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Assessing bioaccessible fractions of arsenic, chromium, lead, selenium and zinc in coal fly ashes

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Abstract The utility of a physiologically based extraction test for evaluating the bioaccessibility of metals from fly ash in the human gastrointestinal system was evaluated in the present research. Calcium-rich and silica-rich fly ashes collected from eight power plants in India and United States of America were assessed for bioaccessibility for arsenic, chromium, lead, selenium and zinc. The results from the physiologically based extraction test were compared with those from a sequential extraction procedure that is often applied to solid wastes. Based on the physiologically based extraction test results, more than 40 % of the arsenic was found to be bioaccessible for all the ashes while selenium was very accessible for the calcium-rich ashes. Lead was found to be insignificantly bioaccessible in calcium-rich as well as silica-rich fly ashes. The mobilization of metals in the first three steps of the sequential extraction procedure was similar to the mobilization in the physiologically based extraction test for selenium for all ashes and for arsenic and chromium for most ashes, but the sequential extraction procedure mobilized more zinc than did the physiologically based extraction test. These results indicate that while sequential extraction procedures can provide good estimates of the bioaccessibility of many elements, extraction tests that more closely simulate physiological conditions can provide more accurate measures of bioaccessible concentrations of metals.

Keywords Bioaccessibility · Coal fly ash · Leaching · Metals · Physiologically based extraction · Sequential extraction procedure

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Introduction

About 40 % of global electricity is generated from coal-fired thermal power plants that consume over 5 billion tons of coal (Mukherjee et al. 2008) and produce more than 700 million tons of coal fly ash each year (Prakash and Sridharan 2009). In addition to impacts of coal-fired power plants on air quality through atmospheric emissions, the generation of metal-rich fly ash poses additional environmental concerns. Increasing coal consumption in thermal power plants implies increased emission of metals in gaseous forms and in the form of fly ash (Kim et al. 2002; Vassilev and Vassileva 2005). The toxic metals that are naturally present in coal are enriched in the coal fly ash as a result of combustion. As, Pb, Se, Cr, Ni, Cd, Zn and Hg are common potentially harmful elements carried by coal fly ash (Dayan and Paine 2001; Sonmez and Pierzynsk 2005).

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The availability and the mobility of metals occurring in coal fly ash depend on the physicochemical forms of the metals (Smeda and Zyrnicki 2002), and the total metal contents of the ash are generally poor predictors for the leachable concentrations of the metals (Thorneloe et al. 2010). The environmental conditions as well as the physical and chemical properties of the coal fly ash have a great impact on the mobility of coal fly ash constituents. The metal-related risks associated with coal fly ash should not be determined by the total metal concentrations in the fly ash but rather by the fractions that may be mobilized (i.e., leached) in aquatic systems. Metal mobility can be affected by changes in pH, redox potential, ionic strength and the presence of complexing agents (Popovic and Djordjevic 2009). Metal speciation is influenced by the mechanisms of metal association with the coal fly ash, which include chemical and physical adsorption, precipitation and encapsulation.

There are several metals that may be readily bioavailable, which leads to growing environmental concerns regarding fly ash disposal and utilization (Singh 2005). The bioaccessibility means the amount of metal and metalloids is mobilized and hence, become available to human body under different exposure conditions and environment. For example, the amount of metal that is available for absorption after indigestion is a key parameter in estimating potential human exposure. Various extraction processes are used to determine the potential for metal release from solids at specific environmental conditions to classify materials as hazardous, and to assess metal bioaccessibility. The toxicity characteristic leaching procedure (TCLP) is extensively used in the United States to classify materials as hazardous or non-hazardous based on the extent of leaching of toxic constituents from the material. There are sequential extraction procedures, which can be used to infer mechanisms of metal binding to coal fly ash (Kosson et al. 2002; Worathanakul et al. 2008). These have been used in various forms to determine the amounts of metals in fly ash that are water soluble, ion exchangeable and other extractable forms (Huang et al. 2007). In addition, physiologically based extraction procedures have been proposed specifically to quantify human exposure to toxic metals and metalloids via the oral ingestion pathway.

Physiologically based extractions have been applied to different metal-containing solids to assess the bioaccessibility of metals when the solids are in contact with solutions designed to simulate the human gastrointestinal tract. The physiologically based extraction test (PBET) was developed by Ruby et al. (1996) to simulate the behavior of material in the stomach and the small intestine by providing the appropriate pH, solid-to-liquid ratio and mixing and emptying rates. The PBET is a two-step test that uses hydrochloric acid, pepsin, tri-sodium citrate, sodium malate, lactic acid and acetic acid mixture to simulate the stomach environment with 1-h residence time and a neutralized solution containing additional bile salt and pancreatin compounds to simulate the small intestine with 2-h residence time (Ruby et al. 1996). Wragg and Cave (2002) demonstrated the PBET as a practical methodology for in vitro measurement of the bioaccessibility of metals and metalloids. The PBET has been applied to soils, mussel tissues, airborne dusts, mine-waste contaminated soils, mining wastes and magnetic fractions of coal fly ashes (Bruce et al. 2007; Roe and Klinck 2007; Wragg et al. 2007; Navarro et al. 2008; Lu et al. 2009; Sialelli and Urquhart 2010).

The objective of the present study work was to assess the bioaccessibility of significant trace elements in coal fly ash through the use of a physiologically based extraction test. The extraction method was applied to a range of coal fly ashes from the thermal power plants in India and in the United States that differed in their origin and physical and chemical properties. The research was conducted at Washington University, USA from September 2010 to December 2010 and at IIT Bombay, India from July 2009 onwards till date.

Materials and methods

Materials

Three fly ashes (IN-A, IN-B and IN-C) from three full-scale Indian power plants and five fly ashes (US-A, US-B, US-C, US-D, and US-E) from five U.S. power plants were collected from hoppers of the electrostatic precipitators. All fly ash samples were sieved to finer than 250 μm before experiments. The fly ashes were analyzed by powder X-ray diffraction (Rigaku Geigerflex, Japan) to identify the crystalline phases present in the fly ash for physical characterization of its mineralogy. All the fly ash samples were evaluated for their mineralogical compositions by the above XRD spectrometer with graphite monochromator and Cu-Kα radiation. The samples were scanned from 2θ of $0°–180°$.

Ultra pure water produced by Millipore ultrapure water kit (Milli-Q Academic, USA) was used for washing of glassware and preparation of reagents. Ammonium nitrate, acetic acid, sodium dithionite, sodium citrate, sodium bicarbonate, and concentrated nitric acid and hydrochloric acid were used to prepare extractants for the sequential extraction procedure. Pepsin, sodium malate, sodium citrate, lactic acid, acetic acid, bile salt and pancreatin were used for the preparation of stomach and intestinal fluid for use in the PBET. Nitric acid, hydrochloric acid and acetic acid were trace metal grades. All chemicals were of

analytical reagent grade and were purchased from Fisher Scientific (Pittsburgh, USA). A mutli-element custom standard (ICSU-2726) from Ultra Scientific Analytical Solutions (N. Kingstown, USA) was used for calibration of the inductively coupled plasma mass spectrometer (ICP-MS). An aliquot of this standard was also used as control during the experiments.

Methods

Sequential extraction procedure

The sequential extraction procedure (SEP) used here has been modified from that proposed by Noel et al. (2007) and is shown in Fig. 1. The fly ashes were subjected to the following five steps: (1) ultrapure water was used to extract water soluble metals; (2) 1.0 M ammonium nitrate was used to remove ion exchangeable metals; (3) 0.11 M acetic acid targeted acid soluble metals; (4) a solution of 0.128 M sodium dithionite, 0.3 M sodium citrate and 0.1 M sodium bicarbonate was used to remove reducible metals; and (5) finally a 4:1 mixture of concentrated nitric acid and hydrochloric acid at 100 °C in Hot Block (Environmental Express, USA) dissolved the remaining solids. Based on optimization tests carried out at 30 rpm in a specifically fabricated end-over-end mixer, a solid-to-liquid ratio (1:100) of 0.5 g ash/50 mL extractant (10 g/L) was used. The optimum agitation times were found to be 24 h for the acid soluble and reducible steps, while 4 h was optimum for the remaining steps. 0.5 g ash was mixed with 50 mL extractant in 100-mL centrifuge tube for the prescribed time at 30 rpm. After agitation, the suspension was centrifuged for 10 min at 10,000 rpm. Nearly, all of the supernatant was decanted and filtered with a 0.2-μm PTFE filter. The supernatant was acidified to 2 % (by mass) by adding required nitric acid. The solids remaining from the centrifugation were then gathered with the next extractant in the sequence. Concentrations of metals of interest in various acidified samples were obtained using ICP-MS.

Physiologically based extraction test

The various parameters for conducting the PBET, viz. gastric and intestine pH, sample mass-to-fluid ratio, stomach mixing, stomach emptying rate and intestinal transit rates, were chosen on the basis of previous studies (Ruby et al. 1996, 1999; Hamel et al. 1998; Rodriguez et al. 1999; Roe and Klinck 2007; Wragg et al. 2007; Sialelli and Urquhart 2010). The details of PBET procedure are shown in Fig. 2. 1.0 g fly ash was taken in 250-mL I-CHEM certified glass bottle. In the first step, which is to simulate the stomach phase, 100 mL gastric solution (a mixture of 1.25 g pepsin, 0.50 g sodium malate, 0.50 g sodium citrate,

420 μL lactic acid and 500 μL acetic acid made up to 1 L with freshly prepared ultrapure water, adjusted to pH 2.5 with concentrated hydrochloric acid) was added to each bottle, thus maintaining solid-to-liquid ratio of 1:100. The suspension was agitated at 30 rpm at 37 °C in a controlled water bath in a PBET setup fabricated as per EPA (2008). A period of 1-h contact was provided to simulate the typical residence time of solids in the stomach. At the conclusion of this hour, a 5 mL stomach sample was drawn from the bottle. Equivalent amount (5 mL) of stomach phase gastric solution was replaced to the bottle. After the stomach phase, bile salt (70 mg/100 mL) and the pancreatin (50 mg/100 mL) were added to each bottle and the pH was adjusted to 7.0 with saturated sodium bicarbonate solution to simulate the small intestinal conditions. Intestinal samples (5 mL each) were collected during the small intestinal phase after 3 and 5 h and are referred to as intestinal phases 1 and 2. Extracted samples were centrifuged for 10 min at 10,000 rpm. The supernatant was filtered with 0.2-μm PTFE filter and then acidified to 2 % (by mass) HNO_3. The concentrations of metals of interest in stomach, intestinal phases 1 and 2 samples were analyzed using ICP-MS. The higher of the two metal values in intestinal phases 1 and 2 samples was taken as metal extracted in intestine phase.

The bioaccessible fraction is the amount of the element in the ash that can be solubilized in the solutions representing either the stomach or small intestine. The percentages of metal leached in the simulated human gastrointestinal environment of stomach and intestine phases were calculated (Roe and Klinck 2007) as follows:

Bioaccessible factor
$$= \frac{\text{Metal extracted in stomach/intestine phase}}{\text{Total extractable metal}} \times 100$$
(1)

where total extractable metal is the maximum metal that can be directly extracted by acid digestion, that is, 0.5 g fly ash digested with 4:1 mixture of concentrated nitric acid (10 mL) and hydrochloric acid (2.5 mL) at 100 °C in Hot Block for 4 h.

Determination of metals concentrations

Concentrations of trace metals in samples from SEP and PBET were obtained using an Agilent ICP-MS (Model 7500ce, USA). Prior to analysis, the samples were diluted with 2 % HNO_3 solution. Samples from the SEP were diluted 1:10 for the water soluble step, 1:20 for the acid soluble step and 1:50 for the other three steps. PBET samples used a 1:10 dilution factor. Calibration standards were analyzed in the same matrices as the samples.

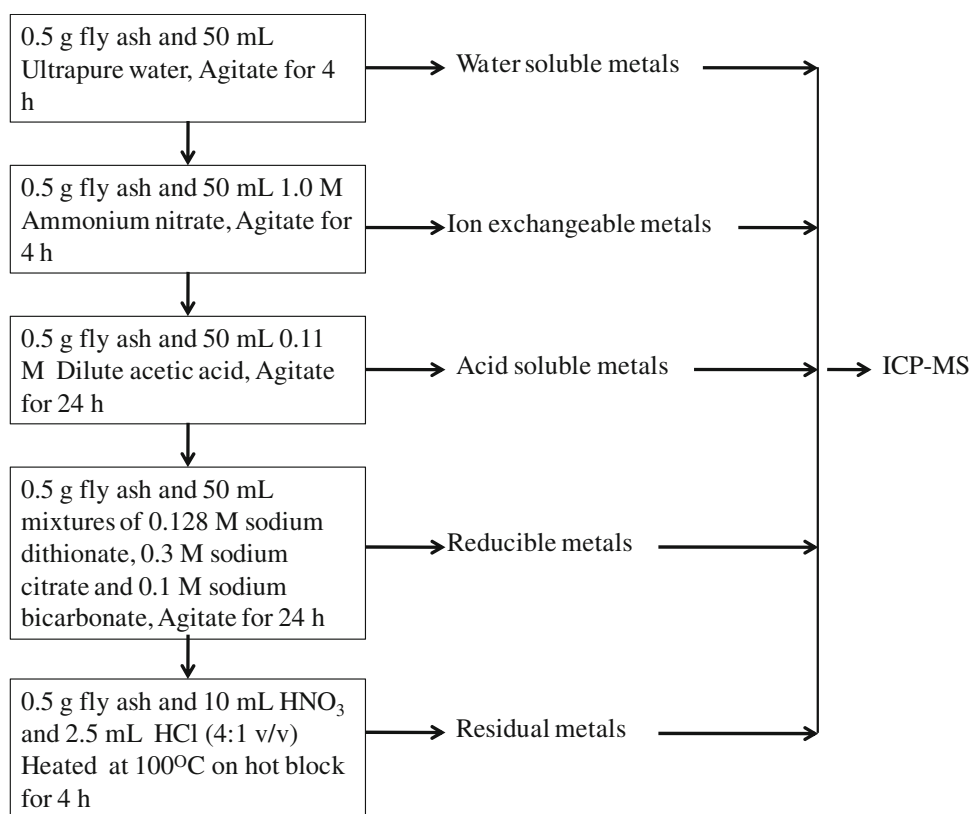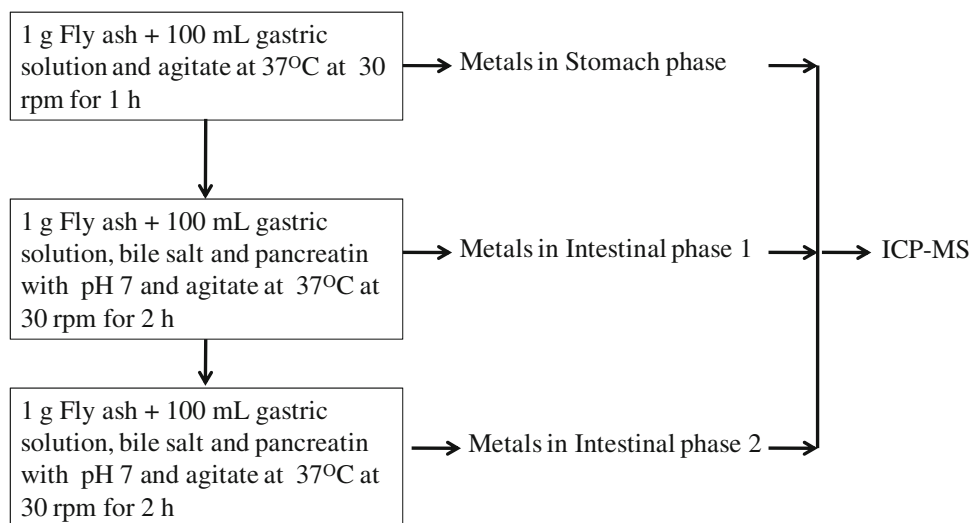**Fig. 1** Sequential extraction for assessing the leaching potential of metals

| 0.5 g fly ash and 50 mL Ultrapure water, Agitate for 4 h | → Water soluble metals |

| 0.5 g fly ash and 50 mL 1.0 M Ammonium nitrate, Agitate for 4 h | → Ion exchangeable metals |

| 0.5 g fly ash and 50 mL 0.11 M Dilute acetic acid, Agitate for 24 h | → Acid soluble metals |

| 0.5 g fly ash and 50 mL mixtures of 0.128 M sodium dithionate, 0.3 M sodium citrate and 0.1 M sodium bicarbonate, Agitate for 24 h | → Reducible metals |

| 0.5 g fly ash and 10 mL HNO_3 and 2.5 mL HCl (4:1 v/v) Heated at 100^OC on hot block for 4 h | → Residual metals |

→ ICP-MS

Fig. 2 Extraction of toxic metals by physiologically based extraction test

| 1 g Fly ash + 100 mL gastric solution and agitate at 37^OC at 30 rpm for 1 h | → Metals in Stomach phase |

| 1 g Fly ash + 100 mL gastric solution, bile salt and pancreatin with pH 7 and agitate at 37^OC at 30 rpm for 2 h | → Metals in Intestinal phase 1 |

| 1 g Fly ash + 100 mL gastric solution, bile salt and pancreatin with pH 7 and agitate at 37^OC at 30 rpm for 2 h | → Metals in Intestinal phase 2 |

→ ICP-MS

Quality control/quality assurance

The quality control (QC) samples were analyzed as part of the ICP-MS analytical runs to check for instrument drift, accuracy and precision. Spiked blanks of the mutli-element custom standard (ICSU-2726) were used as control for ICP-MS during the experiments. Secondary standards were also used frequently to check the accuracy. SEP and PBET also involved the extraction and analysis of blank samples and standard reference fly ash material (NIST 1633b). All analytical and sampling experiments were carried out in duplicates. The minimum detectable limit for the metals ranged from 0.01 ppb for minor metals to 1 ppb for major metals.

Results and discussion

Indian and the U.S. coal fly ash properties

Two power plants in India are using bituminous coal mined from Indian coal fields while one is using sub-bituminous coal imported from Indonesia. The ash content of

Indonesian coal was about 1.9 % while that of Indian coals was 25 and 38 %, respectively. Usually coal fly ashes are classified as class C and class F based on their calcium oxide contents. Class C ashes are calcium-rich with greater than 10 % calcium oxide while class F ashes are silicon-rich having less than 10 % calcium oxide. Coal fly ash IN-B is class C ash being calcium-rich while IN-A and IN-C are silica-rich class F ash.

The U.S. power plants all use Powder River Basin sub-bituminous coals that typically have 4–7 % ash content (WGS 2011). All five of the U.S. ashes are class C ashes. The crystalline phases present in the fly ashes are shown in Fig. 3 while Table 1 shows mineralogy and composition of all fly ashes.

Metals extracted in sequential extraction procedure and physiologically based extraction test

The SEPs were carried out for 25 major and minor metals present in all the eight fly ash samples. On the basis of the concentrations, five metals viz. arsenic, chromium, lead, selenium and zinc were found to be the most significant, and hence these five elements were evaluated for bioaccessibility for assessing human exposure by accidental or otherwise ingestion.

Leaching and dilution of toxic metals in the simulated conditions and residence time of acidic stomach phase and the neutral intestinal phase were dependent on the form of metals present in the coal fly ash. Significant amount of metals solubilization taking place in the stomach phase and the intestinal phase environment was strongly depended upon the pH of the gastrointestinal fluid, presence of calcium, silica and other minerals oxides present in the coal fly ash. The results from PBET were compared with the first 3 steps of SEP results, which are very similar to the TCLP. The total metal extracted through acid digestion was considered as the total extractable metal. Finally, bioaccessible fractions for various metals were determined in using Eq. (1). The results are shown in Fig. 4a–e and are discussed below for each of the five metals.

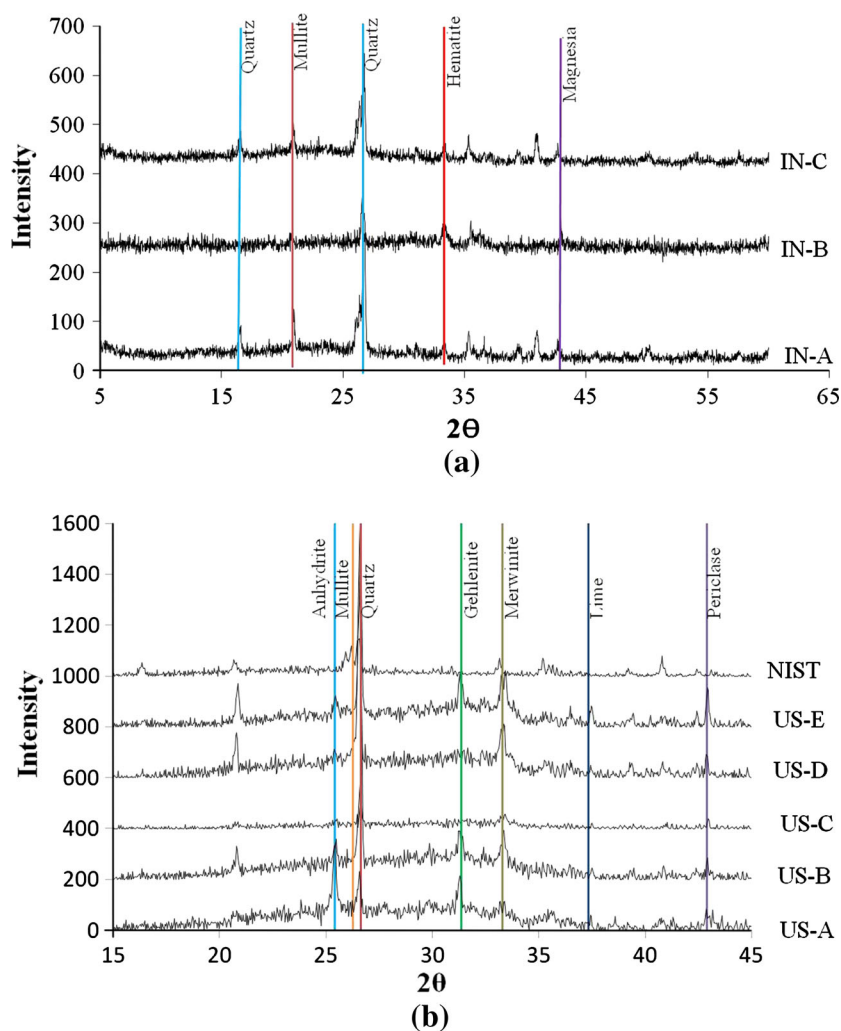**Fig. 3** Crystalline phases present in **a** Indian fly ashes and **b** the U.S. fly ashes

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Table 1 Composition and mineralogy of fly ash materials studied

Fly ash	LOI (%)[a]	As (μg/g)	Cr (μg/g)	Pb (μg/g)	Se (μg/g)	Zn (μg/g)	Ash class	Major minerals
IN-A	1.4	12.8	11.5	8.0	31.0	73.2	F	Quartz, mullite
IN-B	1.1	52.9	39.3	28	17.5	204.8	C	Quartz, magnesia, hematite
IN-C	1.6	6.1	3.2	4.6	23.4	64.0	F	Quartz, mullite
US-A	17.5	22.7	64.9	43.5	15.0	230.3	C	Anhydrite, quartz, gehlenite, merwinite, periclase, lime
US-B	0.3	24.1	82.2	33.1	7.4	218.0	C	Anhydrite, quartz, gehlenite, merwinite, periclase, lime
US-C	0.7	26.9	85.3	38.0	14.5	332.7	C	Anhydrite, quartz, merwinite, periclase, lime
US-D	1.6	25.1	62.8	24.0	10.1	45.0	C	Anhydrite, quartz, merwinite, periclase, lime
US-E	0.4	21.4	64.3	28.2	13.5	34.1	C	Anhydrite, quartz, gehlenite, merwinite, periclase, lime

[a] LOI is loss on ignition, which represents the unburned carbon content in the fly ash samples

Arsenic

Potentially As leaching took place in the acidic environment in the case of Ca-rich fly ash because pH of the leaching solution was 2.5. The percentages of leaching of As in the case of Ca-rich coal fly ash ranged from 40 to 57 % (Fig. 4a). In the Si-rich coal fly ash, As leaching took place in the intestinal phase 1 at pH 7 in the neutral environment of the system. Here, redox reactions occurred in neutral environment of the system due to As bound with oxides and hydroxides in the silicon content of the coal fly ash. As mineral solubilities vary widely according to arsenic oxidation state. As leaching in the intestinal phase of the Si-rich coal fly ash depended on the pH, concentration of the bile salt and the pancreatin solution present in the gastric solution and ranged between 64 and 100 %.

In Ca-rich coal fly ash, As leaching from the stomach phase were in the range of 12–21 μg/g of ash whereas the three-step SEP As leaching were 1–17 μg/g of the ash and the 23–53 μg/g of ash as total As.

For most of the ashes, the greatest amounts of As were leached from the ash in the acidic environment of the PBET. With only one exception (IN-C), the PBET extracted more As than did the 3-step SEP. The difference is particularly striking for the U.S. ashes D and E. The regulatory TCLP test, which is similar to the 3-step SEP, may underestimate the bioaccessibility of As in fly ash. As adsorbs well to iron oxides in mildly acidic solutions, so the mobilization of As in the PBET may be driven more by effects of the organic components of the extraction solutions than by the acidity of the solutions. A recent X-ray absorption spectroscopy of the five U.S. ashes determined that the As was primarily As(V) and largely present as calcium pyroarsenate ($Ca_2As_2O_7$) (Luo et al. 2011). As release

during the PBET may be controlled by dissolution of this phase.

Chromium

As seen from Fig. 4b, the significant amount of Cr leaching (10–55 %) took place in the stomach phase for the Ca-rich coal fly ash. This is due to the formation of soluble species stable at acidic pH environment and Cr co-adsorbed with iron oxide mineral substrate. In Si-rich coal fly ash, the Cr leaching occurred in the intestinal neutral environment of the gastric solution. This is due to the solubilization of Cr in the neutral pH condition. It ranged from 43 to 59 %.

The 3-step SEP results of the Ca-rich coal fly ashes ranged from 9 to 30 μg/g of ash whereas in case of Si-rich coal fly ash, these were in the range of 0.4–3 μg/g. Total Cr amounted from 11 to 13 μg/g in the case of Ca-rich coal fly ash whereas in silica-rich coal fly ash, the same ranged between 18 and 58 μg/g of ash.

More Cr leaching took place from the Ca-rich ashes (U.S. ashes and IN-B), which is consistent with their substantially greater Cr contents. The mobility and toxicity of Cr are strongly dependent on the oxidation state, Cr(III) versus Cr(VI), but unfortunately no measurements of the Cr oxidation state were available. Cr(VI) is present as anionic species ($HCrO_4^-$ and CrO_4^{2-}) and is much more toxic than Cr(III). Since the pattern of Cr results is not very similar to that of As, which is present as anionic arsenate for the ashes, it may indicate that the Cr is present as Cr(III) and not Cr(VI).

Lead

Pb leaching took place in the stomach phase of the Ca-rich coal fly ash due to the release of Pb in the gastric solution
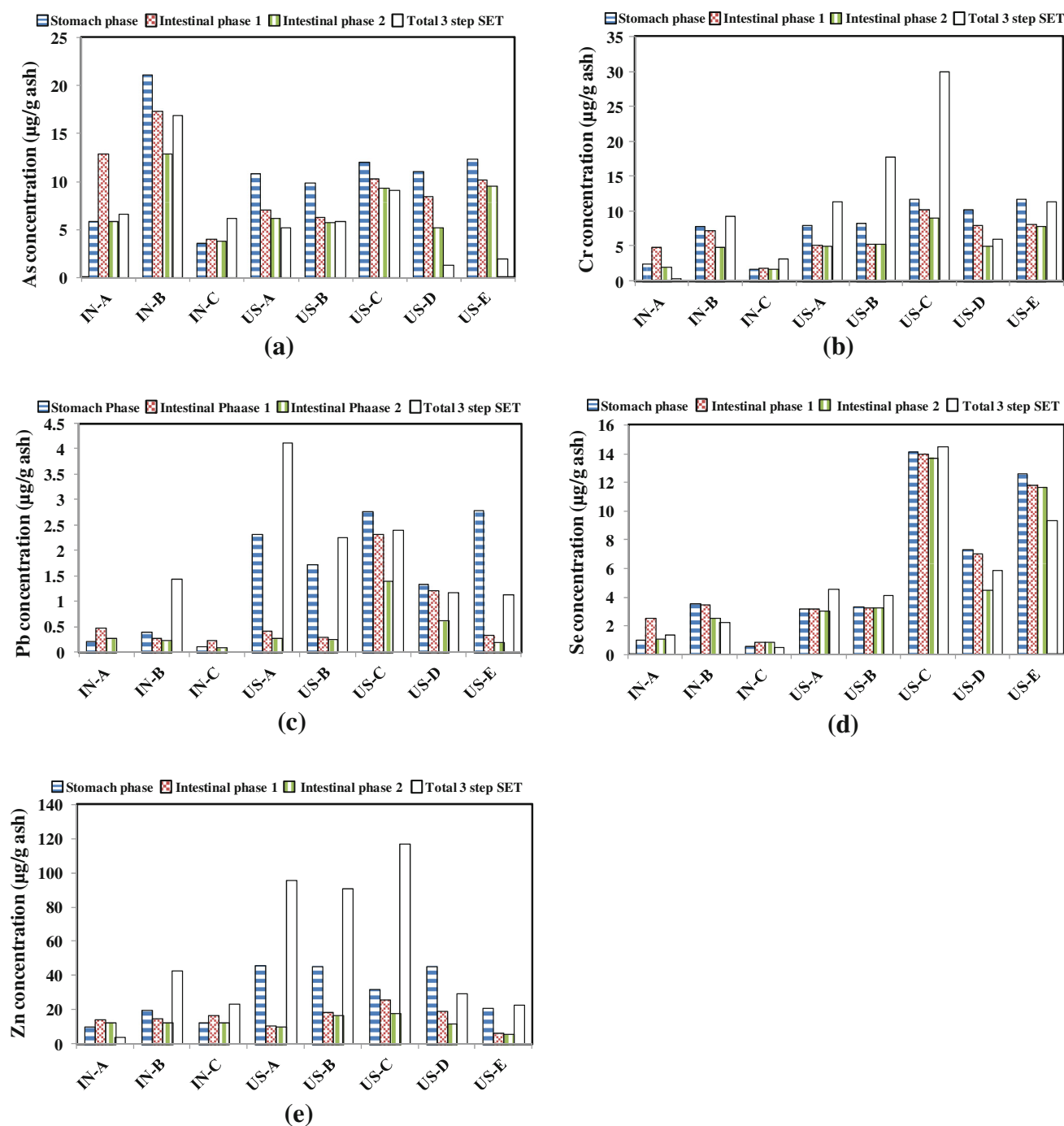
Fig. 4 The amount of **a** arsenic, **b** chromium, **c** lead, **d** selenium and **e** zinc extracted in stomach, intestinal phase 1, intestinal phase 2 and 3-step sequential extraction procedures

in the acidic environment and then in the intestinal phase where pancreatin and bile salts were added and the pH of the solution was increased to neutral condition, the leaching of Pb in the intestinal phase was decreased.

In Ca-rich coal fly ash, metal leaching of Pb in the stomach phase was in the range of 0.4–3 μg/g of ash

whereas the three-step SEP Pb leaching ranged between 1 and 4 μg/g of the ash (Fig. 4c), and between 24 and 44 μg/g of ash as total Pb. The extractability of Pb leaching by PBET and SEP revealed that the huge amount of Pb leaching occurred in the SEP for the same solid-to-liquid ratio. In the case of Si-rich coal fly ash, minor quantities of
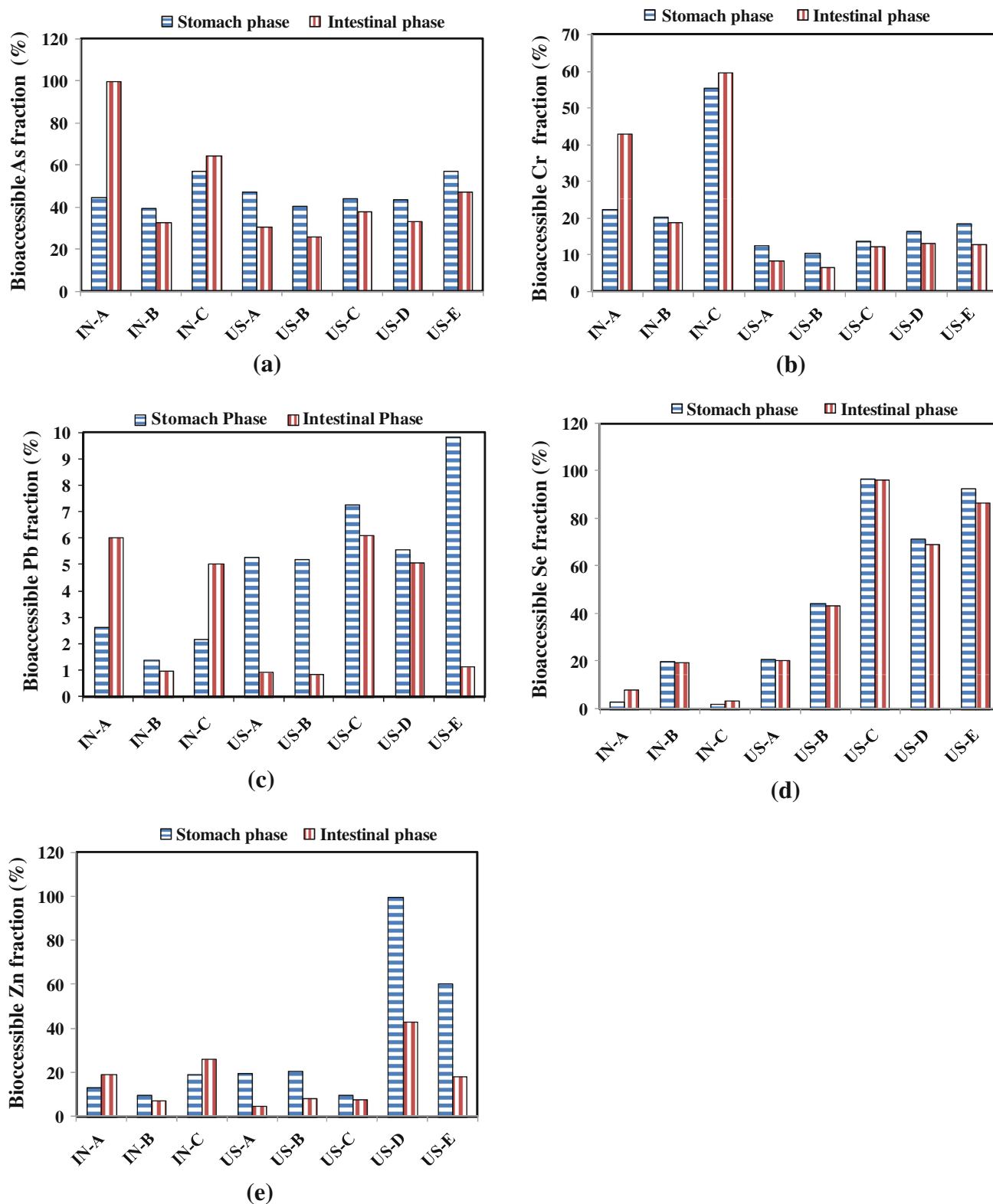
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Fig. 5 Bioaccessible fraction of **a** arsenic, **b** chromium, **c** lead, **d** selenium and **e** zinc from various coal fly ash samples as determined by PBET

Pb leaching took place in the intestinal phase and were range between 0.2 and 0.5 μg/g of ash. The three-step SEP in the coal fly ash was zero, and the total Pb ranged between 5 and 8 μg/g of ash. The quantities of Pb leaching in the case of Si-rich coal fly ash in the intestine phase were ranged between 5 and 6 %.

Selenium

During the PBET, considerable Se leaching took place in the stomach phase for the Ca-rich coal fly ash due to its leaching in acidic environment and the bioaccessible Se ranged from 20 to 97 % (Fig. 4d). In Si-rich coal fly ash, the leaching occurred in the intestinal phase and it ranged from 3 to 8 %.

The 3-step SEP of Se in the case of Ca-rich coal fly ash was from 2 to 9 µg/g of ash whereas total Se ranged between 7 and 17 µg/g of ash. In the case of Si-rich coal fly ash, the three-step SEP Se extracted ranged from 0.5 to 1 µg/g of ash whereas the total Se ranged between 23 and 31 µg/g of ash.

More Se was extracted from the Ca-rich ashes (all five U.S. ashes and IN-B) than from the Si-rich ashes, although the Si-rich ashes (IN-A and IN-C) actually had the highest Se contents of the eight ashes studied (Table 1). The solid phase speciation of Se clearly influences the leachability of Se more than does the total Se content. The Se speciation is probably much different for the Si-rich ashes than for the Ca-rich ashes. Because of the limited Se content of the Ca-rich ashes, the X-ray absorption spectroscopy study could only determine that the Se was predominantly Se(IV) (Luo et al. 2011) and it could not provide additional structural information. The 3-step SEP was an excellent predictor of the Se that can be mobilized in the PBET and consequently TCLP measurements may provide a good estimate of Se bioaccessibility.

Zinc

Considerable Zn leaching took place in the acidic environment of the calcium-rich coal fly ash and ranged between 10 and 100 % (Fig. 4e). In silica-rich coal fly ash, the Zn leaching occurred in the intestinal phase 1 of the neutral environment and ranged between 19 and 26 %. The three-step SEP of the calcium-rich coal fly ash ranged from 23 to 117 µg/g ash whereas the total Zn ranged from 34 to 333 µg/g of ash. In the case of silica-rich coal fly ash, the three-step SEP ranged between 3 and 23 µg Zn/g of ash whereas the total Zn ranged from 64 to 73 µg/g of ash.

The 3-step SEP extracted considerably more Zn than did the PBET for almost all of the Ca-rich ashes. For the Ca-rich ashes, the amount of Zn remaining in the extractant decreased considerably in the stomach phase. Ashes IN-B and US-A, US-B and US-C had both the highest total Zn contents and the highest SEP extractable amounts of Zn.

Bioaccessibility of metals

The fraction of the metals in the ashes that are bioaccessible as defined by Eq. (1) varied depending on the source of the ash, the element of the interest and the portion of the gastrointestinal tract (Fig. 5a–e). A portion of the bioaccessible fraction may then be bioavailable for uptake from the human gastrointestinal tract into the bloodstream. Arsenic in the ash was very bioaccessible with 40–57 % of the total As being bioaccessible for the Ca-rich ashes and 64–100 % for the Si-rich ashes. The bioaccessible fraction of Se was also very high for the most Ca-rich ashes (20–97 %), but it was much lower (3–8 %) for the Si-rich ashes. In contract, the bioaccessible fraction of Cr was much lower for the Ca-rich ashes (10–20 %) than the Si-rich ashes (43–59 %), but it should be noted that the Cr contents of the Si-rich ashes were much lower than those of the Ca-rich ashes. The Zn bioaccessible fractions were lower than 25 % for most of the ashes, but two low Zn Ca-rich ashes did have much higher bioaccessible fractions.

The bioaccessible fractions were usually quite similar for the stomach phase and the intestinal phase. This was particularly true for Se which had nearly identical bioaccessible fractions for the stomach and small intestine phase. Arsenic was consistently more bioaccessible in the stomach phase for the Ca-rich ashes, but it was more bioaccessible in the intestinal phase for both Si-rich ashes. The bioaccessibility of As in the Ca-rich ashes may be influenced more by pH differences between the stomach and intestinal phases than in the Si-rich ashes. Similarly, the Cr bioaccessible fractions were slightly higher in the stomach phase for all of the Ca-rich ashes but lower for the two Si-rich ashes. The behavior of Zn was most variable with respect to bioaccessibility with no consistent trends based on ash type. Pb was bioaccessible for Si- rich fly ashes ranged from 5 to 6 % and for Ca-rich fly ashes it ranged from 1 to 10 %.

Conclusion

Elements posing the greatest risks will be those with both high concentrations in the ash and large proportions of the element in bioaccessible forms. The results of the present study suggest that while As has relatively low concentrations in the ash, the fraction of the As that is bioaccessible can be quite high. Similarly, for Se in Ca-rich class C ashes, although Se contents may not be very large, most of the Se can be bioaccessible. In contrast, while the Zn contents of the ash were high, the bioaccessible fractions were low relative to those of Se and As. The solid phase speciation of the elements can strongly affect the bioaccessibility of the element; this is illustrated by the much lower Se bioaccessible fractions for the Si-rich class F ashes despite their having higher total Se contents than the class C ashes. The bioaccessibility of As and Se can make them the primary drivers of environmental risks associated with ash disposal.

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The PBET procedure can be an effective tool for assessing the bioaccessibility of different toxic metals in coal fly ash. For certain ashes and elements, the results with the PBET were considerably different from those with a 3-step SEP. In some cases, the TCLP provided a good measure or a conservative estimate of the physiologically extractable element (e.g., Se and Cr). However, for other elements (e.g., As), the physiologically extractable amount of element was higher than that from the SEP and estimates of bioaccessibility based on the TCLP or SEP might underestimate the risk posed by arsenic in fly ash.

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