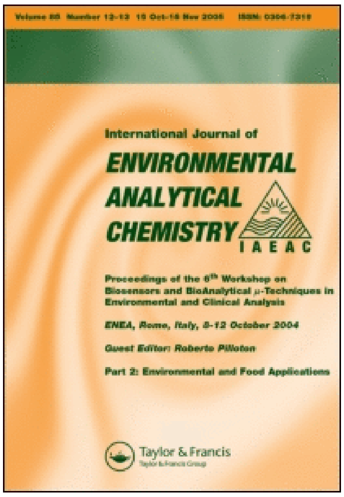

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ORGANIC RESIDUES IN SOILS: MECHANISMS OF RETENTION AND EXTRACTABILITY

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Retention of pesticides and related organic chemicals by the soil is an important process that affects the fate of these chemicals in the environment. Although a number of binding mechanisms have been postulated for the retention of these chemicals in the soil, few experimental methods are available to characterize the specific bonds involved in the retention process. Common indices used to depict soil sorption of pesticides are of limited value to elucidate the bonding mechanisms or bond strengths. This paper discusses the potential of using the solvent extraction procedure to gain an insight on the binding mechanisms. It can be demonstrated that the solvent action during an extraction is specific in removing a portion of the chemical which is presumably held by similar bonds in the soil. Examples of efficient extraction of chemicals held by ion exchange, hydrogen bonding, and metal complexation are given to illustrate this potential.

KEY WORDS: Pesticides, adsorption, binding mechanisms, solvent extraction, atrazine.

INTRODUCTION

Pesticides and related organic chemicals are retained to a greater or lesser extent in the soil. Retention is a major process which affects the volatilization, leaching, degradation, and the eventual fate of pesticides in the environment. Therefore, an understanding of the mechanisms of retention and factors affecting the retention process is important in assessing the environmental impact of pesticides. A number of physical and chemical bonds have been postulated to be the mechanisms and forces involved in the retention process. However, how these bonding mechanisms are actually involved in the retention of pesticides has seldom been elucidated or demonstrated. Few experimental methods are presently available for characterizing and differentiating the various mechanisms or the extent of each mechanism involved in the retention of organic residues in soil.

Retention is defined as the interaction of a chemical with the soil particle surface that results in a restriction or retardation of the mobility of the chemical in the soil solution. Although in this paper we will deal mainly with the retention of organic chemicals by soil particles, the mechanisms discussed are equally applicable to inorganic chemicals. The retention process differs from the transformation process in that the structure of the organic molecule is not altered in retention.

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The retention process may or may not be reversible depending on the energy required and available for the reverse process.

Indices such as the chemical's solubility in water or its distribution between an aqueous phase and an octanol phase (K_{ow}) characterize the adsorptivity of a chemical on the basis of only the properties of the chemical. No consideration is given to the influence of the soil in the adsorption process. These indices can at best be considered as rough indicators of the adsorbability of the chemical. Even though these indices have been shown to be correlated to other more precise indices for certain types of chemicals,[1,2] they are not useful in providing any insights on the mechanism of retention of these chemicals by different soils. For measuring the retention of an organic chemical in soils, the general approach has been to estimate the chemical concentration remaining in the solution following equilibration of the chemical with the soil. The reduction in solution concentration of the chemical after equilibration is taken as a measure of the amount retained by the soil particle surface.

INDICES FOR CHARACTERIZING SOIL RETENTION OF CHEMICALS

A number of indices have commonly been used to indicate the extent of retention of pesticides by soils under batch equilibration conditions. When retention is measured at a single concentration of the chemical, the ratio of the chemical in the adsorbed phase and that remaining in the equilibrating solution is known as the partition or distribution constant, K_D. The usefulness of K_D is based on the assumption that the value of K_D does not vary with the concentration of chemical present in the system. In reality, K_D values derived from single determinations are valid only when the concentration of the chemical in the soil does not vary greatly. Applying the K_D values to a wide range of pesticide concentrations in the soil could lead to erroneous conclusions.

A more useful adsorption constant than K_D is K_F, the Freundlich constant, derived from the Freundlich isotherm equation: $x/m = K_F C^{1/n}$, where x/m is the amount of chemical adsorbed by soil, C is the amount of chemical remaining in the equilibrating solution, and K_F and n are constants. The K_F in the Freundlich equation is derived from a range of chemical concentrations in the soil. Only when $n = 1$ will $K_F = K_D$. If 1/n is less than 1, less chemical will be adsorbed with increasing concentration of the chemical in the soil. Although the Freundlich isotherms have been widely used to characterize soil adsorption of pesticides, the validity of these estimates has not always been established. Our studies[3,4] have shown that degradation of the pesticide during the equilibration process could pose problems in obtaining a realistic estimate of the amount of pesticide actually adsorbed, and variations in experimental conditions could change the so-called constants many fold. However, the most notable shortcoming of this approach for characterizing chemical adsorption is the fact that the Freundlich isotherms shed little light on the mechanism or the strength of the retention bonds.

As for other indices in common use, an adsorption constant (K_{oc}) is often expressed in terms of the organic matter content of the soil, assuming that only the organic matter fraction would interact with and adsorb these organic chemicals. The K_{oc} is derived from dividing the K_D or K_F by the percentage of organic carbon in the soil; therefore, it is still based on the same approach by which the distribution constants are derived. Moreover, there is ample evidence showing that the assumption that only soil organic carbon is involved in the retention process is not generally valid.[5] Soil minerals are known to influence the retention of pesticides in the soil.[6] Thus, it is clear from this discussion that the batch equilibration methods for characterizing soil retention of pesticides are of limited use for elucidating the mechanisms of pesticide retention by soil.

CHARACTERIZING RETENTION BY SOLVENT EXTRACTION APPROACH

If the mechanisms involved in the retention of pesticides in the soil are physical and chemical bonds between the chemical and soil particle surface, it should be possible to characterize the bonding mechanisms from the ease by which these bonds are broken. One may view the action of a solvent in extracting a pesticide from the soil as the breaking of bonds between the pesticide chemical and the soil particle surface. The effectiveness of the solvent can be judged on how readily the solvent can compete with the soil surface in attracting the pesticide molecule. Although the aim of an analytical chemist in developing a solvent extraction procedure for removing pesticides from the soil is mainly to strive for completeness of pesticide recovery from the soil sample, the solvent extraction approach can be used to elucidate the mechanism of retention of pesticides in the soil. As a matter of fact, a major problem confronting an analyst in the development of an effective method for estimating pesticide residues in the soil has been the lack of a systematic approach in developing a procedure for extracting the target chemical from the soil. Development of extraction methods has seldom been linked to how effectively the solvent can break the bonds between the chemical and the soil surface. However, selection of effective solvents for extraction can be facilitated by knowing the nature of bonds that retain the pesticide on the soil particle surface.

The forces and processes participating in the binding of a pesticide on soil range from general to specific in nature, vary from weak to strong in strength, and involve both the molecular and ionic forms of the chemical. These include London-van der Waals forces, hydrogen bonding, protonation, cation and water bridging, cation and anion exchanges, ligand exchange, covalent bonding, and physical trapping, among others. The purpose of this paper is to evaluate the possibility of relating the effectiveness of solvent extraction action to the ability of the solvent in breaking specific bonds. It is readily recognized that solvent actions are not singular, and certain pesticide-soil interactions involve multiple bonds which would require a mixture of solvents or a multi-step extraction procedure to break all the bonds.

SPECIFICITY OF THE SOLVENT ACTION

A large number of solvents have been used for the extraction of a variety of chemicals from the soil. These include water; salt solutions (e.g., 1 or 2 *M* KCl); acids (e.g., HCl) or bases (e.g., KOH); complexing agents such as Na pyrophosphate, oxalate, citrate, EDTA, and DPTA; oxidants or reductants; and numerous organic solvents ranging from the highly polar and water miscible methanol to the totally non-polar hexane. Among the commonly used organic solvents are also ethanol, propanol, acetone, acetonitrile, chloroform, dichloromethane, cyclohexane, and heptane, to name a few. When several types of binding mechanisms are involved in the retention of a pesticide by soil, extraction by a mixture of solvents may be advantageous.

To establish the relationship between solvent action and bond breakage, it will be necessary to demonstrate that pesticides are retained by specific bonds and the solvent action is directed specifically to breaking these bonds. A series of studies were performed to examine the extractability of atrazine residues in variously treated soils.[7] Two soils from Germany were used in this study. The Eschweiler soil (E1 and E2) is a sandy loam-degraded loess; it has a pH of 5.2 and contains 1.35% C, 0.112% N, 12.0% clay, 28.4% silt, and 59.6% sand. The Neuhofen Neu soil (N3 and N4) is a sandy soil; it has a pH of 7.0 and contains 3.02% C, 0.255% N, 8.3% clay, 7.6% silt, and 84.1% sand. The soils were treated with ^{14}C-labeled atrazine (2-chloro-4-(ethylamino-6-(isopropylamino)-*s*-triazine), planted to corn (Zea mays), and incubated under controlled temperature and moisture regime for three months. The atrazine residue remaining in the treated soils was repeatedly extracted with 0.05 *M* $CaCl_2$, 1 *M* KCl, acetone, acetonitrile, methanol, acetone + $CaCl_2$, or methanol + $CaCl_2$ until no significant amount of radioactivity could be removed further by a solvent. For each extraction, a soil:solvent ratio of 1:10 was used. The soil-solvent mixture was equilibrated on a shaker for 30 min; then the extract was separated from the soil by centrifugation and decantation. After removal of the solvent from the extract by evaporation, the ^{14}C radioactivity was measured and the value obtained was corrected for quenching. The amount of radioactivity found in the extract as a percentage of the ^{14}C originally added was calculated. For exhaustive extraction, the procedure was repeated with the same type of solvent until the amount of radioactivity extracted decreased to below 1% of the original level added.

For comparison of solvent efficiency, soil samples were exhaustively extracted either separately with each solvent or sequentially with the solvents in various orders. The amount of radioactivity extracted by each solvent from separate soil samples is shown in Table 1. The data indicate that a particular solvent would only remove a specific portion of the radioactivity remaining in the soil. Once that portion was removed, further extraction by the same solvent would remove no more. This result indicates that solvent actions are specific in breaking certain types of bonds. The efficiency of the solvent action depends on the nature of the bonds broken and the affinity of the chemical for the solvent. In this case, water and salt solutions (0.05 *M* $CaCl_2$ and 1 *M* KCl) were not very effective in removing atrazine residue from the treated soil. The organic solvents were only slightly more effective. However, significant amounts of radioactivity could be removed by the mixture of an aqueous salt solution and a miscible organic solvent, far more than the sum of the amounts removed by the salt solution and the organic solvent

Table 1 Extractability of ^{14}C-residue from ^{14}C-atrazine-treated soils

Solvent	*No. of extraction*	*Soil E1*	*Soil E2*	*Soil N3*	*Soil N4*
0.05 *M* $CaCl_2$	8	6.6	7.4	9.7	9.8
1 *M* KCl	2	8.0	8.9	11.2	11.0
Acetone	8	13.0	18.7	19.3	22.6
Acetonitrile	8	13.1	17.7	20.3	22.0
Methanol	8	26.2	32.2	37.6	41.4
Acetone + $CaCl_2$	8	50.8	59.4	57.7	66.0
Methanol + $CaCl_2$	5	52.6	58.8	59.7	61.2
Sequential-exhaustive[a]	29	60	66	63	67

[a] Sequentially with acetone, acetonitrile, and methanol in different orders followed by acetone + $CaCl_2$ and methanol + $CaCl_2$. Samples were exhaustively extracted by one solvent before extraction by a subsequent solvent. Data are averages of 4 replicates.

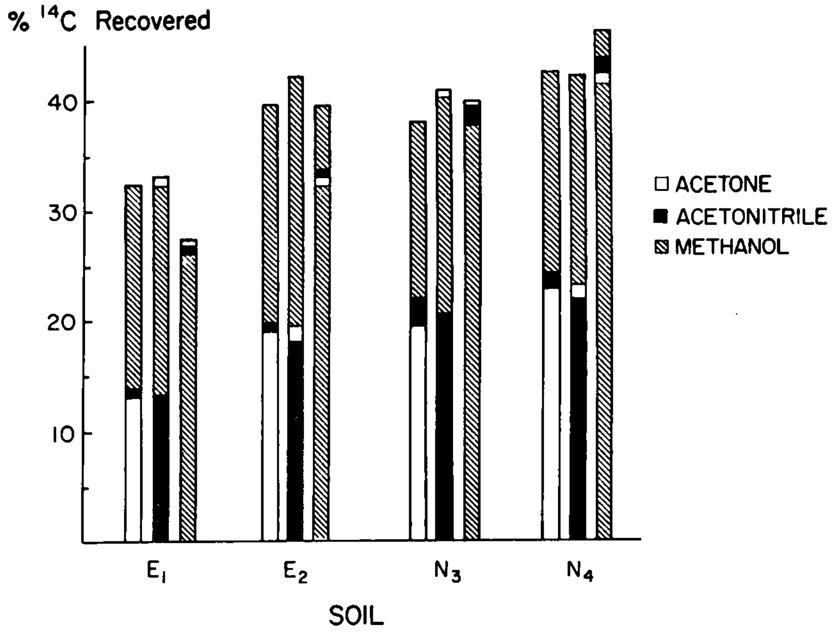

Figure 1 Recovery of ^{14}C-atrazine residue in soils by sequential-exhaustive extraction with various solvents.

separately. It is known that hydrogen bonding between the chemical and soil surface can be reduced when organic solvents are present in an aqueous solution. It appears likely that the atrazine residue found in the extract was bound to the soil particle surface predominantly by hydrogen bonding.

Results of sequential extraction of soils containing atrazine residue are shown in Figure 1. When methanol was used for extraction following exhaustive extraction of the atrazine-treated soil with acetone or acetonitrile, methanol was able to remove a significant amount of atrazine residue. However, when the order of extraction was reversed, little additional atrazine residue could be recovered by either acetone or acetonitrile following an exhaustive extraction by methanol. This means that methanol could remove most of the atrazine residue which acetone or acetonitrile could remove, but not vice versa. On the other hand, even though acetone did not remove a great deal of the atrazine residue following the extraction with methanol, additional residue was extracted by methanol following the acetone extraction, indicating that acetone could be useful in enhancing methanol extraction (see Soils E2 and N4). In all cases, the total amount of atrazine residue extracted was similar regardless of the squence of extractants used. This further supports the observation that the solvent actions are specific in removing a portion of the atrazine residues which are likely held by similar bonds. It should be noted, however, that extraction by the mixed solvent of acetone or methanol with $CaCl_2$ alone was practically as effective as the combined sequential-exhaustive extraction. The radioactivity remaining the soil and not extractable by these solvents is probably that portion which has been incorporated into the soil humus.

RELATIONSHIP BETWEEN SOLVENT ACTION AND BOND BREAKING

In light of the observation that the solvent action during extraction can be considered as bond breaking, we can examine how the effectiveness of various solvent extraction methods can be credited to their ability in breaking specific bonds. Thus the commonly used Freundlich isotherm approach for characterizing adsorption and desorption is no more than an extraction by water, the weakest of the solvents. Few bonds would be broken by water extraction except those that can be readily overcome by the force of mechanical agitation. However, other solvents are more effective in breaking various bonds. For instance, a concentrated salt solution such as 2 *M* KCl can readily remove not only many inorganic cations and anions from soil exchange complexes, but also organic ions such as a number of organic acid type pesticides in their anionic form. Cheng[8,9] has shown that the anionic form of the herbicide picloram (4-amino-3,5,6-trichloropicolinic acid) can be quantitatively extracted by 2 *M* KCl if the soil pH is maintained at 7, with little dissolution of soil organic matter. The frequent use of polar organic solvent and aqueous solution mixtures for pesticide extraction would indicate that hydrogen bonding could be a major force in the pesticide retention process.[10,11,12,13]

The capability of solvents to break bonds can be attested not only for single types of bonds, but also in complex bonding situations. Phenolic compounds such as catechol, phenol, and their chlorinated analogs are very reactive in the soil, as they are readily oxidized to corresponding quinones and polymerized products or complexed with metals. A mixed solvent system consisting of ascorbic acid, citric acid, and acetone has proved to be an effective extractant for removing these phenolic compounds from treated soils.[14] It is reasonable to assume that the effectiveness of this solvent mixture supports the premise that ascorbic acid helps to maintain the soil medium under a reduced condition to minimize oxidation reactions, while citric acid is probably a stronger metal complexer than the phenolic compounds and can help to decomplex the phenolics, and the presence of acetone in the aqueous solution should lower the hydrogen bonding tendencies.

CONCLUSION

A number of examples have been given to illustrate that the effectiveness of certain solvents in extracting specific pesticides can be related to their ability in breaking certain bonds that are responsible for retaining the pesticide chemical on soil particle surfaces. The potential usefulness of the solvent extraction approach toward elucidating the mechanisms of retention of pesticides in the soil has not been extensively explored. Future endeavors in exploring this approach could prove fruitful. Furthermore, an understanding of the bonding mechanisms involved in the retention process can also help to develop more effective extraction procedures for removing pesticides and other trace organic chemicals in the soil.

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