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Effect of Added Reactive Aluminum on Aldicarb Adsorption by a High Organic Soil

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Aldicarb and its metabolites have been detected in the ground water of 19 states (Lorber et al. 1989). Eleven of these states have reported aldicarb residue levels at greater than the health advisory of 10 $\mu g/L$ (Lorber et al. 1989). There is little argument that soil factors such as soil moisture, aeration, and soil pH may influence the disappearance of aldicarb and other pesticides in soil (Kuhr & Leistra 1980). Aldicarb is less likely to reach groundwater when applied to moist, alkaline soils than when applied to dry, acidic soils. Other factors which may affect aldicarb's movement to groundwater include ground water vulnerability, agricultural practices and the chemical characteristics of aldicarb. These factors are discussed in detail elsewhere (Bromilow & Leistra 1980, Dierbert & Given 1986, Jones & Back 1984, Jones et al. 1986, Leistra et al. 1976, Wyman et al. 1985).

Aluminum release from rocks and minerals under acid conditions has been well documented (Stumm & Morgan 1979). Mobile or reactive aluminum tends to form ligands with organic molecules present in soil. The formation of aluminum-organic matter complexes in soil has also been well described in the literature (Hodges & Zelazny 1983, Huang & Keller 1972, Kwong et al. 1981, Schnitzer & Skinner 1963).

The role of metal interaction with pesticides has not been reported extensively in the literature. However, there is indication that metals may play an integral role in the degradation of aldicarb in soil (Bromilow et al. 1986, Supak et al. 1978). Bromilow and co-workers (1986) report that aldicarb, aldicarb sulfoxide and aldicarb sulfone degrade more rapidly under anaerobic than aerobic conditions and that ferrous ions play an important role in this rapid degradation.

Analysis of data from an aldicarb adsorption study conducted by Supak

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(1978) suggests that organo-aluminum or organo-iron complexes may have prevented aldicarb from being adsorbed to the organic material in an acidic (pH 5.4) soil. In the experiment, soils to which aldicarb did not adsorb contained high levels of organo-aluminum and iron complexes. Soils low in these complexes were able to retain the pesticide. Although no experimentation was performed by these researchers to specifically investigate the influence of these complexes on aldicarb adsorption, the interaction warrants further consideration.

The effect that aluminum release and its subsequent complexing with organic matter in acid soils has on the adsorption of pesticides is not well understood and is not discussed in the literature. It is hypothesized here that aluminum may interfere with aldicarb adsorption by soils. The metal may bind with the organic fraction of the soil thus inhibiting pesticide interaction. Alternatively, aluminum may interfere by tying up functional groups on the aldicarb molecule itself. The research study described herein investigates the premise that aluminum plays an important role in the interference of adsorption of aldicarb by soil constituents.

MATERIALS AND METHODS:

A Rowland sandy loam soil was collected under the leaf debris from the 0-3 inch layer from the Hutcheson Memorial Forest in Somerset, New Jersey. Soil characteristics are presented in Table I. The area from which the soil was removed is characterized by shaded, virgin forest which has never been treated nor cultivated. It is in the floodplain of the Millstone River. Immediately after transportation to the laboratory, the soil was sieved through a 1.44 millimeter sieve and stored at 4 $^{\circ}$C.

Two hundred gram aliquots of soil were removed and treated with lime in the form of dry calcium carbonate to raise the pH. Soil pH was measured on the day of collection and again immediately before use (Table I outlines the field soil characteristics). Limed soils were incubated for 2 to 7 months before use to ensure that equilibrium between the lime and soil had been reached. The samples were removed from the refrigerator and allowed to equilibrate to room temperature for 24 hours prior to experimentation.

Three soil masses (1.0 gram, 5.0 grams and 10.0 grams of field moist soil) at three pH ranges (3.0-4.9, 5.0-5.9 and 6.0-7.5) were used in batch experiments. One set of experiments was carried out to investigate the absorption of aldicarb onto the untreated soil. In the second set, exchangeable aluminum dissolved in dilute hydrochloric acid was added in addition to aldicarb to investigate its influence on aldicarb adsorption. The initial aqueous concentrations for the three series of soils were: 0.06, 0.6 and 6.00 mg/L aldicarb in the first set (aldicarb but no aluminum added); and 6.00, 0.60 and 0.06 mg/L exchangeable aluminum and 0.06, 0.60 and

Table 1. General characteristics of soil.

Series	Rowland
Texture	sandy loam
TVOC (%)	27.00
Total Aluminum (mg/g)	0.15
Reactive Alum (meq/g)	0.23
FeOx (mg/g)	1.12
CEC (mequ/100g)	26.00
Exchangeable Cations	
Calcium	1.92
Magnesium	0.63
Potassium	0.36
Sodium	0.03
Mechanical Analysis	
sand (%)	77
silt (%)	12
clay (%)	11
Lime Requirement	
pH 5.0	69.89
pH 6.0	469.6
pH 7.0	1018.4
Acidity	
pH 5.0	0.303
pH 6.0	0.519
pH 7.0	0.736
Moisture (%)	
Field	46
Stored	52

6.00 mg/L aldicarb respectively in the second set (aldicarb and aluminum added). For reference, soils treated with both aluminum and aldicarb are called "treated",and soils to which aldicarb but no aluminum was added are called "untreated". Appropriate quality assurance and quality control samples were run and analyzed to examine interference of aldicarb and aluminum in the absence of soil. These samples indicated that aldicarb was not adsorbed onto the glass vials, syringes nor cellulose filter paper. Also, it was not adsorbed onto the lime. The pH measured in the batch solutions was not significantly altered by the addition of aluminum solution.

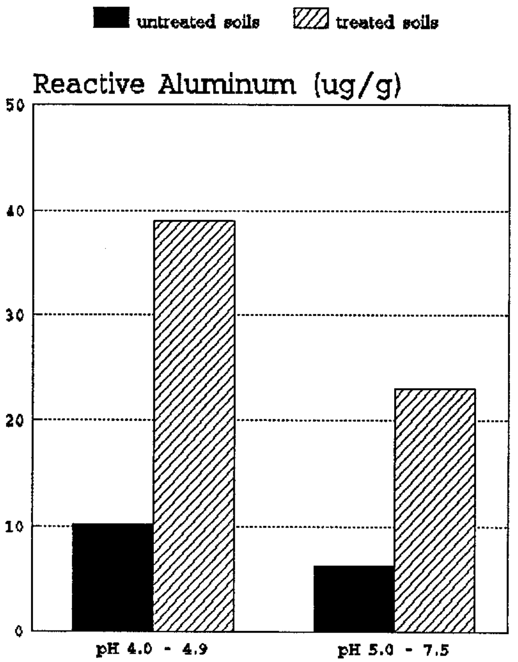

Figure 1. Reactive aluminum in treated and untreated soils

The vials were placed on a mechanical shaker and agitated for 3 hours. Other researchers have reported that equilibrium for aldicarb is achieved within 2 hours (Felsot & Dahm 1979, Uchrin & Mangels 1985). To confirm this time, one vial at each concentration was left on the shaker for 24 hours and aliquots of supernatent analyzed for aldicarb each hour for the first 12 hours, then every 6 hours. The results of this indicated that equilibrium was achieved within 2 hours. After shaking, the samples were centrifuged for 30 minutes at 10,000 rpm. The supernatant was decanted and passed through a 0.45 μm filter via a glass syringe-stainless steel filter holder. The solutions were put into autosampler vials and analyzed immediately for aldicarb residues by HPLC-fluorescence.

Aldicarb adsorption was calculated by subtracting the amount of pesticide added to the vial minus that detected in supernatant after the batch experiments. Samples were analyzed for parent aldicarb as well as for degradation products. This pesticide has a low volatilization, so negligible loss was attributable to this route. Control vials indicated that aldicarb did not adsorb to glass vials, lime or filters. Therefore, it was assumed that all loss of aldicarb in the vials was due to adsorption by the soil matrix.

The remaining soil was removed from the glass vials, transferred to 150 mL plastic bottles and treated with 1.0 N KCl (potassium chloride) solution to extract reactive aluminum according to procedures in Standard Methods (Chapman 1982). The solution was stored at 4°C until ready for analysis. The results were recorded as KCl-extractable aluminum in milligrams reactive aluminum per standard mass of dry soil.

Quality assurance/control samples indicated that aluminum concentrations were stable throughout the duration of the batch experiments and that neither aldicarb nor aluminum loss occurred as a result of adsorption to glass or plastic labware or filter paper. Also, no significant aldicarb degradation occurred in the vials during the batch experiments.

Aldicarb, aldicarb sulfoxide and aldicarb sulfone were measured in aqueous solutions using high pressure liquid chromatography with post-column derivatization and fluorescence detection. Partisil 5 ODS 3 packing material packed into a 25 cm stainless steel chromatography column was used for separation.

Aluminum determinations were completed on a Perkin-Elmer HGA-2100 Graphite Furnace Atomic Absorption Spectrophotometer set at 309.6 nm for optimum detection.

RESULTS AND DISCUSSION

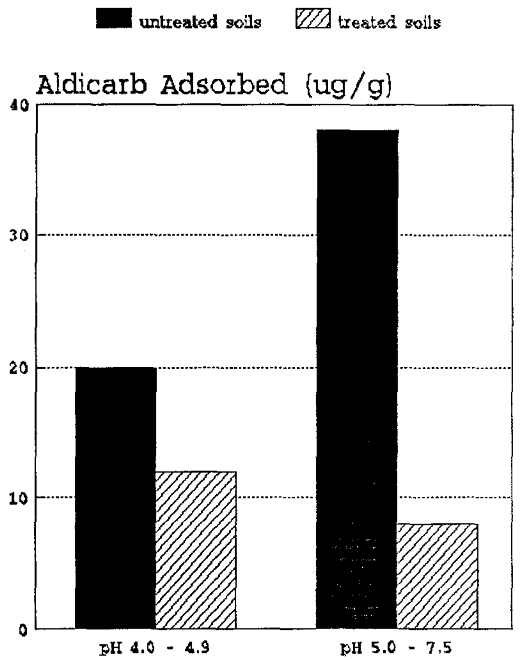

Figure 2. Aldicarb adsorption in treated and untreated soils

This high organic soil behaved predictably to liming; the pH was altered according to the amount of lime added. Thus, there were three pH groups with which to perform batch experiments. The actual pH ranges after liming and storage were 4.0-4.9, 5.0-5.9 and 6.0-7.5. The Wilcoxon and Mann-Whitney tests for nonparametric data sets were used in for statistical testing. The level of significance selected for rejecting the null hypothesis was 0.01 unless otherwise indicated.

Statistical analyses showed that reactive aluminum levels for soils having a pH level of 4.9 or below were significantly higher than for those having a pH level above 4.9 (see Figure 1). For ease in data presentation, the pH ranges are grouped as 4.0-4.9 and 5.0-7.5. Reactive aluminum levels varied significantly with liming according to statistical analyses.

There was a slight increase in aldicarb adsorption for soils having a pH above 4.9. The decrease in reactive aluminum level caused by liming resulted in a small change in the way this soil adsorbs aldicarb. Figure 2 bar graphs present the data for aldicarb adsorption according to reactive aluminum level for this soil.

The addition of reactive aluminum to this soil resulted in increased reactive aluminum levels at both pH ranges (see Figure 1). Reactive aluminum levels were higher in the treated soil than in untreated soils indicating that

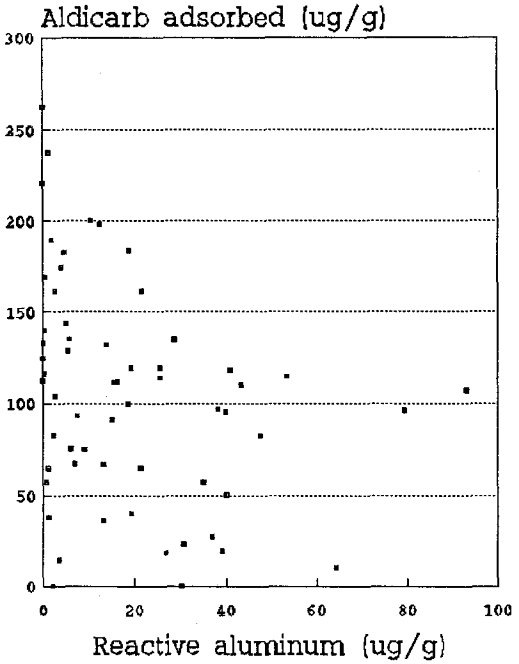

Figure 3. Reactive aluminum levels & aldicarb adsorption

the soil took up some of the aluminum that was added at both pH levels. Adsorption of aldicarb was significantly lower in the treated soil than in the untreated soil at all pH levels as shown in Figure 2. Statistical correlations performed on treated and untreated soil data show that aldicarb adsorption is significantly correlated with reactive aluminum at a 0.01 level of significance. An increase in reactive aluminum level corresponds to a decrease in aldicarb adsorption in this soil at the pH ranges studied.

Figure 3 presents a scatter diagram of reactive aluminum versus aldicarb adsorption for the soil. It is evident from the diagram that aldicarb adsorption by this soil is inversely proportional to the level of reactive aluminum present in the soil.

It can be concluded from the experimental results that the presence of additional reactive aluminum decreases this soil's affinity for aldicarb. Adsorption of aldicarb was lower in the treated soil indicating that the reactive aluminum had some influence in how this soil reacted in the presence of aldicarb. The soils and the conditions under which soils were subjected for the two experimental procedures were identical. The only factor which was altered was the level of reactive aluminum present in the soil solution, which was altered by adding aluminum dissolved in dilute hydrochloric acid (the addition of aluminum did not alter the pH level in these experiments). The presence of increased reactive aluminum level appears to have inhibited the adsorption of aldicarb in the Rowland soil.

There are two mechanisms whereby aldicarb adsorption could have been affected by aluminum: 1) aluminum was preferentially adsorbed by the active sites on the organic matter in the soil thus prohibiting adsorption of the aldicarb molecule, or 2) aluminum was adsorbed to the pesticide's active sites thereby preventing the molecule from reacting with organic matter. In either situation, the adsorption of the pesticide was inhibited by the addition of the reactive aluminum.

Liming soils in agricultural areas to increase pesticide efficacy is a common practice, especially in areas characterized by acidic soils. The results of this study imply that while liming may be effective for some pesticides in some soils, it will not help in all soils, and it may not have a significant effect for aldicarb adsorption. These results are applicable to soils which have recently experienced artificial acidification due to acidic deposition. The presence of additional aluminum released from rocks and minerals in a soil as a result of artificial acidification may prevent some high organic soils from adsorbing aldicarb (and other similar carbamate pesticides) to the extent they may otherwise have been able. This hindrance may not be reversible by liming.

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