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Arsenic Speciation and Reactivity in Poultry Litter

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Recent U.S. government action to lower the maximum concentration levels (MCL) of total arsenic (As) (10 ppb) in drinking water has raised serious concerns about the agricultural use of As-containing biosolids such as poultry litter (PL). In this study, solid-state chemical speciation, desorbability, and total levels of As in PL and long-term amended soils were investigated using novel synchrotron-based probing techniques (microfocused (μ) synchrotron X-ray fluorescence (SXRF) and μ-X-ray absorption near-edge structure (XANES) spectroscopies) coupled with chemical digestion and batch experiments. The total As levels in the PL were as high as ≈50 mg kg^{-1}, and As(II/III and V) was always concentrated in abundant needle-shaped microscopic particles (≈20 μm × 850 μm) associated with Ca, Cu, and Fe and to a lesser extent with S, Cl, and Zn. Post-edge XANES features of litter particles are dissimilar to those of the organo-As(V) compound in poultry feed (i.e., roxarsone), suggesting possible degradation/transformation of roxarsone in the litter and/or in poultry digestive tracts. The extent of As desorption from the litter increased with increasing time and pH from 4.5 to 7, but at most 15% of the total As was released after 5 d at pH 7, indicating the presence of insoluble phases and/or strongly retained soluble compounds. No significant As accumulation (<15 mg kg^{-1}) was found in long-term PL-amended agricultural surface soils. This suggests that As in the PL may have undergone surface and subsurface transport processes. Our research results raise concerns about long-term PL amendment effects on As contamination in surrounding soil−water environments.

Introduction

In the last four decades, the poultry industry has become one of the major livestock operations in the Mid-Atlantic states (e.g., Delaware, Maryland, and Virginia) of the United States. The majority of poultry litter (PL) generated during the operations has been recycled as an organic amendment on agricultural fields to meet N requirements for crops. As the result of (i) long-term amendments of the litter containing a high quantity of P (>10 000 mg kg^{-1}) and (ii) P retention on the soils, many Mid-Atlantic Coastal Plain soils are now classified as agronomically excessive or high P soils (i.e., >28 mg kg^{-1} by the Mehlich 3 extraction) (*1*, *2*). Phosphorus in soils is now considered as the nonpoint nutrient source causing eutrophication and possible outbreaks of *Pfiesteria piscicida* in surrounding water bodies via surface runoff, erosion, and preferential flow of dissolved/particulate P (*3*−*6*). On-site PL management has been evaluated to reduce the P release from soils. However, the effects of poultry litter amendments on trace element contamination (e.g., As, Cu, and Zn) in soils have not been considered in current nutrient management programs.

In recent years, As has became one of the major environmental toxicants in the world due to its high carcionogenicity, phytotoxicity, and biotoxicity (*7*, *8*). Changes in the MCL of total As (10 ppb) in drinking water (*9*) have raised concerns about agricultural uses of As-containing biosolids (e.g., PL) because As contamination in surface water/groundwater could potentially threaten human/ecological health.

Poultry litter has been generally applied at the rate of 8.96−20.16 Mg ha^{-1} on agricultural lands, with total annual As inputs on the Delaware−Maryland−Virginia (Delmarva) Peninsula estimated at between 20 and 50 t of total As (*10*). The origin of As in the PL is organo-As(V) compounds (e.g., 3-nitro-4-hydroxyphenylarsonic acid (roxarsone)) in the poultry feed (*11*). Approximately 25−50 mg of roxarsone is mixed per kilogram of feed for coccidiosis control, as a growth and egg production stimulant, and for improvement of feed conversion (*12*). Feed spillage and digested materials have increased the mean total As concentration in the PL to 14−76 mg kg^{-1} (*13*−*19*). At present, annual total metal(loid) inputs on agricultural lands via PL amendments are not specifically regulated at either the state or federal levels, and continuous litter amendment effects on As contamination in Atlantic Coastal Plain soil/water environments is not known. Preliminary assessments of As contamination in soils via long-term PL amendments are necessary to suggest new policies for reducing As additions from PL and/or to initiate changes in current regulations if contamination is occurring.

To better understand the fate and transport of the organo-As(V) compound from PL, we investigated (i) As levels in the PL and long-term amended agricultural surface soils, (ii) stability of As in the PL as a function of pH, and (iii) As solid-state speciation (oxidation state and chemical speciation) in litter materials using traditional chemical digestion, batch desorption techniques, and μ-SXRF/XANES spectroscopies. Spatially resolved (≈20 μm diameter) spectroscopic techniques (μ-SXRF and μ- XANES) can identify the chemical speciations and elemental associations of As in dilute (<100 mg kg^{-1}) heterogeneous materials such as PL.

Materials

Several agricultural surface (0−30 cm) soils (Evesboro (Ev) loamy sand [Typic Quartzipsamments], Fallsington (Fs) sandy loam [Typic Ochraquults], Pocomoke (Pm) sandy loam [Typic Umbraquults], and Rumford (Ru) loamy sand [Typic Hapludults]) were collected from southern Delaware agricultural fields, which were previously used for a soil phosphorus characterization transect study by Sims et al. (*32*). Three to five soil samples from transects 1 and 3 of site 1 and from transect 4 of site 2 had received over 3 decades of PL surface amendments and had been used row crop production. Prior to chemical digestion, samples were air-dried and ground

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using a mortar and pestle. Four-inch diameter cores were collected from the full depth of the litter (i.e., predominantly wood shavings) in a zigzag manner in a southern Delaware poultry house (approximately 1487.21 m^2) where 6 flocks (approximately 21 000 broiler chicks/flock) were reared annually. Samples were composted/mixed and kept at 3 °C prior to macroscopic and spectroscopic analyses to minimize any changes in As chemical properties. For thin section preparation for the μ-SXRF/XAS analyses, soil and PL samples were first freeze-dried, and then the samples were embedded in a 3M electrical resin (3M Industry, TX). The freeze-drying process was used to remove any moisture that could inhibit the resin curing process and to maintain the physical aggregate properties of the samples. The hardened resin-embedded samples were cut and polished into thin sections ($\approx$30 μm) and mounted on pure silica slides (2.5 cm diameter and 1.6 mm thick) using Superglue. These materials and the resin medium were used to minimize potential trace metal/metalloid contamination in the background during the SXRF and XANES analyses.

Methods

Characterization of Solids. Nitric acid/microwave digestion was performed on triplicates of each soil and PL sample using a solid/solution ratio of 0.5 g/12 mL (*20*). The digested solution was analyzed for Al, As, Ca, Cu, Fe, Mn, P, and Zn using ICP-AES. The quality assurance and check methodologies are described elsewhere (*21*). Total percent carbon, nitrogen, and sulfur were also analyzed using a LECO CNS 2000 analyzer (LECO Equipment Co., St. Josephs, MI). The pH of each sample was also measured in H_2O using a 1:5 solid/solution ratio.

μ-SXRF Analyses. The μ-SXRF analyses on the PL thin section were performed at beamline X-26A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, Upton, NY. The beamline is equipped with a channel cut Si(111) crystal monochromator, and the X-ray beam size (a minimum of 15 μm^2) is produced by micro-focusing mirrors. In this study, the monochromatic beam size was set at approximately 18 μm diameter using a double-elliptical Rh-coated Kirkpatrick−Baez mirror system (*22*). SXRF analyses were collected with the monochromatic beam at the As K edge absorption energy (11 869 eV). The thin section was vertically set on the automated $x-y-z$ sample stage with a plastic sample holder at 45° to the incident beam. Fluorescent X-ray signals were detected using a Si(Li) energy-dispersive detector mounted at 90° to the incident beam, and the elemental maps were taken over an approximately 600 μm × 600 μm area for the elements with K absorption edges below the excitation energy (notably S, Cl, Ca, Ti, Fe, Cu, Zn, and As). The excitation energies below Si were not detectable because of instrumental limitations. Compositional maps were produced by defining regions of interest for selected fluorescent peaks and then scanning the sample horizontally and vertically. Typically these were collected at 20 s/pixel (corrected for detector dead time) and with step sizes of 10 μm. Full energy-dispersive spectra for selected points of interest were also collected (typically 300−500 s/point) to evaluate elemental concentrations that were too low to detect efficiently with the short count times required for efficient mapping and to evaluate potential spectral overlaps.

μ/Bulk-XANES Analyses. Arsenic K edge μ-XANES spectra were collected at the GSECARS's undulator beamline (sector-13D) at the Advanced Photon Source in Argonne, IL. Cryogenic-cooled Si(111) monochromators and a double-elliptical Rh-coated Kirkpatrick−Baez mirror system were used to produce an approximately 5 μm diameter beam. The XANES spectra were collected from 11 800 to 12 200 eV in fluorescence mode using a Ge 16 element detector. Because of beam-induced oxidation effects of As(III), XANES spectra collections were limited to only 3−5 scans. The WinXAS 2.0 program (*23*) was used for the XANES spectra analyses, and linear combination analyses were performed using an approach similar to that described by Fendorf et al. (*24*). Reference materials used in the LC analyses are listed below. The adsorption energy ($\approx$11 874 eV) was calibrated at the half-height of the edge step for ACS grade sodium arsenate salt ($Na_2HAsO_4 \cdot 7H_2O$) (Baker) ($\approx$1 wt % in boron nitride). Several As(III and V) reference materials (approximately 1 wt % in BN) were run at beamline X11A at the NSLS to identify the oxidation state and to compare XANES spectra features with litter particles. They were sodium *m*-arsenite, $NaAsO_2$ (Sigma), orpiment (As_2S_3), $Cu_3(AsO_4)_2 \cdot 27H_2O$, and roxarsone premixed in feed additives. Our attempt to collect the bulk-XANES spectrum of the PL sample was not successful because of the low levels of total As in the PL (i.e., <50 mg kg^{-1}). The As K edge XANES measurements at X11A were performed as described by Arai et al. (*25*). The spectra were collected in fluorescence mode with a Lytle detector filled with krypton gas. The ionization chamber (I_o) was filled with 90% N_2 and 10% Ar. A Ge filter was used to remove elastically scattered radiation from the fluorescence emissions. The monochromator consisted of two parallel Si(111) crystals with a vertical entrance slit of 0.5 mm. The $Cu_3(AsO_4)_3 \cdot 27H_2O$ solubility product was synthesized on the basis of the MINEQL+ chemical modeling speciation program (*26*). A total of 125 mL of 0.005 M copper chloride solution was mixed with 125 mL of a 0.001 M sodium arsenate solution at pH 6, and the mixture was equilibrated for 48 h. The precipitates were washed with deionized water at pH 6 to remove excess salts.

Desorption Experiments. The stability of As in the PL was investigated using a batch desorption method. The batch method was chosen over continuous flow methods due to high levels of dissolved organic carbon, which clogged the filter in the continuous flow systems. pH 4.5 and pH 7.0 were chosen in these studies to simulate soil pH values of Atlantic Coastal Plain agricultural soils before and after liming. A total of 10 mM sodium acetate or HEPES [*N*-(2-hydroxyethyl)-piperzine-*N′*-2-ethanesulfonic acid] in 0.01 M NaCl was used as desorption reagents, and pH values were adjusted to 4.5 and 7.0, respectively, using 0.1 M HCl and NaOH. A total of 2 g of air-dried PL was placed in 50 mL polypropylene high-speed centrifuge tubes. The solids were reacted with 15 mL of the desorption reagents for 24 h at 60 rpm on an end-over shaker. Suspensions were centrifuged at 11950*g* for 7 min at 22 °C (±2) and decanted, and then 15 mL of fresh desorption reagents were added to continue the desorption processes. This desorption procedure was repeated 5 times (i.e., 5 d). The supernatant solutions were first passed through a 0.45 μm Gelman Supor-200 membrane filter (Pall Corp., MI), and filtrates were subsequently analyzed for total Al, As, Ca, P, Cu, Fe, Mn, and Zn using ICP-AES. In this study, we only focused on total As concentrations since As speciation can be rapidly altered during the batch desorption procedure via microbial and photodegradation of organo-As compounds (e.g., roxarsone) (*27*, *28*).

Results and Discussions

Total Metal(loid) Levels in Litter and Amended Soils. Total metal(loid) concentrations and pH of the PL and long-term amended soils are shown in Table 1. While the pH of the PL was near-neutral, soil pH values were moderately acidic. These pH differences might have caused dissolution/desorption of As that was retained in the PL-amended soils. Although the total As level was approximately 50 mg kg^{-1} in the PL, over 3 decades of PL amendments did not seem to have resulted in any significant As accumulation ($\leq$15 mg kg^{-1}) in the surface soils (Table 1). These values are in good agreement with previously reported values (*13*−*19*, *29*). The

TABLE 1. Total Elemental Analyses of Poultry Litter and Long-Term-Amended Soils[a]

		total metal (loid) and nutrient										
		%			mg kg^{-1}							
sample	pH	C	S	N	P	Al	Fe	Ca	Mn	Cu	Zn	As
litter	7.53 ± 0.04	19.04	0.43	2.02	15200	5490	6098	17863	390	345	386	47.8
		(0.13)	(0.06)	(0.21)	(875)	(195)	(692)	(659)	(26.2)	(36.8)	(27.7)	(2.3)
Ev	5.32 ± 0.02	1.22	0.010	0.130	1226	8951	2936	852	76.9	22.31	39.9	12.0
		(0.04)	(0.001)	(0.001)	(45)	(102)	(85)	(43)	(3.5)	(0.5)	(1.7)	(1.5)
Fs	4.96 ± 0.02	7.50	0.040	0.37	769	6738	1207	1623	28.2	19.0	22.2	15.0
		(0.18)	(0.001)	(0.01)	(63)	(70)	(282)	(101)	(1.6)	(1.6)	(2.5)	(0.1)
Pm	5.03 ± 0.02	1.48	0.010	0.13	764	5667	2239	1131	18.9	9.6	11.3	14.6
		(0.16)	(0.001)	(0.02)	(53.6)	(202)	(12)	(82)	(3.6)	(1.6)	(1.5)	(0.3)
Ru	5.52 ± 0.02	0.99	0.010	0.110	561	4115	2268	80.8	37.6	11.7	25.4	13.3
		(0.07)	(0.001)	(0.002)	(0.2)	(272)	(12)	(10.2)	(2.4)	(1.2)	(0.1)	(0.2)

[a] Mean (standard deviation), $n = 3$.

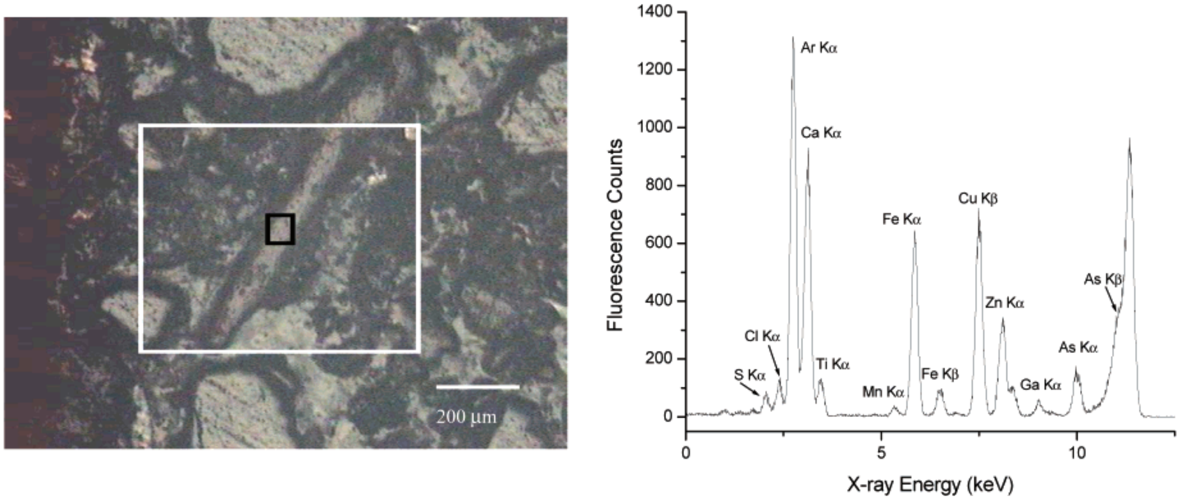

FIGURE 1. Photographic image of a poultry litter thin section and a synchrotron-based microfocused X-ray fluorescence spectrum of an arsenic-rich particle taken at a black open square. A white open square (approximately 600 × 600 μm) indicates a selected area for microfocused X-ray fluorescence maps shown in Figure 2.

total As levels in the surface soils, which are slightly higher than the background As level in soils (5 mg kg^{-1}) (*30, 31*), are similar in all soils regardless of the total carbon content of the soils (i.e., 0.99−7.5%) suggesting that As might not be strongly associated with organic carbon in the soils. A similar finding was previously reported by Jackson and Bertsch (*40*), who found a predominant portion of water-extractable As in the PL that was not associated with Sepak C_{18} extractable hydrophobic dissolved organic carbon. All soils contained significant amounts of total Al (>4000 mg kg^{-1}) and Fe (>1200 mg kg^{-1}), and operationally defined oxalate extractable Al and Fe were >2400 mg kg^{-1} in the Pm and Ev surface soils (*32*). It is possible that amorphous aluminum and iron oxides act as sinks for dissolved As. Noticeable amounts of Ca, S, P (>10 000 mg kg^{-1}), Cu, and Zn were also found in the PL. The origin of P, calcium, transition metals (i.e., Cu, Fe, and Zn), and S are likely to be in the poultry feed. $CuSO_4$ (total Cu, 6−100 mg kg^{-1}), $ZnSO_4$ (total Zn, 55−100 mg kg^{-1}), limestone and dicalcium phosphate (total Ca, 66.5 mg kg^{-1}), and $FeSO_4$ (total Fe, 40−55 mg kg^{-1}) are commonly mixed in the feed (*33*−*35*). It is interesting that As, Cu, and Zn accumulation is similar in all soils (i.e., approximately 10−40 mg kg^{-1}) even though Cu and Zn input levels were much higher than that for As (Table 1), suggesting that Cu and Zn transport processes had occurred.

***μ*-SXRF Analyses.** A photomicrograph of one of the As-rich particles (Figure 1) shows the distinctive elongated particle morphology in the litter. These particles (approximately 20 × 850 μm) were abundantly present in sample matrixes. Our X-ray fluorescence analyses at the center of this particle (indicated by a black open square) show that elevated As levels are associated with Ca, Fe, and Cu and to a lesser extent with Zn, Ti, Cl, and S (Figure 1).

A total of 17 similar particles was found in nearly half of the thin section (∼200 mm^2). Due to the use of trace metal free (i.e., trace metal content was not detectable using the SXRF) resin and quartz slides, the occurrence of these elements indicates that they strictly originated from the PL samples. Elemental maps generated within a white open square region in Figure 1 also show that the distribution of As is highly associated with Cl and Cu. Assuming no significant changes in the sample thickness and the density of the particle, the flux-normalized fluorescence counts in Figure 2 can be correlated to relative elemental concentrations for each element. It is possible that the formation of mixed metal−As, As−S precipitates, and/or As sorption complexes on metal oxide precipitates were occurring in the litter and/or during poultry digestion. The presence of Ca, transition metals (i.e., Cu, Fe, and Zn), and S in the PL is expected as observed in the previous total digestion data (Table 1), but chlorine is not expected. The source of Cl is probably sodium chloride mixed in the feed at 600−1000 mg kg^{-1} (W. Saylor, personal communication). Our preliminary μ-XRD analyses at beamline X26A at the NSLS showed no distinctive diffraction patterns on these particles, indicating the amorphous nature of the As-containing particles.

Inhalation/ingestion of As-rich microscopic particles could potentially cause detrimental effects to agricultural

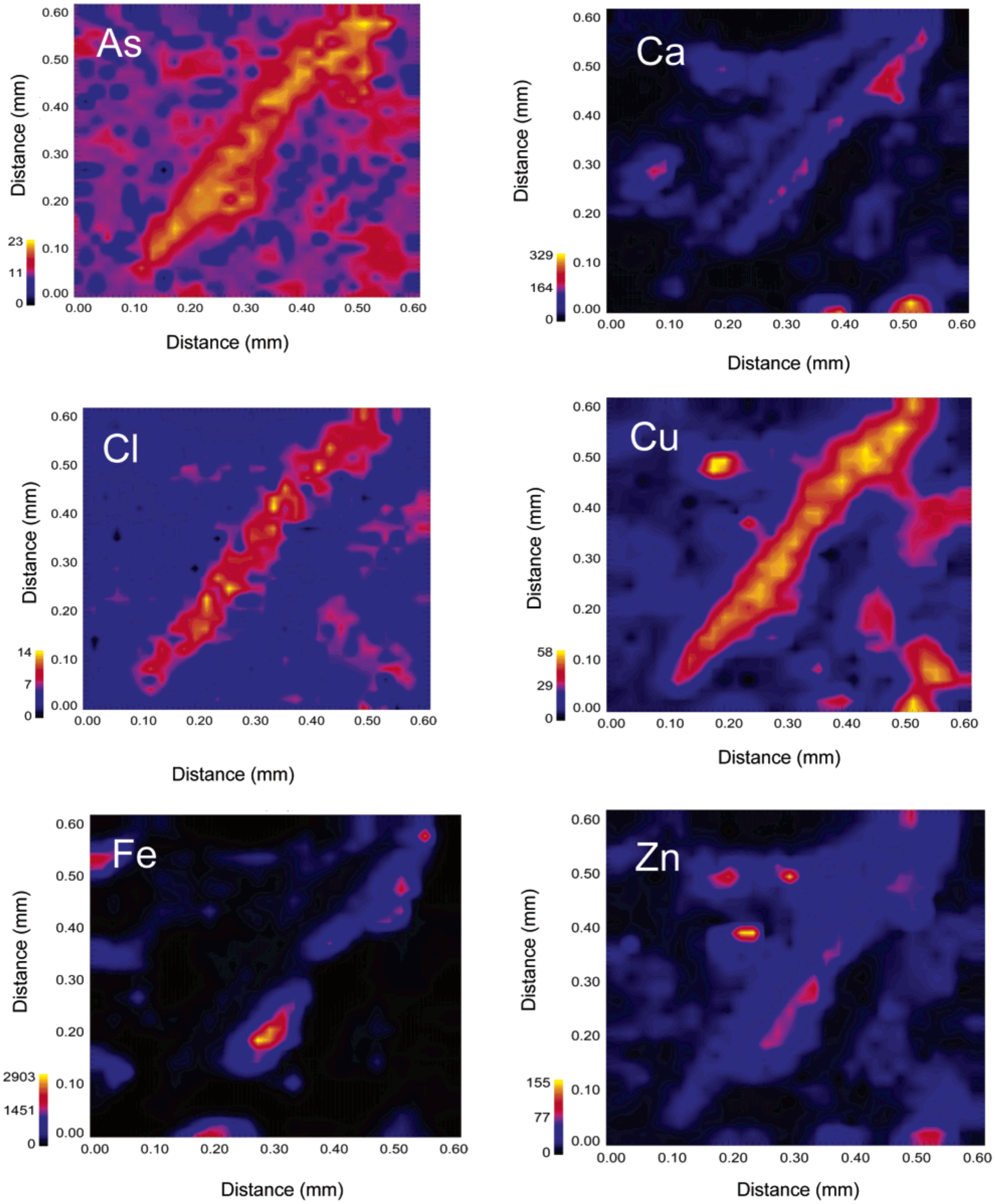

FIGURE 2. Synchrotron-based microfocused X-ray fluorescence maps (600 × 600 μm) of a white open square area in the photographic image in Figure 1. Flux normalized fluorescence counts/20 s are shown for each element.

workers. To minimize possible human health risks, new procedures for safely handling litter materials may be needed.

We have subsequently performed μ-SXRF analysis on long-term litter-amended DE soils. Unlike the PL, As hot spots were not located in the PL-amended soils. We did not observe any detectable As fluorescence counting for 500 s due to well-homogenized low levels of As (i.e., approximately 5 mg kg^{-1}) in the soils.

Although the μ-SXRF analyses provide spatially resolved elemental distribution with respect to As in the samples, it is still unclear if organo-As(V) compounds persist in the PL. In the next section, results of μ-XANES measurements on these particles are discussed to gain insights into the As chemical speciation in the PL.

μ/Bulk-XANES Analyses. The μ-XANES measurements were performed on the particle in Figure 1 (i.e., particle A in Figure 3b) and several additional As-containing particles (only particles B and C are shown in Figure 3a,b). They all produce similar XRF spectra to particle A (data not shown). Wide whiteline peaks are consistently observed in particles A−C

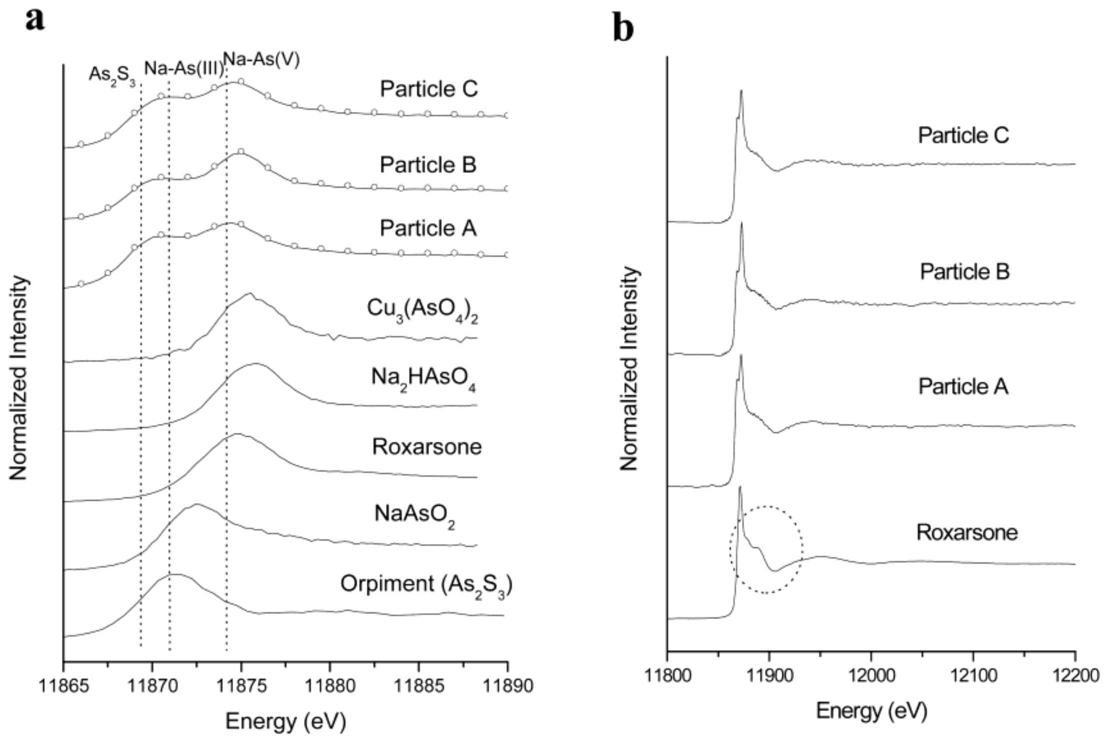

FIGURE 3. (a) Short-range normalized XANES spectra of As reference materials (sodium arsenate (Na_2HAsO_4), sodium *m*-arsenite ($NaAsO_2$), $Cu_3(AsO_4)_2 \cdot 27H_2O$, orpiment ($As_2S_3$), and roxasorne), and As-rich particles in poultry litter are shown. The open-circles overlying on the sample spectra are the best fit from the linear combinations of model compounds. Spectra contribution (%) of roxarsone and As_2S_3 are 54 and 46 for particle A; 64 and 36 for particle B; and 53 and 47 for particle C, respectively. Three vertical dashed lines are at the absorption edge energy positions of orpiment (As_2S_3 ≈ 11 869 eV), sodium *m*-arsenite (Na−As(III) ≈ 11871 eV), and sodium arsenate salt (Na−As(V) ≈ 11 874 eV), respectively. In panel b, long-range normalized XANES spectra of As-rich particles A−C and roxarsone are shown.

(Figure 3a,b), indicating the presence of mixed oxidation states in these particles. The mixed oxidation state was consistently present in the 17 particles previously observed in the SXRF analyses. We subsequently performed XANES analyses on the reference roxarsone in the resin, and there were no changes in its As(V) oxidation. This suggests that the reduced As valence state in the litter sample was not due to the artifacts created during the thin section preparation. Specific XANES post-edge features (as indicated by a dotted circle in Figure 3b) in roxarsone are dissimilar to those in particles A−C, suggesting a possible degradation of roxarsone. To resolve the multi-As oxidation states in the litter, magnified XANES spectra of reference materials are compared (Figure 3a). Whereas the absorption edge energy position of As(V) mineral/salt(s) is ≥11 874 eV, sodium arsenic(III) salt exhibits an absorption edge energy position of ≈11 871 eV. However, when As(II/III) associates with sulfide (i.e., mineral realgar (AsS) and orpiment(As_2S_3)), the As(III) energy position further decreases to ≈11 869 eV (*36*, *37*). On the basis of the absorption edge energy positions, the As valence state of the unknown samples can be assigned. Two absorption edge positions were observed in particles A−C, and they are similar to those of the As(V) mineral/salt and arsenic(II/III) sulfide. The mixed oxidation states were consistently present in other particles found in the thin sections (Supporting Information Figure 1). If one assumes that As(II/III and V) is associated with elements (Cu, Fe, Zn, and S) being determined via μ-SXRF analyses, arsenic(II/III) sulfide-like minerals and metal−As(V)-like precipitates might be forming in the PL. Dissolution of $CuSO_4$ in the feed additive might have contributed to sulfide sources in realgar-like phases. Hydrogen sulfide, which is known as a strong reductant for arsenate (*38*), may have been playing a significant role in the abiotic reduction of inorganic/organic arsenate species. A linear combination of the absorption edge profile fit was performed using the spectra of roxarsone for the As(V) and As_2S_3 for the arsenic(III) sulfide reference at the near-absorption edge energy range (i.e., 11 860−11 885 eV). The results suggest that at most 64% As(V) was present in these particles. Although the absorption energy position at ≈11 871 eV might indicate the presence of the arsenic(II/III) sulfide species, the exact As(V) species are difficult to elucidate based on the absorption edge LC fit since the energy positions for different As(V) standards closely occur within 0.8 eV (Figure 3a). We were unable to perform extended region LC analyses to differentiate the ratio of various organic/inorganic As species due to the amount of noise in the extended region of the unknown samples. Moreover, correct reference spectra of an unknown high molecular weight biodegraded species in the PL (*39*) and the mixed metal−As species observed in our XRF/XANES analyses are difficult to define. As several researchers have previously suggested that As(III), As(V), roxarsone, and degraded compounds such as DMA and/or 3-amino-4-hydroxyphenylarsonic acid are present in the PL water extract (*28*, *40*), complex mixtures of the organic/inorganic As species are likely to be present in these As-rich particles.

Metal(loid) and Nutrient Desorption. Results of metal(loid) and phosphorus desorption (i.e., cumulative release) experiments are shown in Figure 4a−c. The extent of As and P desorption increases with an increasing number of replenishments and as pH increases from 4.5 to 7 (Figure 4a). Interestingly, less than 15% of total As was desorbed after 5 replenishments at pH 7 (Figure 4a and Table 2). The slow desorption processes might be attributed to the presence of insoluble phases and/or strongly retained soluble compounds. pH-dependent desorption behavior clearly indicates that As in the litter could undergo different desorption processes before and after liming of soils. Recent research has shown that roxarsone in the litter solution undergoes the photo-/microbial degradation to inorganic As(V) (*27*, *28*, *40*). It is possible that arsenate ions (e.g., $H_2AsO_4^-$) were

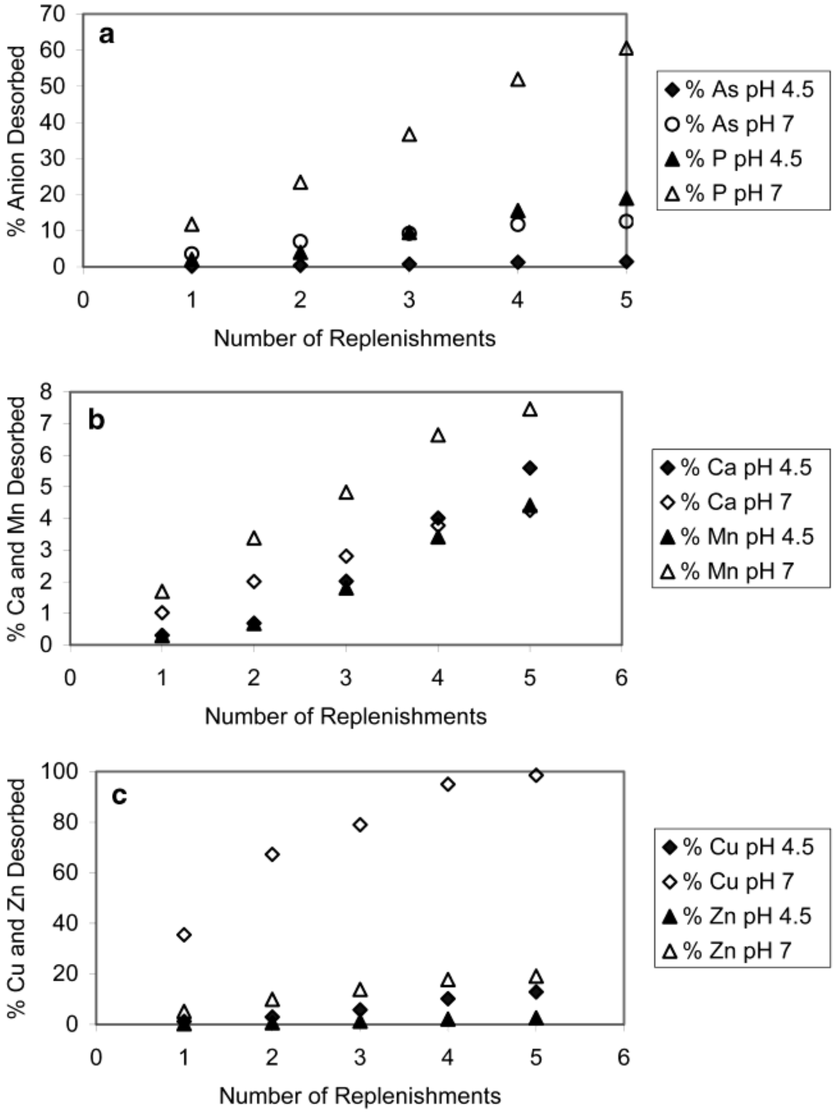

FIGURE 4. (a−c) Metal(loid) (As, Ca, Mn, Cu, and Zn) and phosphorus (P) release from poultry litter at pH 4.5 and 7.

TABLE 2. Total Metal(loid) and Phosphorus Released from Poultry Litter at pH 4.5 and pH 7 after Replenishments (5 d)

reaction conditions	total metal(loid) and nutrient desorbed (mg kg^{-1}, (%))							
	As	Al	Ca	Cu	Fe	Mn	Zn	P
pH 4.5	0.71 (1.50)	8.86 (0.2)	998 (5.6)	44.4 (12.8)	42.2 (0.7)	17.3 (4.4)	9.83 (2.5)	519 (3.4)
pH 7	6.01 (12.6)	10.0 (0.2)	760 (4.3)	341 (98.5)	147 (2.4)	29.2 (7.5)	73.8 (19.1)	1322 (8.7)

predominantly present during desorption and that adsorption sites were out-competed by hydroxyl ions at higher pH, resulting in more As desorption at pH 7. Moreover, total desorbed phosphate was approximately 2.5 times higher at pH 7 than at pH 4.5 (Figure 4a and Table 2), and this provided more favorable competitive anion sorption conditions for dissolved As(V) at pH 7. The photodegradation and biodegradation of roxarsone into arsenate anions also may explain the differences in As extractability from PL in the study of Jackson and Bertsch (*40*) and our desorption study. Whereas Jackson and Bertsch found that >92% of total As, predominantly containing roxarsone, was soluble after 2 h of water extraction (*40*), at most of 12.6% of total As was recovered in our 5-d replenishment desorption study. The recent paper by Garbanino and co-workers reported that the biodegradation of roxarsone into arsenate anions was a function of incubation time and water content (*39*), suggesting that our longer extraction times probably enhanced the formation of more degraded species such as arsenate anions. Re-adsorption of charged arsenate ions (e.g., $H_2AsO_4^-$) on reactive sites in the PL might have resulted in less As recovery in our study.

A similar pH-dependent desorption behavior was also observed for Ca, Cu, Mn, and Zn, indicating a potential nonpoint source metal contamination via litter application. Increased levels of Cu, Mn, and Zn in runoff from PL-amended fields have been previously reported (*16*, *41*, *42*). While less than 8% of total Ca and Mn were released after 5 replenishments at both pH values (Table 2), pH had a significant influence on Cu and Zn release (Figure 4c). In the case of Cu, nearly 100% of Cu was desorbed at pH 7 (Figure 4c and Table 2), and this raises concerns about possible Cu toxicity to crops and waters receiving agricultural runoff. It is possible that organic acid-promoted and/or microbially mediated reductive dissolution of amorphous As metal phases observed in the SXRF analyses were occurring at the neutral pH.

Fate and Transport of Roxasorne in PL. In this study, we have presented spectroscopic evidence for metal/anion associated As(II/III and V)-rich microscopic particles in the PL and that As was not readily desorbable at near-neutral pH. Despite the long-term amendments of As-containing PL, there was no significant As accumulation in the agricultural surface soils, suggesting that As in the litter has probably been transported via leaching/surface runoff/surface erosion and/or uptake by agricultural crops. No evidence for significant As accumulation in agricultural crops (e.g., corn) harvested from PL-amended soils (*43*, *44*) has been shown. These results suggest the importance of hydrogeological transport paths with respect to the fate of As in PL. In fact, several field-scale studies have shown evidence for both vertical (i.e., leaching) and lateral (i.e., runoff) As transport (*16*, *18*, *45*). Dissolved total As concentrations ranged from 0.1 to 28.7 ppb in shallow groundwater/shallow pore water near PL-applied agricultural fields (*45*), indicating that As was leached to subsurface environments. The runoff water (i.e., horizontal transport) from amended (8.96 Mg ha^{-1}) soils also contains approximately 200 ppb of total As (*16*, *18*). Multi-organic As species (e.g., DMA and roxarsone) might be initially present in the litter leachate/runoff as Jackson and Bertsch found in water extracts of PL (*40*). However these species can be rapidly transformed into inorganic As (e.g., AsO_4^{3-}) via microbial activity and/or an exposure to UV irradiation (*27*, *28*), and then inorganic As(V) would predominate in PL-amended soils (*28*).

To predict the fate and transport of As in the PL-amended soils, it seems critical to understand inorganic As(V) retention/release mechanisms in these agricultural soils. Several researchers have reported a strong As(V) retention capacity (i.e., inner-sphere adsorption complexes) on soil mineral components such as aluminum/iron oxides (*25*, *46*, *47*).Unfortunately, chemisorbed As(V) in soils can be often displaced by other anions such as phosphate (*48*−*51*). We observed high levels of dissolved P (<240 ppm) and low levels of As (<0.2 ppm) throughout the litter desorption experiments at near-neutral pH. A similar trend has been reported in PL-amended soils and soil solutions (*52*, *53*). It is likely that dissolved P plays an important role in controlling desorption of sorbed As(V) in Atlantic Coastal Plain agricultural soils.

Some studies have already shown elevated levels of As in pore water from amended agricultural fields (<29 μg L^{-1}) and in river sediments near poultry farms (11.78 mg kg^{-1}) (*45*, *54*). This indirect evidence might suggest that long-term PL amendments could be a possible source of As contamination on the Delaware−Maryland−Virginia Peninsula. Further field-scale research is needed to prove linkages between PL amendments and As contamination.

Recently, PL amendments on high P soils have been evaluated in the Mid-Atlantic states (e.g., Delaware and Maryland) to assess negative environmental impacts (e.g., eutrophication) on surrounding water bodies. Cessation of litter amendments and/or metal salt (e.g., aluminum sulfate) mixing into the PL prior to application on land has been proposed to reduce P loss from surface and subsurface soils. While aluminum sulfate amendments have shown promising results in reducing dissolved As, Cu, and Zn in runoff water from PL-amended loamy Arkansas soils, effects on acidic sandy Atlantic Coastal Plain soils are not well-understood. Currently allowable trace element loading levels in biosolid application on lands are only limited by the Federal EPA 530 rule.

Although the concentration of trace metal(loid) and nutrients vary in PL from different regions in the United States, increased levels of As, Cu, and Zn in PL and amended soils have been reported by several researchers (*16*, *17*, *42*, *55*, *56*). Our macroscopic and spectroscopic research results suggest that further studies are needed to assess the long-term As and other trace metal contamination effects via PL application on ecological and human health in the Delmarva Peninsula. These must be carefully investigated along with current nonpoint nutrient (i.e., P and NO_3^-) issues and potential human health effects from inhalation/ingestion of As-rich microscopic particles.

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Supporting Information Available

A figure showing normalized XANES spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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