Influence of Cation Content on the Biological Activity of Fensulfothion in Plainfield Sand[1]

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ABSTRACT

A study was conducted to assess the influence of cations on the biological activity of the organophosphorus insecticide, fensulfothion (O, O-diethyl O-[p-(methylsulfinyl)phenyl] phosphorothioate) (Dasanit®) in soil. Bioassays were done using first stage crickets, *Gryllus* spp. as test insects and a Plainfield sand without and amended with various concentrations of reagent chloride salts of NH_4^+, Ca^{2+}, Fe^{3+}, and Al^{3+}. The toxicity of fensulfothion decreased with increasing cation content, with the effect being most pronounced with trivalent > divalent > monovalent cations. Results of the bioactivity study paralleled those of an earlier adsorption study on fensulfothion-cation montmorillonite suspensions.

Additional Index Words: bioassay, *Gryllus* spp., sulfoxide insecticide, Dasanit®

EXCHANGEABLE CATIONS influence adsorption of polar organic molecules in clays and soils (1, 2, 3, 29). There appear to be three principal adsorption mechanisms involving cations, i.e. H-bond formation between a functional group of the organic molecule and the polarized hydration water of the exchangeable cation (water bridge) (9, 33), protonation of a functional group of an organic molecule by the hydrated cation, and a direct ion-dipole interaction between the exchangeable cation and a functional group. Numerous studies have shown that exchangeable cations influence the adsorption of carbamate (25, 30), aminotriazole (32, 36), phenylurea (20, 28), s-triazine (19, 20, 31, 37) and bipyridinium (10, 39) herbicides. Insecticides have received less attention. There appears to be no direct evidence of cation influence on adsorption of organochlorine insecticides in soils, although Champion and Olsen (12) reported that DDT adsorption was affected by pH and anion exchange capacity. They also suggested that DDT adsorption on soil might be related to the presence of iron and aluminum oxides. Cation-adsorption effects have been reported for organophosphorus and carbamate insecticides involving malathion (diethyl mercaptosuccinate S-ester with O,O-dimethyl phosphorodithioate *(9, 28)* fensulfothion (O,O-diethyl O-[p-(methylsulfinyl) phenyl] phosphorothioate) (8) parathion (O,O-diethyl O-p-nitrophenyl phosphorothioate) (15, 26) and carbaryl (1-naphthyl methylcarbamate) (26) among others.

There is a considerable amount of indirect evidence which indicates that the biological activity of an insecticide in soil is dependent on the extent to which it is "adsorbed" by the soil. Factors such as soil moisture, type, and temperature play an important role (21). It is possible that the nature of the exchangeable cation could also influence the biological activity of insecticides whose adsorption patterns are influenced by cations in the soil. There is some indirect evidence that this may be the case. Downs et al. (17) attributed rapid inactivation of DDT on mud surfaces of adobe huts to high iron content of the soil. However, the iron present in the mud would not have been in an exchangeable form. Peterson et al. (35) reported that 0.1N HCl-extractable iron in *22* soils exhibited a small positive relationship to the LD_{50} of DDT to *Drosophila melanogaster* (Meigen). There appears to be no evidence in the literature linking insecticide activity directly with cation content of the soil. Recently Bowman (8) demonstrated that adsorption of the sulfoxide insecticide, fensulfothion, in montmorillonite suspensions was affected by saturating cations. We subsequently initiated a study to determine if cations would influence the biological activity of fensulfothion in soil, the results of which are reported here.

MATERIALS AND METHODS

Tests were done by bioassay under controlled conditions. Test insects were 24 to 48-hour-old first-stage nymphs of the field cricket, *Gryllus* spp. reared as described by Harris and Svec (22). The Ap horizon of Plainfield sand (Table 1) was used for the bioassay studies. This calcareous soil is representative of sandy soils used to grow tobacco in southern Ontario. Approximately 200 kg of sand were collected in the field, air dried, sifted through a 0.64-cm screen and thoroughly mixed. Prior to use, aliquots of approximately 20 kg were oven dried for 24 hours at 105ºC.

Cation solutions were prepared by dissolving appropriate amounts of reagent chloride salts of NH_4^+, K^+, Ca^{2+}, Fe^{3+}, and Al^{3+} in distilled water so that a 5-ml aliquot of salt solution applied to 100 g of oven-dried soil would produce the desired cation level and also bring the soil up to approximate field moisture capacity. The solutions were prepared to allow addition of the various cations as follows: NH_4^+— 5.5, 27.7, 55.4, 277.2 µmoles/g; K^+—2.6, 12.8, 25.6, 127.9, 179.0 µmoles/g; Ca^{2+}— 2.5, 12.5, 25.0, 124.8, 249.5 µmoles/g; Fe— 1.8, 9.0, 17.9, 89.5, 169.6 µmoles/g; Al^{3+} —3.7, 18.5, 37.1, 111.2 µmoles/g. Limited water solubility of the NH_4^+, K^+, Fe^{3+}, and Al^{3+} salts prevented using higher levels. Calcium chloride was completely soluble over the concentration range studied. Cation exchange capacities of the Plainfield sand and its five cation amendments were determined by the

Table 1—Characteristics of Plainfield sand.

Sand (>20 µm)	92%
Silt (2-20 m)	2%
Clay (<2 m)	6%
Predominant clay mineral	Illite
Organic matter (Walkley-Black)	0.48%
Cation exchange capacity (Na	6.39 meq/100 g
Carbonate (as %	18.0
pH (distilled H_2O)	6.90
(0.01M $CaCl_2$)	6.10

Na saturation method (13) and Na^+ analysis was performed by atomic adsorption spectroscopy. pH measurements were made using a 1:2 soil/solution ratio using 0.01M $CaCl_2$ (34).

For bioassay, 200-g aliquots of oven-dry sand were weighed into jars and sufficient amounts of aqueous cation solutions pipetted onto the soils to bring the soil up to 5% water (oven-dry basis) and the appropriate cation concentration. The samples were then mixed thoroughly on a roller as described by Lichtenstein and Schulz (27). The fensulfothion (> 99% purity), purified as described previously (8) was applied to the soil in distilled, chromatographed n-pentane and the jars again rolled to allow thorough mixing of the insecticide and evaporation of the pentane. Eighty-five gram aliquots of the treated soil were placed in waxed paper cups 6.5 cm diam. x 6.5 cm high and compacted to a volume of 50 ml. The test insects were introduced 1 hour after the insecticide was applied to the soil. The containers were then covered with 9-cm glass petri dishes and placed in a controlled environment maintained at 27±1ºC, 65±5% RH and 24-hour photoperiod. Mortality counts were made 18 hours later. Bioassays were conducted using from 6 to 10 concentrations of insecticide producing mortalities in the 15–90% range. Duplicate groups of 10 insects were tested at each concentration and controls using cation and/or solvent treatment only were run with all tests. Three assays were conducted at each cation concentration and these results were pooled prior to analysis of the dosage-mortality data. The data were computed using probit analysis (18). LD_{50} values were used as a basis for comparison.

RESULTS AND DISCUSSION

Dosage-mortality curves for the Fe^{3+} - fensulfothion series of assays are shown in Fig. 1. The toxicity of fensulfothion decreased significantly with increasing Fe^{3+} content of the sand. At the maximum concentration of Fe^{3+} added to the soil (169.6 µmoles/g soil), approximately 19 times as much fensulfothion was required to cause 50% mortality of the test insects as compared to the control sand. A similar trend was apparent in tests with the other series of cation-amended soils, i.e. the toxicity of fensulfothion decreased (LD_{50} increased) with increasing cation content. LD_{50} values are presented graphically as a function of cation content in Fig. 2. The magnitude of toxicity reduction decreased with decreasing cationic valence, i.e. trivalent (Al^{3+}, Fe^{3+}) > divalent (Ca^{2+}) > monovalent (NH_4^+, K^+). Thus, at a cation concentration of 100 µmoles/g, fensulfothion was approximately 1/14 as toxic in Fe^{3+}-, 1/6 as toxic in Ca^{2+}– and 1/4 as toxic in K^+-amended soil as in the control soil. In the K^+- and NH_4^+-amended soils it appeared that maximum toxicity reduction was being approached at 179 and 277 µmoles/g, respectively, whereas there was no sign that this was the case with the divalent and trivalent cations tested.

The bioactivity data correlate well with earlier adsorption data for fensulfothion in montmorillonite suspensions (8). In that study fensulfothion was adsorbed most strongly in the Fe^{3+}-saturated suspension > Cu^{2+} > Pb^{2+} > H^+ > Al^{3+} > Mg^{2+} ≥
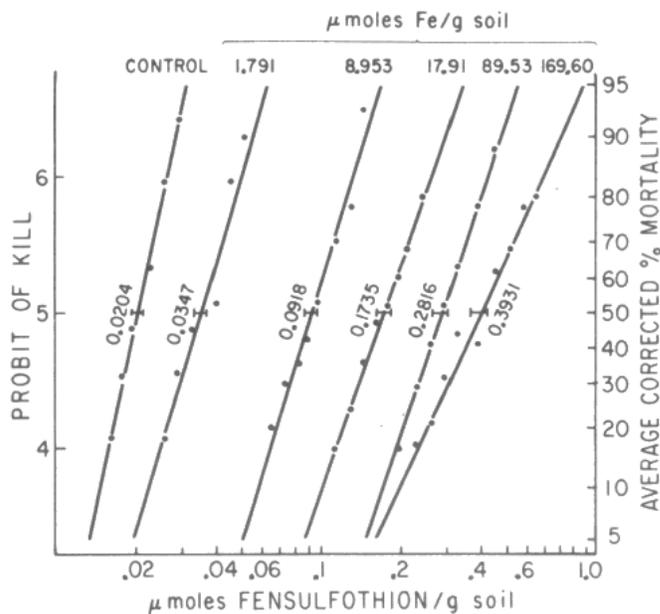

Fig. 1—LD_{50} values for fensulfothion in sand without and with addition of Fe^{3+}

$Ca^{2+} > Li^+ > Na^+$. For the predominant soil cations, the decreasing adsorption sequence was: trivalents > divalents > monovalents. The same general sequence was obtained in the bioactivity assays. The LD_{50} for fensulfothion in the Al-amended sand was slightly less than in the Fe-amended sand at low cation additions (<10 μmoles/g), but was greater at higher cation contents. In the earlier adsorption study (8), fensulfothion adsorption was distinctly greater on Fe-clay than on Al-clay. The difference between the fensulfothion adsorption data and the bioactivity data may be attributable to different reactions that the two elements might undergo in clay as opposed to a sandy soil, e.g., presence of carbonates in sand, greatly different surface areas and cation exchange capacities.

The carbonates present in the Plainfield sand (18% wt/wt) that reacted with the $FeCl_3$ or $AlCl_3$ solutions was evidenced by strong effervescence and gas evolution according to the following equations. The overall reaction can be represented by Eq. [3], showing the precipitation of the hydroxy compound; where M represents Fe or Al. There was no visible reaction with the soil on addition of the three basic salts ($CaCl_2$, KCl, NH_4Cl) to the sand. Addition of $FeCl_3$ to montmorillonite produces positively charged ferric dihydroxy cations which are held on exchange positions (7, 23). Aluminum has also been shown to form hydroxy interlayers in montmorillonite (11, 24). Unlike the situation with the sand, the hydroxy complexes are confined to the interlayer region of the montmorillonite. The fensulfothion appears to have interacted with a hydroxy complex of Fe or Al

Fig. 2— **Biological activity of fensulfothion in soil as a function of cation content.**

in both the Plainfield sand and the montmorillonite of the previous study (8) although the environment and probably the nature of these complexes could be expected to be somewhat different.
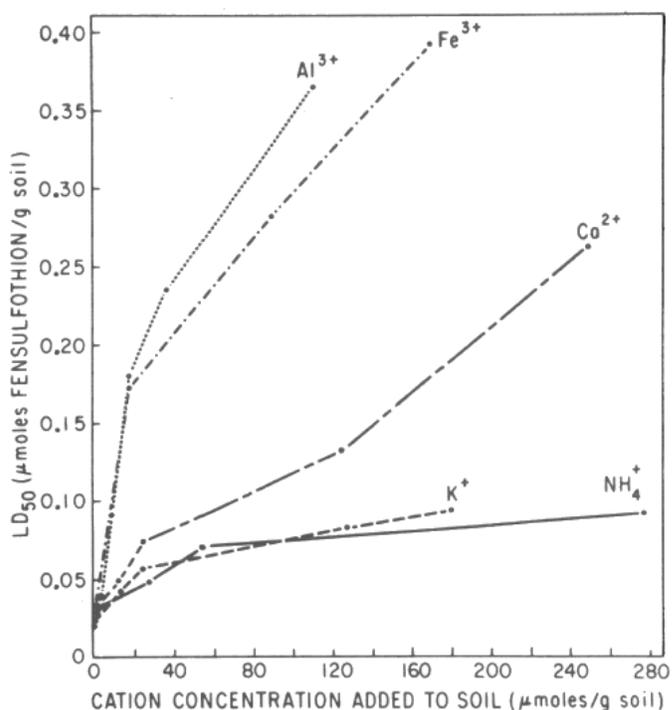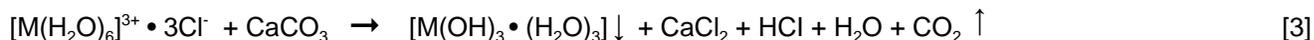
$$[M(H_2O)_6]^{3+} \cdot 3Cl^- \longrightarrow [M(OH)_3 \cdot (H_2O)_3] \downarrow + 3\ HCl \qquad [1]$$

$$CaCO_3 + 2\ HCl \longrightarrow CaCl_2 + H_2O + CO_2 \uparrow \qquad [2]$$

$$[M(H_2O)_6]^{3+} \cdot 3Cl^- + CaCO_3 \longrightarrow [M(OH)_3 \cdot (H_2O)_3] \downarrow + CaCl_2 + HCl + H_2O + CO_2 \uparrow \qquad [3]$$

In the present bioassay study the chloride ion was not washed out of the sand as it was in the earlier fensulfothion-clay studies (8) because the aliquot of salt solution used to supply the required cation also was used to bring the soil mass up to its moisture-holding capacity for the bioassay tests. In a preliminary study a different treatment procedure for applying iron was tested whereby the Cl^- ion was washed out. A given volume of 1N $FeCl_3$ solution was leached through a sand column, followed by several volumes of distilled water to remove excess Cl^- ion. No measurable amount of iron was observed in the effluent during the washing procedure, and in fact the iron complex which formed near the top of the soil column greatly reduced the porosity of the column to further leaching. This resulted in uneven addition of iron to the soil. After drying the soil some of the sand grains had high concentrations of iron associated with them whereas others had a minimal amount (average iron content was 95-100 μmoles/g). Bioassay tests with this washed soil (excess Cl^- removed) indicated that fensulfothion toxicity was significantly less than that observed in the control soil. However, the results using this iron application technique were not reproducible from one batch to the next and, therefore, the direct application technique outlined above was used for all cations in the present study. This uniform application technique produced reproducible results from one batch of soil to the next, as well as allowing a range of cation concentrations to be studied.

In the earlier adsorption study of fensulfothion-cation-montmorillonite systems (8) it was suggested that the interaction between the cation and the fensulfothion molecule occurred with the sulfoxide oxygen atom as is the case with most sulfoxide-cation complexes (4, 5, 16, 38). Recently (6) it has been demonstrated that palladium (Pd^{2+}) complexes with some phosphorodithioate and phosphorothioate insecticides through the P→S group. Zn^{2+} has also been shown to complex with the P→S group of parathion (14). It is possible that fensulfothion, with both P→S and S→O groups might interact with cations through either or both of these groups.

Although there appears to be a close correspondence between the fensulfothion-cation effect on adsorption in montmorillonite and on bioactivity in Plainfield sand, the low cation exchange capacity (CEC) of the Plainfield sand (6.39 meq/100 g) suggests that the predominant interaction in the sand might not be with exchangeable cations. The cations in

both the montmorillonite and the calcareous sand can be divided into two groups: (i) the acidic cations, Fe^{3+} and Al^{3+}, which form hydroxy complexes; and (ii) the basic cations, Ca^{2+}, K^+, and NH_4^+ which exist as simple cations. The CEC of each of the five cation-amended sands was determined. The CEC of the three basic cation-amended samples was within 3% of that of the control sand (6.39 meq/100 g). However, the CEC of the Fe^{3+}- and Al^{3+}-amended sand was 9.71 and 10.86 meq/100 g, respectively, an increase of 52 and 70%, respectively. This significant CEC increase was unexpected since the hydroxy compounds formed with Fe^{3+} and Al^{3+} tend to have a positive charge, if any, or would tend to block normal exchange sites. Perhaps the hydroxy precipitates in the soil created a larger surface area on which some Na^+ ions (in the CEC determination) physically adsorbed, thereby increasing the total Na^+ retention and giving increased CEC values. The CEC values were obtained for a cation-addition level of 100 µmoles/g sand. At this level the sequence of fensulfothion toxicity reduction was Al^{3+}-sand > Fe^{3+}-sand, the same order as the CEC values for the respective systems. pH values (in 0.01M $CaCl_2$) showed that the Al-system was more acidic (4.90) than the Fe-system (5.45), or the original Plainfield sand (6.10). At this point it is impossible to assess the relative importance of pH, CEC, the cationic valence, or the presence of the hydroxy compounds as they affect the fensulfothion toxicity, since these parameters are all interrelated.

In the present study, one can not rule out the possible participation of the Cl^- anion in the cation-fensulfothion interaction in Plainfield sand. It was, however, established in the preliminary bioassay study using the Fe-amended Plainfield sand with the Cl^- anion removed, that there was a significant cation-fensulfothion effect. The greater toxicity reduction of fensulfothion using the current application technique (relative to the column leaching method) is largely attributed to the more uniform distribution of the cation which should provide a more efficient exposure to the fensulfothion molecules throughout the soil mass.

The results of this and the earlier fensulfothion-montmorillonite adsorption study (8) indicate that, in at least some instances, it may be possible to correlate results obtained in model insecticide adsorption studies with bioactivity data. The practical implications of the study in terms of the significance of cations as a factor influencing the biological activity of this class of insecticides in soil cannot be assessed at this stage. However, it is worth noting, in reference to Fig. 2, that a significant toxicity reduction (>2X) occurred at relatively low cation additions of 20 µmoles/g soil for the three basic cations (Ca^{2+}, K^+, NH_4^+), which are commonly used in soil amendments (fertilizers, liming). Further studies are in progress on the effect of cation-amended soil on other groups of insecticides, and also on the exact nature of the cation-soil-insecticide interaction. Other soil insecticides without the P→S and S→O groups are probably less influenced by cation content than fensulfothion. In addition the simplified bioassay procedure adopted will not be representative of the complex interactions which occur in soil under practical conditions.

ACKNOWLEDGMENTS

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