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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 of total arsenic (As) in drinking water (currently 10 parts per billion) has raised serious concerns about the agricultural use of As-containing biosolids such as poultry litter (PL). Microfocused ( $\mu$ ) Synchrotron X-ray Fluorescence (SXRF) and  $\mu$ -X-ray Absorption Near Edge Structure Spectroscopic (XANES) analyses showed that As(III and V) was always concentrated in abundant needle-shaped microscopic particles (approximately  $20 \mu\text{m} \times 850 \mu\text{m}$ ) that are 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. Our research results raise concerns about long-term PL amendment effects on As contamination in surrounding soil-water environments.*

In the last four decades, the poultry industry has become one of the major livestock operations in the middle Atlantic states of the U.S. While PL has been recycled on agricultural lands as an N amendment, much of the trace metal(loid) input (total annual As inputs between 20 and 50 metric tons) into the environments has been neglected. The origin of As in PL is an organo-As(V) compound (3-nitro-4-hydroxyphenylarsonic acid (roxarsone)) for coccidiosis control in the poultry feed (approximately 25 - 50 mg of roxarsone is mixed per kilogram of feed). Feed spillage and digested materials have increased the mean total As concentration in PL to 14 - 76 mg kg<sup>-1</sup>. 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 PL amendment effects on As contamination in Atlantic coastal plain soil/water environments remain virtually unknown. To better understand

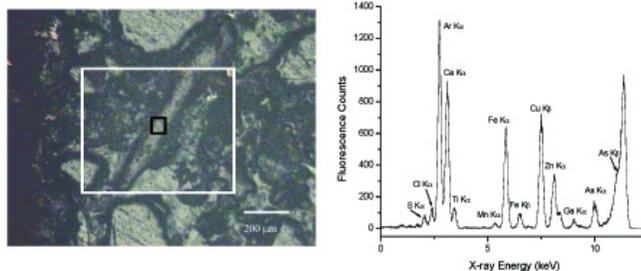


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the reactivity of As from PL to surface and ground water, the As solid-state speciation in

the PL was investigated using SXRF and  $\mu$ -XANES at beamline X26A at the National Synchrotron Light Source and at the GeoSoilEnviro Consortium for Advanced Radiation Sources at Argonne National Laboratory's Advanced Photon Source.

A photomicrograph of one of 17 As-rich particles (approximately  $20 \times 850 \mu\text{m}$ ) found in an approximately 200 mm<sup>2</sup> area (**Figure 1**) shows the distinctive elongated particle morphology. The XRF analyses at the center of this particle

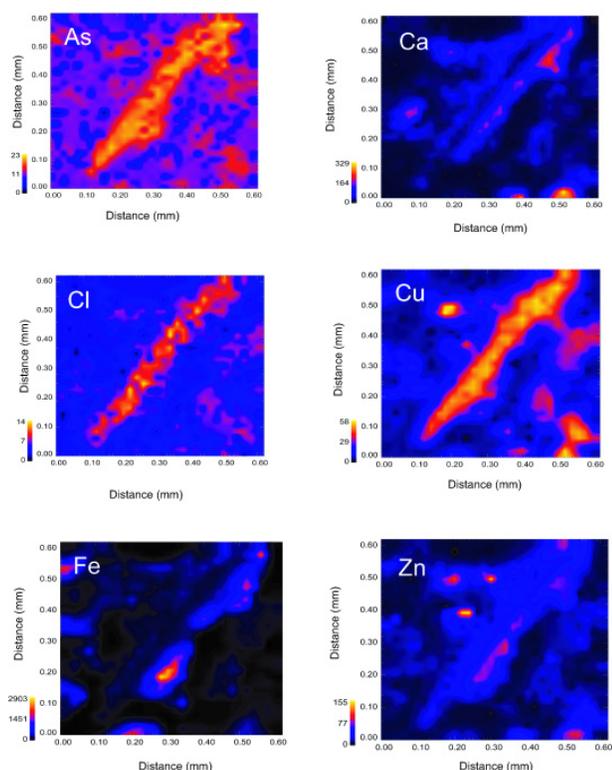


**Figure 1:** A photographic image of a thin section of poultry litter and a synchrotron based microfocused X-ray fluorescence spectrum of an arsenic-rich particle inside the black open square region. The white open square (approximately  $600 \times 600 \mu\text{m}$ ) indicates the selected area for microfocused X-ray fluorescence maps shown in Figure 2.

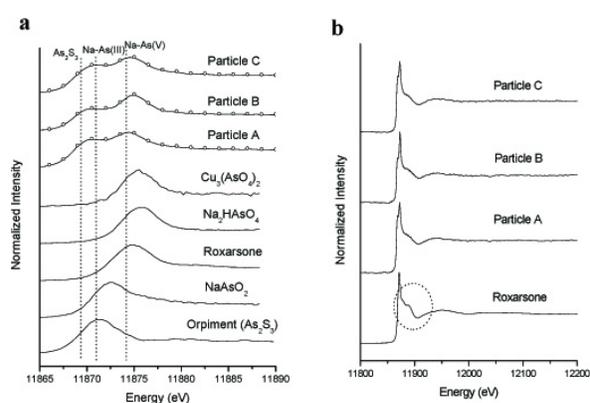
(indicated by a black open square) show that elevated As levels are associated with Ca, Fe and Cu, and to a lesser extent with Zn, Ti, Cl, and S (**Figure 1**). A total of 17 similar particles were found in nearly half of the thin section (about 200 mm<sup>2</sup>). Elemental maps (**Figure 2**) generated from the region in the white open square 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 pre-

cipitates and/or As sorption complexes on metal oxide precipitates were occurring in the litter and/or during poultry digestion. Our preliminary microfocused X-ray diffraction analyses at the NSLS showed no distinctive diffraction patterns on these particles, indicating the amorphous nature of the As-containing particles. The  $\mu$ -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 **Figures 3a and 3b**). They all produce similar XRF spectra as particle A (data not shown). Wide whiteline peaks are consistently observed in particles A-C (**Figures 3a and 3b**), in-

dicating the presence of mixed As(III and V) oxidation states in these particles. Although the absorption energy position at  $\approx 11871$  eV might indicate the presence of the orpiment-like As(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**). Post-edge XANES features of the particles (indicated by a dotted circle in **Figure 3b**) are dissimilar to those of the organo-As(V) compound in poultry feed, suggesting possible degradation/transformation of roxarsone in the litter and/or in poultry digestive tracts.



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



**Figure 3:** Panel a: short-range normalized XANES spectra of As reference materials (sodium arsenate ( $\text{Na}_2\text{HAsO}_4$ ), sodium m-arsenite ( $\text{NaAsO}_2$ ),  $\text{Cu}_3(\text{AsO}_4)_2 \cdot 27\text{H}_2\text{O}$ , orpiment ( $\text{As}_2\text{S}_3$ ), and roxarsone) and As-rich particles in poultry litter are shown. The open circles overlying the sample spectra are the best fit from the linear combinations of model compounds. Spectra contribution (%) of roxarsone and  $\text{As}_2\text{S}_3$  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 ( $\text{As}_2\text{S}_3 \approx 11869$  eV), sodium m-arsenite ( $\text{Na-As(III)} \approx 11871$  eV), and sodium arsenate salt ( $\text{Na-As(V)} \approx 11874$  eV), respectively. Panel b: long-range normalized XANES spectra are shown for roxarsone and As-rich particles A, B, and C.