Long-term leaching of As, Cd, Mo, Pb, and Zn from coal fly ash in column test

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Abstract Globally, millions of tons of coal fly ash (CFA) are generated per year, and the majority of this material is usually stored in stock piles or landfills, and in a long-term, it can be an environmental hazard if rainwater infiltrates the ashes. Long-term leaching studies of Brazilian ashes are scarce. The purpose of this study was to evaluate arsenic, cadmium, molybdenum, lead, and zinc leaching behavior from a Brazilian CFA by a column experiment designed to simulate field conditions: slightly acid rain considering seasonality of precipitation and temperature for a long-term leaching period (336 days). All elements were leached from CFA, except lead. Elements leaching behavior was influenced by leaching time, leaching volume, and temperature. Higher leachability of As and Cd from CFA during warm and wet season was observed. Results indicate a potential risk to soil and groundwater, since ashes are usually stored in uncovered fields on power plants vicinity.

Introduction

Coal fly ash (CFA) is a by-product generated from coal power plants. CFA worldwide production is estimated on 415–600 million ton annually and is considered as an environmental concern (Gomes et al. 2016). Brazilian production of CFA reaches around 3 million ton per year (Ferrarini et al. 2016) and only 30% have been applied as raw material for cement and concrete production (Fungaro et al. 2013). The remaining CFA are usually dumped in the vicinity of the power plants (Fungaro et al. 2013; Rohde et al. 2006). CFA has been used worldwide for building material applications, asphalt, concrete pavements, soil stabilization, road base, structural fill, embankments, mine reclamation, mineral fillers or fertilizers, zeolites, and geopolymers (Izquierdo and Querol 2012).

The disposal of these ashes in uncovered fields might lead to the release of potentially toxic leachates, since Brazilian CFA is commonly composed by environmentally harmful elements such as As, Cd, Mo, Pd, and Zn (Flues et al. 2013; Depoi et al. 2008). Atmosphere surrounding coal power plants is usually associated with acid rain (Flues et al. 2002) and might increase leaching of these elements from CFA.

Laboratory experiments are well known as an alternative to simulate CFA leaching and are helpful to evaluate elements release under distinct conditions (Depoi et al. 2008; Querol et al. 2000; Querol et al.

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2001; Pires and Querol 2004; Ludwig et al. 2005; Ram et al. 2007; Izquierdo et al. 2008; Dutta et al. 2009; Ward et al. 2009; Neupane and Donahoe 2013; Dudas 1981; Wang et al. 2008a, b; Fytianos et al. 1998; Sandeep et al. 2016; Liu et al. 2016; Yılmaz 2015; Gallardo et al. 2015; Lieberman et al. 2014). The leaching rate of elements from CFA depends on parameters such as pH, leaching time, solid/liquid ratio, leaching medium, and temperature (Izquierdo and Querol 2012; Querol et al. 2001; Ram et al. 2007; Dutta et al. 2009; Ward et al. 2009; Neupane and Donahoe 2013; Wang et al. 2008a, b; Fytianos et al. 1998; Sandeep et al. 2016; Lieberman et al. 2014; Khanra et al. 1998; Wang et al. 2008a, b.

The long-term environmental effects of CFA dumped in landfills exposed to weathering are not fully understood (Kim et al. 2017); however, long-term leaching tests are scarce (Dutta et al. 2009; Catalano et al. 2012; Neupane and Donahoe 2013; Dudas 1981). Batch leaching tests for periods above 180 days using deionized water, synthetic rainwater, and sulfuric acid (pH 1.3) were reported by Neupane and Donahoe (2013), Catalano et al. (2012), and Dutta et al. (2009), respectively. Dudas (1981) evaluated CFA column leaching with distilled water during 2 years.

In the last decade in Brazil, in spite of coal power plants have been operating in their maximum capacity and have enhanced the production of CFA, the long-term leaching of harmful elements from this ash still received little attention. Batch leaching tests with Brazilian CFA using water with shaking for 24 h were reported by Depoi et al. (2008) and Pires and Querol (2004), whereas long-term leaching studies were not found in the literature.

Therefore, studies on long-term leaching of Brazilian CFA may provide valuable information to support remediation procedures, as well as encourage improvements in the management practices of ash landfills. Environmental implications of ash disposal could be evaluated by the comparison between toxic elements concentration in leachate and groundwater and soil guidelines values.

Figueira Coal Power Plant (CPP) has been operating since 1963 in the south of Brazil and presently generates 20 MW. Figueira CFA presents toxic metals and arsenic in concentrations higher than most Brazilian CFAs (Depoi et al. 2008). Dumped piles of CFA have been growing along the years, first with unfiltered ashes, and since 1998 with bag filters (Flues et al. 2013).

The paper proposes a laboratorial column leaching test to evaluate the leachability of toxic elements from CFA disposed over land and subjected to environmental conditions, using synthetic acid rain, and considering seasonality of precipitation and temperature for a long-term period of 1 year, using Figueira CFA as a study case.

Experimental

CFA

One kilogram of CFA samples were collected from the bag filter of Figueira CPP every 2 months during a year. A composite sample was prepared by mixing and homogenizing individual samples. More information about the site and sample collection method was published previously (Flues et al. 2013).

CFA column setup

The columns, filled with 50 g of air-dried and homogenized CFA, were supported by funnels, which in turn were put inside graduated cylinders (Fig. 1). The column setups were prepared as follows: (i) a funnel was inserted inside a graduated cylinder; (ii) a perforated polyethylene disc covered with a qualitative filter paper was placed inside the funnel; (iii) the acrylic column (inner diameter of 8 cm) was put over the disc; (iv) the column was filled with inert sand till forming a 5-cm thick layer; and (v) a cup of qualitative filter paper (to prevent fly ash loss) filled with 50 g of air-dried and homogenized CFA was placed inside the column over the sand; the thickness of the CFA layer was ~ 2 cm.

The columns were leached with a synthetic acid rain solution composed of HNO_3 and H_2SO_4 (analytical grade) mixed on 1:1 proportion with pH 4.5, based on previous studies (Flues et al. 2002; Rocha et al. 2003), during 336 days. At every 28 days, a volume of this solution, based on monthly rainfall data from 1933 to 2008 for the city of São Paulo (IAG 2008), was added to the columns according to Fig. 2; these volumes were divided into four equal parts added weekly to avoid clogging. This solution was introduced into the CFA columns using gravity enteral feeding equipment with an average flux of 0.5 mL min^{-1}. The CFA leachate was collected each 28 days, stocked in a polyethylene bottle, and refrigerated for toxic elements determination. The total solution volume added in each column was 6,300
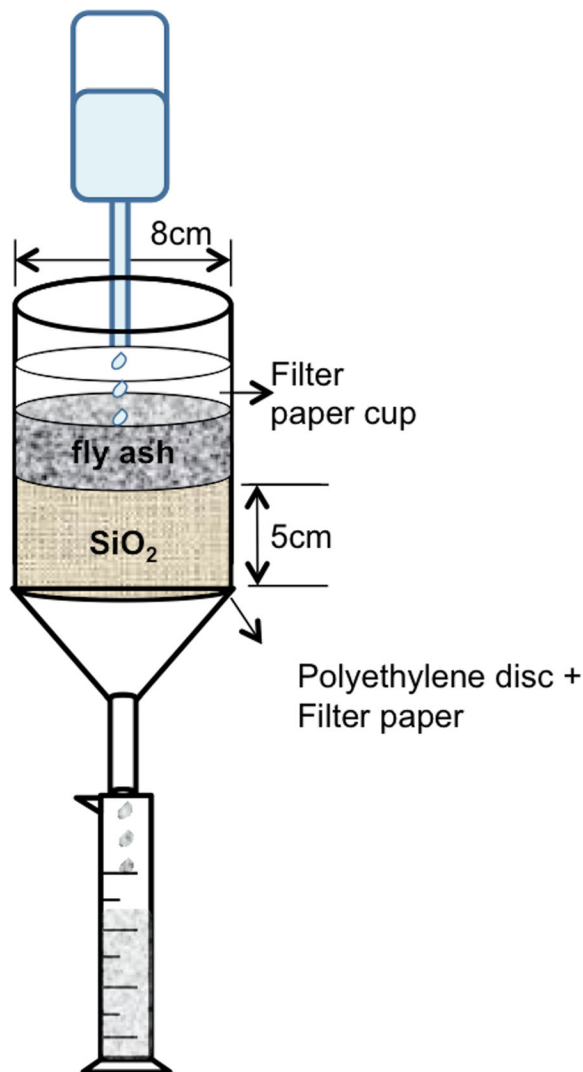
Fig. 1 Scheme of column leaching filled with CFA

mL. Room parameters of CFA, temperature, and air humidity were measured over the leaching period, varying from 20.8 to 27.1 °C and 56.3 to 73.8%, respectively.

The solution seeped quickly through the ash and the sand, and the leached volumes were similar but slightly lower than the input volumes, probably due to evaporation. Only during the first month the input volume was greater than the leached volume, because the materials were not saturated in the beginning of the experiment.

CFA characterization

CFA pH was determined from a mixture of 0.800 g of ash plus 40 mL of deionized water stirred for 24 h in a

shaker at 120 rpm, filtered through a 0.45-μm cellulose membrane and measured by a pH meter. The mineralogical composition was determined by the powder method using X-ray diffractometer (PANalytical model X'Pert PRO with X'Celerator detector). Crystalline phase identification was done by comparison with the ICDD (International Center for Diffraction Data) and PANalytical inorganic crystal structure databases. The chemical composition of CFA was determined by semi-quantitative analysis using an X-ray fluorescence spectrometer (PANalytical model Axios Advanced).
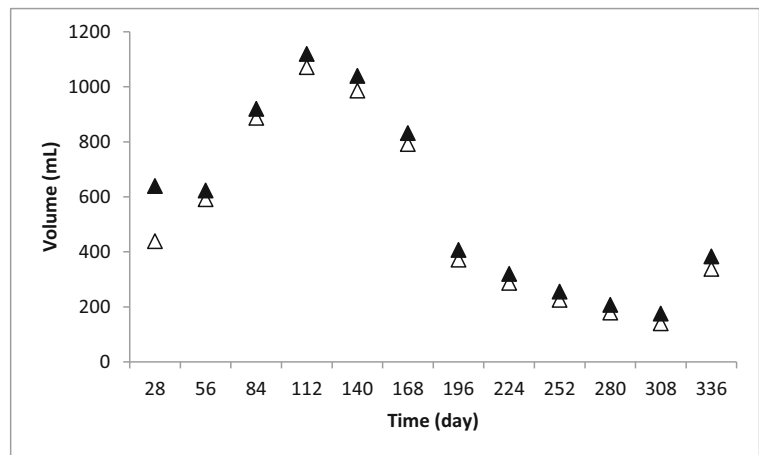
CFA leachate

Total dissolved carbon, pH, and anion concentration were determined for the leachate samples every 28 days. The leachate was filtered through a 0.45-μm acetate membrane for the anion and dissolved carbon analyses. Anions (SO_4^{2-}, NO_3^-, F^-, Cl^-, NO_2^-, and PO_4^{3-}) concentrations were measured using a Dionex DX120 Ion Chromatograph (IC) with IonPac AS14 column. Total dissolved carbon, dissolved inorganic carbon, and dissolved organic carbon concentrations were measured using a Shimadzu VCPH total organic carbon analyser (TOC).

Elements concentration

Elements concentrations were determined in CFA leachate and CFA samples. At every 28 days, 50 ml of stocked CFA leachate was filtered through a 0.45-μm acetate membrane and acidified to 2% with HNO_3 (analytical grade). Duplicate CFA samples were submitted to acid digestion, with 0.500 g of each sample treated with a mixture of 9 mL of concentrated HNO_3 (analytical grade) and 3 mL of concentrated HCl (analytical grade) in a digestion vessel and processed in a microwave oven according to method USEPA 3051-A (USEPA 2001). The extracts were diluted to 50 mL with deionized water and filtered by a filter paper of 6 μm of porosity.

The concentrations of major and toxic elements in CFA leachate were determined by inductively coupled plasma optical emission spectrometer (ICP-OES, Spectro Analytical Instruments, model SpectroFlame M120 E) for Al, Mn, Fe, Zn, Mo, Cd, Na, Mg, Si, K, and Ca and graphite furnace atomic absorption spectrometry (GF-AAS, from Perkin-Elmer Corp., model Analyst/HGA 400) for As and Pb. For the CFA acid-digested samples, all elements concentrations were determined by ICP-OES.

Fig. 2 Volume of synthetic acid rain solution added to CFA, compared to leached volume collected over 336 days; ▲ synthetic solution; △ CFA leachate

Usual quality control procedures were executed. Blanks were prepared for the samples of leachate and acid-digested CFA. For all procedures, analytical grade reagents were used. Precision, recovery, and limit of quantification of the elements concentration were evaluated using a multielementar synthetic solution prepared with element standards from Merck to determine As, Cd, Mo, Pb, and Zn concentrations. Precision ranged from 0.6 to 4.4% and recovery ranged from 92 to 99%. The limits of quantification were 0.050 $\mu g \, mL^{-1}$ for As, 0.010 $\mu g \, mL^{-1}$ for Cd, 0.200 $\mu g \, mL^{-1}$ for Mo, 0.100 $\mu g \, mL^{-1}$ for Pb, and 0.010 $\mu g \, mL^{-1}$ for Zn.

The precision of the methodology to determine the elements concentrations (As, Cd, Mo, Pb, and Zn) in the CFA acid-digested sample was evaluated using NIST SRM2689 (CFA) and varied from 3.8 to 12%. The recovery was not determined because certified and non-certified values were related to total concentration in SRM 2689.

Leaching of toxic elements

The leached cumulative concentration of each element relative to dry CFA mass was calculated by Eq. 1.

$$\text{Cumulative concentration} = \sum_{t=28}^{336} \frac{(Cl_t \times Vl_t)}{Mc} \quad (1)$$

where Cl_t is the element concentration in the leachate (mg L^{-1}) collected at determined time (t), Vl_t is the leachate volume (L) collected at determined time (t), and Mc is the mass of CFA (kg) added to the column top.

The total leached percentage of each toxic element was calculated by the sum of the element masses in the leachate samples obtained over a 336-day period (Eq. 2).

$$\text{Total leached percentage} = \sum_{t=28}^{336} (Cl_t \times Vl_t) \times \frac{100}{Cc \times Mc} \quad (2)$$

where Cc is the element concentration in CFA obtained by acid digestion (mg kg^{-1}).

Statistical analysis

Pearson correlation analysis with significance levels of 0.01 and 0.05 was performed in order to evaluate the influence of temperature, air humidity, leaching volume, and time on toxic elements leaching from the CFA, using EXCEL electronic sheet (Microsoft Office 2010).

Results and discussion

Characterization

CFA chemical composition

The CFA is composed mainly of SiO_2 (54.4%), Al_2O_3 (18.0%), and Fe_2O_3 (8.08%) (Table 1). The higher contents of the toxic trace elements found in the CFA were As (0.14%) and Zn (0.13%). Quartz (SiO_2), mullite ($3Al_2O_3.2SiO_2$), hematite (Fe_2O_3), and magnesioferrite ($MgFe_2O_4$) minerals were identified in the CFA.

Arsenic, Cd, Mo, Pb, and Zn concentrations were determined in the CFA extracts obtained by acid digestion (Table 2). The elements concentration followed the sequence: As > Zn > Pb > Mo > Cd. These elements

Table 1 Chemical composition (wt.%) in CFA obtained by X-ray fluorescence

SiO_2	Al_2O_3	Fe_2O_3	K_2O	SO_3	TiO_2	CaO	Na_2O	MgO	P_2O_5
54.4	18.0	8.08	2.63	2.39	1.09	1.07	1.07	0.87	0.23
As_2O_3	ZnO	ZrO_2	BaO	PbO	V_2O_5	MnO	SrO	Cr_2O_3	U_3O_8
0.19	0.16	0.12	0.07	0.06	0.06	0.05	0.05	0.03	0.03
Cl	Y_2O_3	MoO_3	NiO	CuO	GeO_2	Rb_2O	Nb_2O_5	Co_3O_4	LI
0.02	0.02	0.01	0.01	0.01	0.01	0.01	nd	nd	9.30

Nd, not detected (< 0.01%); *LI*, losses during ignition (1050 °C)

were selected for this study considering their concentration in the CFA, toxicity, and soil contamination around Figueira coal power plant (Flues et al. 2013; Flues et al. 2008). In general, these concentrations were higher when compared to other countries (Table 3). Figueira ash also showed higher concentrations than ash of other cities from the states of Brazil. Elements concentration in CFA depends on coal geochemical composition and coal combustion processes.

Major elements, anions, and carbon concentrations in CFA leachates

Figures 3 and 4 show major elements, anions, and dissolved carbon in CFA leachates. It can be observed that sulphate and Ca are predominant in the leachates. Calcium concentrations were higher than other alkaline earth and alkaline elements, as **the** following: Ca > Na > K > Mg. The presence of an easily dissolved free lime and salts fraction might explain this high content of Ca (Flues et al. 2013; Lieberman et al. 2014; Lieberman et al. 2016). Leaching of Fe was not detected (< 0.020 $\mu g\ mL^{-1}$). Sulphate concentration was higher than other anions, followed by fluoride. Sulfate presence can be explained by its predominance in the surface of the ash and by the solubility of most sulphate compounds (Izquierdo and Querol 2012). Fluoride from coal enter into fly ash composition after combustion by condensation, and their inorganic forms are predominant on

the ash surface in comparison with their organics (Deng et al. 2016). Their solubility is pH-dependent; acidity increases solubility (Izquierdo and Querol 2012). Thus, the experimental conditions (synthetic acid rain solution pH 4.5) favored the mobilization of F^-.

Aluminum and Mn were present in low concentrations in the leachates (< 0.010–0.026 $\mu g\ mL^{-1}$ and < 0.01–0.103 $\mu g\ mL^{-1}$, respectively) and were not leached continuously during the experiment. Aluminum is usually associated to the glassy matrix (Al, Si) and Mn to ferromagnetic particles (Mn) and oxyhydroxides (Fe) whose dissolution is low under near neutral conditions. Nitrate (< 0.10–2.36 $\mu g\ mL^{-1}$), Cl^- (< 0.10–1.70 $\mu g\ mL^{-1}$) and PO_4^{3-} (< 0.20–1.23 $\mu g\ mL^{-1}$) were not leached continuously from the CFA during the leaching period. Nitrite was not detected (< 0.10 $\mu g\ mL^{-1}$).

The dissolved organic carbon concentration was higher than that of the dissolved inorganic carbon concentrations (Fig. 4). Furthermore, the dissolved organic carbon concentrations in the CFA leachates are related to elements mobility, since elements bonded to organic material can become mobile when organic material is dissolved.

pH of CFA and CFA leachates

CFA pH is considered a key parameter for elements leachability (Izquierdo and Querol 2012; Ram et al. 2007; Ward et al. 2009; Neupane and Donahoe 2013; Wang et al. 2008a, b). Arsenic and Mo have their

Table 2 Elements concentration in CFA extracts obtained by acid digestion

Concentration (mg kg^{-1})

	As	Cd	Mo	Pb	Zn
Mean ± s	1635 ± 64	37.0 ± 0.6	81.8 ± 1.9	154 ± 2	778 ± 18
Range	1590–1680	36.6–37.4	80.4–83.1	151–157	765–791

s standard deviation

Table 3 Concentration of toxic elements in worldwide CFA

	Australia[a]	Asia[b]	Europe[c]	North America[d]	Argentina[e]	Brazil		
						Rio Grande do Sul[f]	Santa Catarina[f]	Figueira[f,g]
Concentration (mg kg^{-1})								
As	11	5.7–490	60–1411	17–167	77	11.9–35.6	37.2	110–1820
Cd	0.9	0.137	1.54–14.4	2–20	1.54	0.41–0.77	1.32	4.9–34.9
Mo	3	7.561	–	52	7.46	3.93–4.95	5.65	62.2–386.6
Pb	75	7.5–181	123–143	12–100	30	26.2–57.3	52.7	20.1–3477
Zn	150	73–290	59.6–133	67–103	54.6	83.6–134	222	1125–5798.5

[a] Ward et al. 2009; [b] Dutta et al. 2009; Wang et al. 2008a, b; Chaudhary and Banerjee 2007; [c] Fytianos et al. 1998; Bolanz et al. 2012; Sočo and Kalembkiewicz 2007; [d] Neupane and Donahoe 2013; Dudas 1981; [e] Smichowski et al. 2008; [f] Depoi et al. 2008; [g] Levandowski and Kalkreuth 2009

mobility enhanced in pH 7–11 range (Izquierdo and Querol 2012; Wang et al. 2008a, b), and Cd and Zn are consistently immobile in near neutral and alkaline conditions, but more mobile at pH 4.5 (Izquierdo and Querol 2012). CFA pH was determined in water and presented an average value of 7.4, near neutral acidity. This value was similar to the average pH value (7.1) of CFA leachates during 336 days (Fig. 5). The experimental conditions (synthetic acid rain solution pH 4.5 and leachate pH 6.9–7.4) favored the mobilization of As, Cd, Mo, and Zn, which are bound to the exchangeable fractions of the CFA particles surface (Izquierdo and Querol 2012; Neupane and Donahoe 2013; Smichowski et al. 2008; Lieberman et al. 2016; Querol et al. 1996).

Arsenic, Cd, Mo, Pb, and Zn leaching from CFA

The 28-day concentrations of As, Cd, Mo, and Zn mobilized from CFA, indicated as serial concentrations in Fig. 6, decreased during the 336 days of percolation. Cumulative concentrations were calculated by Eq. (1).

Molybdenum was the most leached element from CFA (70.7%), followed by As (36.8%), Cd (22.6%), and Zn (0.2%) (Table 4), according to Eq. (2). The high Mo mobility from CFA can be explained considering that Mo has higher solubility under near to neutral conditions (Izquierdo and Querol 2012) and is more associated with exchangeable fractions (Smichowski et al. 2008; Querol et al. 1996) rather than to other CFA fractions (oxides, organic matter, sulfide, and residual). Smichowski et al. (2008) and Querol et al. (1996) studied the Mo distribution on different fractions of CFA and reported an association of this element

between 45 and 77.5% with exchangeable and soluble fractions. Neupane and Donahoe (2013) showed Mo leaching percentage of 47–89% from acidic and alkaline CFA using synthetic acid rain and water. Depoi et al. (2008) reported that 11.1 to 50.8% of Mo was leached from Brazilian CFA-using water.

The mobility of As, Cd, and Zn were lower than Mo under experimental conditions. After the leaching tests, more than 63% of As concentration remained immobilized in CFA, probably because this element is more commonly bound to oxides than soluble, exchangeable, organic matter, and residual fractions (Bolanz et al. 2012; Querol et al. 1996; Jegadeesan et al. 2008; Quispe et al. 2012).

As noted, more than 77% Cd concentration was not leached from CFA, since the association of this element is more related to silicate than non-silicate fractions. As reported previously (Smichowski et al. 2008; Querol et al. 1996; Quispe et al. 2012; Kim and Kazonich 2004), this association could represent 80 to 100% of Cd distribution in CFA. According to these authors, Cd mobilization, related soluble and exchangeable CFA fractions, can vary from 0 to 5%, approximately.

Up to 99% of Zn concentration was not mobilized from CFA. Some authors (Chaudhary and Banerjee 2007; Smichowski et al. 2008; Querol et al. 1996; Jegadeesan et al. 2008; Quispe et al. 2012) have reported that this element is commonly distributed in CFA as the following: 70 to 90% in silicate fractions, 5 to 15% in Fe and Mn oxide fractions, and 1 to 5% in soluble and exchangeable fractions.

Lead was not detected in the CFA leachates (< 0.001 μg mL^{-1}). Izquierdo and Querol (2012) reported that Pb tends to present low solubility in acidic and
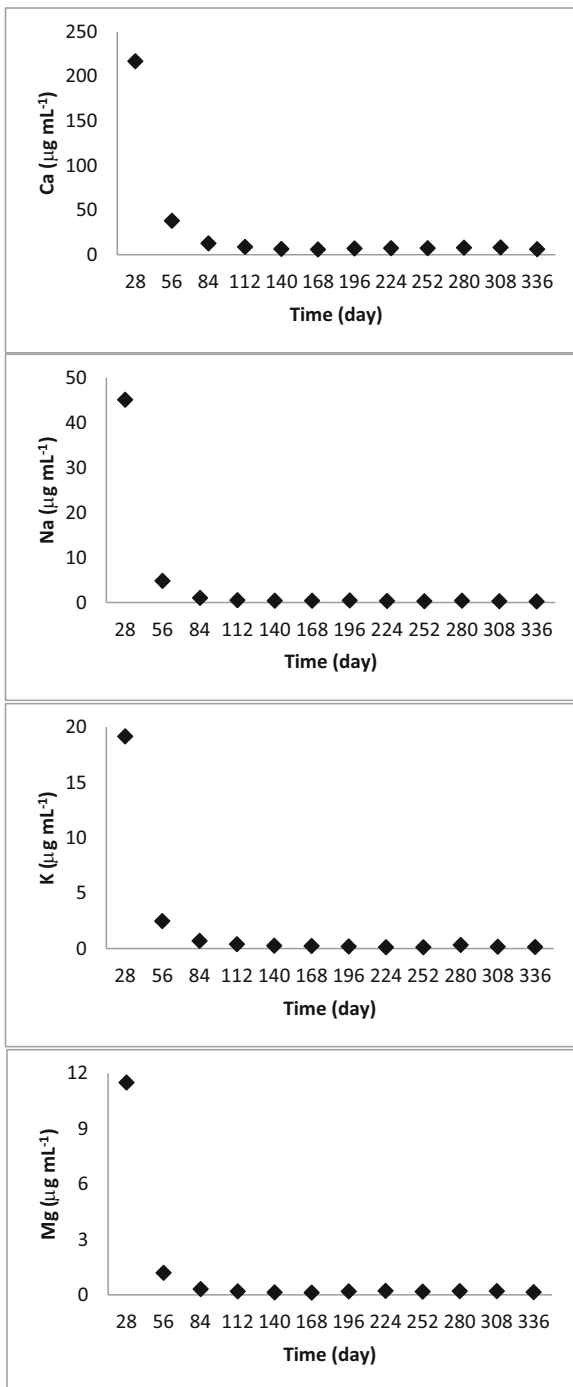
Fig. 3 Concentration of major elements in CFA leachates over a 336-day period

Fig. 4 Concentration of anions and carbon in CFA leachates over a 336-day period. DOC, dissolved organic carbon; DIC, dissolved inorganic carbon

alkaline pH. The low solubility of Pb can be explained because Pb is mostly associated with the silicate fraction of CFA and is less associated with soluble and exchangeable fractions (Chaudhary and Banerjee 2007;
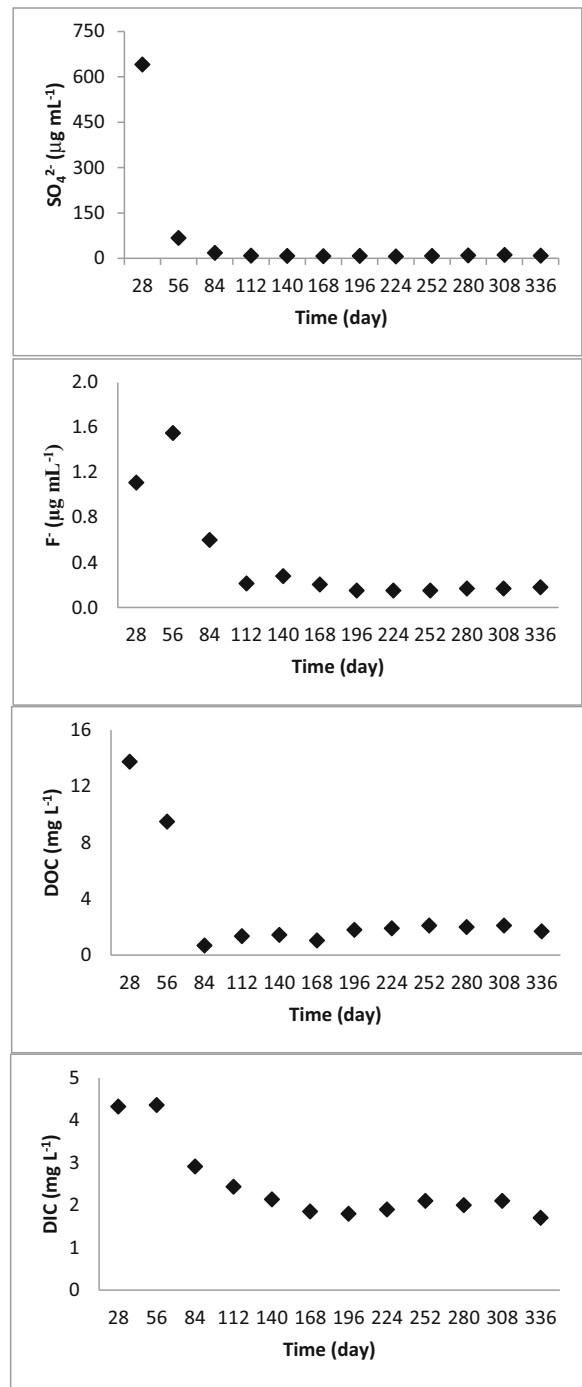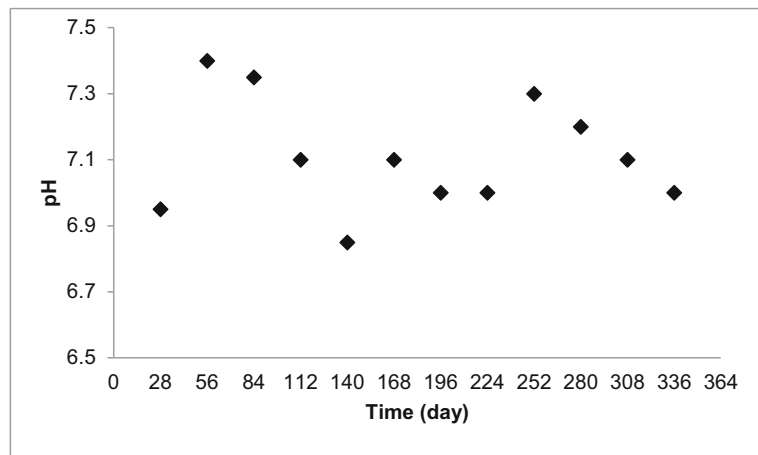
Smichowski et al. 2008; Jegadeesan et al. 2008; Kim and Kazonich 2004).

Molybdenum concentration decreased sharply while As, Cd, and Zn concentration decreased

Fig. 5 pH of CFA leachates over a 336-day period

gradually over 336 days of percolation (Fig. 6): 60% of the total leached mass was released in the first 28 days. This can be explained because Mo is more readily soluble since this element is more associated with CFA soluble and exchangeable fraction than As, Cd, and Zn that are also partially associated with oxides and silicate fractions. The leaching curve of Mo is similar to Ca, Mg, K, Na, and SO_4^{2-} curves (Figs. 3 and 4) since Mo, sulphate, and these major elements are mainly associated on the particles surface of CFA (Izquierdo and Querol 2012; Neupane and Donahoe 2013). The other elements were released gradually, so that the cumulative concentration versus time curve could be fitted by a linear equation, until 112–148 days for As and 148–166 days for Cd and Zn; for longer times, cumulative concentrations tend to stabilize to a maximum value, what however must be further investigated.

The sequence of elements concentration in CFA leachates, As > Mo > Cd > Zn (Fig. 6), was different from CFA, As > Zn > Pb > Mo > Cd (Table 2). This indicates that availability of these elements does not depend exclusively on element concentration in CFA; for example, Pb was not detected in the leachates and Zn presented low concentrations. According to Izquierdo et al. (2008), in general, the leachable concentration of an element is not necessarily correlated with its concentration in CFA; however, it can be correlated when the element solubility is mainly controlled by a single phase and when elements are present as soluble salts, as observed for Mo. However, if the single phase is crystalline or oxides, correlation may not be observed.

Correlation analysis

The long-term leaching tests carried out in this experiment provide a better representation of field conditions of CFA dumps exposed to climate. This method allowed correlating elements leaching with natural variation of extrinsic parameters, such as temperature, air humidity, and precipitation volume (Table 5).

Molybdenum concentrations did not correlate to leaching volume, room temperature, nor air moisture at the significance level of 0.05: since 60% of the leached mass had already been released in the first 28 days (Fig. 6), there was not time enough to observe the influence of environmental conditions on leached concentrations. A significant positive correlation between As and Cd concentrations and room temperature was observed, indicating that As and Cd can be more easily leached from CFA in summer period when temperatures are higher. Khanra et al. (1998) showed that As concentration increases with increasing temperature between 30 and 80 °C under acidic leaching.

Cadmium showed significant positive correlation with leachate volume ($r = 0.70$, $p < 0.01$), suggesting that higher volume of synthetic acid rain results in higher Cd leaching from CFA. This indicates that the leachability of Cd from CFA can increase during summer, where rain volume is higher than other periods.

Environment impact of As, Cd, Mo, and Zn leachate from CFA

Arsenic, Cd, Mo, and Zn leached from CFA in contact with soil can suffer natural attenuation or can also be transported to groundwater.
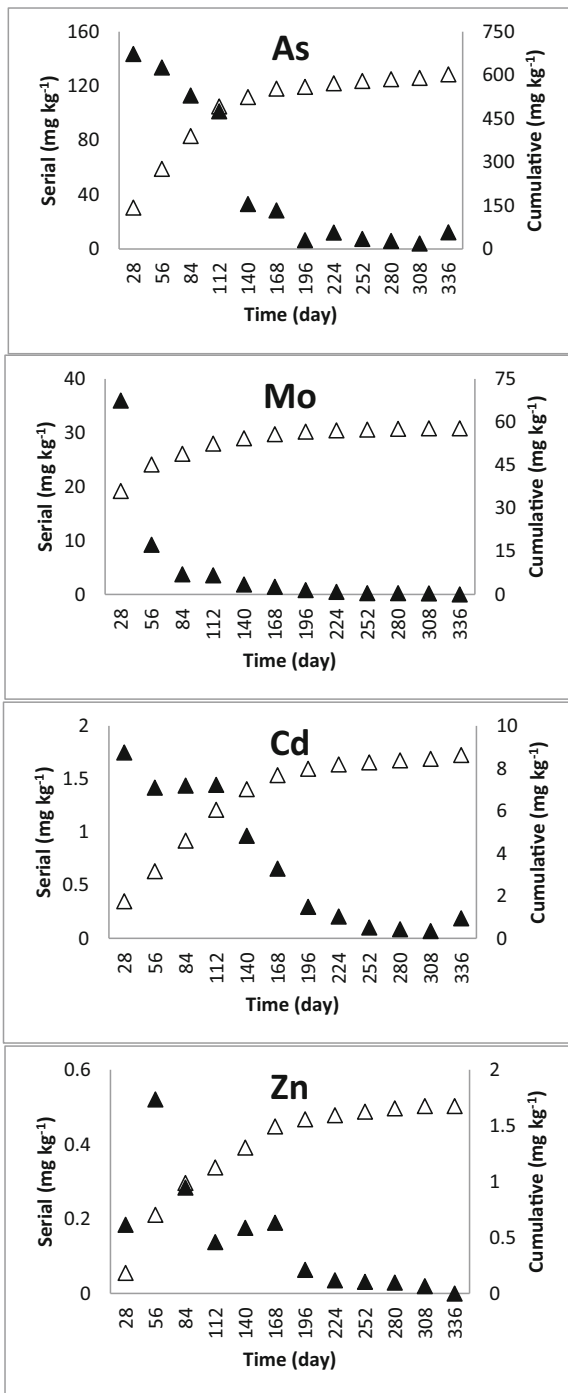
Fig. 6 Serial (▲) and cumulative (△) concentration of As, Mo, Cd, and Zn released from CFA over a 336-day period

The cumulative concentration of As, Cd, Mo, and Zn leached from CFA was 603 mg kg^{-1}, 8.6 mg kg^{-1}, 57.8 mg kg^{-1} and 1.7 mg kg^{-1}, respectively. In general,

Table 4 Total leached percentage (%) over a 336-day period

Total leached (%)			
As	Cd	Mo	Zn
36.8	22.6	70.7	0.2

these concentrations of As and Cd leached were higher when compared to CFA from other countries (Table 3).

Elements concentrations in leachates varied from 0.9 to 16.4 μg mL^{-1} for As, from < 0.05 to 4.23 μg mL^{-1} for Mo, from 0.023 to 0.20 μg mL^{-1} for Cd, and from < 0.005 to 0.044 μg mL^{-1} for Zn. These values cannot be compared directly with limit values for groundwater because of natural attenuation of soil. Therefore, elements concentration was divided by a natural attenuation factor 10, as recommended by CETESB. Just for illustrative purpose, these values were compared with toxic elements concentration limits established by CETESB (Casarini et al. 2001). Of course, in a real field conditions, the leached concentrations will be still attenuated by soil partition, not addressed in the present study. Figure 7 shows the elements concentration in leachates divided by factor 10, and also the limit values for groundwater. Note that, with exception of Zn, these graphics suggest that As, Cd, and Mo concentration in groundwater, down gradient from the ash disposal zone, could be above the limits established and needs to be prospected.

One of drawbacks on coal utilization as fossil fuel is the production of fly ashes waste which is frequently dumped without management practices to avoid the contamination of the surrounding environment due to hazardous trace elements such as As, Cd, Mo, Pb, and Zn. In this study, these elements were leached from Figueira CFA under synthetic acid rain over 336 days

Table 5 Correlation coefficient (r) between toxic elements concentration in the leachates and extrinsic parameters. Sample size n = 12

	As	Mo	Zn	Cd
Leaching volume	0.57	0.17	0.52	0.76[a]
Room temperature	0.76[a]	0.45	0.62[b]	0.89[a]
Air moisture	0.63[b]	0.42	0.38	0.68[b]

[a] Correlation is significant at the 0.01 level
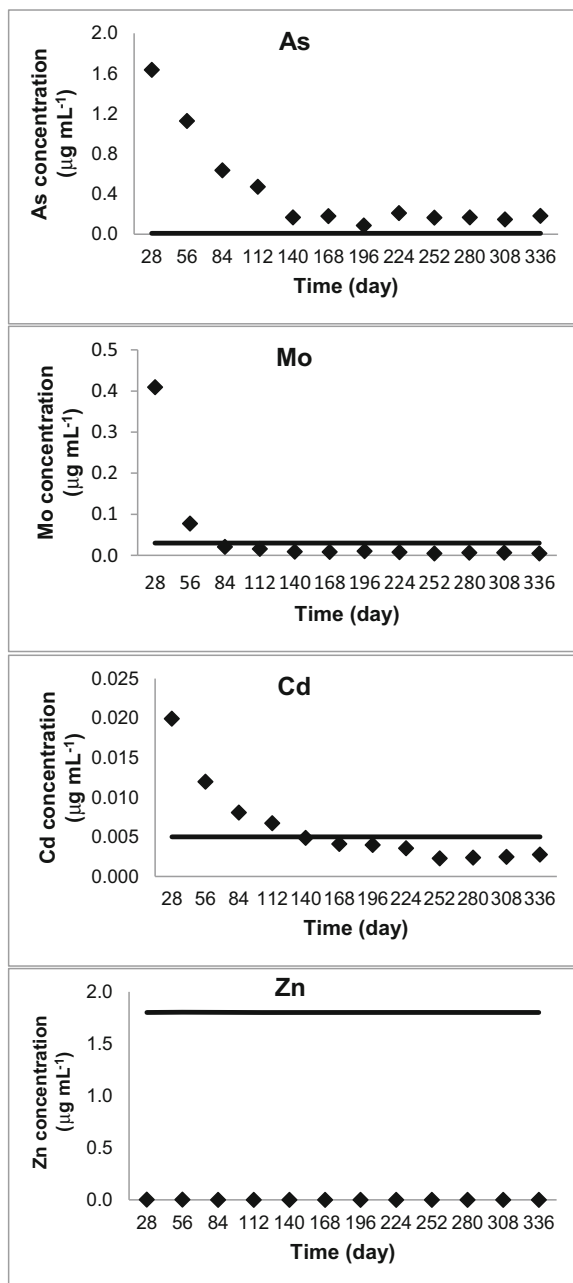
[b] Correlation is significant at the 0.05 level

Fig. 7 Concentration of As, Mo, Cd, and Zn leached from CFA divided by a natural attenuation factor 10 and limit value for groundwater established by São Paulo State Environmental Agency (CETESB 2017)

concentration indicated that these elements have higher leachability from CFA during summer period when temperature and rain volume are higher than other seasons.

The concentrations of most of the elements decreased rapidly with respect to time, except for As. The results for As, Cd, and Mo in CFA leachate indicate an environmental concern, since the concentration in groundwater could be exceeding guideline values. This fact suggests that open dumping should be avoided to prevent groundwater contamination. Arsenic can be considered as a more critical element than Cd, Mo, Pb, and Zn in Figueira CFA due to its high concentration in CFA (1635 mg kg^{-1}) and the fraction leached (603 mg kg^{-1}). Although Pb and Zn presented high concentration in CFA, these elements are not environmental concern considering weathering action due to the fact that they are not considerably leached from CFA.

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of percolation, indicating that these elements can be leached in natural environment conditions when CFA is deposited on a soil exposed to weathering. These elements leachability showed to be leaching volume and temperature dependent. The temperature and leaching volume correlation with Cd and As

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