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Environmental Fate of Roxarsone in Poultry Litter. Part II. Mobility of Arsenic in Soils Amended with Poultry Litter

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Poultry litter often contains arsenic as a result of organo-arsenical feed additives. When the poultry litter is applied to agricultural fields, the arsenic is released to the environment and may result in increased arsenic in surface and groundwater and increased uptake by plants. The release of arsenic from poultry litter, litter-amended soils, and soils without litter amendment was examined by extraction with water and strong acids (HCl and HNO₃). The extracts were analyzed for As, C, P, Cu, Zn, and Fe. Copper, zinc, and iron are also poultry feed additives. Soils with a known history of litter application and controlled application rate of arsenic-containing poultry litter were obtained from the University of Maryland Agricultural Experiment Station. Soils from fields with long-term application of poultry litter were obtained from a tilled field on the Delmarva Peninsula (MD) and an untilled Oklahoma pasture. Samples from an adjacent forest or nearby pasture that had no history of litter application were used as controls. Depth profiles were sampled for the Oklahoma pasture soils. Analysis of the poultry litter showed that 75% of the arsenic was readily soluble in water. Extraction of soils shows that weakly bound arsenic mobilized by water correlates positively with C, P, Cu, and Zn in amended fields and appears to come primarily from the litter. Strongly bound arsenic correlates positively with Fe in amended fields and suggests sorption or coprecipitation of As and Fe in the soil column.

Introduction

Arsenic is present in most of the litter coming from commercial broiler chicken operations because of the use of the arsenic-containing feed additive, roxarsone. Roxarsone (3-nitro-4-hydroxyphenylarsonic acid) is widely used as a feed additive in the broiler poultry industry to control

coccidial intestinal parasites. In 2000, approximately 70% of the broiler chickens on starter rations and approximately 74% of those on grower rations in the United States were fed roxarsone (1). According to the National Agricultural Statistical Service (NASS) of the U.S. Department of Agriculture, 8.26 billion broiler chickens were produced in the United States in 2000. Therefore, approximately 5.8 billion chickens were fed roxarsone in the year 2000. Using the estimate by Muir (2) that a broiler chicken fed rations containing the recommended dosage of 45.4 g of roxarsone per ton for the 42 days life cycle, will excrete approximately 150 mg of roxarsone in total, we can calculate that approximately 9×10^5 kg of roxarsone or 2.5×10^5 kg of arsenic was present in the manure from these chickens.

Poultry litter consisting of bedding material (e.g., sawdust or wood chips) and excrement is generally disposed of by spreading onto agricultural fields near the poultry houses (3, 4). This practice could result in locally elevated concentrations of arsenic in water and soil. Routinely, Co, Cu, Fe, Mn, Se, and Zn are also added to poultry rations to maintain the health of the birds (4, 5). Gupta and Charles (6) found that fields in the Delmarva Peninsula of Maryland fertilized with poultry litter over a long period of time had higher As, Cd, Cu, and Mn concentrations in the soil than nearby fields that had not received poultry litter. Han et al. (5) found that the surface soil of a pasture of a Mississippi poultry farm that had been amended with poultry litter for approximately 25 years had much higher total concentrations of Cu, Zn, and Mn than the surface soil of an adjacent forest that had not been amended.

Of more importance than the total concentrations of trace metals is that these metals can readily enter the pore water of the soil. These water-soluble components are available for uptake by plants and other soil organisms. Elevated concentrations of metals in soil water can lead to elevated metal concentrations in plants, which may be phytotoxic or render the plants unsuitable for human or animal consumption (7, 8). High metal concentrations in soil water can also contribute to surface water and groundwater contamination. Because collecting and measuring soil pore-water samples can be difficult and expensive, water extraction of the soils has been used as being proportional to potential pore-water concentrations. It would be expected that water extraction would underestimate the actual pore-water concentrations (9).

Part I of this study (10) established that roxarsone in poultry litter quickly degrades into inorganic arsenic. This report, Part II of the study, examines the ease of arsenic release to water from poultry litter after it has been applied to soil. We examined the content of arsenic and other transition metal feed additives (Cu, Zn, and Fe) in a typical poultry litter and its ability to be extracted by water. Soil samples from fields that have been amended with poultry litter and similar control fields with no amendment were extracted with water and strong acids to examine the abundance of weakly and strongly bound As, Cu, Zn, Fe, and P components. Comparison of water-soluble and more tightly bound fractions of these elements will contribute to a better understanding of the mobility of arsenic from agricultural operations and its potential to contaminate surface water and groundwater.

Experimental Section

Three samples of poultry litter used to amend the test plot at the University of Maryland Agricultural Experiment Station were obtained and analyzed. Detailed analysis of this litter

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is available in Part I (10). Analytical data for litters used to amend the Delmarva agricultural soil and the Oklahoma pasture soil were not available.

Soil samples were obtained from the University of Maryland Agricultural Experimental Station, Wye Research and Education Center. The soil is a clay silt loam. More than 99% of the samples were less than 0.125-mm particle size. The fine fractions (<0.125 mm) contained 0.2 to 3.4% organic carbon. Poultry litter was applied to the test plots during June of 1998 and 2000 at the rates of 0, 3, and 6 tons per acre and tilled to a depth of approximately 20 cm. Each plot was sampled at three locations per plot and two depths per location (0–15 cm and 15–30 cm). The 0–15-cm samples are considered to be well mixed, whereas the 15–30-cm samples are considered untilled. These plots had no prior history of poultry litter application.

Soil samples from a tilled field with a history of long-term (20–30 years) poultry litter application were obtained from the Delmarva Peninsula (DAS) and from an adjacent forested lot (DFS) with no history of litter amendment. Poultry litter had been applied at rates between 1.5 and 3 tons per acre on a 2-year cycle since records were started in 1994. A single representative sample was taken from the surface (0–12 cm) at each site. The soil is a poorly drained sandy loam. About 12% of the field soil and 5% of the forest soil was less than 0.125-mm particle size. The fine fraction of the field soil contained 16% organic carbon and the same fraction of the forest soil contained 5% organic carbon.

Soil samples from an Oklahoma pasture with a history of long-term (>30 years) poultry litter application and a similar nonadjacent pasture with no history of litter application were collected at four locations per pasture and at eight, 7.5-cm depth intervals per location. The litter was applied to the surface without tilling. The litter was applied annually, but the rate of application is not known. The soil is a silt loam. Between 90 and 99% of the soil is less than 0.125-mm particle size. The fine fractions contained 0.2 to 3.5% organic carbon. All samples were analyzed by water extraction and acid extraction. Samples from the top two depth intervals of one hole in each field were also analyzed by sequential water extraction.

All soil and litter samples were air-dried. The Maryland litter was ground with a Wiley mill and used without further preparation. Soil particle size was determined by sieving. All soil extractions were performed on the less than 0.125-mm size fraction to ensure a homogeneous sample medium and to facilitate comparison among fields. The results presented in this report are for the fine fraction only (<0.125 mm) and have not been normalized to a whole-soil concentration.

Water extraction for litter and soil samples consisted of a single extraction with a constant solid-to-water ratio of 1 g of sample to 20 mL of deionized water. Samples were mixed for 16 h and centrifuged (1 h at 3000 relative centrifugal force) to separate colloids. A subset of samples was sequentially extracted with water using the same procedure as outlined above, except that after the aqueous sample was withdrawn and the excess water was aspirated off, additional water was added and the extraction was repeated. The sequential extractions were repeated (13×) until further extraction resulted in small and consistent recoveries.

Soil samples were also extracted with strong acid. A 0.2-g sample was treated with 5 mL of concentrated nitric acid and 5 mL of concentrated hydrochloric acid. The sample was heated until dry and redissolved in 10 mL of concentrated nitric acid by heating at 40 °C overnight. The sample was brought to volume (25 mL) with 1% nitric acid. A subset of soil samples was subjected to total dissolution by treatment with concentrated HCl, HNO₃, HClO₄, and HF acids (11).

Litter samples were subjected to total dissolution by digestion in 30% hydrogen peroxide until a clear solution

TABLE 1. Results of Single-Water Extraction and Total Dissolution of the University of Maryland Experiment Station Litter^a

	total determined by total dissolution mg/kg	single-water extraction mg/kg
As	29 (2.7)	22 (1.6)
P	24000 (1300)	3900 (290)
Cu	400 (12)	200 (2.3)
Zn	430 (5.7)	86 (0.9)
Fe	2000 (530)	170 (10)

^a Results are average of three samples. The number in parentheses is the standard deviation.

was obtained, and then heated to dryness. The solid residue was dissolved in concentrated nitric acid and hydrochloric acid and boiled to dryness. The sample was then dissolved in concentrated nitric acid and diluted to volume (25 mL).

Inductively coupled plasma–mass spectrometry (ICP–MS) was used for the determination of As, Cu, Zn, Fe, and P (11, 12). Total carbon was determined by combustion in oxygen and coulometric detection. Carbonate carbon was determined by acidification and coulometric detection of evolved carbon dioxide. Organic carbon (OC) was calculated by subtracting the carbonate carbon from the total carbon.

Results

Soils and poultry litter samples were extracted with water as a reasonable approximation of the leaching of soils by precipitation. For soils, the first water extraction accounted for 23% of the cumulative arsenic extracted after 13 extractions. The correlation between a single extraction and the cumulative sum of 13 extractions is 0.95 ($n = 21$). The arsenic concentration in a single water extraction readily distinguished between poultry-litter-amended and unamended soils, even for soils that had only two litter applications. A single water extraction of the Maryland poultry litter accounts for 80% of the cumulative arsenic from 13 consecutive water extractions.

The water extraction procedure releases weakly bound metal ions in the soils. These labile metals constitute only a small part of the total metal concentration in soils. To estimate the total metal concentration bound to hydrous metal oxide coatings, carbonates, clay minerals, and micas, a strong acid extraction was used. The strong acid extraction does not release metals that occupy sites in the crystal lattices of minerals such as feldspars, therefore, a subset of soil samples was subjected to total dissolution. For all elements to be discussed in the following sections, there was good correlation ($r^2 > 0.90$, $n = 29$) between strong acid extraction and total dissolution concentrations. The strong acid extraction procedure recovered the following percentage of the total dissolution: As, 60%; P, 74%; Cu, 64%; Zn, 34%; and Fe, 73%. Further information is available in the Supporting Information.

Three samples of litter used to amend the test plot at the University of Maryland Experiment Station were extracted with water both as single and sequential extractions. The results for arsenic and other elements of interest based on single water extractions and by total dissolution are listed in Table 1. The total arsenic in the litter is 29 mg/kg as determined by total dissolution. Arsenic in the litter is readily extractable with water, with 22 mg/kg (76%) extractable with one extraction and 27.8 mg/kg (95%) extractable with 13 extractions. Most of the arsenic was extracted with four

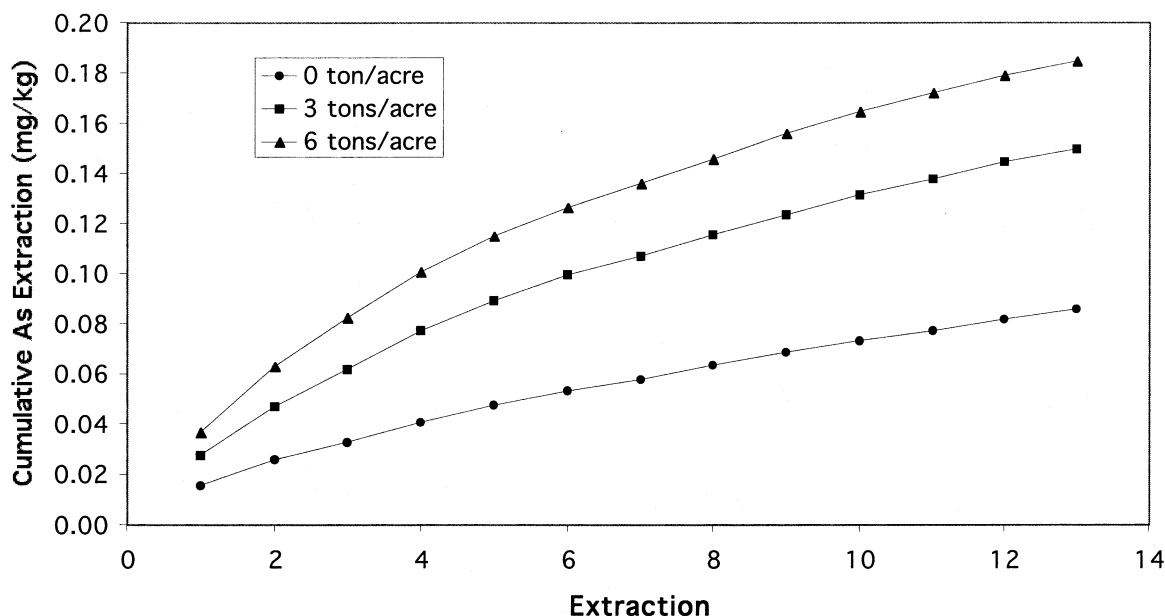


FIGURE 1. Sequential water extraction of soils from test plots at the University of Maryland Agricultural Experiment Station after the second application of 3 and 6 tons/acre litter and a control plot with no litter application. The results shown are an average of three analyses for each test plot. Samples are from the top 15 cm sampled in July 2000.

extractions. The extracted arsenic was determined to be present as inorganic arsenate (10). Other metals commonly used as feed supplements (Cu, Zn, and Fe) all show higher total concentrations than arsenic in the litter and higher concentrations in the water extract. Expressed as a percentage of the total, however, the water extractability (single extraction) of these metals is lower than that of arsenic (Cu, 51%; Zn, 20%; and Fe, 8%). Further information is available in the Supporting Information.

Water extraction of the University of Maryland test plot samples, taken after the 1998 and 2000 applications, showed no statistical differences for any elements between plots at the 15–30-cm depths (untilled); however, for the 0–15-cm depth (tilled), statistical differences were found for As, Cu, and Zn. For water extractable arsenic in the 0–15-cm depth (tilled), there was a statistically significant increase after a single application of 6 tons/acre compared to the 0 ton/acre plot. After two applications of litter, there was a significant increase in water-soluble arsenic at both 3 and 6 tons/acre application rates compared to the 0 ton/acre plot. The increase in water-soluble arsenic appears to persist over a 2-year period and to accumulate in the soil (data shown in Supporting Information). The sequential water extraction results of the unamended soil (0 tons/acre) shown in Figure 1, indicate that the indigenous component of water extractable arsenic in the soil is about 0.08 mg/kg. Two applications of litter over 2 years resulted in an increase of water-soluble arsenic by a factor of 2 to 3. Water-extractable Cu and Zn in the 0–15-cm depth samples showed significant differences (*t* test statistic of 0.1 or less) between the control and the 3 and 6 tons/acre test plots after two applications of litter. Iron showed a statistically significant difference only for the 6 tons/acre test plot. The water extraction results for samples collected in July 2000 are listed in Table 2. Water-extractable arsenic showed a strong correlation with water-extractable P, Cu, and Zn ($r^2 = 0.97, 0.98, \text{ and } 0.92$, respectively). No change in total carbon or strong-acid-extractable As, Cu, Zn, or Fe was observed between the amended and unamended test plots after two applications. The acid extraction results for samples collected in July 2000 are listed in Table 3.

Sequential water extractions of samples from fields with a history of long-term poultry litter application from the Delmarva Peninsula and Oklahoma, along with samples taken

TABLE 2. Water-Extractable As, P, Cu, Zn, and Fe from Test Plots at the University of Maryland Agricultural Experiment Station after the Second Application of 3 and 6 Tons/Acre Litter and a Control Plot with No Litter Application^a

tons/acre	As (mg/kg)	P (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Fe (mg/kg)
0	0.015 (0.00023)	2.89 (0.55)	0.058 (0.011)	0.0168 (0.004)	6.65 (0.65)
3	0.027 (0.0036)	6.53 (2.32)	0.131 (0.017)	0.0248 (0.002)	6.68 (0.61)
6	0.037 (0.0095)	10.31 (6.13)	0.170 (0.059)	0.0323 (0.010)	7.29 (0.62)

^a Samples are from the top 15 cm sampled in July 2000. Results are the average of three locations per plot. The standard deviations are shown in parentheses. Results are for a single-water extraction.

TABLE 3. Acid Extractable As, P, Cu, Zn, and Fe from Test Plots at the University of Maryland Agricultural Experiment Station after the Second Application of 3 and 6 Tons/Acre Litter and a Control Plot with No Litter Application^a

tons/acre	As (mg/kg)	P (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Fe (mg/kg)
0	2.36 (0.216)	461 (8.89)	10.1 (1.56)	30.0 (3.63)	10200 (436)
3	2.25 (0.027)	472 (45.6)	10.1 (0.41)	29.5 (1.64)	10100 (445)
6	2.31 (0.052)	459 (21.5)	11.2 (1.15)	30.8 (3.30)	9970 (242)

^a Samples are from the top 15 cm sampled in July 2000. Results are the average of three locations per plot. The standard deviations are shown in parentheses. Results are for a single-water extraction.

in an adjacent forested lot or nearby pasture with no history of litter use, are shown in Figure 2. Water-extractable arsenic is 6.4 times higher for the litter-amended Delmarva agricultural soil (DAS) than an unamended nearby forest soil (DFS). For Oklahoma pasture soils from the top 7.5 cm, the litter-amended pasture (B-1) had 2.7 times the water-extractable arsenic than the same depth in the unamended pasture (A-1). For soil from 7.5–15-cm depth, the amended pasture (B-2) had 4.5 times as much water-extractable arsenic

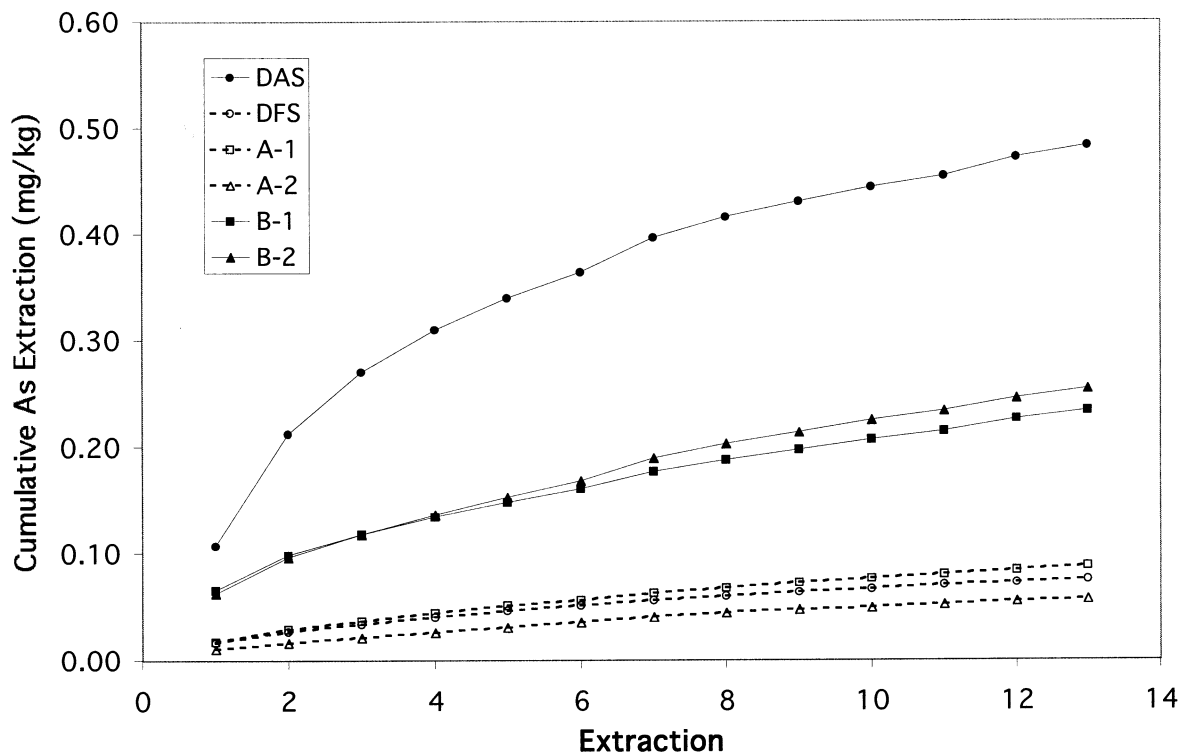


FIGURE 2. Sequential water extraction of agricultural soils with long-term application of litter [Delmarva agricultural soil (DAS) and Oklahoma pasture soils (B-1 and B-2)] and similar soils with no history of litter application [Delmarva forest soil (DFS) and Oklahoma pasture soils (A-1 and A-2)].

TABLE 4. Water-Extraction of Oklahoma Pasture Soils

depth	arsenic		dissolved carbon		phosphorus		copper		zinc		iron	
	unamended field (mg/kg)	amended field (mg/kg)	unamended field (mg/kg)	amended field (mg/kg)	unamended field (mg/kg)	amended field (mg/kg)	unamended field (mg/kg)	amended field (mg/kg)	unamended field (mg/kg)	amended field (mg/kg)	unamended field (mg/kg)	amended field (mg/kg)
0–	0.0165	0.0721	252	395	6.86	62.71	0.096	0.347	0.0409	0.1702	2.70	2.65
7.5 cm	(0.0107)	(0.0277)	(50)	(42)	(6.82)	(26.50)	(0.041)	(0.162)	(0.0478)	(0.0687)	(1.08)	(0.60)
7.5–	0.0111	0.0482	170	202	2.55	34.58	0.078	0.243	0.0102	0.0568	2.99	9.16
15 cm	(0.0064)	(0.0106)	(72)	(54)	(1.77)	(25.01)	(0.036)	(0.128)	(0.0115)	(0.0370)	(1.23)	(4.94)
15–	0.0092	0.0375	145	163	1.82	16.80	0.068	0.164	0.0042	0.0243	3.08	19.4
22.5 cm	(0.0062)	(0.0095)	(48)	(43)	(1.51)	(13.91)	(0.039)	(0.095)	(0.0084)	(0.0092)	(1.26)	(14.9)
22.5–	0.0073	0.0296	153	173	1.36	12.27	0.055	0.108	0.0054	0.0214	4.71	23.5
30 cm	(0.0051)	(0.0095)	(14)	(34)	(1.13)	(13.23)	(0.044)	(0.030)	(0.0064)	(0.0094)	(2.27)	(17.4)
30–	0.0069	0.0253	165	144	0.81	5.16	0.038	0.105	0.0054	0.0225	5.55	25.7
37.5 cm	(0.0043)	(0.0062)	(59)	(47)	(0.58)	(5.28)	(0.027)	(0.025)	(0.0044)	(0.0065)	(1.58)	(13.2)
37.5–	0.0063	0.0198	108	130	0.58	1.45	0.027	0.091	0.0098	0.0236	7.36	25.5
45 cm	(0.0029)	(0.0026)	(30)	(43)	(0.36)	(1.02)	(0.014)	(0.010)	(0.0055)	(0.0042)	(1.42)	(5.46)
45–	0.0074	0.0177	103	126	0.54	1.09	0.029	0.068	0.0131	0.0230	8.00	24.6
52.5 cm	(0.0048)	(0.0014)	(28)	(47)	(0.39)	(0.60)	(0.019)	(0.010)	(0.0019)	(0.0038)	(0.86)	(7.12)
52.5–	0.0067	0.0150	113	109	0.41	0.64	0.023	0.059	0.0136	0.0226	7.91	21.3
60 cm	(0.0036)	(0.0021)	(19)	(22)	(0.27)	(0.58)	(0.015)	(0.022)	(0.0112)	(0.0085)	(2.76)	(0.38)

^a Results are the average of four samples per field. Numbers in parentheses are the standard deviations.

as the unamended pasture (A-2). The cumulative arsenic extracted after 13 water extractions from fields with long-term application was 2.6 times higher for the Delmarva agricultural soil and 1.3 times higher for the Oklahoma surface soil (B-1) compared to the Maryland Agricultural Station soil after two applications of 6 tons/acre. There was no significant difference in water-extractable arsenic among the unamended soils. The arsenic determined by total dissolution for the Delmarva agricultural soil (DAS), Delmarva forest soil (DFS), the unamended Oklahoma soils (A-1 and A-2), and the amended Oklahoma soils (B-1 and B-2) was 4.0, 3.5, 3.2, 3.1, 4.2, and 7.5 mg/kg, respectively.

Results of the water extraction of As, P, C, Cu, Zn, and Fe from litter-amended and unamended Oklahoma pasture soils are listed in Table 4 and Figure 3. Water-extractable As, C, P, Cu, and Zn decreases with depth in both fields and is

higher at the surface in the amended field than in the unamended field for all elements. Water-extractable Fe increases with depth in both fields and is the same for both fields at the surface. The difference between amended and unamended fields for water-extractable arsenic decreases steadily with depth, with the amended field being 4.4 times higher at the surface than the unamended field and 2.2 times higher at the lowest depth. The differences in mean concentration are significant at the 90% confidence level at all depths. The differences between water-extractable C, P, Cu, and Zn concentrations in amended and unamended soil at the surface (0–7.5 cm) were significant at the 90% confidence level. The water-extract concentrations for C, P, Cu, and Zn were 1.6, 9.1, 3.6, and 4.2 times greater, respectively, in the amended field at the surface. Differences between the amended and unamended soils were less prominent for lower

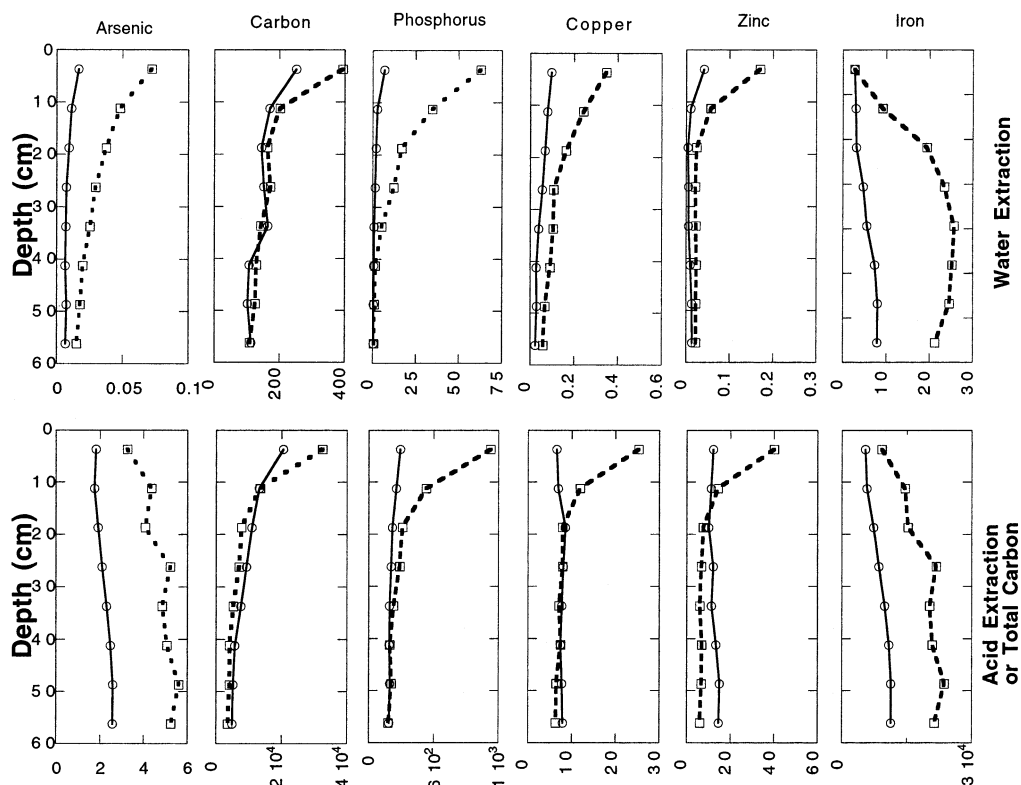


FIGURE 3. Water extractions, strong acid extractions, and total carbon of Oklahoma pasture soils. All units are mg of element per kg of soil. Square symbols and dashed lines are the amended field. Circles and solid lines are the unamended fields.

TABLE 5. Strong Acid Extraction of Oklahoma Pasture Soils and Total Organic Carbon^a

depth	arsenic		total carbon		phosphorus		copper		zinc		iron	
	unamended field (mg/kg)	amended field (mg/kg)	unamended field (%)	amended field (%)	unamended field (mg/kg)	amended field (mg/kg)	unamended field (mg/kg)	amended field (mg/kg)	unamended field (mg/kg)	amended field (mg/kg)	unamended field (mg/kg)	amended field (mg/kg)
0–	1.82	3.26	2.06	3.80	291	1129	6.57	25.32	12.2	40.1	5380	9240
7.5 cm	(0.16)	(0.88)	(0.66)	(0.79)	(84)	(279)	(1.02)	(9.46)	(3.1)	(14.1)	(644)	(3980)
7.5–	1.76	4.37	1.32	1.35	254	532	6.94	11.97	11.2	14.4	5740	14600
15 cm	(0.19)	(1.45)	(0.61)	(0.42)	(70)	(174)	(0.88)	(4.22)	(3.2)	(4.5)	(1230)	(5850)
15–	1.92	4.08	1.10	0.78	219	313	8.58	7.97	10.1	7.6	7250	15300
22.5 cm	(0.15)	(1.72)	(0.36)	(0.20)	(41)	(46)	(0.98)	(2.22)	(2.1)	(1.1)	(1430)	(9000)
22.5–	2.10	5.23	0.93	0.71	205	287	8.07	7.97	12.2	6.8	8530	21800
30 cm	(0.33)	(1.88)	(0.32)	(0.44)	(37)	(80)	(1.09)	(0.82)	(2.3)	(1.6)	(2290)	(10800)
30–	2.31	4.86	0.76	0.53	192	230	7.73	7.10	11.4	6.0	9820	20300
37.5 cm	(0.30)	(1.60)	(0.24)	(0.25)	(27)	(40)	(1.12)	(0.75)	(2.4)	(1.6)	(1220)	(8900)
37.5–	2.49	5.08	0.58	0.42	190	196	7.44	7.47	13.4	6.9	10800	20900
45 cm	(0.33)	(1.40)	(0.18)	(0.16)	(32)	(37)	(1.22)	(2.85)	(1.5)	(1.6)	(1210)	(7620)
45–	2.60	5.61	0.52	0.42	195	211	7.76	6.48	15.1	6.8	11300	23700
52.5 cm	(0.47)	(1.57)	(0.14)	(0.19)	(48)	(50)	(0.46)	(0.81)	(1.6)	(1.6)	(1510)	(9390)
52.5–	2.59	5.25	0.49	0.36	187	182	7.97	6.36	14.6	6.1	11300	21400
60 cm	(0.25)	(1.82)	(0.15)	(0.14)	(37)	(52)	(0.61)	(1.06)	(3.0)	(1.6)	(856)	(10400)

^a Results are the average of four samples per field. Numbers in parentheses are the standard deviations.

depths. Water-extractable arsenic has a strong positive correlation ($r^2 > 0.90$) with water-extractable C, P, and Cu for both fields, and Zn in the treated field. Water-extractable arsenic has a strong negative correlation ($r^2 = -0.93$) with water-extractable Fe in the treated field.

The observed changes in acid-extractable elemental concentrations with depth were more variable than those observed for the water-extractable concentrations. These results are shown in Table 5 and Figure 3. Although the total C and concentrations of P, Cu, and Zn in the acid extracts were greater than those in the water extracts, similar trends showing decreasing concentrations with soil depth were observed. The differences between acid-extractable C, P, Cu, and Zn concentrations in the amended and unamended soil at the surface (0–7.5 cm) were significant at the 90%

confidence level. The total C and acid-extractable concentrations for P, Cu, and Zn were 1.8, 3.9, 3.9, and 3.0 times greater, respectively, at the surface in the amended field. There were some significant differences (>95% confidence level) between fields at lower depth intervals for some elements. Acid-extractable Cu and Zn concentrations in unamended soil were higher than those in the amended soil between 30 and 60 cm and between 22.5 and 60 cm, respectively. Only acid-extractable As and Fe concentrations increased with depth in both fields. Concentrations of As were approximately twice as high in the amended field at all depths compared with those in the unamended field (differences were significant at the 95% confidence level for all depths). The Fe concentrations were 1.6–2.9 times higher in the amended field as in the unamended field; these differ-

ences were significant at all depths (>89% confidence level). Acid-extractable arsenic has strong positive correlation ($r^2 = 0.99$) with acid-extractable Fe in the treated field.

Discussion

The application of poultry litter containing roxarsone or its degradation products to agricultural fields results in increased concentrations of water-extractable arsenic species compared to that in fields that have not been amended. This relation was observed at three different amended and unamended field sites examined in this study. The hypothesis that water-extractable arsenic is derived primarily from poultry litter amendments is supported by the following observations. Mobilization of arsenic, as well as the other feed additives, such as Cu and Zn, was observed when poultry litter was extracted with water. There is a strong positive correlation ($r^2 > 0.90$) between water-extractable concentrations of As, C, P, Cu, and Zn for soils amended with poultry litter, and these concentrations decrease with increasing depth (greater distance from the application of litter) and increase with increasing application rate.

The capability of water extraction to detect arsenic introduced by litter amendment when total dissolution showed no difference in arsenic concentrations was observed in fields having only two applications of poultry litter as well as fields which had long-term application of litter. The amount of arsenic added to the tilled portion of a field at a rate of 3 and 6 tons per acre would increase the total arsenic concentration of a soil containing a background concentration of 3.5 mg/kg arsenic by 1.5 to 3% per application. Because the arsenic in the litter is readily water extractable, it can contribute to a detectable increase in the water-extractable concentration although having a negligible effect on total concentration. The bulk of the arsenic in the soil that corresponds to strongly bound arsenic contributes less to the water-extractable arsenic than the litter.

Although the arsenic in the poultry litter is easily mobilized by water, its leach rate from amended soils appears to be slow enough that it accumulates in the soils as demonstrated by the Maryland test plots for the 2-year application cycle. There was a significant difference between water-extractable arsenic in the amended soil after one application at 6 tons per acre and after two applications at 3 and 6 tons per acre compared to the unamended plot. Even though these applications were 2 years apart, there was a measurable increase in water-extractable arsenic between the first and second applications. The Delmarva agricultural field, with long-term application on a 2-year cycle, showed 2.6 times more water-extractable arsenic than the highest Maryland test plot. The water-extractable arsenic from all the unamended soils was not significantly different.

The soil profile from the Oklahoma pasture soils showed a significant increase in strong-acid-extractable arsenic with litter application and with increasing depth in the soil column.

The strong correlation ($r^2 = 0.99$) between acid-extractable As and acid-extractable Fe in the treated field is probably indicative of the sorption of As by Fe oxyhydroxides or coprecipitation with the Fe (13–16).

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Supporting Information Available

Tables and figures of data relating to various aspects of this study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Chapman, H. D.; Johnson, Z. B. *Poultry Sci.* **2002**, *81*, 356–364.
- (2) Muir, L. A. *Safety of 3-Nitro to Humans and the Environment*; Alparma: Fort Lee, NJ.
- (3) Edwards, D. R.; Daniel, T. C.; Marbun, O. *Water Resour. Bull.* **1992**, *28*, 487–494.
- (4) Sims, J. T.; Wolf, D. C. In *Advances in Agronomy*; Sparks, D. L., Ed.; Academic Press: San Diego, CA, 1994; vol. 52, pp 1–83.
- (5) Han, F. X.; Kingery, W. L.; Selim, H. M.; Gerard, P. D. *Soil Sci.* **2000**, *165*, 260–268.
- (6) Gupta, G.; Charles, S. *Poultry Sci.* **1999**, *78*, 1695–1698.
- (7) Krishnamurti, G. S. R.; Naidu, R. *Environ. Sci. Technol.* **2002**, *36*, 2645–2651.
- (8) Marin, A. R.; Pezeshki, S. R.; Masscheleyn, P. H.; Choi, H. S. *J. Plant Nutr.* **1993**, *16*, 865–80.
- (9) Blaser, P.; Zimmermann, S.; Luster, J.; Shotyk, W. *Sci. Total Environ.* **2000**, *249*, 257–280.
- (10) Garbarino, J. R.; Bednar, A. J.; Rutherford, D. W.; Beyer, R. S.; Wershaw, R. L. *Environ. Sci. Technol.* **2003**, *37*, 1509–1514.
- (11) Arbogast, B. F., Ed. *Analytical Methods Manual for the Mineral Resources Survey Program*; USGS Open-File Report 96-525; U.S. Geological Survey: Washington, DC, 1996.
- (12) Garbarino, J. R.; Taylor, H. E. *Inductively Coupled Plasma-Mass Spectrometric Method for the Determination of Dissolved Trace Elements in Natural Water*; USGS Open-File Report 94-358; U.S. Geological Survey: Washington, DC, 1994; 28 pp.
- (13) Howell, R. J. *Appl. Geochem.* **1994**, *9*, 279–286.
- (14) Voigt, D. E.; Brantley, S. L.; Hennet, R. J.-C. *Appl. Geochem.* **1996**, *11*, 633–643.
- (15) Smith, E.; Naidu, R.; Alston, A. M. *J. Environ. Qual.* **1999**, *28*, 1719–1726.
- (16) Grafe, M.; Eick, M. J.; Grossl, P. R.; Saunders, A. M. *J. Environ. Qual.* **2002**, *31*, 1115–1123.

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