Microscale Speciation of As in Poultry Litter

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Introduction

In the last four decades, the poultry industry has become one of the major livestock operations in the Mid-Atlantic States. The majority of poultry litter (PL) generated during the operations has been recycled as an organic amendment on agricultural fields to meet nitrogen requirements for crops. The PL contains large quantities of phosphorus (P), which contribute to water pollution and are also the source of trace elements, such as arsenic (As). Poultry litter is generally applied at a rate of 8.96 to 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 [1]. The origin of As in the PL is organo-As(V) compounds (e.g., 3-nitro-4-hydroxyphenylarsonic acid [roxarsone]) in the poultry feed [2]. To better understand the fate and transport of the organo-As(V) compound from PL, we investigated As solid-state speciation (oxidation state and chemical speciation) in PL by using micro-scanning x-ray fluorescence (μ-SXRF) and micro-x-ray absorption near-edge structure (μ-XANES) spectroscopies. These and other macroscopic data on the PL are found in Arai et. al [3].

Methods and Materials

The μ-SXRF analyses on the PL thin section were performed at beamline X-26A of the National Synchrotron Light Source (NSLS). The size of the monochromatic beam diameter was set at approximately 18 m by using a double-elliptical, Rh-coated Kirkpatrick-Baez (K-B) mirror system. The SXRF analyses were done with the monochromatic beam at the As K-edge absorption energy (11,869 eV). Elemental maps were taken over an area of approximately 600 × 600 μm for the elements with K absorption edges below the excitation energy (notably S, Cl, Ca, Ti, Fe, Cu, Zn, and As). 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.

As K-edge μ-XANES spectra were collected at the GSECARS undulator beamline 13-D at the APS. Cryogenic-cooled Si(111) monochromators and a double-elliptical, Rh-coated K-B mirror system were used to produce an approximately 5-m-diameter beam. The XANES spectra were collected from 11,800 to

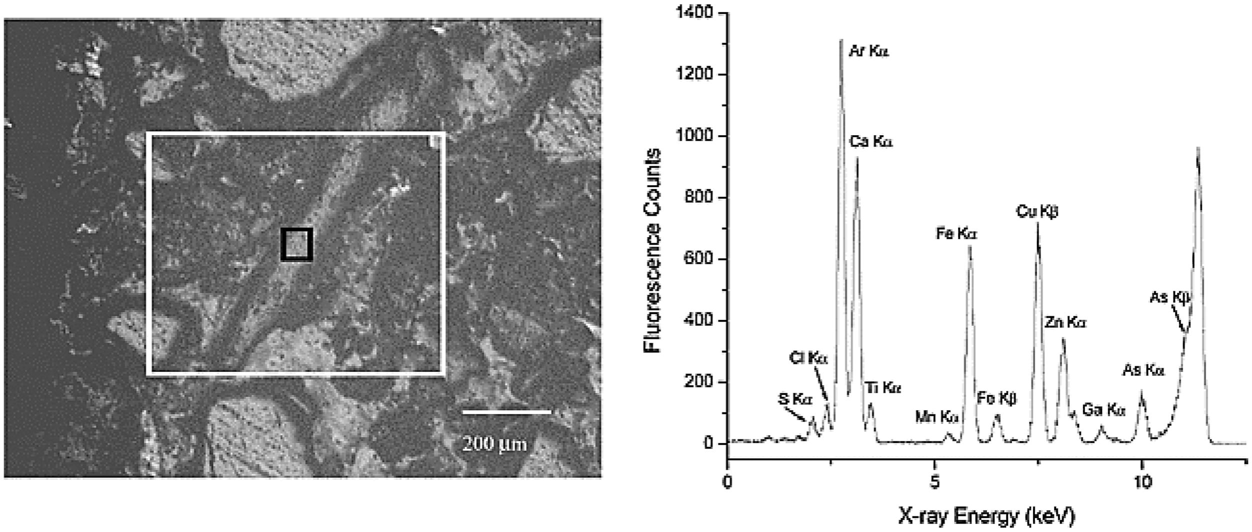

FIG. 1. Photomicrograph of a thin section of poultry litter and synchrotron-based, microfocused x-ray fluorescence spectrum of an As-rich particle taken at the spot indicated by the black open square. The white open square (approximately 600 × 600 μm) indicates an area selected for microfocused x-ray fluorescence maps (not shown).

12,200 eV in fluorescence mode by using a Ge 16-element detector. Because of the beam-induced oxidation effects of As(III), XANES spectra collections were limited to only three to five scans. The WinXAS 2.0 program was used for the XANES spectra analyses, and linear combination analyses were performed.

Results and Discussion

Although not shown, the total As level was approximately 50 mg kg^{-1} in the PL, while more than three decades of PL amendments did not seem to have resulted in any significant As accumulation (<15 mg kg^{-1}) in the surface soils that were investigated. A photomicrograph of one of the As-rich particles (Fig. 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, Zn, Ti, Cl, and S (Fig. 1).

The μ-XANES measurements were performed on the particle shown in Fig. 1 (i.e., particle A in Fig. 2b) and on several additional As-containing particles (only particles B and C are shown in Fig. 2). All of them produce XRF spectra similar to those of particle A (data not shown). Wide white-line peaks are consistently observed in particles A-C (Fig. 2), indicating the presence of mixed oxidation states in these particles. Mixed oxidation states were 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 thin-section preparation. Specific XANES post-edge features (as indicated by a dotted circle in Fig. 2b) 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 (Fig. 2a). Whereas the absorption-edge energy position of As(V) mineral/salt(s) is >11,874 eV, sodium As(III) salt exhibits an absorption-edge energy position of ≈11,871 eV. However, when As(II/III) associates with sulfide (i.e.,

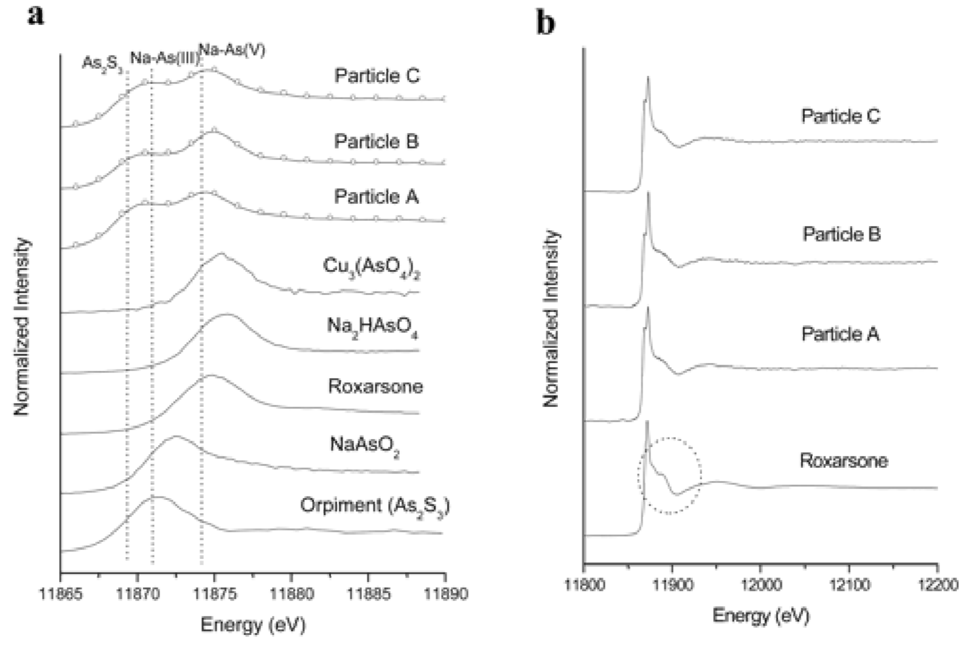

FIG 2. In panel a, short-range normalized XANES spectra of As reference materials and As-rich particles in poultry litter are shown. The open circles overlying the sample spectra are the best fit from the linear combinations of model compounds. The spectral contributions (%) from roxarsone and As_2S_3 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 of ≈11,869 eV), sodium m-arsenite [Na-As(III) of ≈11,871 eV], and sodium arsenate salt [Na-As(V) of ≈11,874 eV], respectively. In panel b, long-range normalized XANES spectra of As-rich particles A-C and roxarsone are shown.

mineral realgar [AsS] and orpiment [As_2S_3]), the As(III) energy position further decreases to ≈11,869 eV [4, 5]. 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 As(II/III) sulfide. The mixed oxidation states were consistently present in other particles found in the thin sections. If one assumes that As(II/III and V) is associated with elements (Cu, Fe, Zn, and S) being determined via μ-SXRF analyses, As(II/III)-sulfide-like minerals and metal-As(V)-like precipitates might be forming in the PL.

Although the concentrations of trace metal(loid)s and nutrients vary in PLs 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 [6]. Our macroscopic and spectroscopic research results suggest that further studies are needed to assess the long-term effects of As and other trace metal contamination via PL application on ecological and human health in the Delmarva Peninsula.

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