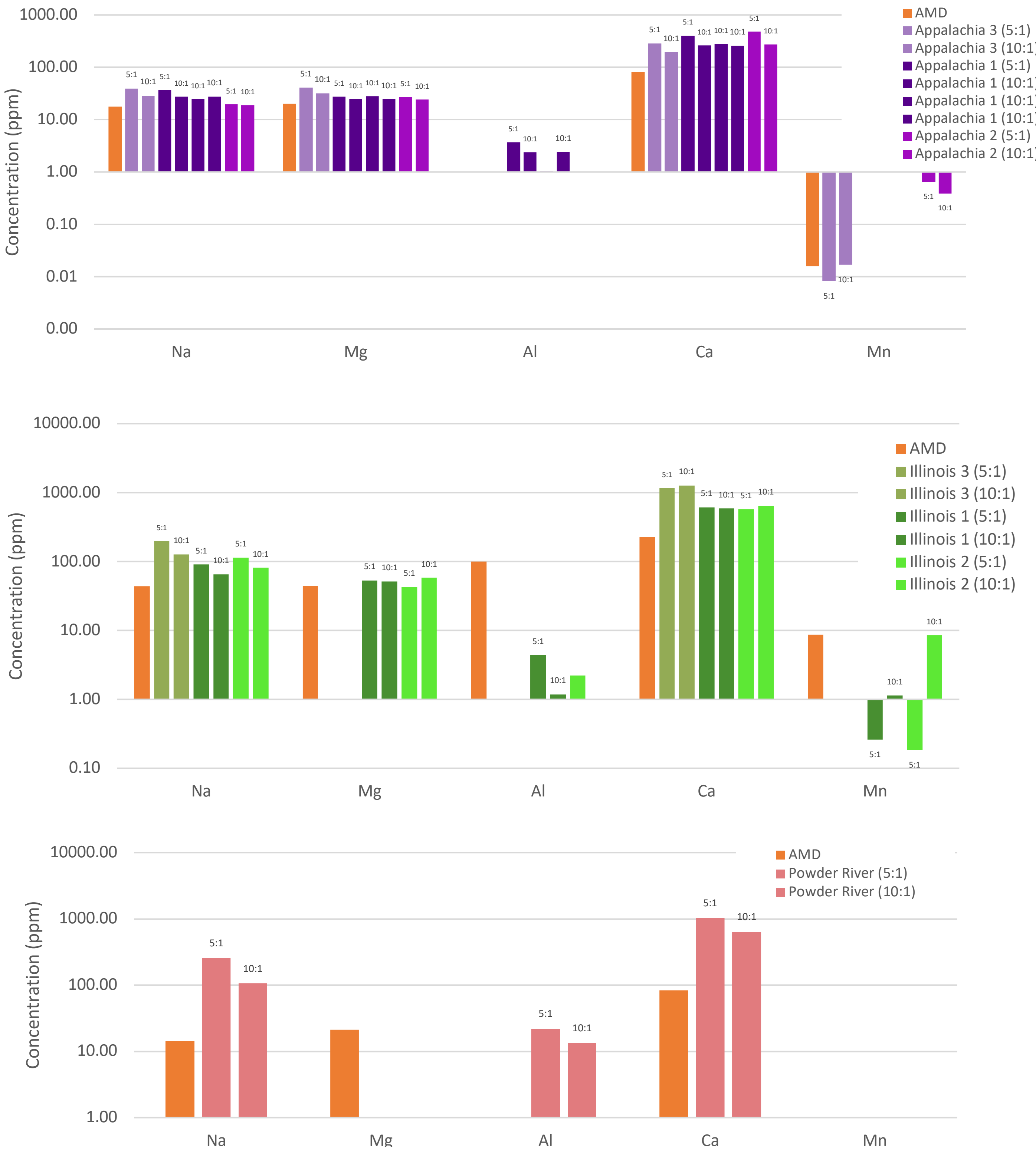


Figure 10. Initial and final concentration of major elements in synthetic AMD and leachate after 24hr leaching with fly ashes from three different basins in the United States at different L/S ratios (5:1, 10:1)

Figure 11. Initial and final concentration of trace elements in synthetic AMD and leachate after 24hr leaching with fly ashes from three different basins in the United States at different L/S ratios (5:1, 10:1)

Figure 12. Enrichment of major and trace elements in leachate samples that reached a pH > 6.2 after 24hr leaching with fly ashes from three different basins in the United States at different L/S ratios (5:1, 10:1)

Table 11. Enrichment ratios of major and trace elements in leachate samples that reached a pH > 6.2 after 24hr leaching with fly ashes from three different basins in the United States at different L/S ratios.

Fly Ash	AMD	Ratio	Initial pH	Final pH	Na	Mg	Al	K	Ca	Mn	Co	As	Pb	U
Bull Run	App High	5:1	5.04	6.96	2.20	2.04	N/A	0.76	3.51	0.51	0.12	N/A	N/A	N/A
Bull Run	App High	10:1	5.04	6.84	1.60	1.59	N/A	0.39	2.38	1.05	0.24	N/A	N/A	N/A
AP 93172	App High	5:1	5.04	9.05	2.05	1.37	N/A	0.24	4.91	N/A	N/A	N/A	N/A	N/A
AP 93172	App High	10:1	5.04	8.63	1.55	1.24	N/A	0.20	3.20	N/A	N/A	N/A	N/A	N/A
AP 93172	App Low	10:1	2.8	9.3	1.72	1.33	N/A	0.89	3.31	N/A	N/A	N/A	N/A	N/A
AP 93172	App High	10:1	5.21	9.15	1.50	1.21	N/A	0.14	2.90	N/A	N/A	N/A	N/A	N/A
AP 93441	App High	5:1	5.04	6.91	1.10	1.35	N/A	0.32	5.82	40.1	12.64	N/A	N/A	N/A
AP 93441	App High	10:1	5.04	6.47	1.06	1.19	N/A	0.35	3.32	24.1	9.38	N/A	N/A	N/A
IL 93879	India	5:1	2.38	13.11	4.54	N/A	N/A	6.23	5.11	N/A	N/A	15.1	0.20	5.65
IL 93879	India	10:1	2.38	13.1	2.91	N/A	N/A	3.40	5.53	N/A	N/A	25.8	0.14	6.70
IL 93630	India	5:1	2.38	9.05	2.06	1.19	0.04	1.93	2.67	0.03	N/A	64.24	N/A	61.4
IL 93630	India	10:1	2.38	8.48	1.48	1.15	0.01	1.01	2.57	0.13	N/A	38.55	N/A	63.9
IL 93796	India	5:1	2.38	8.79	2.59	0.96	0.02	0.38	2.50	0.02	N/A	28.82	N/A	0.96
IL 93796	India	10:1	2.38	7.54	1.85	1.30	N/A	0.22	2.80	0.98	41.6	4.72	N/A	N/A
PR 93925	App Low	5:1	2.8	12.92	17.91	N/A	N/A	4.64	12.3	N/A	N/A	N/A	N/A	N/A
PR 93925	App Low	10:1	2.8	12.87	7.45	N/A	N/A	2.26	7.62	N/A	N/A	N/A	N/A	N/A

Figure 12 shows the enrichment of major and trace elements in the leachates separated by the coal sources from the different US basins. Enrichment ratios could only be calculated when the element was present in both the leachates and the synthetic AMD solution used for the experiments. Values above 1 indicate that the element was enriched due to the interaction with the coal ash, while values below 1 indication removal of the element after AMD-fly ash interaction (Table 11).

Figures 13 and 14 show, the relationship between final pH and concertation of major and trace elements. While there is less of a clear trend among all of the US samples, because the chemistry of each fly ash and AMD differs, there is a general increase in calcium and sodium concentrations with increasing final pH (Fig 13). Human health and ecological standards from the EPA, Bureau of Indian Standards (BIS), and WHO (BIS, 2012; EPA, 2015b; EPA, 2015c;

WHO, 2017) are presented to show which toxic elements occur above recommended drinking water and ecological threshold values. Arsenic generally increased with pH, and then decreased substantially with pH values > 10. Aluminum increased with pH for the Illinois fly ashes, but didn't show a clear trend for Powder River and Appalachian fly ashes (Fig 13; Fig 14).

Manganese concentrations in solutions after 24h interaction were mostly low, even though the manganese concentration in the initial synthetic AMD used with the Illinois ashes was substantially higher (Fig 13). Final concentrations of toxic elements such as arsenic, boron, molybdenum, antimony, selenium, and thallium were above human health and ecological standards for multiple fly ash samples in the neutral pH range (Fig 14). Arsenic exceeded drinking water standards in all but four samples, but was under the ecological standard for all by one sample (Fig 14). Chromium concentrations were near both drinking water and ecological standards, with some samples below all three, others slightly exceeding limits, and two Illinois samples substantially above all three standards (Fig 14). Lead, copper, and iron concentrations were all under drinking water and ecological standards (Fig 14).

Major Elements

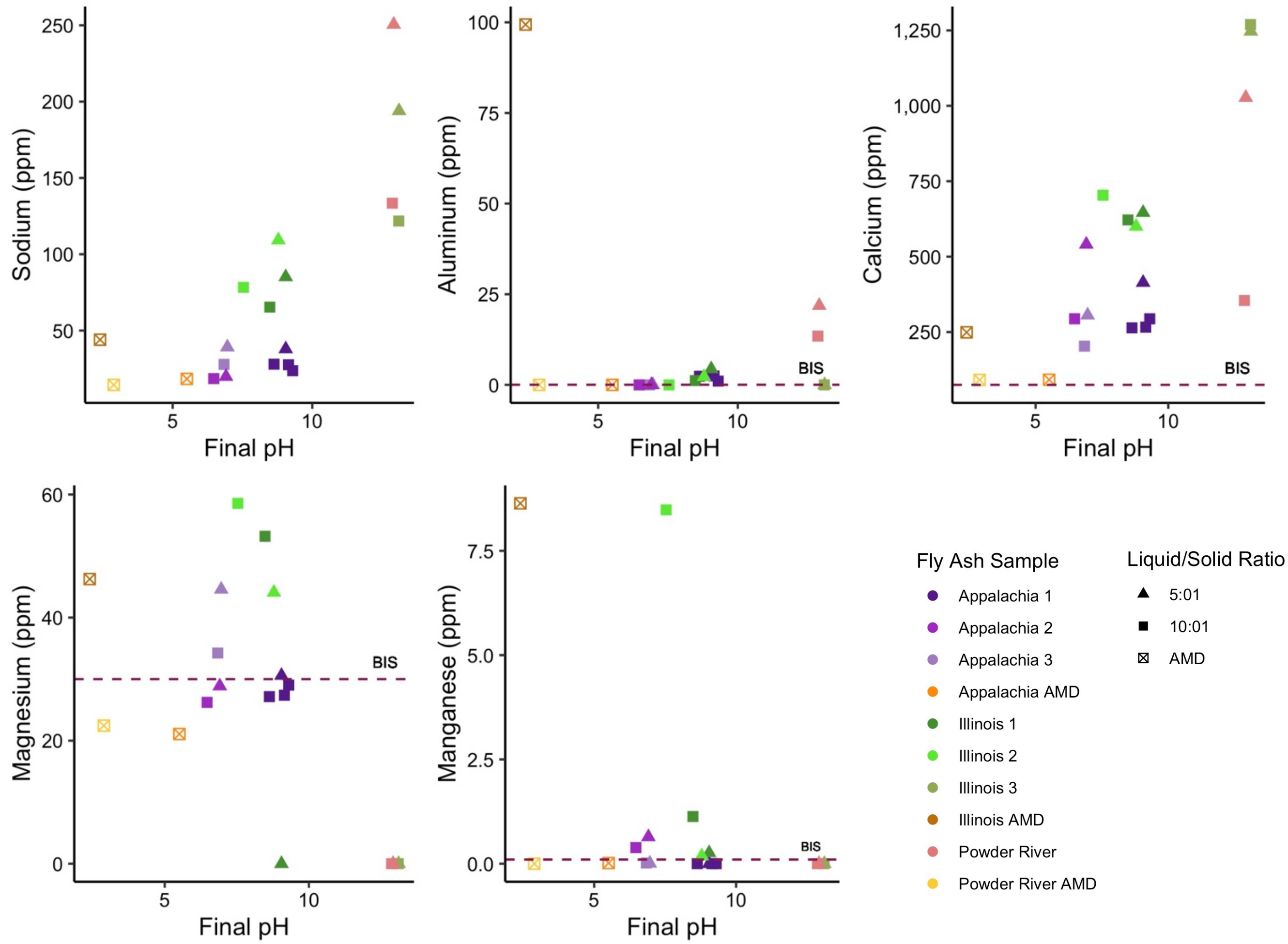
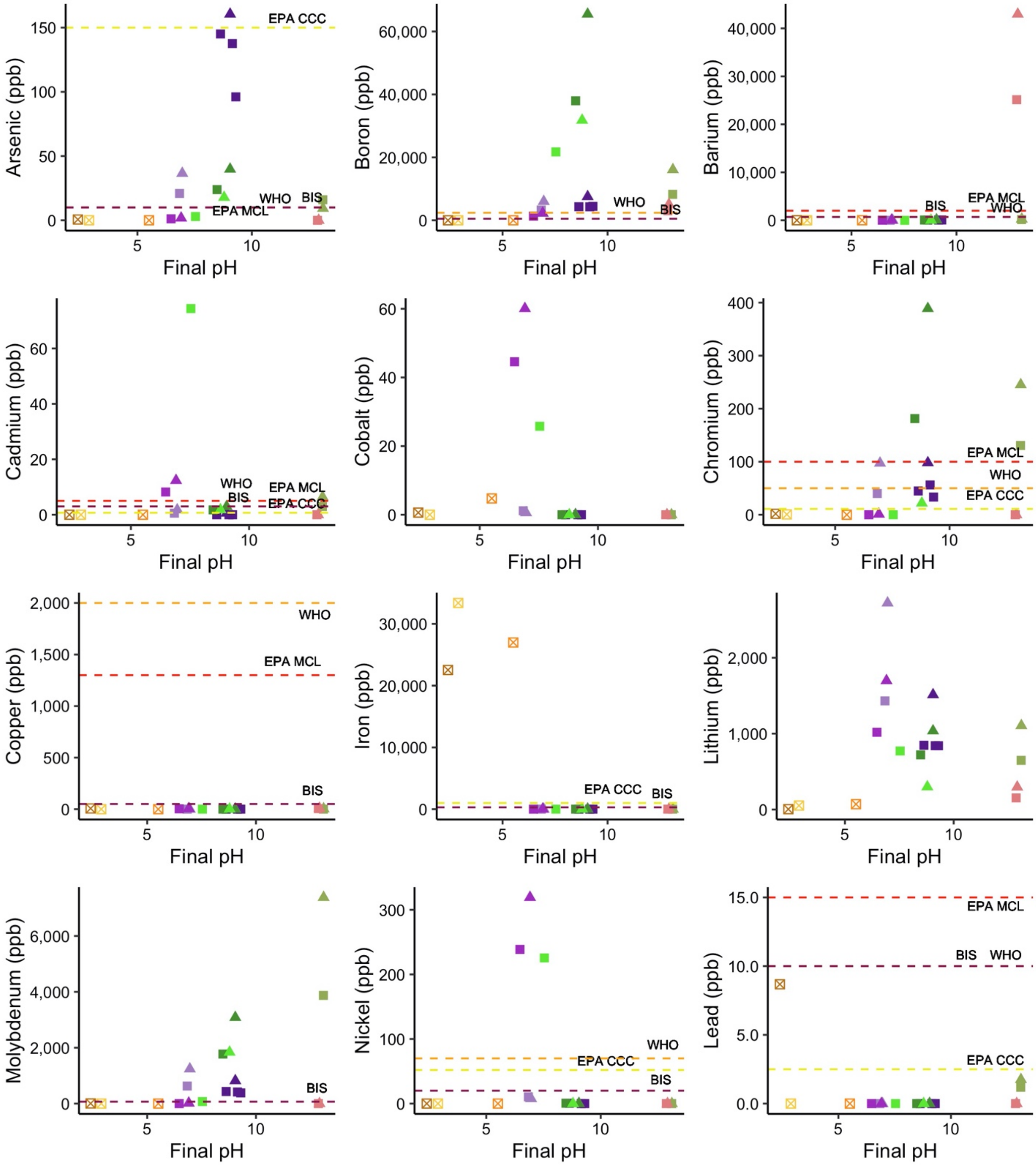


Figure 13. Final concentration of major elements in comparison with final pH for each fly ash sample at different L/S ratios. Original concentration of each element in AMD is shown by the orange squares. WHO guideline value, Bureau of Indian Standards, EPA MCL, and EPA CCC are shown by dotted line when applicable.

Trace Elements



Trace Elements

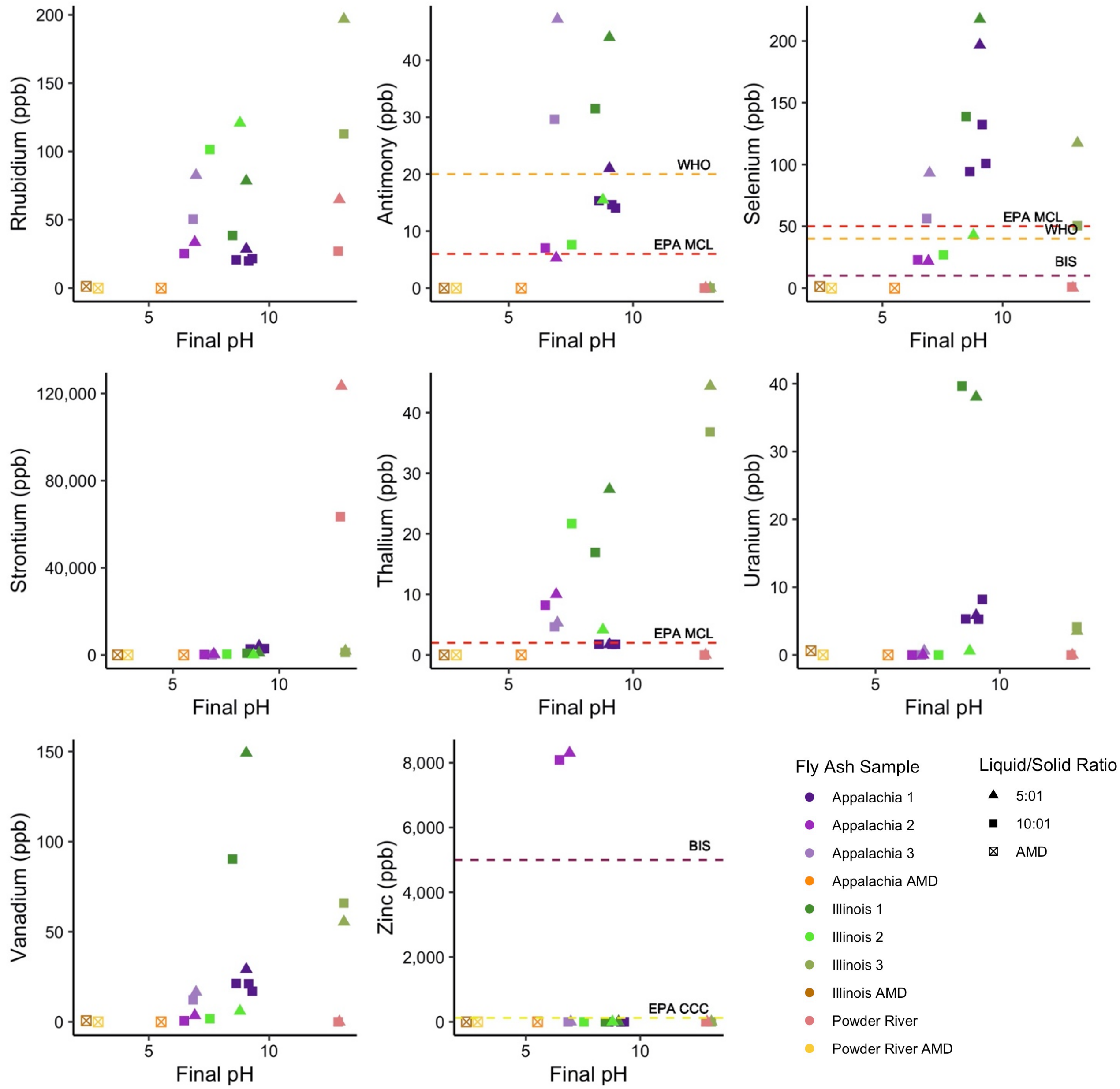


Figure 14. Final concentration of trace elements in comparison with final pH for each fly ash sample at different L/S ratios. Original concentration of each element in AMD is shown by the orange squares. WHO guideline value, Bureau of Indian Standards, EPA MCL, and EPA CCC are shown by dotted line when applicable.

5. Discussion

The results of the experiments conducted as part of this MP show that certain fly ashes at the L/S ratios tested in our experiment (3:1, 5:1, 10:1) can effectively neutralize AMD, but not without consequences for degradation of water quality of the neutralized effluents. Therefore, it is necessary to weigh the benefits and detriments of utilizing fly ash to neutralize AMD before applying this practice in the field. Additionally, it is important to examine the chemistry of the fly ash in order to evaluate its suitability for neutralization.

As shown in previous studies and reinforced by the results of the lab experiments of this study, two major factors influence neutralization capacity: the AMD to fly ash ratio (L/S ratio) and the chemical composition of fly ash. The L/S ratio had substantial influence on the neutralization of multiple Indian ashes, with ability to reach neutralization only at a lower L/S ratio, inferring that a larger mass of fly ash is needed to reach neutral pH. The difference in neutralization capacity of the US ashes and Indian ashes highlights the important role that calcium plays in neutralization. Our finding is consistent with results of previous fly ash leaching studies that have shown that the concentration of calcium in the fly ash is the leading factor that controls pH variations of the leachates (Gitari et al., 2006; Izquierdo & Querol, 2012; Qureshi et al., 2016). When selecting a fly ash medium to be used for neutralization, it is important to select a fly ash with a higher calcium concentration. In our experiments, we found a Ca threshold of ~9,000 mg/kg in the fly ash to ensure an effective neutralization of most fly ash samples at a 10:1 L/S ratio. This information is valuable because rather than conducting leaching experiments to determine which fly ash has the highest neutralization potential, it is possible to predict the fly ash neutralization capability based on the chemistry of the fly ash itself.

The results show less of a clear trend between element concentrations and final pH in the US samples as compared to the India samples. From figures 8 and 9 and figures 13 and 14, it looks like there is more chemical variation across fly ash samples derive from individual coal basins in the US, rather than a general trend across the country as a whole. Therefore, it would be valuable to examine if fly ash from a specific coal basin would follow a similar trend in final pH vs. concentration of each element that we have seen in the results of the India fly ash samples. Our data show that the final pH as well as the initial chemistry of both the AMD and fly ash would influence the mobilization and occurrence of toxic elements in the final effluent. A review of multiple fly ash leching experiments identified the leaching of certain elements from fly ash to be dependent on solution pH rather than the metal concentrations in the fly ash, including Cd, Co, Cu, Fe, Mg, Mn, Ni, Pb, Th, Tl, U, and Zn (Izquierdo & Querol, 2012). These elements were found to have low leachability in the pH 7-10 range. Alternatively, As, B, Cr, Mo, Sb, Se, and V were found to reach maximum leachability at pH 7-10 (Izquierdo & Querol, 2012). This information is valuable to understand which contaminants have the most mobilization potential in the ideal solution pH range of 6.5 – 9.

Boron and calcium are known to be two of the most readily mobilized elements in the fly ash (Gitari et al., 2007; Izquierdo & Querol, 2012). Calcium concentration in the leachates increased with pH across all of our experiments, as expected because higher Ca content fly ashes were significantly correlated with higher final pH values. Boron concentrations also increased with pH across all Indian ash samples and somewhat in the US, but because boron concentration in the fly ash was correlated with final pH, it is more likely that initial concentration has a greater influence than pH on final concentration (Izquierdo & Querol, 2012). In our experiments, the mobilization of aluminum was relatively low in the pH 5-9 range and then higher for the Indian ash samples at low pH values and US ash samples at high pH values, which is consistent with other fly ash leaching studies (Izquierdo & Querol, 2012). The major difference in final manganese concentration between experiments with Indian fly ash and those with US fly ash is most likely a result of manganese's low leachability at near neutral pH values and higher leachability as pH becomes more acidic (Izquierdo & Querol, 2012). Similarly, nickel concentrations were substantially higher with India ashes than US ashes because nickel has its highest mobility at low pH values and minimal mobility in the pH 8-10 range (Izquierdo & Querol, 2012). Our results show relatively low levels of zinc, lead, copper, and manganese for US ash samples, which is consistent with results from Perez-Lopez et al. (2007) column experiment, but our results indicate higher manganese, zinc, and lead concentration at lower pH ranges in the India samples. Further comparison between basins in our experiments can help to identify if final pH is the main factor that controls mobilization and occurrence of toxic elements in the leachate, or if it is more affected by the chemical composition of fly ash and AMD used for neutralization.

While increased pH of AMD benefits the environment and aquatic life, mobilization of certain toxic elements from fly ash could also impair the quality of effluents and thus aquatic life. Specifically, toxic elements such as chromium and cadmium were above ecological standards in many samples after neutralization with both the US and Indian fly ash samples. Additionally, lead was above the EPA aquatic life standard in the India leaching experiments.

In addition to environmental impacts, it is also necessary to examine drinking water standards, as mine drainage sometimes enters drinking water sources through surface and groundwater. Molybdenum and boron were consistently above drinking water standards after experiments with both Indian and US fly ash samples, whereas barium and copper were consistently below standards. Cadmium, antimony, thallium, chromium, arsenic and selenium remained below EPA and or WHO drinking water guidelines during experiments with fly ash from India that reached neutral pH, but exceeded standards in neutralization experiments using the US fly ash samples. Therefore, it is clear that both the chemical composition of the fly ash and the final pH influence the mobilization of these elements into leachates generated from interaction of fly ash with AMD.

While the comparison of the concentration of elements in the leachate with ecological and health standards is valuable, it does not fully resemble natural conditions because toxic trace elements that might be in natural AMD were not included in the synthetic solutions. Therefore, calculating the enrichment of each element and comparing that with the range of chemistry of natural AMD gives a better prediction for possible outcomes in field settings. When enrichment of each element under experimental conditions was added to the initial concentration of each element in the AMD, all of the toxic elements except iron and thallium were above the Indian drinking water standards, which are in many cases more strict than the US EPA and WHO standards. A comparison of the toxic metals concentrations in the Indian AMD (Table 2) to their concentrations in effluents that reached neutralization (Table 7) show that magnesium, aluminum, manganese, iron, cobalt, nickel, copper, zinc, arsenic, selenium, rubidium, strontium, and cadmium were lower in the leachates (mixture of synthetic AMD and fly ash) than in the naturally occurring AMD. Whereas, concentrations of lithium, boron, calcium, vanadium, molybdenum, and antimony were higher in the leachates than in the naturally occurring AMD from India. While this is a valuable comparison, there are many factors that may influence the final concentrations of elements, and therefore, this method does not capture the exact concentrations of each element were this to be conducted in the field. As previous studies have shown, there are multiple factors that influence the nature of the final leachate. Consistent with previous studies, our experiments show, L/S ratio, final pH, chemistry of fly ash, and chemistry of AMD are the major factors that control the quality of the final leachate (Gitari et al., 2006; Izquierdo & Querol, 2012; Kim, 1999; Prasad and Mortimer, 2011; Qureshi et al., 2016).

6. Conclusion

This study highlights the benefits and detriments to water quality upon experimental interaction of AMD with fly ash samples from India and the United States. The results show that specific elements in fly ash such as calcium would control the neutralization potential, in addition to other factors such as AMD chemistry and the experimental L/S ratios, which is overall consistent with the results of previous studies. The original pH of the AMD did not impact the neutralization potential, as was demonstrated by the experiments with fly ash samples from Appalachia mixed with AMD with a starting pH of both 2.8 and 5 and resulting in the same final pH. The variations of the neutralization potential upon the L/S ratios have important implications for field-scale tests and the ability to evaluate the capability and sustainability of this method on real field conditions. The study also found that the greatest pH changes generally occurred within the first hour of the experiment, and therefore the neutralization of AMD through interaction with fly ash does not require a significant amount of contact time. While neutralization was achieved in many fly ash samples, particularly those from the US, the data show both contaminant retention from the AMD and mobilization from the Indian and US fly ash samples. The magnitude of mobilization versus retention varied, and was found to be dependent primarily on the chemical characteristics of the fly ash samples used in the neutralization experiments. The final pH of the leachate, which was a response to the L/S ratios and fly ash types, also influenced the mobilization of some contaminants from the fly ash versus retention of others. In many cases, particularly for the US fly ash samples originated from the Appalachian and Illinois coals, the neutralized pH leachates contained contaminant levels exceeding the drinking water and ecological standards, reflecting a negative outcome, rather than improving the overall water quality. Fly ash from Powder River Basin in the US had much higher calcium content, which resulted in a higher final pH (up to 12), but substantially lower concentration of most contaminants in the high-pH leachates. In contrast, neutralization of AMD with fly ash samples from India resulted in lower contaminants levels in the neutral pH range of

6-9. Overall, the results of this study show that there is potential to utilize fly ash as a medium for to neutralization of low-pH AMD, and yet, the chemistry of the fly ash would affect the performance of this treatment method and resulting environmental impact. Therefore, only fly ash containing high levels of calcium and low mobilization potential of toxic elements should be used to neutralize AMD and improve quality of AMD and surrounding waters to meet drinking water and aquatic health standards.

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