DEGRADATION OF ROXARSONE IN POULTRY LITTER

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Roxarsone (fig. 1), 3-nitro-4-hydroxyphenylarsonic acid, is an arsenic-containing feed additive that is used extensively in the broiler poultry industry to promote growth by controlling coccidial intestinal parasites. Most of the roxarsone is excreted unchanged (Morrison, 1969; Gregory, 1993) in the manure to accumulate in the poultry bedding. Each broiler excretes about 150 milligrams (mg) of roxarsone in the 42-day growth period for administering roxarsone. Litter collected following this period contains from 30 to 50 milligrams per kilogram (mg/kg) of total arsenic. In poultry houses where more than 200 million broilers per year are raised, a volume not uncommon for major poultry-producing areas, litter that contains more than 8 x 10^3 kg of arsenic would be produced. Generally, all the litter is used as nitrogen-containing fertilizer in nearby fields. Litter is routinely tilled into cornfields or applied to pastureland at a rate of between 1 and 2 metric tons per hectare. If a 100-hectare field was fertilized at 2 metric tons per hectare, about 10 kg of arsenic would be introduced to the environment. During crop rotation, the litter is stored in covered or uncovered windrows for up to 1 year. Soils amended with arsenic-containing poultry litter and the practice of using uncovered windrows for litter storage could be providing sources for arsenic contamination of surface and ground water. However, the extractability of roxarsone from the poultry litter and the stability of the mobilized roxarsone in the environment are unknown.

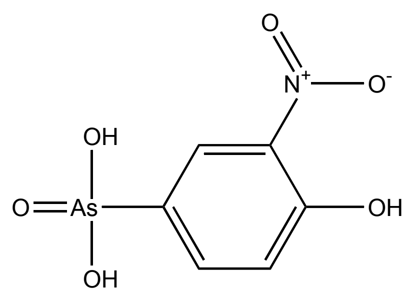

Figure 1. The molecular structure of roxarsone or 3-nitro-4-hydroxyphenylarsonic acid.

The aqueous extractability of roxarsone from the broiler litter was determined by mixing a known weight of litter in deionized water at room temperature for 1 hour. After centrifugation, the total arsenic concentration in the extract was determined to be about 70 percent of the total arsenic available. Nevertheless, speciation of the water extract was found to be primarily roxarsone with arsenite (As^{3+}), dimethylarsinate (DMA), and unknowns as minor components (fig. 2). The high extractability of roxarsone from poultry litter suggests that roxarsone can easily be mobilized to the environment by either agricultural field irrigation or rainfall on uncovered windrows. Degradation could be possible through biotic and abiotic processes after roxarsone is mobilized. The stability of roxarsone in the litter extract was investigated under various conditions. Under anaerobic conditions at room temperature, roxarsone was totally transformed into different arsenic-containing components within about 48 hours (fig. 3). The rate of the transformation was dependent upon temperature; an increase in temperature accelerates the transformation, whereas a decrease in temperature retards it. However, if the litter extract was sterilized, the roxarsone was stable for a period of at least 10 days. Such findings suggest that bacteriological processes are responsible for the degradation of roxarsone. Electrospray ionization mass spectrometric analysis of the fraction that corresponds to the major unknown component gave a molecular ion at 233 atomic mass units. This analysis suggests that this byproduct could be 3-amino-4-hydroxyphenylarsonic acid. However, the retention time did not match that of a standard, and the broad chromatographic peak for the byproduct (see peak at ~10 minutes in chromatogram shown in fig. 3) most likely indicates that the arsenic-containing molecule is much larger than 3-amino-4-hydroxyphenylarsonic acid.

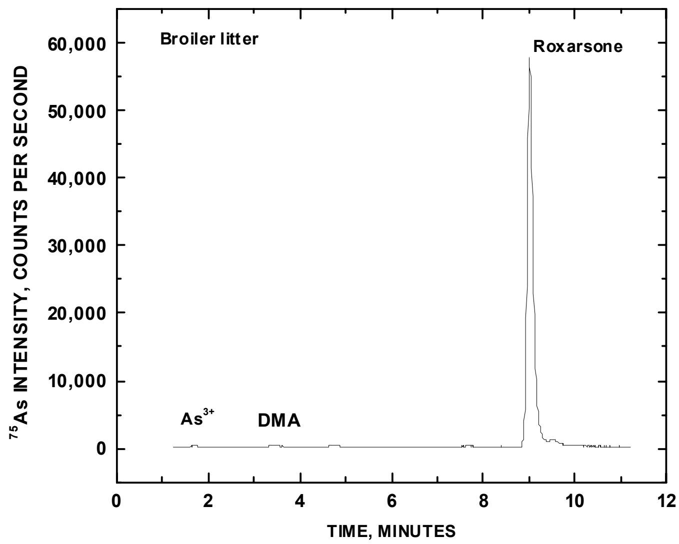

Figure 2. Chromatogram of the aqueous extract of broiler litter. Nearly all the arsenic is present as roxarsone. Total arsenic concentration in the litter is 44 milligrams per kilogram.

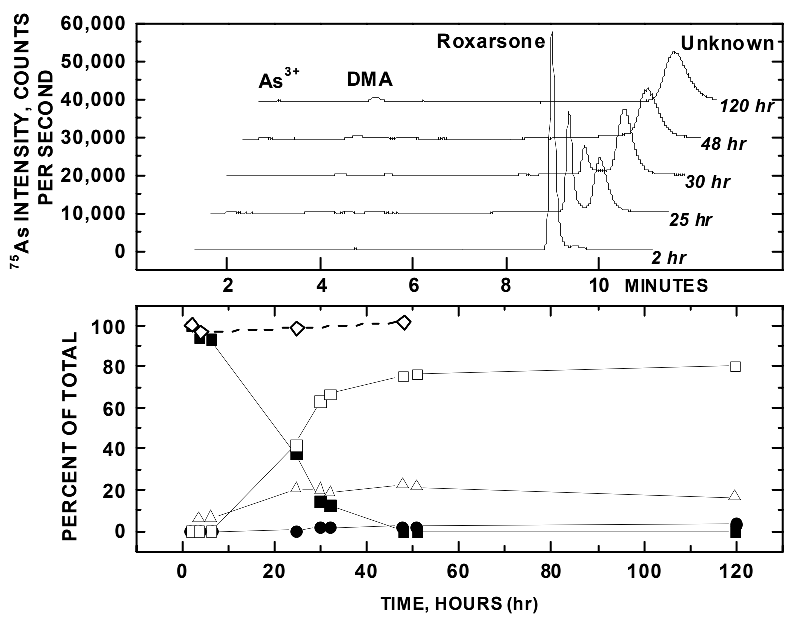

Figure 3. All the roxarsone (solid square) in aqueous broiler-litter extract is rapidly degraded primarily into one unidentified species (open square), dimethylarsinate (solid circle), and other unidentified arsenic species (open triangles). However, when the aqueous broiler-litter extract is sterilized (open diamond), the roxarsone is stable.

Indirect evidence indicates that roxarsone undergoes more extensive degradation after it is introduced into the soil. Soil samples were collected from a pasture and an agricultural field that had been amended with poultry litter within the past year (2000). Soil samples from nearby fields that have similar soil types, but that have not been recently amended, also were collected for controls. The soil types were different; the pasture soil was primarily silt and clay, whereas the agricultural soil was primarily sand. In addition, the amended soils had about 2 to 3 times more organic carbon. The fine [<0.250 millimeter (mm)] and very fine (<0.125 mm) fractions of the pasture and agricultural soils, respectively, were extracted with water for 24 hours. Arsenic speciation of the soil extracts show that the amended soils have 5 to 10 times more extractable arsenic than the controls, and that arsenate (As^{5+}) is the predominant species (figs. 4 and 5). A onetime water extraction mobilized only 1 to 3 percent of the total arsenic present. The use of other extraction reagents showed that most of the water-extractable arsenic is bound to organic matter. In contrast, arsenite (As^{3+}) is the predominate species in the extract of the fine fraction of bed sediment from a ditch adjacent to the agricultural field (bottom graph in fig. 5). It is likely that in such an anoxic environment, bacteria are promoting the reduction of arsenate to arsenite and the methylation of arsenate to dimethylarsinate.

References

Gregory, D.E., 1993, The microscopic and ultrastructural lesions of peripheral nerves caused by feeding toxic levels of roxarsone and lasalocid to broiler chickens: Oklahoma State University, Stillwater, Okla., unpublished M.S. thesis, 55 p.

Morrison, J.L., 1969, Distribution of arsenic from poultry litter in broiler chickens, soil, and crops: Journal of Agricultural and Food Chemistry, v. 17, p. 1288–1290.

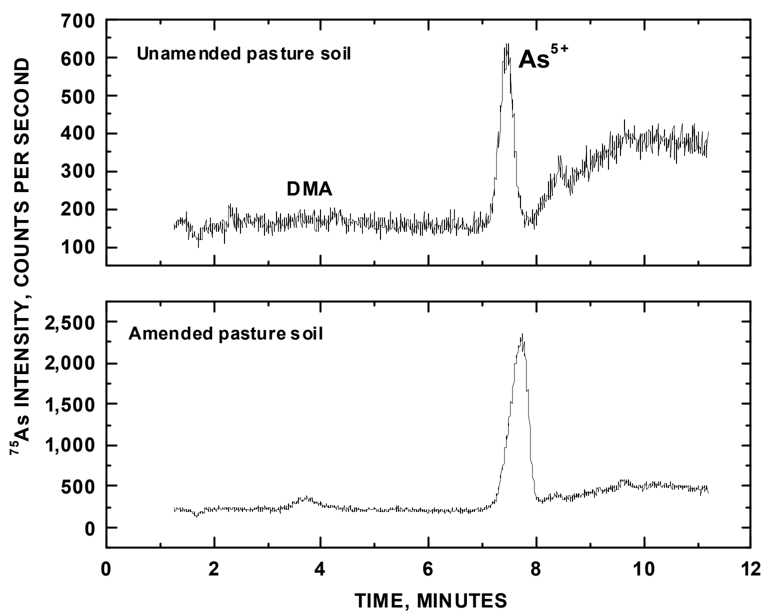

Figure 4. The aqueous extract of a silted and clayey pasture soil that had been amended with poultry litter contained mostly arsenate (As^{5+}). The soil has about 4 times greater extractable arsenic than the unamended soil. The total arsenic present in the amended soil was 4 milligrams per kilogram.

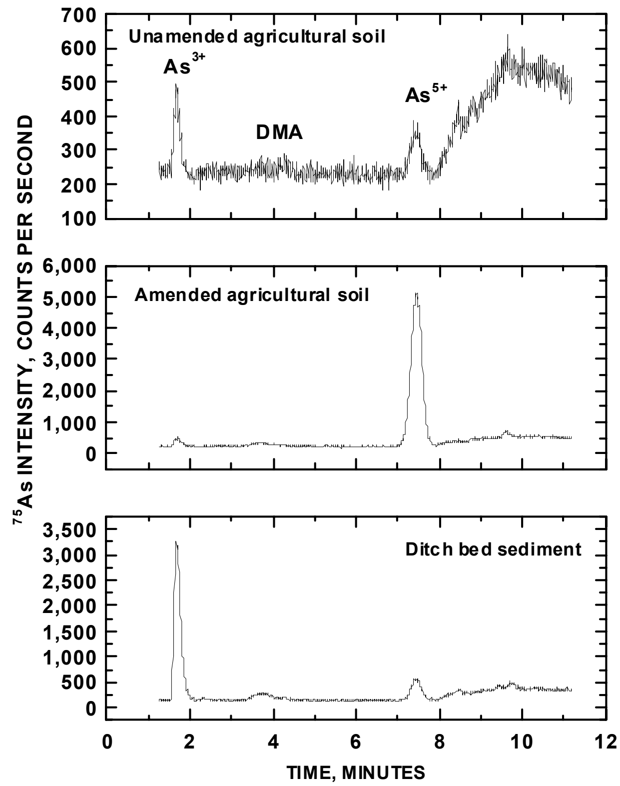

Figure 5. The aqueous extract of a sandy agricultural soil that had been amended with poultry litter contained mostly arsenate (As^{5+}). The soil has about 10 times greater extractable arsenic than the unamended soil. In contrast, extract of bed sediment from a nearby drainage ditch contained mostly arsenite (As^{3+}). The total arsenic present in the amended soil and bed sediment was 5 and 2 milligrams per kilogram, respectively.