

Humus-Pesticide Interaction in Soil

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The soil environment serves as the primary recipient of diverse pollutants, especially pesticides used in agriculture. It comprises abiotic (non-living) and biotic (living) components, hosting a myriad of organisms like nematodes, fungi, bacteria, algae, and earthworms. These organisms interact in a complex web, influencing the fate of applied chemicals. Pesticides tend to persist in the soil for extended periods, necessitating evaluation of their toxicity and stability within this environment. Xenobiotics (foreign substances) in soil undergo transformation through biological and non-biological processes. Ideally, they mineralize into harmless elements, yet often form toxic intermediates. These chemicals and their by-products can move through soil via leaching, bioconcentration, and volatilization. Understanding these processes is crucial for assessing their impact on soil health and ecosystems.

Pesticide interactions with soil greatly influence their environmental fate, impacting degradation, volatilization, and leaching. Xenobiotics engage with soil through adsorption and covalent bonding processes. (Bollag et al. 1992)

The most enduring pesticide complexes form via direct covalent bonds with soil humic matter or clay, especially when pesticides share chemical characteristics with humus components. Adsorption occurs through various mechanisms such as:

1. Van der Waals forces
2. ion exchange
3. hydrogen bonding
4. transfer complexation,
5. hydrophobic interactions.

The strength and nature of adsorption depend on the xenobiotic's structure and chemistry, making it sensitive to environmental changes. Pesticides resembling phenolic compounds can bind covalently to humus, creating stable complexes resistant to degradation.

Over time, adsorbed residues become more stable and resistant to extraction or microbial breakdown. Soil-pesticide interactions are influenced

by factors like soil properties, pesticide characteristics, climate, and agricultural practices.

Soil properties like texture, clay type, organic matter, and pH affect pesticide retention, with organic matter, particularly humic substances (HS), playing a significant role. Studies show HS's reproducible behavior in pesticide interactions, where pesticides favor humic acid (HA) over fulvic acid (FA) and exhibit greater affinity for HS rich in aromatic carbon.

Various characterization techniques like spectroscopy aid in understanding pesticide sorption to HS. These parameters significantly impact pesticide fate models used in regulatory assessments, where spatial variability of these parameters in landscapes holds more importance than the choice of the fate model itself.

Advancing knowledge of HS distribution in soil landscapes can refine exposure assessments reliant on pesticide fate models, potentially improving regulatory assessments and risk evaluations.

Categorization of Pesticides

Pesticides can be categorized as **cationic**, **ionizable** (i.e., weakly acidic, weakly basic, or zwitter ionic), or **non-ionic** (nonpolar) molecules.

- ✓ **Charge transfer and ionic bonding** are mechanisms that specifically apply to the sorption of cationic pesticides by HS.
- ✓ For **non-ionic pesticides**, **hydrophobic bonding** (partitioning) is most common, but other possible mechanisms for sorption by HS include charge-transfer complexes, covalent bonding, hydrogen bonding, and Van der Waals attractions.
- ✓ **Bonding mechanisms** commonly observed for ionizable pesticides and HS include charge-transfer (electron donor-acceptor) complexes, hydrogen bonding, ligand exchange, and Van der Waals attractions.

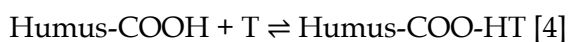
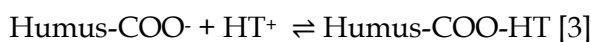
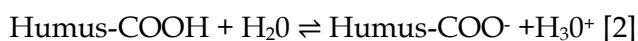
Bonding mechanisms of herbicides with humus

Bonding mechanisms for the adsorption of herbicides by humus include ion exchange, H-

bonding, van der Waals forces, and coordination through an attached metal ion.

- Ion exchange** is of special significance because herbicides adsorbed in this manner are particularly ineffective in controlling weeds; furthermore, the adsorbed molecule may not be easily attacked by soil micro-organisms.
- Cationic herbicides** are also tightly bound to clay - some can be held within the expandable lattice layers of montmorillonite.
- Adsorption through ion exchange** is restricted to those herbicides which either exist as cations (diquat and paraquat) or which become positively charged through protonation (e.g., the s-triazines). Diquat and paraquat, being divalent cations, can react with more than one negatively charged site on soil humic colloids, such as through two COO⁻ ions (illustrated for diquat).

Adsorption of diquat through Ion exchange



T is the s-triazine molecule, HT⁺ the protonated molecule, and H₃O⁺ the hydronium ion.

- Reaction [1] represents the pH-dependent protonation of s-triazines in the soil solution, while
- reaction [2] represents ionization of the humus colloid COOH group.
- Ionic adsorption of the cationic s-triazine molecule, formed by reaction [1], is shown by reaction [3];
- adsorption through protonation on the surface of the organic colloid is shown by reaction [4].

Adsorption of Pesticides on Soils

- Adsorption is an attraction/repulsion phenomenon as a resultant of the interaction between the fields of force emanating from the surface of the adsorbent and the molecules or ions of the adsorbate.

Table 1: Typical bonding mechanism for the adsorption of herbicides by soil humus

	PHENYLCARBAMATES	SUBST UREAS	s- TRIAZINES	PHENOXYALKANOIC ACIDS
VAN DER WAALS	+	+	+	+
H-BONDING	+	+	+	-
LIGAND EXCHANGE	+	+	-	-
SALT LINKAGE	-	-	-	+

- The adsorption of pesticides by soils is a complex process but one of great importance for an understanding of the behaviour, efficacy and fate of pesticides in the soil environment.
- Adsorption processes play a vital role in determining the environmental fate of pesticides and in determining their efficacy for crop protection.
- United States Environmental Protection Agency (USEPA) has proposed guidelines for registration of pesticides requiring adsorption and movement studies in soils because adsorption helps to better understand the judicious use of pesticides.
- It controls the quantity of a pesticide in soil solution which impacts almost all the specific fate processes, including volatilization, bioavailability to flora and fauna, biodegradability, photolysis, hydrolysis, its persistence, mobility, toxicity, transformation and bioaccumulation.

Adsorption of pesticides on soil surfaces is mainly governed by

- Soil properties**
 - amount and nature of organic matter
 - the type and amount of clay minerals
 - CEC and the hydroxide content
 - particle size distribution
 - moisture, pH and ionic strength
- Physical and chemical parameters of the pesticides**

- a. shape, configuration, molecular structure,
 - b. chemical functions, water solubility, polarity, polarizability, charge distribution and
 - c. acid and base nature of the pesticide molecule
- Temperature and
 - other environment conditions (presence of organic solvents and other chemicals like surfactants).

Degradation of pesticides in soil

Degradation of pesticides is an important process in determining the fate of pesticides in soil and water environments. Extraction and chemical analysis, bioassays, oxygen uptake and evolution of carbon dioxide are several methods which have been used in study of degradation of pesticides in soil. In general, conditions that promote microbial activity enhance the rate of loss and those that inhibit the growth of microorganisms reduce the rate.

Biodegradation of pesticides in soils

- Microbial degradation plays an important role in the fate and behaviour of the pesticides in soils.
- Factors affecting the microbial degradation of pesticides in soil include pH, temperature, sorption, soil water content and soil type.
- The effect of temperature on the degradation process was more pronounced than the effect of soil type. Soil microorganisms are able to interact physically and chemically with pesticides and inducing the physical change or the complete change of pesticides.
- Soil microorganisms metabolize pesticides either aerobically or anaerobically and usually microorganisms degrade the pesticides and utilize them as a source of energy and nutrients or use them through co-metabolism.

Leaching of pesticides in soils

- Knowledge of pesticides leaching is important to understand the problems of contamination of natural water and soil environments.
- Pesticides mobility is governed by the interactions of specific physical and chemical properties of soils which determine the

potential bonding mechanism and magnitude of retention to soil.

- Leaching of pesticide in unsaturated soil is largely determined by the physical and chemical properties of both the pesticide and soil.

Effect of organic matter on leaching of pesticides in soils

- a. Dissolved organic matter is able to complex with the pesticides and increases the mobility of pesticides in the soil profile.
- b. It is able to affect the dissolution and facilitated the transport of pesticides.
- c. Therefore, application of certain types of organic fertilizer to some agricultural soils may not be advantageous as far as pesticide leaching is concerned because it may enhance or facilitate pesticide leaching through the soil profile.

Concluding Remarks and Recommendations

- Humic substances may interact with pesticides in different modes, of which adsorption is probably the most important one.
- A major question is the reversibility or irreversibility of the adsorption process, that is, whether the bound residues can be considered definitely inactivated and have become common components incorporated in the humic polymer, or they are only momentarily inactivated in reversibly-bound forms, thus representing a possible source of contamination by a time-delayed release of toxic units.
- Although experimental evidence of at least partial re-mobilization of pesticide residues has been obtained as, for example, for dichloroaniline derivatives of propanil, intact methoxychlor, methyl parathion, dinitroanilines and methabenzthiazuron, the question is still unresolved and needs further research.
- Other modes of interaction between HS and pesticides include catalytic effects of HS in hydrolysis and dealkylation reactions, photosensitization effects in various photo-

degradation reactions and solubilization effects.

- The knowledge of the chemical nature, reactivity and properties of HS, the major materials interacting with pesticides in the soil, is extremely important in determining the mode and extent of the interaction.
- Our understanding of HS and of their multiple modes of interaction with pesticides needs further research by a more extended application of advanced techniques such as NMR, ESR, FT-IR and fluorescence spectroscopies.
- Adsorption of pesticides onto soil HS gives rise to a problem in the analytical, qualitative and quantitative, determination of pesticide residues in soil and water. Thus, it appears necessary to develop new procedures and methods which take into consideration these aspects and may bring a solution.
- Joint interdisciplinary research efforts thus appear necessary for the establishment of predictive measures to face and minimize pesticide pollution problems for soil, water, organisms and the global environment. (Senesi 1992)

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