

Soluble Arsenic and Selenium Species in Fly Ash/Organic Waste-Amended Soils Using Ion Chromatography—Inductively Coupled Plasma Mass Spectrometry

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Mixing coal fly ash with an organic waste increases macronutrient content and may make land application of fly ash a viable disposal alternative. However, trace element chemistry of these mixed waste products warrants investigation. Speciation of As and Se in soil solutions of fly ash-, poultry litter- and sewage sludge-amended soils was determined over a 10-day period by ion chromatography coupled to inductively coupled plasma mass spectrometry (IC–ICP–MS). Detection limits were 0.031, 0.028, 0.051, 0.161, 0.497, and 0.660 $\mu\text{g L}^{-1}$ for dimethylarsinate (DMA), As(III), monomethylarsonate (MMA), As(V), Se(IV), and Se(VI), respectively (100 μL injection). Arsenic was highly water-soluble from poultry litter and appeared to be predominantly As(V). Arsenic(V) was the predominant species in soil amended with two fly ashes. Application of fly ash/poultry litter mixtures increased As solubility and led to the prevalence of DMA as the major As species. DMA concentrations in these soil solutions decreased rapidly over the sampling period relative to As(V), suggesting that DMA readily underwent mineralization in the soil solution. Se(VI) was the predominant soluble Se species in all treatments indicating rapid oxidation of Se(IV) initially solubilized from the fly ashes.

Introduction

Analytical methods for As and Se speciation are limited by the necessity of separating and detecting the low concentrations of these species normally encountered in environmental samples. In the past decade, hyphenated techniques, whereby chromatography is used to effect species separation, coupled to a sensitive element-specific detector, have been extensively applied to the speciation of As and Se. Detection limits of 0.8 $\mu\text{g L}^{-1}$ for As(III) and As(V) in sediment extracts were obtained by ion chromatography (IC) coupled to hydride generation atomic absorption spectrophotometry (HGAAS) (1). As(III), As(V), DMA, and Se(IV) were quantified by IC coupled to inductively coupled plasma atomic emission spectrometry (ICP–AES) with hydride generation (2); detection limits ranged from 17, 640, 230, and 100 $\mu\text{g L}^{-1}$ for As(III), As(V), Se(IV), and DMA, respectively. Sheppard et al. (3) used IC–ICP–MS to effect the separation and quantification of As(III), As(V),

DMA, and MMA with detection limits of 4.9, 6.0, 1.2, and 3.6 $\mu\text{g L}^{-1}$, respectively.

Coal fly ash, a byproduct of coal combustion, often contains elevated concentrations of As and Se. Eary et al. (4) reported concentration ranges of 2–440 and 0.2–130 mg kg^{-1} for As and Se, respectively, in coal fly ashes as compared to background soil ranges of 1–50 (As) and 0.1–2 (Se) mg kg^{-1} . Land application of fly ash is considered an attractive alternative for disposal of this waste material as compared to the current procedure of land-filling (5). However, concern of trace element contamination has been one factor that has limited widespread land application (6). Another major limiting factor is the lack of macronutrients in the ash, which is consequently of little agronomic value. Recent research has shown that the mixing of fly ash with an organic waste product such as poultry litter or sewage sludge can produce a balanced soil amendment with equivalent nutrient availability to conventional fertilizers (7), and this may lead to a viable means for large-scale reuse of this industrial byproduct. However, consideration must also be given to changes in trace element speciation and availability resulting from these mixed waste products.

Arsenic and Se in fly ash predominately exist as As(V) and Se(IV) (8). Mixing of fly ash with an organic waste may affect both the solubility and the speciation of As and Se. A lowering of the soil redox potential due to the application of a readily oxidizable organic waste, such as poultry litter, may effect reduction of As(V) to the more toxic and mobile As(III) species. Poultry litter itself may be significant source of As to the soil as organo-arsenical compounds are used in the poultry industry as growth promoters (9). These compounds are reported to be rapidly excreted with little or no breakdown to the more toxic inorganic arsenic compounds (10).

In the normal pH range (4–8) of soils, As(V) is present as the oxyanion H_2AsO_4^- and, at $\text{pH} > 7$, HAsO_4^{2-} ; while As(III) exists as the uncharged H_3AsO_3 . In the absence of methylating organisms, E_h/pH conditions control the ratio of As(V)/As(III) in the soil solution. Microbial action can also promote oxidation or reduction. The soil solution chemistry of As is further complicated by the biomethylation of inorganic As compounds to form organo-arsenic compounds. Microbial action also promotes methylation resulting in monomethylarsonic acid (MMA), $\text{CH}_3\text{AsO}(\text{OH})_2$ (pK_a values of 4.19 and 8.77), dimethylarsinic acid (DMA) also known as cacodylic acid, $(\text{CH}_3)_2\text{AsO}(\text{OH})$ (pK_a of 6.27), trimethylarsinic oxide, $(\text{CH}_3)_3\text{AsO}$, and methyl arsines $(\text{CH}_3)_n\text{AsH}_{3-n}$ (11). Arsines are volatile; consequently, one fate of As in soils may well be volatilization. However, Gao and Burau (12) reported that volatile As loss from soils treated with 100 mg kg^{-1} As(III), As(V), DMA, and MMA was minimal (0.001–0.4%). Indeed, mineralization of the organo-arsenicals was much more prevalent than further methylation and volatilization. The inorganic and simple methylated species of As are all fairly strongly sorbed by soil particle surfaces with As(V) being the most strongly sorbed (11).

In aerobic soils selenium is present as selenate, Se(VI), or selenite, Se(IV); both these species are oxyanions, the speciation of which is governed by pH. Selenate is present as SeO_4^{2-} over the entire pH range of soils, while the major Se(IV) species is HSeO_3^- at $\text{pH} < 7$ and SeO_3^{2-} at $\text{pH} > 7$. Selenium has similarities with As, which often lead to their concurrent study. They are both potentially toxic trace elements, both exhibit varying oxidation states, and both occur as oxyanions. The adsorption characteristics of Se(IV) in soils are also similar to those of As(III) and As(V). Selenite is adsorbed by ligand exchange inner-sphere mechanisms

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(13), and as such, adsorption is little affected by the ionic strength of the soil solution (14). However, selenate is generally considered to be rather weakly adsorbed by soils, with sorption occurring by outer-sphere mechanisms that are dependent on the ionic strength of the solution and the anion exchange capacity of the soil (15).

Previous studies on As and Se soil solution speciation have focused almost exclusively on flooded soil systems and have involved either soil spiked with inorganic salts (16, 17) or anthropogenically contaminated soils (18, 19). While flooded soil conditions are obviously of importance for redox-sensitive elements such as As and Se, the speciation in aerobic soil systems is also of interest. Kinetically slow redox equilibria for As and Se may result in a different species distribution in the soil solution than that predicted from a purely thermodynamic standpoint (20). In addition, few studies have determined the prevalence of organic As compounds in waste-amended soils, and IC-ICP-MS previously has not been employed for simultaneous speciation of As and Se in soil solution.

The objectives of this study were to assess the utility of IC-ICP-MS for the multi-element speciation of As(III), As(V), MMA, DMA, Se(IV), and Se(VI); to employ this method for the determination of As and Se in the aqueous extracts of two fly ashes, poultry litter, sewage sludge, and mixtures of the three; and to determine As and Se speciation in the soil solution from a soil amended with these wastes as a function of time.

Experimental Section

Analytical Determination of As and Se Speciation. A Dionex model DX500 HPLC system with an AS3500 Dionex autosampler equipped with a Rheodyne 9010 injection valve (Dionex, Sunnyvale, CA) and a 100- μ L injection loop were used. A Dionex IonPac NG1 guard column (4 mm \times 50 mm), AG5 guard column (4 mm \times 50 mm), and AS4A anion exchange column (4 mm \times 250 mm) (Dionex) were used for As and Se speciation. The end of the analytical column was connected to the cross-flow nebulizer of the ICP-MS (Elan 6000, Perkin-Elmer, Norwalk, CT) by a 53 cm length of PEEK tubing (0.25 mm i.d. and 1.55 mm o.d.) coupled to a 12 cm length of polyethylene tubing (0.575 mm i.d. and 0.95 mm o.d.). A 4 mM carbonate and 1 mM bicarbonate solution was used as the eluant. A step gradient program was used to give adequate resolution between DMA and As(III). From 0 to 2.5 min, 30% carbonate buffer and 70% DI water was used as the eluant at a flow rate of 1 mL min⁻¹; after this time the eluant was stepped to 100% carbonate buffer and the flow rate was stepped to 2 mL min⁻¹. This separation program is a modification of that used by Sheppard et al. (3) for the separation of As(III), As(V), MMA, and DMA.

Data Processing. Data processing was performed using the PE Nelson Turbochrom software program that was adapted to facilitate processing of chromatographic data generated by the ICP-MS. The ICP-MS was connected to the inject-out terminal of the 12 pin connector on the AS3500 autosampler by an external cable. A timed-event relay upon sample injection triggered the start of data collection by the ICP-MS software; the gradient program of the pump was also triggered by timed-event relays from the autosampler. The datafile generated by the ICP-MS software was then converted within Turbochrom to a compatible format for further data processing. Data were collected at two *m/z* values (75 for As species and 82 for Se species). Chromatograms could then be generated singly for each *m/z* value, or one chromatogram for both *m/z* values could be generated by summation within the software.

Reagents and Standards. Sodium arsenite (Fisher Scientific, Fair Lawn, NJ), sodium arsenate heptahydrate (Sigma, St Louis, MO), sodium cacodylate (Fisher Scientific), calcium

selenate (Cerac, Milwaukee, WI), and selenous acid (Fisher Scientific) were used to prepare 1000 mg L⁻¹ stock solutions (as As or Se) of arsenite, arsenate, DMA, selenate, and selenite, respectively. Monosodium monomethane arsonate (Crescent Chemical, Hauppauge, NY) was obtained as a 100 mg L⁻¹ solution in methanol. All solutions were prepared in 18.3 M Ω deionized water. Daily working standards were prepared by serial dilution of the stock solutions. Individual species standards were analyzed by IC-ICP-MS to assess any changes in element speciation. No interconversion between elemental species was observed over the duration of experimentation, and multi-species mixed standards were used for calibration of the IC-ICP-MS system.

Waste Products and Soil Amendments. Two fly ashes (FA1 and FA2) were obtained from power plants in the southeastern United States. Dewatered anaerobically digested sewage sludge (S) was collected from the municipal treatment plant, Athens, GA; and broiler poultry litter (PL) was collected from a poultry farm in the Athens area. These wastes were a subset of those used in a larger study on the nutrient availability from fly ash-biosolid mixtures (7). FA/PL and FA/S mixtures were prepared at the ratio of 4:1 and 2:1 (dry weight), respectively. The application rates used in this study were based on the application rates used in a field trial of the fly ash organic waste mixtures. In the field trial, only the mixtures were employed, and the ratios of 4:1 for fly ash:poultry litter and 2:1 for fly ash:sludge (application rate of each fly ash was 80 Mg ha⁻¹ in each mixture) were used so that each mixture would supply an equivalent amount of total N (from the organic waste), while maximizing the limited nutrient properties of the fly ashes. In this study the individual wastes and waste mixtures (8 treatments FA1, FA2, PL, S, FA1/PL, FA1/S, FA2/PL, FA2/S + 1 control) were mixed with soil (Cecil sandy loam Ap horizon) at application rates of 32.3, 8.1, and 16.1 g kg⁻¹ soil for fly ash, poultry litter, and sewage sludge, respectively, wet to 17% moisture and incubated over 33 days. During the incubation period, soil solution was periodically extracted from the treatments by centrifugation. Aliquots of the extracted solution were filtered (0.2 μ m) and analyzed for As and Se speciation, after appropriate dilution, by IC-ICP-MS. Speciation analysis was performed within 12 h of the soil solution extraction to minimize any changes in the species distribution. Aliquots of the filtered soil solution were also taken for measurement of total carbon (TOC 5050A, Shimadzu). The anions Cl, NO₃, and SO₄ were measured by ion chromatography (DX 500, Dionex, Sunnyvale, CA); Na, Mg, Al, P, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Cd, and Pb were measured by ICP-MS, and the results are reported elsewhere (21). Measurements of pH and *E_h* were made on a slurried (1:2 soil:H₂O) subsample of the incubated soil. *E_h* measurements were corrected for the potential of the Ag/AgCl reference electrode by addition of 220 mV and converted to pe via the equation *E_h* (V) = 0.059 pe (22).

To assess the speciation of readily soluble As and Se, water-soluble extracts of the wastes and waste mixtures were also performed. One gram dry weight of solid was weighed into a 50 mL centrifuge tube, 20 mL deionized water was added, and the resultant supernatant was shaken on an end-over-end shaker for 2 h. After centrifugation (10 min, 3200 rpm), the supernatant was filtered (0.22 μ m) and analyzed for total soluble trace elements by ICP-MS and for As and Se speciation by IC-ICP-MS.

Results and Discussion

As and Se Speciation Analysis. The separation of As(III), As(V), DMA, and MMA by anion exchange chromatography with a 5 mM carbonate buffer in 2% propanol and detection by ICP-MS has been described previously (3). Jackson and Miller (8) have shown that Se(IV) and Se(VI) can be

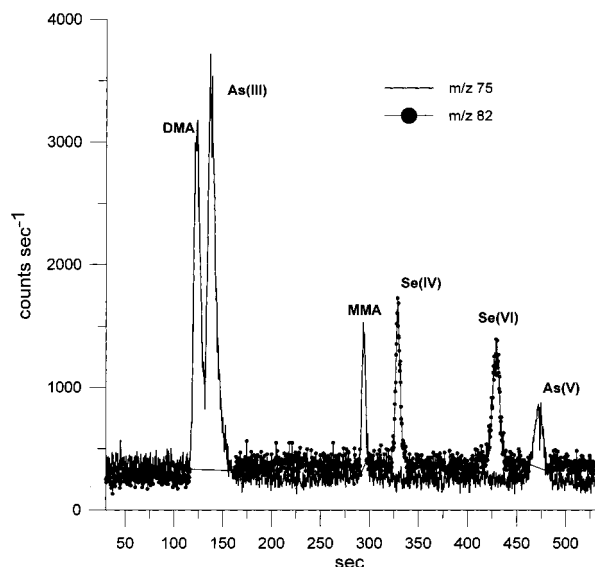


FIGURE 1. Ion chromatogram of mixed As ($1 \mu\text{g L}^{-1}$ As) and Se ($5 \mu\text{g L}^{-1}$) species.

incorporated easily into speciation analysis of inorganic As species using IC-ICP-MS by simultaneous monitoring of mass/charge (m/z) 82. The similarity in m/z values for As and Se, 75 and 82, respectively, results in an almost identical optimum lens voltage for both elements. In this experiment, optimum resolution of the six As and Se species was obtained with a step gradient program of 30% 5 mM carbonate buffer and 70% deionized water at 1 mL min^{-1} for 2.5 min, followed by 100% carbonate buffer at 2 mL min^{-1} until the end of the run (8.5 min). No organic solvent was added to either eluant. An example chromatogram of $1 \mu\text{g L}^{-1}$ mixed As species standard and $5 \mu\text{g L}^{-1}$ Se species is shown in Figure 1. The baseline intensity for Se increased as the flow rate increased from 1 to 2 mL min^{-1} and coincided with the tail end of the As(III) peak. In a previous study on IC-ICP-MS of inorganic As and Se species using an isocratic elution (8), baselines for As and Se were stable throughout the run, which allowed post-analysis summing of the m/z 75 and 82 signal intensities to produce a single chromatogram of the four species. In the present case, although all six species were resolved, the increasing Se baseline, coincident with the tail of the As(III) peak, prohibited summing the signal intensities. Instead, intensities for m/z 75 and m/z 82 were processed independently, resulting in two chromatograms for each sample. Retention times for the six species were 2.06, 2.30, 4.88, 8.10, 5.53, and 7.21 min for DMA, As(III), MMA, As(V), Se(IV), and Se(VI), respectively. Detection limits, calculated from the 3σ baseline intensity were 0.031, 0.028, 0.051, 0.161, 0.497, and $0.660 \mu\text{g L}^{-1}$ for DMA, As(III), MMA, As(V), Se(IV), and Se(VI), respectively, for a $100 \mu\text{L}$ injection volume. Detection limits for Se species are higher than those for As species due to polyatomic interferences that occur for the major Se isotopes (e.g., $^{80}\text{Ar}_2$ interference with ^{80}Se) and thus necessitate measuring the ^{82}Se isotope, which is only 9% abundant. Detection limits of As species compare well with those reported previously of 4.9, 6.0, 1.2, and $3.6 \mu\text{g L}^{-1}$ for As(III), As(V), DMA, and MMA, respectively (3), and reflect both a difference in the chromatographic separation and general advances in sensitivity of quadrupole ICP-MS that have occurred over the past 5 years.

As and Se Speciation in Waste Extracts. Total soluble As and Se concentrations and As and Se speciation were determined in water extracts of the wastes and waste mixtures (Table 1). Although such an unbuffered extract is not necessarily representative of the solubility upon land application, it does provide an indication of the initial speciation

of soluble As and Se. As(V) and Se(IV) were the only two species of these elements detected in the water-soluble extraction of the two fly ashes. Previous reports of As and Se in fly ash extracts have also identified these two species as the predominant soluble forms (8, 23, 24). The high solubility of As from the poultry litter sample was surprising; $25 \mu\text{g g}^{-1}$ soluble As, equivalent to 71% of the total As, was solubilized under the conditions of the extraction. Arsenic occurs in poultry litter as a result of the use of organo-arsenical compounds as growth additives in poultry feed (9). It has been reported that this As compound is excreted without changes in its chemical form or at least with little conversion to the more toxic inorganic forms of the element (10). However, in this experiment all four As species were identified as present in the water-soluble extraction with >92% extractable As occurring as As(V) (Figure 2). However, it is possible that an organo-arsinical could be co-eluted with As(V) under these experimental conditions. A recent study indicated that *p*-arsanilic acid (an additive to poultry feed) had a similar retention time to As(V) when analyzed by reversed-phase ion pair chromatography (25). In the mixed FA/PL wastes (4:1, FA:PL), all four As species were identified, with As(V) being the major species. The increase in soluble As(V) in the FA/PL extracts as compared to the FA extracts was attributable to As solubilized from the poultry litter. No As or Se species was detected in the aqueous extract of the sewage sludge sample, and As and Se solubilized from the FA/S mixtures were attributed to As and Se from the fly ashes.

As and Se in Soil Solution. Previous studies of soil solution As and Se speciation (17, 19) have focused on speciation changes under flooded conditions. The intention of this study was to investigate As and Se speciation resulting from land application of fly ash and organic wastes and mixtures of the two under the more common field situation of aerobic conditions. Consequently, the incubated soil/waste treatments were kept moist but below field capacity. From a purely thermodynamic standpoint, As(V) is predicted to be the major species of this element when $\text{pe} + \text{pH} > 8$ (26). For Se, $\text{pe} + \text{pH} > 14.5$ is predicted to give rise to a prevalence of the Se(VI) oxidation state (27). Inspection of the $\text{pe} + \text{pH}$ conditions for the waste-amended soils in this study (Figure 3) indicates that from a thermodynamic standpoint As(V) would be expected to be the major soluble As species, while Se(VI) should predominate for Se species; although for this element, lower concentrations of Se(IV) might also be expected. However, these predictions are based solely on thermodynamics and thus take no account of microbial mediation of redox reactions or methylation, nor do they account for kinetics.

As and Se speciation analysis of the soil solutions was hampered by high ionic strengths; a result of soluble salts from the waste applications. Excessive concentrations of soluble salts have been identified as a major drawback to land application of unweathered fly ashes (6). Consequently, soil solutions required dilution ($5\times$ dilution for PL-treated soil solutions, $3\times$ dilution for all other treatments) prior to speciation analysis to prevent overloading the exchange capacity of the column, with the unfortunate consequence of dilution of As and Se species concentrations prior to analysis. In analytical terms this meant that the speciation analysis was carried out on solutions that ranged from <1 – $7 \mu\text{g L}^{-1}$ total As. Nevertheless, total As and Se soil solution concentrations remained high enough over the first 10 days of the incubation study to allow for speciation analysis. Total As concentrations were highest in the FA2/PL treatment; Figure 4 shows the As chromatogram for day 3 soil solution extract of this treatment. High concentrations of soluble Cl were present in the soil solutions of the PL treatments. Cl is a potential interferent in the determination of As by ICP-MS due to the formation in the plasma of the $^{40}\text{Ar}^{35}\text{Cl}$ polyatomic

TABLE 1. Water-Soluble As and Se Speciation in FA, PL, and S Wastes and Total Elemental Concentrations^a

	pH of extract	water-soluble speciation								total digest concn	
		DMA ($\mu\text{g g}^{-1}$)	As (III) ($\mu\text{g g}^{-1}$)	MMA ($\mu\text{g g}^{-1}$)	As(V) ($\mu\text{g g}^{-1}$)	Se(IV) ($\mu\text{g g}^{-1}$)	Se(VI) ($\mu\text{g g}^{-1}$)	$\Sigma\text{As}_{\text{soluble}}$ ($\mu\text{g g}^{-1}$)	$\Sigma\text{Se}_{\text{soluble}}$ ($\mu\text{g g}^{-1}$)	As ($\mu\text{g g}^{-1}$)	Se ($\mu\text{g g}^{-1}$)
FA1	11.2	nd ^b	nd	nd	1.59	2.54	nd	1.59	2.54	55.10	8.13
FA1/PL	9.1	1.79	nd	0.56	5.81	0.68	nd	8.16	0.68	51.10	7.54
FA1/S	7.4	0.03	0.03	nd	0.12	nd	nd	0.18	nd	37.03	5.76
FA2	11.7	nd	nd	nd	0.43	8.07	nd	0.43	8.08	117.00	25.63
FA2/PL	9.2	0.19	nd	0.09	5.11	3.59	nd	5.39	3.59	100.62	21.54
FA2/S	8.2	nd	nd	nd	0.43	0.25	nd	0.43	0.25	89.69	18.82
PL	6.4	0.70	0.42	1.01	23.27	nd	nd	25.40	nd	35.10	5.20
S	7.6	nd	nd	nd	nd	nd	nd	nd	nd	0.89	1.03

^a Water-soluble concentrations are presented as μg of soluble As or Se/g of waste. ^b nd, not detected.

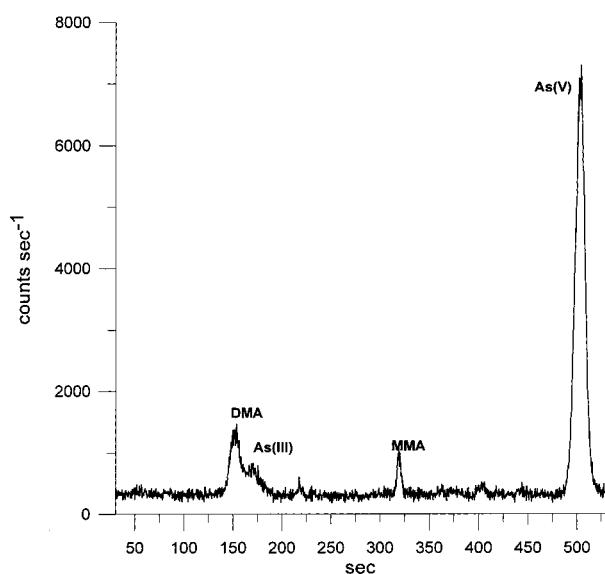


FIGURE 2. Water-soluble As species from poultry litter (0.5 g of solid, 30 mL of deionized H₂O; extract diluted a further 20 \times prior to IC-ICP-MS analysis).

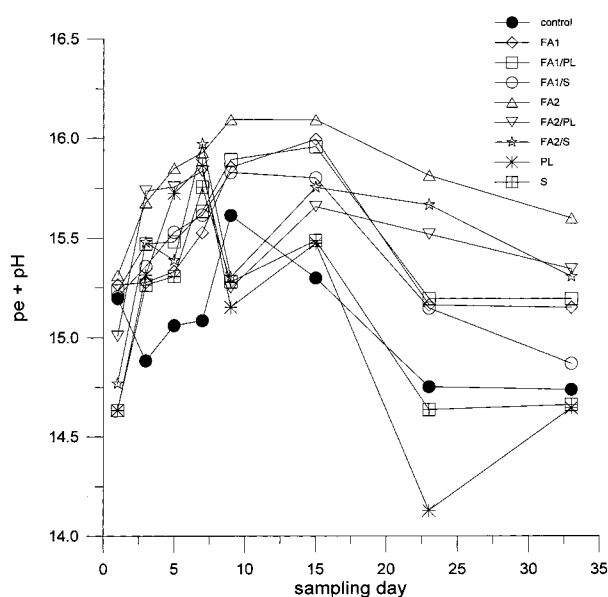


FIGURE 3. $pe + pH$ changes over time for the incubated soil treatments.

species, which is detected at m/z 75 and therefore interferes with the detection of As at this m/z value. IC-ICP-MS has been demonstrated as an effective analytical technique for

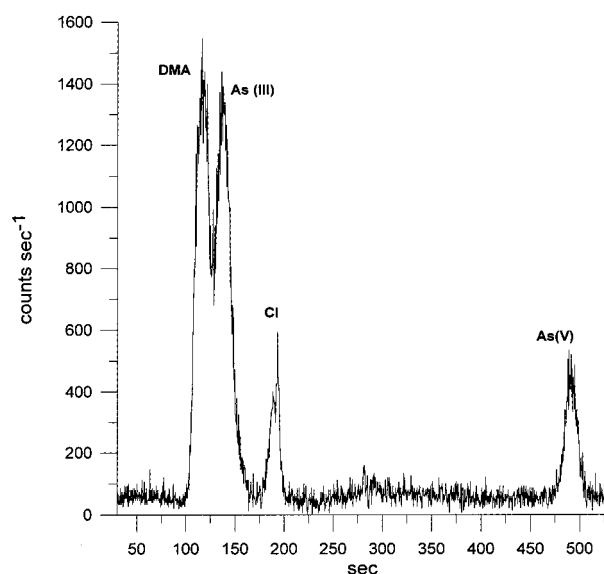


FIGURE 4. Soil solution As species in FA2/PL treatment after 3 days incubation.

analysis of As by ICP-MS because Cl, being anionic, is separated from the anionic As species by IC prior to analysis by ICP-MS (3), so obviating the need for Cl correction equations when determining As by this method. Figure 4 shows the peak at m/z 75 corresponding to approximately 60 mg L⁻¹ Cl and its separation from the As species at concentrations <1 $\mu\text{g L}^{-1}$.

Comparative As species distributions in the FA and FA/PL treatments exhibited some general trends (Figure 5a–d) that were similar for both fly ashes and their respective organic waste mixes, with the magnitude of soluble As reflecting the greater total As concentrations of FA2. In the fly ash-only waste-amended soil, As(V) was the major As species, with lower concentrations of DMA and As(III) also detected. The presence of As(III) in the soil solution, despite highly oxidic conditions for the bulk treatment, may point to the existence of microsites with transient anaerobic conditions. The FA/PL treatments exhibited increased total soluble As concentrations with DMA as the major As species. Given the high concentrations of soluble DMA exhibited in the aqueous extraction of the poultry litter, it could be concluded that this waste was the source of soluble DMA in the FA/PL treatments; however, no similar level of soluble DMA was detected in the PL-only treatment. Despite the high solubility of As from the poultry litter, the low application rate of this waste (0.8 g of PL/100 g of soil) resulted in low concentrations of As in the soil solution. However, total soluble As concentrations in the PL treatment were similar to the fly ash-only treatments, yet poor recovery of As species in relation to total soluble As was noted only for the PL treatment. The

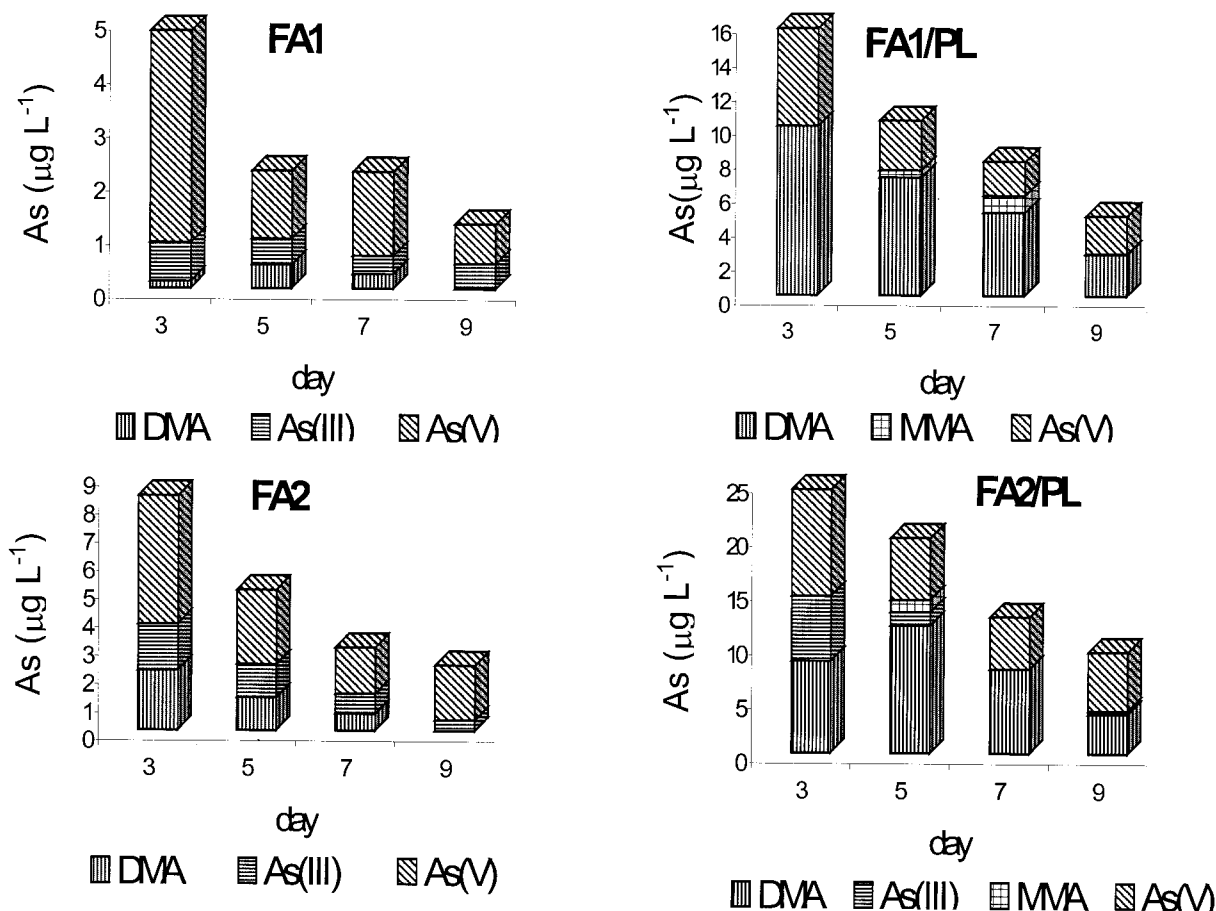


FIGURE 5. Soil solution As speciation in FA and FA/PL treatments.

reasons for this poor recovery were not immediately apparent. However, application of poultry litter to the soil resulted in a highly dispersive system that was qualitatively apparent by the difficulty encountered in filtering of soil solution from this treatment. Hence, it is possible that As identified as soluble by ICP-MS may have actually been colloiddally bound and did not pass through the guard column in the IC-ICP-MS speciation analysis.

DMA concentrations in the FA/PL treatments decreased over time at a greater rate than As(V), the other prevalent soluble As species in the soil solution. Further methylation of DMA would result in the production of methyl-arsines which, being volatile, would escape the aqueous phase (11). However, in a recent study designed to assess the rate of volatilization of these organic As compounds, it was found that mineralization to inorganic species was a more likely reaction pathway than further methylation and volatilization (12). Hence, one possible explanation for the decline in DMA concentrations and the stability of the As(V) concentrations over the sampling duration is that mineralization of DMA to the inorganic species occurred. However, because of the low total As loading rates for any of the treatments a full mass balance was not conducted, and therefore the fate of DMA, either volatilization, mineralization, or sorption, cannot be deduced from the results of this study. Low concentrations of MMA were also detected in the soil solution of both FA/PL treatments.

While mixing fly ash with poultry litter caused an increase in soil solution As over an equivalent application of fly ash alone, mixing of fly ash with sewage sludge had the opposite effect. DMA and As(V) were detected in both FA/S mixtures, but at lower concentrations than the FA treatments, suggesting that solid phases in the sludge may be controlling As

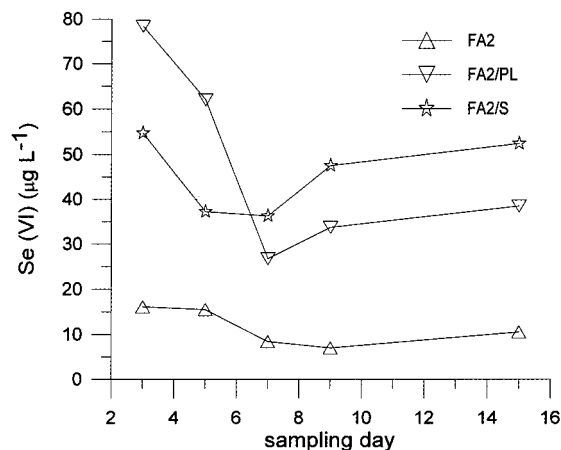


FIGURE 6. Se(VI) solubility in FA2 treatments.

solubility in this mixture. Chemical analysis of the sludge sample showed it contained high concentrations of Al and Fe (possibly added during the water treatment phase to control soluble P in the treatment plant), and the oxyhydroxides of these two elements are highly effective sorbents of As (28). Total As concentrations and As speciation in the sludge treatment were similar to the control treatment, where DMA and As(V) were also identified as present in the soil solution at trace concentrations (results not shown).

Soluble Se was detected in the soil solution of FA2 and its mixes with the organic wastes (Figure 6). Se in the soil solution was present exclusively as Se(VI). Selenate is rather weakly adsorbed by soil minerals through outer-sphere mechanisms and therefore is more soluble than Se(IV) (29). The results of the aqueous extraction showed that soluble Se

from both fly ashes was in the form of Se(IV), suggesting that rapid oxidation of Se(IV) occurred in the soil solution. Alkaline oxidizing conditions increase solubility of Se through oxidation to Se(VI) (27). Since both fly ashes were alkaline and increased soil solution pH, this may explain the predominance of the Se(VI) species. Adsorption of Se(IV) at soil colloid surfaces cannot be the only explanation for the lack of soluble Se(IV), as As(V) is predicted to be more strongly adsorbed than Se(IV) (15), yet As(V) was detected in the soil solution of the waste-amended soils.

Soluble Se was higher in both mixtures of FA2 with organic waste than FA2 as a single treatment. Both organic waste mixtures were low in Se, so that soluble Se in the FA2/PL and FA2/S treatments was a result of Se solubilized from FA2. Because the application rate of FA2 was equal in all three treatments, it may be expected that Se solubility would have been approximately equal for the three treatments. Clearly there were interactive effects of mixing FA2 with an organic waste that increased Se solubility. It may be that the higher ionic strength of the soil solution as a result of soluble salts from the two organic waste mixtures, especially increased soluble SO_4^{2-} concentrations, increased soluble Se(VI) through anion exchange reactions at soil mineral surfaces.

It was apparent from this experiment that mixing of fly ash with either poultry litter or sewage sludge for land application affected both the solubility and speciation of As and Se in the resulting soil solution. For As it appeared that the poultry litter was itself a significant source of soluble As. The soil solution speciation of As in the FA/PL treatments was also different than in the fly ash-only treatments. Mixing fly ash with either organic waste increased selenium solubility but did not affect the prevalent speciation in comparison with the fly ash-only treatment.

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