

THE SORPTION AND EXTRACTION OF ARSENIC IN SOILS THAT HAVE BEEN AMMENDED WITH CHICKEN MANURE, Rutherford, D.W.<sup>1</sup>., Garbarino, J.R.<sup>2</sup>., Kennedy, K.<sup>1</sup>, Wershaw, R.L.<sup>1</sup>.

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## **INTRODUCTION**

Organic arsenic compounds are extensively added to the feed of broiler chickens to control coccidial intestinal parasites. Roxarsone (3-nitro-4-hydroxyphenylarsonic acid) is the most commonly used organic arsenic feed additive. Very little roxarsone is retained in chicken meat (the Food and Drug Administration limit is 0.5 ppm in the chicken muscle tissue) with most roxarsone excreted unchanged (Morrison 1969, Gregory 1993). Arsenic is added to the environment during disposal of the chicken manure with most manure being used as fertilizer on fields. The single published study on the environmental persistence of roxarsone (Morrison 1969) does not provide any information on the fate of roxarsone or the degradation pathways of the compound in soils and natural waters. Ongoing studies have indicated that Roxarsone degrades rapidly and that the arsenic(V) species was the only species detected in amended soils (Garbarino, J.R. and others, 2001).

This study examines and compares the sorption characteristics of Roxarsone and arsenate ion on common soil components to determine where arsenic will be sequestered in soils, and its ability to be remobilized. The extraction of arsenic from soils which have been amended with arsenic containing chicken manure is investigated by various extraction methods to determine binding mechanisms for arsenic, potential reservoirs in soils, and the potential for future mobilization.

## **APPROACH**

Sorption studies were carried out in batch mode. Soil samples were placed in a centrifuge tube with a known volume of water and arsenic compounds added. The samples were equilibrated on a rotary mixer for 24 hours, centrifuged, and the aqueous portion analyzed for arsenic. The amount of arsenic sorbed was determined by difference. Soil components examined were iron oxide, aluminum oxide, silica, kaolinite and montmorillonite. A Florida peat was used as a representative for natural organic matter.

Soils for extraction studies were obtained from the Delmarva Peninsula and northeastern Oklahoma. At each site soils were obtained from a field with a known application of arsenic-containing chicken manure and from a nearby field or woods with no history of manure application. The Delmarva site consisted of a tilled field and a nearby woods, where the samples were taken in the top 6 inches. The Oklahoma site consisted of pastures where the manure was applied to the surface and not tilled. Samples were taken from the top 3 inches (A-1 and B-1) and from 3 to 6 inches (A-2 and B-2). Manure had been applied at site B.

Soils were extracted with water to determine the mobile arsenic component. Hydrogen peroxide was used in another extraction to determine the amount of arsenic bound by natural organic matter. An extraction using oxalic acid and sodium dithionite was used to release arsenic bound by metal oxy-hydroxides. Total arsenic was determined by a total acid digestion of the soils.

Arsenic was analyzed by direct injection into an inductively coupled plasma mass spectrometer.

Effect of pH and ionic strength: Varying pH had a similar effect on the sorption of Roxarsone to iron oxide as it did with the arsenate ion. Arsenate sorption decreased from .035 mmoles per gram at pH 2 to 0.01 mmoles per gram at pH 8. Roxarsone sorption decreased from .033 mmoles per gram at pH 2 to .005 mmoles per gram at pH 8.

Because of the buffering ability of natural organic matter, it was not feasible to vary pH widely because of the possibility of altering the peat. Within the range of pH 4.5 to 6 no significant effect on sorption of either arsenate or Roxarsone was noted. For this study the pH of stock solutions were adjusted to pH 5.5. The pH of the batch experiments was measured after equilibration and was found to remain between 5 and 6.

The effect of ionic strength was examined for Roxarsone and arsenate sorption to natural organic matter. Both Roxarsone and arsenate showed increased sorption as the background concentration of calcium chloride was increased from 0 to .004 M, and remained constant from .004 M to .02M of CaCl<sub>2</sub>. Therefore, it was decided to use an ionic strength of .005M calcium chloride for all comparison isotherms.

## **RESULTS AND DISCUSSION**

Uptake by soil components: Figure 1 shows the sorption of Roxarsone and arsenate ion from aqueous solution to iron oxide and peat. Similar results were observed for aluminum oxide. No measurable sorption was observed for Roxarsone on silica.

Roxarsone shows lower sorption to iron oxide than arsenate suggesting that the larger Roxarsone molecule cannot pack as efficiently onto a metal hydroxide surface.

Figure 1 also shows the sorption of Roxarsone and arsenate ion from aqueous solution to peat. In this case, roxarsone show higher uptake by organic matter than the arsenate ion. This indicates that the organic portion of the Roxarsone molecule aids in the sorption to the peat.

Comparison of the sorption of the arsenate ion to both iron oxide and Roxarsone to iron oxide and peat show that at low concentrations the Roxarsone and arsenate ion are less strongly sorbed by organic matter than by iron oxides

Since the arsenic from chicken manure is added to the environment in organic matter, it would be expected to be more mobile than arsenic in the soil that has been sequestered by metal oxides.

Desorption from Soils: Figure 2 show the extraction of arsenic from soil by water. All soils showed continued extraction of arsenic by water with continued treatment but at a decreasing rate.

Both the Oklahoma and Delmarva soils where chicken manure had been applied (filled symbols) show higher water extractable arsenic even though in the case of the Delmarva field and woods soils there was no significant difference in total arsenic concentration.

There is good correlation between the first water extraction and subsequent extracts so that a single water extraction was used for subsequent evaluation of water extractable arsenic.

Correlation of Extraction Techniques: Table 1 shows the correlation of arsenic removal by extraction method and soil organic carbon and iron content. The high correlation between water extractable arsenic and the hydrogen peroxide extraction and organic carbon content, and the low correlation with total arsenic and iron content suggests that the mobile arsenic is being released from the organic matter. The high correlation of the oxalic/dithionite extraction with total

arsenic and iron content indicates that most of the arsenic in soil is sequestered in the metal oxy-hydroxides.

Table 1: Correlation coefficients of arsenic removal by extraction method and soil organic carbon and iron content.

	H2O2 Ext.	Oxalic / Dithionite Ext.	Total Arsenic	Organic Carbon Content	Iron Content
Water Ext.	0.90	0.26	0.21	0.84	-.02
H2O2 Ext.		0.00	0.02	0.75	-0.48
Oxalic/Dithionite Ext.			0.96	-0.15	0.70
Total Arsenic				-0.28	0.54
Organic Carbon Content					-0.19

## **CONCLUSIONS**

Although the relative amount of arsenic being added to soil by chicken manure is a small percentage of the total arsenic in the soil, it has a higher mobility in water due to the sorption characteristic of arsenic in organic matter compared to arsenic sequestered by metal oxides. This may lead to higher arsenic in water leaching from fields treated with arsenic containing chicken manure until such time that this arsenic can be bound by metal oxy-hydroxides.

## **REFERENCES**

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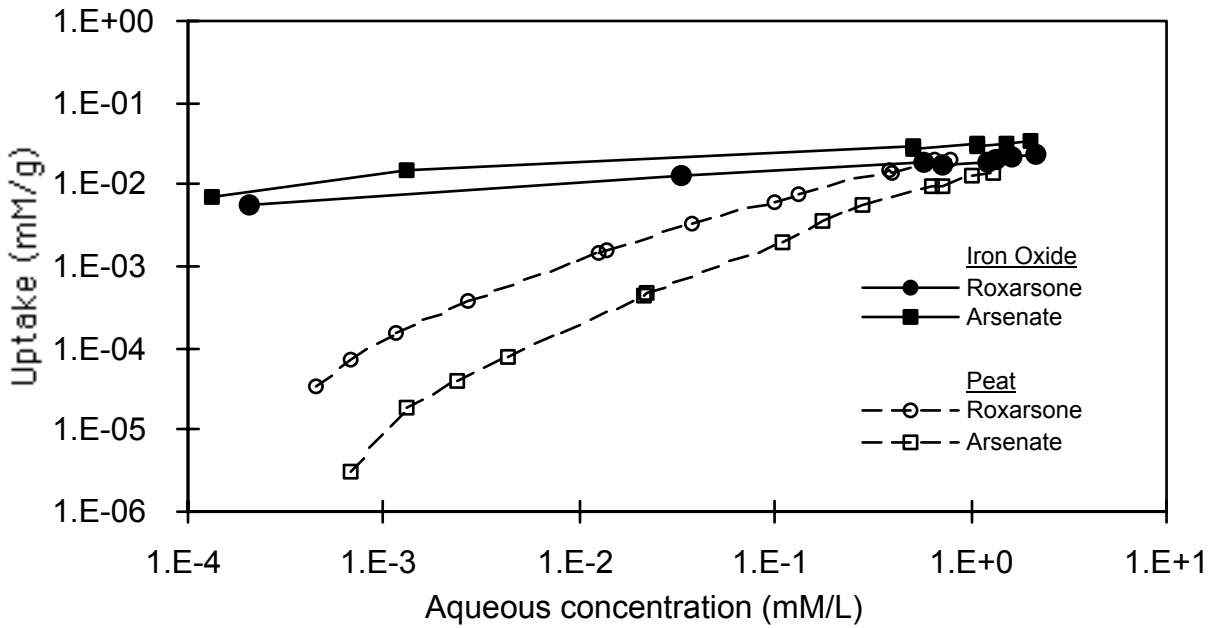


Figure 1: Uptake of roxarsone and arsenate from aqueous solution by iron oxide and peat

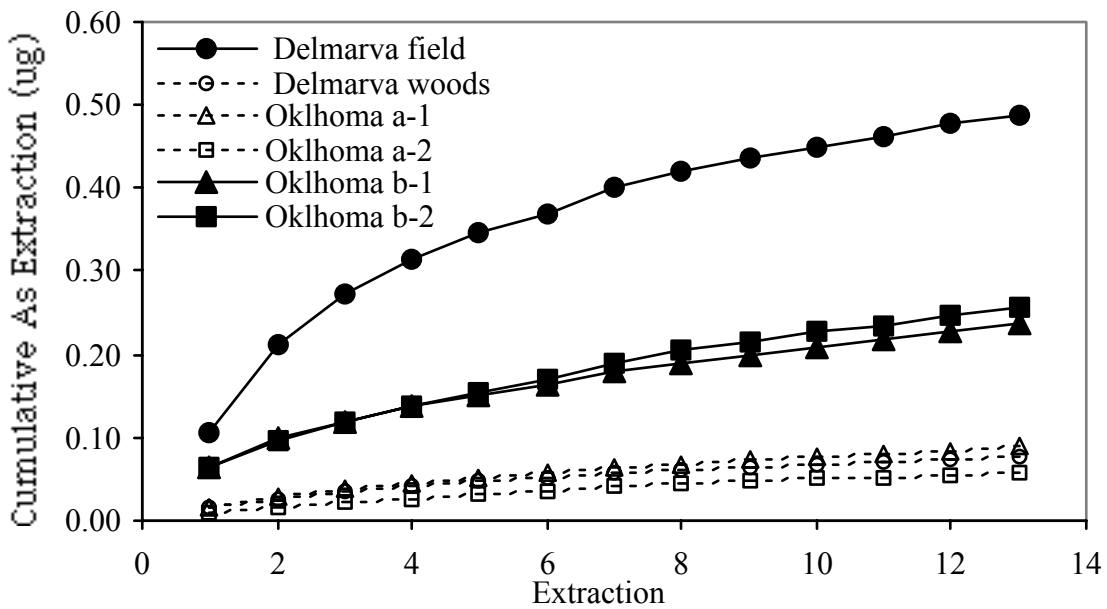


Figure 2: Sequential water extraction of soils. Filled symbols are soils which have had chicken manure application.