THE BINDING OF ORGANIC CONTAMINANTS TO HUMIN

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ABSTRACT It has been recognized for some time that a significant fraction of most organic contaminants that are introduced into a soil becomes rapidly and irreversibly bound to the humin fraction of naturally-occurring organic matter. The insolubility of humin in essentially any solvent has made the study of these "bound residues" difficult. The ability to fractionate humin into four components (extractable lipids, bound-humic acid, bound lipids, and mineral matter) using the methyl-isobutylketone partitioning procedure is providing new insights into the phenomenon of bound-residue formation and the fate of anthropogenic organic compounds in natural environments. Results will be presented describing the formation of PCB- and PAH-bound residues in humin using ^{14}C-labeled compounds. The distribution of the radioactivity among the components of humin will be compared and contrasted.

KEYWORDS: soil organic matter, humin, bound residues, PCB, PAH

INTRODUCTION

Organic matter in soils can be divided into humic and nonhumic substances. Nonhumic substances are organic compounds that belong to recognizable compound classes such as waxes, fatty acids, carbohydrates, and proteins. Humic substances are brown to black polyelectrolytes formed by the profound alteration of nonhumic substances. They are divided into three operationally-defined fractions based on their solubility as a function of pH: humic acid is soluble in basic solutions but insoluble in acidic solutions, fulvic acid is soluble at any pH value, and humin is insoluble at all pH values [1]. Each of these fractions has been shown to play a significant role in the fate of hydrophobic organic contaminants introduced into a natural system.

Most previous work on the nature of contaminant binding to soil organic matter has utilized ^{14}C-labeled compounds to reconstruct the fate of contaminants introduced into the soil system [2-7]. Essentially all of these studies have stopped at the point of assigning a fraction of the bound-radioactivity to one of the humic fractions of soil organic matter; no studies have been able to definitively characterize the actual nature of bound-residues or the nature of their interaction with a humic material.

The humin fraction of humic substances is usually the predominant organic material in most soils and sediments; humin organic-carbon typically represents more than 50% of the total organic-carbon in a soil [6, 8-10], and a significant fraction of most anthropogenic organic compounds (e.g., pesticides, herbicides, polynuclear aromatic hydrocarbons [PAHs] and polychlorinated biphenyls [PCBs]) bind rapidly, and in many cases, irreversibly, to it [2-6, 8, 11-13]. Yet, despite these compelling reasons for a detailed understanding of the nature of contaminant binding to humin, very little is known about its environmental chemistry probably because its insolubility makes it difficult to characterize by most analytical methods.

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This study utilizes a new technique that not only directly isolates humin but, for the first time, permits the separation of humin's organic components from its inorganic component and then fractionates the organic components into recognized compound classes (lipids, humic acid-like, and a mineral-dominated insoluble residue). This method uses the water-immiscible organic solvent methyl-isobutylketone (MIBK) and an aqueous phase whose pH is varied to isolate and subsequently fractionate humin [8]. The MIBK method thus represents a fundamental advance necessary to study contaminant binding to humin. The goal of this study is to develop a better understanding of how polynuclear aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) bind to soil organic matter, particularly to the humin fraction.

MATERIALS AND METHODS

The carbon-14 labeled polynuclear aromatic hydrocarbons napthalene, phenanthrene, and benzo[*a*]pyrene, and the polychlorinated biphenyls 4,4'-dichlorobiphenyl and 2,2',5,5'-tetrachlorobiphenyl were incubated with three soils of different composition in separate experiments: a sandy soil referred to as the Allivar soil, the Poinsett silt-loam soil, and a clay soil referred to as the Hetland soil. The incubation experiments were run in triplicate to assess the reproducibility of the binding phenomenon.

The organic components of each soil were isolated by a traditional alkaline extraction method [1]. Humin was fractionated into its components using the MIBK method [8].

The radioactivity associated with each fraction was determined using a Beckman LS 6000 SE liquid scintillation counter. In order to eliminate color quenching during detection, the "H#" correction routine provided with the instrument operating software was used. All fractions were counted in triplicate and averaged. Errors associated with the values in the tables which follow are standard deviations among each triplicate incubation.

RESULTS AND DISCUSSION

Contaminant binding to whole soil

Table 1 shows the percent of the applied radioactivity bound to the soils for each contaminant in the study. Incubation of the Allivar soil with each contaminant generally resulted in less radioactivity being bound than with the other two soils. The exceptions to this are the experiments with napthalene which seems to show no difference in binding to each soil. The PAHs (benzo[*a*]pyrene, napthalene, and phenanthrene) also seem to be more readily

TABLE 1. FRACTION OF APPLIED RADIOACTIVITY BOUND TO THE WHOLE SOIL.

% Bound	Allivar Soil	Hetland Soil	Poinsett Silt-loam Soil
2,2',5,5'-tetrachlorobiphenyl	16.6 ± 9.4%	25.3 ± 4.8%	19.2 ± 2.6%
4,4'-dichlorobiphenyl	8.0 ± 0.7%	29.4 ± 5.9%	25.9 ± 6.4%
benzo[*a*]pyrene	29.3 ± 4.2%	54.7 ± 5.7%	42.2 ± 5.2%
napthalene	87.2 ± 3.3%	87.8 ± 3.7%	85.5 ± 3.5%
phenanthrene	17.7 ± 1.4%	*	*

* indicates the incubation and fractionation are being repeated. See text for further details. Errors are standard deviations

bound than the PCBs used in this study.

The data for the binding of phenanthrene to the Hetland and Poinsett silt-loam soils are not included because most of the radioactivity applied to the soils in the incubation experiments could not be accounted for in the mass balance. It appears that the amount applied at the start of the incubation experiments was incorrectly recorded. These experiments are being repeated.

Contaminant distribution among humic fractions

It is clear from the examination of the data in Table 2 that the majority of all radioactivity bound to each soil is associated with the humin fraction; in all cases at least 50% of the bound radioactivity is found associated with humin. The only contaminant that seems to have a significant affinity for any of the other humic fractions is napthalene which seems to bind readily to humic and fulvic acids as well as to humin.

Contaminant distribution among components of humin

Examination of the data in Table 3 shows that the radioactivity bound to humin is distributed primarily between the bound-humic acid and lipid components of humin. What is interesting to note at this point is the amount of radioactivity associated with the insoluble reside component. This material is essentially inorganic; typically it contains about 3% or less organic matter by weight. This represents about 1-2% of the organic matter in humin and less than 0.5% of the total organic matter in the soil. Yet as much as 23% of the radioactivity bound to humin (Table 3) is associated with it. This indicates that this fraction’s chemical characteristics, and how it reacts with these contaminants,

TABLE 2. DISTRIBUTION OF RADIOACTIVITY BOUND TO THE SOIL AMONG THE THREE HUMIC MATERIALS.

	Humic Acid	Fulvic Acid	Humin
Allivar Soil			
2,2’,5,5’-tetrachlorobiphenyl	13.5%	27.5%	59.0%
4,4’-dichlorobiphenyl	14.0%	11.0%	75.0%
benzo[*a*]pyrene	6.6%	0%	93.4%
napthalene	12.8%	28.2%	59.0%
phenanthrene	13.9%	9.6%	76.5%
Hetland Soil			
2,2’,5,5’-tetrachlorobiphenyl	7.7%	8.2%	84.1%
4,4’-dichlorobiphenyl	5.7%	7.0%	87.3%
benzo[*a*]pyrene	6.9%	0.7%	92.4%
napthalene	33.3%	13.5%	53.2%
phenanthrene	*	*	*
Poinsett Silt-loam Soil			
2,2’,5,5’-tetrachlorobiphenyl	13.7%	4.0%	82.3%
4,4’-dichlorobiphenyl	28.9%	11.0%	60.3%
benzo[*a*]pyrene	12.5%	1.4%	86.1%
napthalene	34.5%	15.1%	50.4%
phenanthrene	*	*	*

* indicates the incubation and fractionation are being repeated. See text for further details.

should be studied further.

By advancing our understanding of contaminant binding to humin, it may be possible to predict their fate in natural soils. An understanding of the factors that control the binding and desorption of contaminants to humin will provide information that can be used to better model their transport in natural systems. Ultimately, the results of this study could lead to the development of remediation strategies based on humin's insolubility and its ability to bind organic contaminants. By understanding how and why contaminants bind to humin, it may also be possible to design organic molecules that perform more effectively and have less environmental impact.

CONCLUSIONS

In all cases, more than 50% of the radioactivity bound to each soil is associated with humin for each PAH or PCB studied. When humin is fractionated, it is found that the radioactivity is distributed approximately equally between the bound-humic acid and lipid fractions for each contaminant. There is a small but significant fraction of the total radioactivity that is bound to the organic matter associated with the insoluble residue component of humin. Despite the fact that this organic matter is a very small percentage of the total insoluble residue (typically < 3%), humin or whole soil, it may have a binding capacity for PCBs and PAHs that is greater than the other organic matter fractions present in the soil.

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TABLE 3. DISTRIBUTION OF RADIOACTIVITY BOUND TO THE COMPONENTS OF HUMIN.

	Bound-Humic Acid	Lipids	Insoluble Residue
Allivar Soil			
2,2',5,5'-tetrachlorobiphenyl	40.7%	58.0%	1.3%
4,4'-dichlorobiphenyl	55.2%	39.7%	5.1%
benzo[*a*]pyrene	44.2%	41.0%	14.8%
napthalene	41.6%	51.8%	6.6%
phenanthrene	43.3%	33.6%	23.1%
Hetland Soil			
2,2',5,5'-tetrachlorobiphenyl	47.6%	52.4%	0%
4,4'-dichlorobiphenyl	5.0%	88.9%	6.1%
benzo[*a*]pyrene	31.0%	48.9%	20.1%
napthalene	59.0%	49.0%	2.0%
phenanthrene	*	*	*
Poinsett Silt-loam Soil			
2,2',5,5'-tetrachlorobiphenyl	32.7%	67.3%	0%
4,4'-dichlorobiphenyl	25.3%	65.8%	8.9%
benzo[*a*]pyrene	31.9%	57.3%	11.6%
napthalene	50.0%	44.2%	5.8%
phenanthrene	*	*	*

* indicates the incubation and fractionation are being repeated. See text for further details.

agency's peer and administrative review and, therefore, may not necessarily reflect the views of the agency. No official endorsement should be inferred.

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