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Trace Element Speciation in Poultry Litter

B. P. Jackson,* P. M. Bertsch, M. L. Cabrera, J. J. Camberato, J. C. Seaman, and C. W. Wood

ABSTRACT

Trace elements are added to poultry feed for disease prevention and enhanced feed efficiency. High concentrations are found in poultry litter (PL), which raises concerns regarding trace element loading of soils. Trace metal cation solubility from PL may be enhanced by complexation with dissolved organic carbon (DOC). Mineralization of organo–As compounds may result in more toxic species such as As(III) and As(V). Speciation of these elements in PL leachates should assist in predicting their fate in soil. Elemental concentrations of 40 PL samples from the southeastern USA were determined. Water-soluble extractions (WSE) were fractionated into hydrophobic, anionic, and cationic species with solid-phase extraction columns. Arsenic speciation of seven As species, including the main As poultry feed additives, roxarsone (ROX; 3-nitro-4-hydroxyphenylarsonic acid) and p-arsanilic acid (p-ASA; 4-aminophenylarsonic acid), was performed by ion chromatography–inductively coupled plasma–mass spectrometry (IC–ICP–MS). Total As concentrations in the litter varied from 1 to 39 mg kg^{-1}, averaging 16 mg kg^{-1}. Mean total Cu, Ni, and Zn concentrations were 479, 11, and 373 mg kg^{-1}, respectively. Copper and Ni were relatively soluble (49 and 41% respectively) while only 6% of Zn was soluble. Arsenic was highly soluble with an average of 71% WSE. Roxarsone was the major As species in 50% of PL samples. However, the presence of As(V) as the major species in 50% of the PL samples indicates that mineralization of ROX had occurred. The high solubility of As from litter and its apparent ready mineralization to inorganic forms coupled with the large quantity of litter that is annually land-applied in the USA suggests a potential detrimental effect on soil and water quality in the long term.

M ORE THAN 11.4 million Mg of poultry litter (PL) were generated in the USA in 1996 and approximately 90% was land-applied (Cabrera and Sims, 2000). The localized nature of poultry farming operations and the cost of transporting PL over long distances has led to limited land areas receiving repeated waste applications. This has raised concerns over P saturation of soils, and similar concerns must also apply to trace element loading.

Poultry litter, indeed animal wastes in general, contain high concentrations of some trace elements. Copper, Zn, and As occur in PL as a result of their use as growth promoters or biocides in poultry feed (Sims, 1995). Reported PL concentrations of Cu and Zn were, respectively, 1196 and 631 mg kg^{-1} (van der Watt et al., 1994), 55 and 647 mg kg^{-1} (Edwards et al., 1997), 748 and 718 mg kg^{-1} (Moore et al., 1998), 97 and 378 mg

kg^{-1} (Nicholson et al., 1999), and 743 and 501 mg kg^{-1} (Jackson et al., 1999). Arsenic concentration in PL is variable, for example Sims and Wolf (1994; and references therein) reported a range in As concentration from 0 to 77 mg kg^{-1}. Other studies have also reported As concentrations within this range, for example 30 to 37 mg kg^{-1} (van der Watt et al., 1994), 43 mg kg^{-1} (Moore et al., 1998), and 35 mg kg^{-1} (Jackson et al., 1999). Furthermore, there is evidence that As in PL may be readily soluble; 72% of total As was solubilized from PL in a water extraction (Jackson and Miller, 1999).

Increased concentrations of Cu and Zn in the surface horizons of soil receiving annual applications of PL have been identified (Kingery et al., 1994). Copper and Zn concentrations in the surface of a soil profile that had received PL applications over 25 yr were significantly higher than an unamended soil. Furthermore the results of this study suggest that Zn is fairly mobile in the profile (Han et al., 2000). Initial soluble As concentrations of >200 µg L^{-1} were reported in runoff from a field soil amended with 9 Mg PL ha^{-1} and runoff concentrations 7 d after application were still >50 µg L^{-1} (Moore et al., 1998). The latter study also reported soluble Cu levels up to 1 mg L^{-1}, which is approaching the USEPA drinking water maximum contaminant level of 1.3 mg L^{-1}.

To better predict the mobility and bioavailability of major and trace elements arising from PL application it is necessary to investigate the speciation of these elements. Copper and Zn are added to animal feeds as the sulfate salt or oxide, and presumably occur in the litter in ionic form. However, both these elements can form stable soluble organic complexes and, given the high concentration of soluble organic C in leachates of PL, it is possible that these metal–organic complexes are important species affecting the mobility of these two elements. For example, in an acidic soil amended with cattle manure, soluble Cu was correlated with dissolved organic carbon (DOC) and a considerable amount of soluble Cu was found associated with nonlabile or high molecular weight complexes (del Castilho et al., 1993). Copper in pig slurry was found to be associated with DOC of molecular weight > 5000 Da, as measured by gel permeation chromatography (Businelli et al., 1999). In soils amended with pig manure, the increase in organic matter increased Zn solubility but decreased Zn lability as measured by differential pulse anodic strip-

Abbreviations: 3-AHPA, 3-amino 4-hydroxyphenylarsonic acid; DMA, dimethylarsonic acid; DOC, dissolved organic carbon; IC, ion chromatography; ICP, inductively coupled plasma; MMA, momomethylarsonic acid; MS, mass spectrometry; p-ASA, 4-aminophenylarsonic acid; PL, poultry litter; ROX, 3-nitro-4-hydroxyphenylarsonic acid; SAX, strong anion exchange cartridge; SCX, strong cation exchange cartridge; WSE, water-soluble extract.

ping voltammetry (Almas et al., 2000). Using sequential extraction techniques, Cu was found to be mostly associated with the organic matter fraction in soils that had a 25 yr history of PL application (Han et al., 2000). In soils leached with PL leachate, Zn solubility from a contaminated soil was increased; however, in an uncontaminated soil, Zn from the PL leachate was retained by the soil matrix (Li and Shuman, 1997).

Anion and cation exchange columns have been used to obtain qualitative speciation data on trace elements in solution (Chakrabarti et al., 1994, Appelblad et al., 1999). Metal ions retained by a cation exchange column are present either as a cation in solution or are bound in relatively labile complexes that dissociate in the time the solution is in contact with the resin. This methodology has been applied to investigate Cu and Zn species in sewage sludge–amended soils, where Cu was found to form mainly anionic species while Zn formed zwitter ions in the soil solution (Vulkan et al., 2002).

Arsenic occurs in PL as a result of the use of 4-aminophenylarsonic acid (*p*-ASA) or 3-nitro-4-hydroxyphenylarsonic acid (ROX) as feed additives for prevention of coccidiosis and for increased weight gain and improved feed efficiency (21 CFR 558.30; U.S. Code of Federal Regulations). Although there are few studies on the resulting long-term speciation of As in PL, the scant consensus in the literature is that the organo–arsenic compounds added to feed are rapidly excreted by chickens and that the compounds are relatively unchanged in chemical form (Andreae, 1986; Calvert, 1975). Morrison (1969) reported that ROX accounted for 36 to 88% of total As in 10 PL samples. There is a general lack of information about the fate of these organo–arsenicals in PL when composted or applied to soils, but the results of one study indicate that mineralization of arsanilic acid to arsenate occurred in each of three soils initially treated with arsanilic acid (Woolson, 1975). The inorganic As species arsenite, As(III), and arsenate, As(V), are more toxic than either ROX or *p*-ASA, hence it is important to understand the chemical species and speciation transformations of As in PL. A recently developed analytical method using ion chromatography

Fig. 1. Ion chromatography–inductively coupled plasma–mass spectrometry (IC–ICP–MS) chromatogram of seven As species standards: 10 µg L^{-1} dimethylarsenic acid (DMA), As(III), monomethylarsenic acid (MMA), 3-amino-4-hydroxyphenylarsonic acid (3-AHPA), and 4-aminophyenlarsonic acid (*p*-ASA), and 50 µg L^{-1} As(V) and 3-nitro-4-hydroxyphenylarsonic acid (ROX).

coupled with ICP–MS separates the two organo–arsenic feed additives from the inorganic and simple aliphatic As species and provides detection limits for each As species below 0.1 µg L^{-1} (Jackson and Bertsch, 2001). Before land application, speciation changes might be expected to occur either through metabolic processes during passage through the digestive system or through biotic or abiotic-mediated processes during PL storage.

The objectives of this study were to determine (i) the concentration and solubility of trace elements in poultry litter, (ii) the extent of complexation of trace metal cations by DOC in the leachates, and (iii) the speciation of As in the PL leachates.

MATERIALS AND METHODS

A total of 40 PL samples were obtained from Alabama, Georgia, and South Carolina (20, 10, and 10 samples, respectively). Samples were air-dried and sieved. Total elemental concentrations were determined after microwave digestion. A 0.25-g sample was weighed into a Teflon microwave digestion vessel and 5 mL concentrated HNO$_3$ was added. The vessel was allowed to react at room temperature for 1 h. After this time 1 mL of concentrated H$_2$O$_2$ was added and the vessels were capped and digested in an MDS 2000 microwave digestion system (CEM, Matthews, NC). After digestion the samples were brought to a final volume of 25 mL with 18 MΩ-cm deionized H$_2$O. Digestion quality control included blanks, laboratory fortified blanks, duplicates, spikes, and certified reference materials (CRM). The CRM used for this study was TORT 2 (NRC–CNRC, Ottawa, ON, Canada) and mean recoveries for Mn, Fe, Ni, Cu, Zn, As, Se, Sr, and Cd were 101, 118, 112, 96, 88, 106, 105, 99, and 97% respectively, for eight replicates of the CRM performed during analysis of the PL samples set. Major element analysis was performed by ICP–optical emission spectrometry (OES) (Optima 4300DV; Perkin-Elmer, Wellesley, MA) and trace element analysis was performed by ICP–MS (ELAN 6000; PerkinElmer). Percent organic matter was determined gravimetrically after ashing 1 g dry weight of PL at 480°C overnight.

Water-soluble extractions (WSE) were performed by shaking 1 g of PL with 10 mL deionized H$_2$O for two hours. The suspension was then centrifuged (15 000 rpm) for 15 min and the resulting supernatant was filtered (0.22 µm) and diluted 20-fold with deionized H$_2$O. Approximately 10 mL of the WSE was passed through a C$_{18}$ column (Sep-pak; Waters, Milford, MA) to remove hydrophobic organic compounds. The C$_{18}$ columns had first been cleaned and preconditioned by passing through 5 mL methanol followed by 10 mL of deionized H$_2$O. Elemental analysis was conducted on the WSE and WSE-C$_{18}$ eluants by either ICP–OES or ICP–MS. Dissolved organic carbon was determined on the WSE eluants with a TOC 5000A (Shimadzu, Kyoto, Japan). Arsenic speciation was determined on the WSE-C$_{18}$ eluants by IC–ICP–MS (Jackson and Bertsch, 2001). Briefly, the separation was conducted on an AS16 anion exchange column (Dionex, Sunnyvale, CA) that was directly interfaced to an ICP–MS. A step gradient elution procedure was used with 20 m*M* tetramethylammonium hydroxide (TMAOH) from 0 to 3 min at a 1 mL min^{-1} flow rate followed by a step gradient to 50 m*M* TMAOH for 3.01 to 10 min at a flow rate of 1.5 mL min^{-1}. An additional As compound, 3-amino 4-hydroxyphenylarsenic acid (3-AHPA), which has been suggested as a degradation product of ROX (Wershaw et al., 1999; Garbarino et al., 2001), was added to the mixed As standard. This compound was well resolved from As(V) and ROX, eluting at 7.6 min. The separation of the seven As species is given in Fig. 1. Three point calibrations were
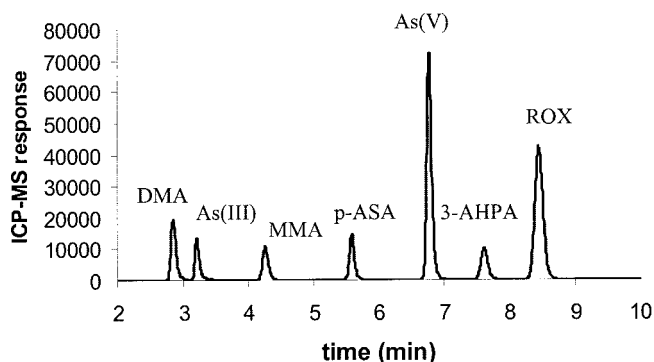
performed daily with mixed As species stock solutions containing As(III), As(V), dimethylarsenic acid (DMA), monomethylarsenic acid (MMA), p-ASA, 3-AHPA, and ROX and 100-μL injection volumes were used for standards and samples. Calibration concentrations were 1, 10, and 20 μg L^{-1} As for DMA, As(III), MMA, p-ASA, and 3-AHPA and 5, 50, and 100 μg L^{-1} for As(V) and ROX. These concentration ranges were based on preliminary results of the range of concentrations of As species in the litter extracts. Calibration correlation coefficients were >0.9998 for all As species and detection limits of 17, 25, 31, 24, 23, 32, and 40 ng L^{-1} were obtained for DMA, As(III), MMA, p-ASA, As(V), 3-AHPA, and ROX, respectively.

For each litter extract, approximately 12 mL of the WSE was passed through either strong cation exchange resin (SCX; benzenesulfonic acid functional group, styrene–divinylbenzene support; Alltech, Deerfield, IL) or a strong anion exchange resin (SAX, tetramethyl ammonium functional group, styrene–divinylbenzene support; Alltech). Trace elements retained by the column were calculated by the difference from the concentration of influent and effluent solutions.

RESULTS AND DISCUSSION

Total Trace Element Data and Water-Soluble Extractions

The total elemental concentrations for the 40 PL samples given in Table 1 are in good agreement with previous compendium reports of PL major and trace element concentrations (Sims and Wolf, 1994; Nicholson et al., 1999; Williams et al., 1999; Adriano, 2001). Arsenic was one of the most variable elements in terms of total concentration, with a range of 1 to 39 mg kg^{-1} for the 40 PL samples. The upper range of total As found in this study is approaching the value of 41 mg kg^{-1}, which, for comparison, is the concentration limit for As for land application of sewage sludge to agricultural, forest, or public contact land as regulated by the USEPA (40 CFR 503; USEPA, 1993). Copper and Zn had mean concentrations of 479 and 372 mg kg^{-1}; these concentrations are well below threshold limit for land application of sewage sludge (1500 and 2800 mg kg^{-1}, respectively); however, they are high enough to indicate that soils subject to long-term PL application may have incurred substantial cumulative loadings of these elements. Indeed, soils subject to long-term PL application have been shown to have increased concentrations of Cu and Zn and there is evidence for increased leaching of these elements (Kingery et al., 1994; Han et al., 2000). The relatively high concentrations of U in the litter (mean = 5.6 mg kg^{-1}) have not previously been reported and presumably result from the use of inorganic phosphates in poultry feed, as these sources have been reported to contain 20 to 120 mg kg^{-1} U (Langmuir, 1997).

The proportion of the total elemental concentration that was solubilized in a water extraction (WSE) is presented in Table 1. The polyvalent cations Al, Ca, and Mg are relatively insoluble, probably due to precipitation as phosphates. The monovalent cations Na and K are, predictably, highly soluble. Of the divalent transition metals, both Ni and Cu (49 and 41% mean percent WSE, respectively) exhibit much greater solubility, and this may be due complexation with DOC. Surprisingly,

Table 1. Average total elemental concentrations and water-soluble fractions for 40 poultry litter samples.

	OM†	Na	Mg	Al	P	K	Ca	Mn	Fe	Ni	Cu	Zn	As	Se	Sr	Cd	Ba	Pb	U
	%										mg kg^{-1}								
Mean	76	10810	7162	3169	17100	33020	22420	449.3	2189	11.09	479.2	372.7	15.65	1.183	82.62	0.252	21.61	2.06	5.601
Standard deviation	7	3149	2157	2277	3541	12000	5538	119.2	1092	3.346	229.6	89.01	9.57	0.295	22.58	0.144	5.626	1.328	1.465
Median	77	11324	7170	2374	17889	35799	22169	460	1914	10.8	413.6	375.6	14.75	1.129	82.93	0.232	21.01	1.781	5.283
Minimum	39	5103	2707	815	8883	8792	8731	158.1	529.4	3.081	86.00	132.8	1.186	0.459	34.17	0.054	9.418	0.803	3.197
Maximum	84	18520	14740	10040	24500	58940	32960	636.2	5713	21.1	1204	594.8	39.36	1.967	135	0.884	33.85	6.213	9.473
												% water soluble							
Mean	12	64	17	0	26	79	3	2	5	49	41	6	71	40	7	15	2	1	0

† Organic matter.

Table 2. Mean percentage of water-soluble trace elements retained by three solid-phase extraction columns (n = 40). Standard errors are given in parentheses.

Column	Mn	Fe	Ni	Cu	Zn	As	Se
				%			
C_{18}†	16 (0.21)	20 (0.32)	12 (0.1)	27 (0.13)	16 (0.24)	11 (0.18)	21 (0.51)
SAX‡	6 (0.18)	37 (0.23)	45 (0.23)	41 (0.26)	6 (0.22)	77 (0.21)	67 (0.23)
SCX§	98 (0.03)	44 (0.18)	70 (0.23)	81 (0.16)	52 (0.31)	33 (0.16)	44 (0.36)

† Retains hydrophobic species.
‡ Strong anion exchange cartridge; retains anionic species.
§ Strong cation exchange cartridge; retains cationic species.

As was one of the most water-soluble elements from PL with a mean WSE value of 71%. This indicates that on initial land application, As will be readily soluble from the PL. The long-term fate of As from the PL will depend on the initial speciation of As in the poultry, biotic and abiotic transformations of these species, and the resulting soil chemistry of these species.

Retention of Trace Elements by C_{18}, Strong Anion Exchange Cartridge, and Strong Cation Exchange Cartridge Solid-Phase Extraction Columns

The proportion of water-soluble trace element retained by various solid-phase extraction columns is given in Table 2. Copper was the most highly retained element on the C_{18} column. This is not surprising given the affinity of Cu for complexation with DOC. Hydrophobic DOC would be expected to partition to the solid phase of a C_{18} column whereas hydrophilic anionic DOC would be expected to bind to the SAX column. The SAX column retained 45% of soluble Ni and 41% of soluble Cu, suggesting that a significant fraction of these elements is complexed by DOC in the poultry extract. The affinity of Cu for DOC is in agreement with the results of Moore et al. (1998), who showed that Cu concentrations in runoff were highly correlated to DOC in runoff from plots fertilized with poultry litter. However, the SCX column retained 70 and 81% of soluble Ni and Cu, respectively, suggesting that a portion of the metal–organic anionic complexes were also labile and dissociated in the SCX column environment. Only a small fraction of soluble Zn was retained by the SAX column, indicating that it was not present as anionic species. However, 48% of soluble Zn was not retained by SCX, indicating that a major species of Zn in the litter is a neutral complex. The SAX column retained 77% of soluble As, consistent with the idea that As is present mainly as anionic species (including

p-ASA, 3-AHPA, and ROX). The As not retained by the SAX column may be a neutral species, for example, As(III), or a cationic species, or may be present as an anionic species not retained by the SAX due to competition with excess PO_4 in the extract. Cationic As species were not expected to be present in the extracts; however, 33% of As was retained by the SCX column, suggesting the presence of either a cationic species or a species that is retained by the stationary phase of the SCX column (Table 2).

Arsenic Speciation Data

The form of As in poultry feed is either ROX or p-ASA, as regulated by U.S. Food and Drug Administration (21 CFR 556.60; U.S. Code of Federal Regulations). It has been reported that these compounds are not efficiently absorbed (or are added to the feed in excess), such that the PL contains relatively high concentrations of As, and that the original As species added to the feed is also the major species in the litter (Andreae, 1986). However, abiotic or biotic reactions are likely during litter storage or handling that could lead to changes in As speciation. A summary of the As species determined in the 40 PL samples examined in this study is given in Table 3. The major species determined in the litter samples were either ROX or As(V), with lesser amounts of DMA, 3-AHPA, MMA, and As(III) also detected. Other smaller (unidentified) As peaks were also obtained at different retention times from the As species standards. For 20 of the 40 PL samples, As(V) was identified as the major As species in the water extract, indicating that mineralization of the initial organo–arsenic had occurred. Representative chromatograms for WSE of a PL with predominantly As(V) and predominantly ROX are shown in Fig. 2A and 2B, respectively. Three possible mechanisms for ROX degradation have been suggested: (i) reduction of the nitro group to form 3-amino; (ii) enzymatic oxidative aro-

Table 3. Summary data of As speciation in 40 poultry litter extracts.

	DMA†	As(III)	MMA‡	p-ASA§	As(V)	3-AHPA¶	ROX#
Maximum concentration detected in solution, μg L^{-1}††	5.39	3.1	2.78	ND‡‡	33.84	7.47	34.63
Maximum as percent of sum of As species, %	25	7	7	ND	80	36	80
Average as percent of sum of As species, %	9	2	2	ND	36	13	40
Median as percent of sum of As species, %	7	1	1	ND	34	12	37

† Dimethylarsonic acid.
‡ Momomethylarsonic acid.
§ 4-Aminophenylarsonic acid.
¶ 3-Amino 4-hydroxyphenylarsonic acid.
# 3-Nitro-4-hydroxyphenylarsonic acid.
†† One gram of poultry litter was extracted in 10 mL deionized water and was further diluted 20-fold.
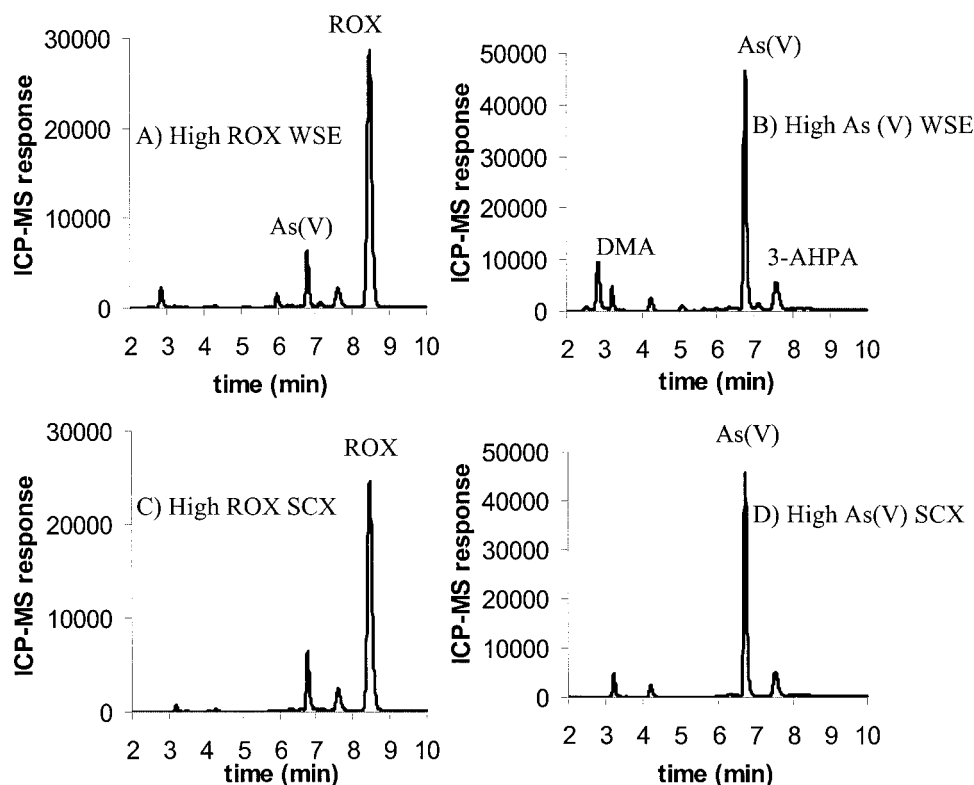‡‡ Not detected.

Fig. 2. Representative chromatograms for poultry litter (PL) water-soluble extraction (WSE) with (*A*) As(V) as the major species, (*B*) 3-nitro-4-hydroxyphenylarsonic acid (ROX) as the major species. (*C*) Sample in 2A after the strong cation exchange cartridge (SCX) column, and (*D*) sample in 2B after the SCX column.

matic ring fission, which in aerobic conditions would produce As(V); and (iii) photolysis of the C–As bond to produce As(V) (Wershaw et al., 1999). Garbarino et al. (2001) have observed that ROX in PL leachate was totally transformed to different As species within 48 h, but in sterilized litter extract ROX was stable for at least 10 d. Garbarino et al. (2001) further noted that transformation of ROX produced an unidentified As species that they proposed was of higher molecular weight than 3-AHPA. The results of our study also indicate that As(V) is a major degradation product of ROX, that is, As(V) was identified in litter leachates with low concentrations of ROX, while litter extracts with high concentrations of ROX had lower concentrations of As(V). A correlation analysis of PL leachates, where total soluble As was >10 μg L^{-1} (36 out of 40 samples), showed that the percent As(V) (as a percent of total soluble As species) was negatively correlated to percent ROX with $R^2 = -0.96$.

When the sum of As species was compared with the total soluble As, incomplete recovery was noted for all PL extracts. Recovery ranged from 29 to 69% with a mean value of 43%. The correlation analysis results indicated that percent recovery was directly correlated to percent ROX and negatively correlated to percent As(V). Three spiked leachate samples gave mean recoveries of 104, 104, 99, 100, 99, and 101 for DMA, As(III), *p*-ASA, As(V), 3-amino, and ROX, respectively. Hence we have a high degree of confidence that these components were not being retained on the anion exchange

column. However, the discrepancy in recovery of As in the speciation scheme suggests an unidentified As species that has a high affinity for the anion exchange resin. It was noted earlier in the solid-phase extraction results that the SCX column retained a mean of 33% of soluble As. Hence we hypothesize that the unidentified As species must have a high affinity for the stationary phase (styrene–divinylbenzene) of exchange columns (i.e., an aromatic As compound). The IC–ICP–MS analysis of two of the SCX extracts gave essentially the same chromatogram as the WSE (Fig. 2C,D), that is, no further As was retained by the anion exchange column once the extract had been passed through a cation exchange column. This observation supports the idea that the unknown As compound is retained by the stationary phase of the exchange columns. Hence, it appears that degradation of ROX results in both As(V) and an unidentified As species of more aromatic character.

CONCLUSIONS

Trace elements Ni, Cu, and As were found to be readily soluble from PL. More than 70% of Ni and Cu was in the cationic form, or bound in relatively labile complexes that dissociated to the cationic species. Hence, trace metal cations from PL are expected to be readily sorbed by soil mineral phases on land application of PL. The organo–arsenic feed additive ROX was found to be the major species in 50% of the litter lea-

chates. However, the prevalence of As(V) as a major species in 50% of the litter leachates means that mineralization mechanisms exist, leading to the degradation of ROX to the more toxic inorganic species. In addition to As(V), it appears that degradation of ROX leads to an, as yet, unidentified As species that had a strong affinity for the stationary phase. We are currently working on methodology to identify this As species. The solubility of As from PL coupled with high concentrations of soluble PO_4 from PL that can displace As from soil sorption sites (Peryea and Kammereck, 1997) suggests that the continued land application of As-containing PL could be detrimental to soil and water quality in the long term.

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