Mobility and speciation of arsenic in the coal fly ashes collected from the Savannah River

Site (SRS)

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Abstract

Arsenic (As) leaching from coal fly ash stockpiled at waste disposal sites is a source of environmental concern. An array of techniques including batch extraction and column leaching tests, in combination with speciation analysis of chemically specific As species, was employed to evaluate the mobility of As in fly ashes collected from the U.S. DOE Savannah River Site. The results obtained using the U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP), a two-step sequential extraction technique, and continuous column leaching experiments suggest that only a small portion of total As in the fly ashes was mobile, but mobilizable As could be a considerable fraction (3.1-43%), varying inversely with alkalinity of fly ash. Speciation analysis by using phosphate extraction suggests that arsenate (As^{V}) was the major extractable species in the fly ash samples. During the column leaching experiment, however, it was observed that arsenite (As^{III}) was an important species leached out of the fly ashes, indicating species conversion during the leaching process. The matrix-bound As^{V} within the fly ash, once being released from the solid matrix, could be converted to As^{III} during its transport inside the column. The pHs of leachates and fly ashes (both acidic in column leaching experiments here) could be related to the dominance of As^{III} in the effluents.

Keywords: Arsenic, coal fly ash, mobility, speciation, Savannah River Site

1. INTRODUCTION

Anthropogenic sources, e.g. mining, manufacturing, coal combustion, and uses in agriculture and forestry, have emitted large quantities of arsenic (As) into the environment (Nikolaidis et al., 2004; Huggins et al., 2007). Of these anthropogenic sources, the accumulation of large amounts of ash from fossil fuel combustion is becoming an environmental concern (Sajwan et al., 1999; Ohki et al., 2005; Zielinski et al., 2007; Ruhl et al., 2010; Khodadoust et al., 2011; Catalano et al., 2012). For example, coal combustion products, particularly fly ash, stockpiled at the U.S. Department of Energy's Savannah River Site (SRS) are a potential source of As, which could be drained into the Savannah River through rainwater runoff or leached into the groundwater beneath the piles. The release of As from fly ash due to leaching and spills into the surrounding environment has been observed (Xu et al., 2001; Otero-Rey et al., 2005; Kim et al., 2009; Ruhl et al., 2010; Su and Wang, 2011; Yang et al., 2015).

In general, coal fly ash can accumulate As compounds in such significant concentrations as to be of environmental concern (Brownfield, 2002; Goodarzi and Huggins, 2005; Ohki et al., 2005). However, not all forms of As in fly ash is subject to be mobilized. Some fractions of As in fly ash are strongly bound to solid phase. Only under very dramatic conditions, these strongly bound As may be released and thus adversely impact organisms or potentially poses health risks to human health through food chain or water supplies (Pantsar-Kallio and Manninen, 1997; Jackson and Miller, 1999; Bankowski et al., 2004; Ohki et al., 2005; Otero-Rey et al., 2005; Huggins et al., 2007). Therefore, it is necessary to assess the leachability of As from large accumulations of coal fly ash stockpile. This work is essential to understand to what extent As from fly ash piles would pose environmental hazard and to assess the potential remedial actions that would be employed to minimize the leaching of As (Zheng et al., 2004).

Total As concentration determined using strong reagents such as concentrated nitric acid extraction may be misleading to actually represent the portion of mobile or mobilizable As in solid materials (Hartley et al., 2004). By using mild extractants, selective extraction procedures simulating the effects of natural leaching conditions have been developed and used to assess realistic environmental risk due to As contamination (Kashiwakura et al., 2010; Su and Wang, 2011). These extraction techniques used by statutory bodies included U.S. Environmental Protection Agency (EPA) toxicity characteristic leaching procedure (TCLP) (USEPA, 1992), the American Society of Testing and Materials (ASTM) extract test (Eisenberg et al., 1986), and the UK Environmental Agency (UKEA) one-hour test (Eisenberg et al., 1986). Besides these batch leaching tests, continuous column leaching test, e.g. the Dutch Environmental Agency long-term leaching test (NEN, 1995), is also a useful tool and probably more realistic to evaluate the mobility of As. Additionally, various sequential extraction procedures have been applied to characterization of As mobility and bioavailability (Keon et al., 2001; Wenzel et al., 2001; Fedotov et al., 2005). A simplified three-level sequential extraction method, which separates metals into mobile, mobilizable, and pseudo total metal fractions, seems to be attractive because of its simplicity (Gupta et al., 1996; Cai et al., 2002).

The leaching tests or sequential extraction procedure for characterizing the mobility of As mentioned above could provide some information on operationally defined speciation of As, but failing to provide exact information on chemical speciation of As in samples. Information about chemical speciation of As in solid samples was also necessary for evaluating the fate and environmental impact of As in fly ashes, since different chemical forms of As have different mobility, transformation pathways, and toxicity (Le et al., 2004; Ilander and Väisänen, 2011). A number of studies have investigated the As speciation involving arsenite (As^{III}) and arsenate

(As^V) in solid phases (e.g., soil and sediment) through extraction by a variety of reagents such as phosphate and phosphoric acid (Ellwood and Maher, 2003; Pizarro et al., 2003; Georgiadis et al., 2006). Yet, speciation of As in fly ashes, in particular during leaching processes, has been scarcely studied.

In this study, the mobility of As from coal fly ash stockpile at SRS site was investigated through TCLP leaching test and a simple two-step sequential extraction procedure. Arsenic species with different oxidation states, i.e. As^V and As^{III}, in fly ash were determined by high performance liquid chromatography coupled with a hydride-generating atomic fluorescence spectrometer (HPLC-HG-AFS), following extraction using phosphate solution with sodium diethyldithiocarbamate trihydrate (NaDDC) (Cai, 2000; Zhang et al., 2002). Column experiments were conducted to further investigate the mobility and speciation of As under the simulated environmental conditions. The present study features speciation analysis of As in the column leaching test as well as a combination of a batch leaching test, a sequential extraction procedure, and a continuous column leaching technique to assess the mobility of As in coal fly ash. The information provided here would be useful to develop remedial strategies to minimize the leaching of As from fly ash and to improve the methodology for assessing the leachability of metals from solid phase in general.

2. MATERIALS AND METHODS

2.1 Materials and reagents

Three SRS field fly ash samples collected from an old filled pond (overflow), the shallow natural ravine (D-area), and a pond where the filled fly ash was recently dug out (reference

pond), and two reference fly ashes (Class C and Class F) were used here. Arsenic and metals standards (ICP grade, 1000 ppm) were purchased from GFS Chemicals, Inc. (Powell, OH, USA) were used for quantification. Detailed information on materials and reagents can be found in Supplementary Materials.

2.2 Instrumentation

Analysis of As and other metals was performed on ICP/MS, and speciation of As was done on HPLC-HG-AFS system. Determination of iron was carried out using atomic absorption spectrophotometer (AAS). Detailed information on instrumentation can be found in Supplementary Materials.

2.3 Batch extraction experiments

2.3.1 Determination of total As and other metals

Fly ash samples were digested using an open vessel digestion before analysis following a procedure reported previously (Cai et al., 2000). Briefly, 0.15 g (dry weight) sample was digested for 1 hr at 120 °C after adding 10 ml of HNO₃. Then 1 ml of hydrogen peroxide (H₂O₂) was slowly added to the sample to digest for another 0.5 hr. The resulting digestate was reduced in volume by heating and then diluted to a final volume of 100 ml. Analysis of total As and other elements (Al, Ca, Mg) was carried out using ICP/MS while Fe was determined by AAS.

2.3.2 TCLP test

The TCLP experiment followed a procedure described in USEPA Method 1311 (USEPA, 1992). Fly ash sample (5 g) was placed in a glass Erlenmeyer flask to which 100 ml of 0.57%

(v/v) acetic acid (CH_3COOH) solution was added, producing a dilution ratio of 20/1 and yielding a pH of 2.88. The sample container was placed in an agitation device for 20 hours at $22 \pm 1^\circ\text{C}$. The mixture was filtered through a $0.45\ \mu\text{m}$ (25 mm) filter and the liquid phase was analyzed for As using ICP/MS.

2.3.3 Two-step sequential extraction

Sodium nitrate (NaNO_3 , 0.1 M, pH 7.0) and potassium dihydrogen phosphate (KH_2PO_4 , 0.1 M, pH 4.7) were used to extract mobile and mobilizable As fraction sequentially (Cai et al., 2002). Fly ash samples were weighed ($\sim 0.5\ \text{g}$) into plastic centrifuge tubes (50 ml) and then 25 ml of 0.1 M NaNO_3 was added. After being shaken for 24 h, the sample was centrifuged at 4000 rpm for 5 min and the supernatant was transferred to a clean 60 ml plastic bottle. The residue was extracted for 1 h using 25 ml of 0.1 M KH_2PO_4 and centrifuged at 4000 rpm for 5 min to get mobilizable As fraction. Both supernatants were adjusted to 2% of HNO_3 and analyzed for As using ICP/MS.

2.3.4 Arsenic speciation analysis

Phosphate-extractable As^{V} and As^{III} in fly ash were estimated by phosphate solution extraction followed by HPLC-HG-AFS analysis (Cai, 2000; Georgiadis et al., 2006). To do this, 0.5 g fly ash sample was weighed into an amber HDPE bottle and then 20 ml of 10 mM phosphate solution ($\text{KH}_2\text{PO}_4:\text{K}_2\text{HPO}_4=1:1$, pH 6.8) with 0.5% NaDDC was added. After being shaken on an orbital shaker for 12 hours, samples were centrifuged at 5000 rpm for 5 minutes and then filtered through $0.45\ \mu\text{m}$ PVDF syringe filters. Five ml of each sample was pipetted into a 15 ml plastic tube and acidified with 50 μL of 6M HCl solution. In an effort to minimize the

effect of corrosion on the HPLC sample introduction system, the pH is then adjusted with 10 μ L of 6 M NaOH prior to HPLC-HG-AFS analysis.

2.4 Column leaching experiment

Four PVC pipes with 5.2 cm inner diameter $\times$ 30.5 cm length were used for the experiments. The inner surface of the pipes was glued with dry and acid-cleaned sand. The columns were packed with wet fly ash samples (around 600 g wet weight for each column) supported by a sponge at the bottom of column. After the columns were packed, 2 mM NaNO₃ is pumped through the column for equilibration (around 5 days). After the equilibrium period, the 2 mM NaNO₃ solution was replaced by artificial rainwater (Strom and Kaback, 1992) as influent (see Supplementary Materials for preparation, Table S1) for columns A and B, whereas columns C and D remained unchanged (serving as controls). The flow rates for both NaNO₃ and artificial rainwater were maintained at 90 ml/d by a peristaltic pump. The effluent samples were collected in 120 mL polystyrene bottle every day for monitoring pH and Eh and analyzed every other day for As speciation using HPLC-HG-AFS.

2.5 Quality control and data processing

QA/QC procedures were strictly followed. For analysis of each type of sample, triplicates of the original samples and two spikes were carried out. In addition, one procedural blank and PACS-2 analyses were included. Data obtained were processed with Microsoft Excel 2003 and all statistical analyses were performed on SPSS (SPSS Inc., Release 11.5.0 Standard version).

3. RESULTS AND DISCUSSION

3.1 Total and extractable As in fly ash measured in batch extraction experiments

Five fly ash samples including two commercial standard fly ashes (class C and F) and three field samples from SRS were analyzed for As concentration using different extraction methods. As seen from Table 1, which lists the As concentrations on a dry weight basis, class F fly ash had high total As concentration ($145.9 \pm 3.8 \mu\text{g/g}$) compared to class C ($23.6 \pm 1.2 \mu\text{g/g}$). This was in agreement with previous reports, suggesting class C fly ash tended to have lower concentration of trace elements (e.g. As, Cd, Co, Cr, Pb, Sb and Zn) than class F (Davison et al., 1974). Brownfield has reported a total As concentration of $170 \mu\text{g/g}$ for a class F fly ash produced from Illinois Basin coals while $18 \mu\text{g/g}$ for class C fly ash produced from coals from Powder River Basin, Wyoming (Brownfield, 2002). Regarding the three field samples, the highest As concentration ($167.6 \pm 33.7 \mu\text{g/g}$) was observed in the overflow fly ash, the lowest ($53.0 \pm 4.7 \mu\text{g/g}$) in the D-area fly ash, and the reference pond fly ash being the intermediate ($82.9 \pm 2.4 \mu\text{g/g}$). Both D-area and the reference pond fly ashes contained significantly lower ($P < 0.001$) As than class F fly ash, possibly indicating loss of As leached out during stockpiling and aging of fly ash. There was no significant difference between concentrations of As in overflow and class F fly ashes.

The percentages of extractable As fractions obtained using different methods, namely TCLP, mobile, and mobilizable As, were calculated against total As concentration and illustrated in Fig 1. For all fly ash samples tested, TCLP As as well as mobile As was rather small portion of the total As (0.1-1.7% and 0.1-2.5% for TCLP and mobile As, respectively), while mobilizable As appeared to be a considerable portion (3.1-43%). Of these three As fractions, TCLP As was the lowest with the exception of D-area fly ash for which mobile As fraction was

the lowest. Mobilizable As fractions were highest for all five fly ash samples tested. For each fly ash sample, the differences between every two of these three As fractions were tested to be statistically significant ($P < 0.001$), indicating that TCLP and the two-step extraction gave different results when evaluating mobility of As in fly ash despite the fact that both TCLP and mobile As were at very low concentration levels.

The percentages of TCLP, mobile, or mobilizable As against total As were different among the studied 5 fly ash samples, indicating different mobility of As present in different samples. Class F fly ash had much higher mobilizable As proportion than class C fly ash, while the percentages of TCLP and mobile As fractions were quite similar. The high alkalinity (see Supplementary Materials) of Class C fly ash could be partially related to reduced fraction of mobilizable As, as alkalinity could buffer the leachate. The mobility of As in the three field fly ash samples, though originated from US eastern power plant with class F fly ash produced, appeared to be remarkably different from the class F fly ash. The major difference was the significantly decreased proportion of the mobilizable As fraction in the field samples. As mentioned above, aging process of fly ash stockpiled at SRS under natural environmental conditions had altered the properties of fly ash as indicated by contents of total elements in Table S2. The altered properties of the fly ashes could contribute to the difference of As mobility in different samples. The low percentages of mobile or mobilizable As against total As suggested that As present in the SRS field samples had limited mobility, probably because the labile As has been leached out of the ash during aging and weathering processes.

Different extractants used in the TCLP test and two-step sequential extraction can leach different As fractions present in fly ash samples. The TCLP test adopted an acetic acid solution as extractant to release the loosely adsorbed As on mineral clays and it was likely unable to

dissolute the mineral oxides due to weak acidic reagent used. In two-step extraction, NO_3^- and H_2PO_4^- were used for replacing the non-specifically and specifically adsorbed As (especially As^{V}), respectively. This sequential extraction has been observed to release As without significant dissolution of the oxides/hydroxides of iron, manganese, and aluminum in soil samples (Cai et al., 2002). It has been observed that As fraction tightly bound to mineral (hydr)oxides, especially crystalline metal (hydr)oxides, was not subject to be desorbed reversibly and hence immobile during two-step extraction (Warren and Dudas, 1985; Mattigod et al., 1990; van der Hoek et al., 1994; van der Hoek and Comans, 1996).

3.2 Total As leached in column experiment

On the basis of batch extraction tests, column leaching experiments were conducted on two field fly ash samples, namely overflow and reference pond fly ashes, to evaluate the mobility of As under simulated field conditions. Speciation analysis rather than total elemental analysis was employed for determining As in effluents for the purpose of obtaining additional information on As species besides total As amount leached from columns. The results suggest that As^{III} and As^{V} were the two major As species in the leachates and organic As species commonly present in the environment, such as monomethylarsonic and dimethylarsinic acids, were not detected in the leaching process. Accordingly for the convenience of discussion $\text{As}^{\text{III}} + \text{As}^{\text{V}}$ was termed as total As in the leachate in the discussion related to column experiments. Fig. S1 shows that the concentration of total As leached from the overflow fly ash was fluctuated during the beginning period of experiment until reaching a relatively stable level around day 18, while As leached from the reference pond fly ash increased steadily with time.

The column leaching experiment was conducted for more than two months under continuous flow rate of 90 ml/d. The overall amount of total As leached from the overflow and the reference pond fly ashes constituted small portions of the total As (Table 2). Only 0.2-0.5% and 0.1-0.2% of total As, approximately identical percentages for the overflow and reference pond fly ash samples, were leached by artificial rainwater and sodium nitrate solution, respectively. These results were in agreement with those obtained with batch leaching experiments, i.e. that As present in fly ashes at SRS had limited mobility. Additionally, Kolmogorov-Smirnov Z tests ($P < 0.001$) suggested that more As was leached out of the overflow or reference pond fly ash by artificial rainwater than by equilibration solution (sodium nitrate). Artificial rainwater appeared to enhance the mobility of As in fly ash in comparison to sodium nitrate solution and probably provides a more accurate estimation of mobile As.

3.3 Speciation of phosphate-extractable As in batch experiment

Chemical speciation of As was conducted on standard class C and class F as well as field samples from SRS through extraction with phosphate buffer containing NaDDC as a chelating reagent. This procedure has been proven to be able to minimize As species conversion during extraction process and has been successfully used to estimate phosphate-extractable As^{V} and As^{III} in soil and sediment samples (Georgiadis et al., 2006).

The results of speciation analysis (Table 3) indicate that fly ashes generally had much higher phosphate-extractable As^{V} concentration than As^{III} with an exception of D-area sample. For this sample, neither As^{V} nor As^{III} was detected during speciation analysis ($< 0.01 \mu\text{g/g}$). This was not compatible with the results of two-step extraction which indicated the occurrence of both mobile and mobilizable As. The reason was not clear, but higher concentration of phosphate in

two-step extraction (0.1 M) might have stronger leaching power than phosphate used in speciation analysis (10 mM). The phosphate-extractable As^{III} concentration in class C fly ash was below the detection limit of the method. For samples in which As species were detected during speciation analysis, phosphate-extractable As^{III} accounted for approximately up to 1% of total As present in the fly ash samples, whereas the percentages of phosphate-extractable As^{V} ranged from 6.3% through 26%.

3.4 Speciation of As leached from columns

Regarding the variation of As species with time during leaching process, different patterns were observed for the overflow and reference pond fly ashes. For the overflow fly ash, both As^{III} and As^{V} were detected throughout the leaching period and the concentrations of As^{III} in the effluents from all columns were much higher than As^{V} . The concentrations of As^{III} and As^{V} in effluents from different columns showed similar time-series trends as seen from Fig. 2, i.e. reaching an approximately stable level after an rising stage at the beginning of the experiment. Fig. 2 illustrated the results of artificial rainwater leaching experiments only, but similar trend was also observed for sodium nitrate leaching experiments (data not shown).

For the reference pond fly ash, As^{V} was not detected in the effluents from columns C and D (sodium nitrate leaching) during the leaching process. Even for columns A and B which were leached with artificial rainwater, As^{V} became detectable only from day 31 and day 11, respectively. As^{III} was observed in the leachates throughout the leaching process and the cumulative amounts of As^{III} and As^{V} leached out of the fly ash were comparable at the end of leaching test. Speciation conversion between As^{III} and As^{V} was clearly observed during the leaching process as shown in Fig. 2. For column A, the concentration of As^{III} decreased

gradually accompanied by increased As^{V} concentration from day 31. Similar trend appeared for column B except that As^{V} occurred from day 11 and began to drop from day 45 after an apparent increase. Overall, As^{III} varied apparently in an opposite manner with As^{V} , whereas total As concentration remained basically stable during this process.

Although As^{V} concentration is much higher than As^{III} for both the overflow and reference pond fly ashes as determined in speciation analysis using phosphate as extractant, the total amount of As^{III} leached was higher than (for the overflow ash) or similar to (for the reference pond ash) As^{V} during the column leaching experiments. This result suggests that As^{III} is an important species for As leaching out of the fly ash, indicating possible species conversion from As^{V} to As^{III} during the column leaching process. The conversion of As^{V} to As^{III} in the effluents was determined to be insignificant (data not shown). Therefore, it seems that the conversion of As^{V} to As^{III} occurred inside the column. Although the majority of As was originally present in the fly ashes in the form of As^{V} , when leaching solutions passed through the column, As^{V} would be released into the solution phase. Once released from fly ash, As^{V} could be converted to As^{III} due to alteration of redox potential and/or microbial activities during its transport in the fly ash column. The redox potentials inside the columns were monitored throughout the leaching process and were basically within the range of 200-400 mV, with higher Eh for reference pond fly ash than overflow (Fig. S2). Under such redox conditions at the experimental pH (about 6.0-6.5, gradually increasing during leaching process in particular for reference pond fly ash, Fig. S3), As^{V} would be the major species according to the pH-Eh diagram of As and simple chemical reduction of As^{V} to As^{III} would not be expected to occur significantly (Ferguson and Gavis, 1972). Therefore redox potential appeared not to be satisfactorily responsible for the conversion of As^{V} to As^{III} in the present study. This species conversion process is likely mediated by

microbial processes. It is also speculated that the different patterns in the speciation profile of leached As between the overflow and reference pond ash could be related to the different microbial community and activity between these two fly ashes.

Another possible reason for higher As^{III} amounts leached out of fly ashes was the difference in mobility between As^{III} and As^{V} . It is known that As^{III} is more mobile than As^{V} in most environmental conditions and thus it is possible that more As^{III} could be leached out of the columns (Pierce and Moore, 1982; Bose and Sharma, 2002). The influent artificial rainwater pH was 4.8, and because the field ashes had acidic pH of eastern US ash (Table S2), the pH values of effluents were still slightly acidic after passing through the columns. Under these acidic leaching conditions, As^{III} was present in the neutral H_3AsO_3 and As^{V} in oxianion H_2AsO_4^- form. The uncharged H_3AsO_3 could be less adsorbed onto minerals and more readily released into solution (and subsequently leaching out of the columns). It should be borne in mind that the issue with respect to what As species could be leached out of fly ash and/or present in the leachates is complicated. The As species in the leachates may be dependent upon the composition and properties of fly ash, the redox potential and pH inside the packed column, the microbial condition (Macur et al., 2001), and the properties of leaching solution used. Indeed, different distribution of As species in the leachate was observed for different fly ashes (overflow and reference pond) as well as for different leaching solutions (artificial rainwater and sodium nitrate solution) in this study. More detailed studies are needed in order to provide an in-depth explanation on the profile of As species in the leachates and to predict the distribution of As species during leaching process.

4. CONCLUSIONS

An array of extraction and leaching tests, in combination with speciation analysis, was conducted to evaluate the mobility of arsenic in fly ashes. Although the fly ash stockpile at SRS was heavily contaminated with As, the results of TCLP, two-step sequential extraction, and column leaching tests showed that only a small portion of total As was mobile, whereas mobilizable As could amount to a considerable fraction. Speciation analysis by using phosphate extraction suggested that As^{V} was the major extractable species for As bound to fly ashes. During the column leaching experiment As^{III} was observed to be an important species leached out of fly ash, with an amount higher than (for the overflow fly ash) or comparable to (for the reference pond ash) As^{V} . It seemed that As^{V} , once released from the fly ash matrix, could be converted to As^{III} during its transport inside the column. More studies are begged for in order to determine and predict the profile of As species in the leachates during As leaching process from fly ashes.

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470

471

472

473 Table 1 Arsenic concentrations ($\mu\text{g/g}$, expressed as mean $\pm$ standard deviation on a dry weight
 474 basis, N=3) in different fly ash samples determined in the batch leaching tests

475

Test methods Fly ash samples	HNO ₃ digestion	TCLP	Two-step extraction	
	total As	TCLP As	Mobile As	Mobilizable As
Class C	23.6 $\pm$ 1.2	0.07 $\pm$ 0.00	0.47 $\pm$ 0.10	3.57 $\pm$ 0.36
Class F	146 $\pm$ 3.8	0.48 $\pm$ 0.01	2.77 $\pm$ 0.25	63.0 $\pm$ 0.3
Overflow	167 $\pm$ 34	0.16 $\pm$ 0.04	0.75 $\pm$ 0.21	6.54 $\pm$ 5.00
D-area	53.0 $\pm$ 4.7	0.91 $\pm$ 0.14	0.03 $\pm$ 0.00	1.63 $\pm$ 0.18
Reference pond	82.9 $\pm$ 2.4	0.88 $\pm$ 0.02	2.07 $\pm$ 0.84	12.2 $\pm$ 1.4

476

477 Table 2 Amounts and percentages of As leached out of the column packed with selected fly
 478 ashes during continuous leaching tests

Fly ash samples column	Overflow fly ash				Reference pond fly ash			
	A ^b	B ^b	C ^c	D ^c	A ^b	B ^b	C ^c	D ^c
Total As leached (µg)	307	135	138	58.3	68.8	175	39.5	33.0
% ^a	0.55	0.24	0.25	0.10	0.22	0.56	0.13	0.11

479 a: Percentage was calculated against total As amount present in the fly ash packed in the column.

480 b: Columns A and B were leached with artificial rainwater.

481 c: Columns C and D were leached with equilibration solution (2 mM NaNO₃) serving as
 482 controls.

483

484 Table 3 Concentrations of phosphate-extractable As^{III} and As^V in the fly ash samples

Fly ash samples	As ^{III}		As ^V	
	Concentration (µg/g)	% ^a	Concentration (µg/g)	% ^a
Class C	-	-	1.81±0.15	7.65
Class F	0.64±0.01	0.44	13.6±0.5	9.31
Overflow	0.91±0.29	0.54	10.6±0.7	6.34
D-area	-	-	-	-
Reference pond	1.08±0.14	1.30	21.2±1.2	26

485 a: Percentage was calculated against total As concentration determined through HNO₃ digestion.

486 -: Below the detection limit (0.01 µg/g).

487

488 FIGURE LEGENDS

489

490 Fig. 1 Percentages of extractable As against total As in the fly ashes as determined by different
491 methods

492

493 Fig. 2 Concentrations of As^{III} and As^{V} in the leachates during artificial rainwater column
494 leaching tests of the overflow fly ash (a and b) and reference pond fly ash (c and d). For each
495 type of fly ash, two duplicate columns, column A and column B, were prepared and the
496 discrepancies in As concentration between A and B could be due to the heterogeneity of the
497 packed columns.

498

Fig. 1

Fig. 2