

# Sorption of Pesticides in Soil and Compost

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## Abstract

A study was carried out on the sorption of the sparingly water-soluble pesticide linuron in various types of soil with different levels of organic matter. The sorption isotherms of the pesticide were obtained in bath-equilibrium experiments and the data were fit to Freundlich and Dual Reactive Domain Models. In general, the sorption was the highest for the soil with greatest content of soil organic matter.

The study also points out the global problem of handling the sewage sludge at wastewater treatment plants. We studied the compost made in Torun's Wastewater Treatment Plant during sludge fermentation. To characterise the compost organic matter UV-Vis and  $^{13}\text{C}$  CP/MAS NMR spectroscopy were used.

Consequences of the compost use in agriculture are also discussed here. Particular attention is given to the changes in the behaviour of pesticides applied to soil in the presence of compost organic substances. The treatment of soils by the compost from sewage sludge may lead to increased retention or removal of hydrophobic compounds like linuron.

**Keywords:** sorption, pesticides, soil analysis, compost

## Introduction

The widespread use of various chemicals in agriculture, especially herbicides, has resulted in growing concern about soil and the whole natural environment [1]. The main problem is that chemicals like pesticides once introduced to soil environments can behave in different ways: (i) existing in an unchanged form for a long time being

sorbed by different soil compartments, (ii) transforming to other compounds, sometimes even more dangerous than the original ones, (iii) leaching from soil and pollute the surface or ground waters [2, 3-6].

It is therefore necessary to carry out studies on the main processes governing the transportation, sorption and mobility of soil contaminants.

Sorption of chemicals by soils has been extensively studied [3-8, 9-11, 12, 13]. There are many models descri-

bing the sorption phenomena of xenobiotics by soil but the Langmuir and Freundlich isotherms remain still the most commonly used adsorption equations. Recently, a Dual Reactive Domain Model (DRDM) for sorption of hydrophobic organic compounds by soils has been developed [14-17]. DRDM includes a linear phase-partitioning component and the single limited-site Langmuir-type isotherm component. It has been extensively discussed elsewhere [14].

The content of Soil Organic Matter (SOM) in soil has the greatest effect on sorption of Hydrophobic Organic Compounds (HOCs). The term SOM is generally used to represent the organic constituents in soils including undecayed plant and animal tissues, their partial decomposition products, and the soil biomass. Thus, this term includes: identifiable, high-molecular-weight organic materials such as polysaccharides and proteins, simpler substances such as sugars, amino acids, and other small molecules and humic substances [18, 19]. Humic substances

make up approximately 85-90% of the total organic carbon in soils [20, 21]. The SOM may range in soils from 0.1% in desert soils to 90% in organic ones.

Sewage sludge is produced during the sewage purification process by wastewater treatment plants. The chemical composition of sludge will vary depending on the properties and origin of the sewage (municipal or industrial) and kind of purification process (mechanical, biological, chemical). Sludge handling is a major problem facing wastewater treatment plants due to the high costs of treatment and disposal. However, sludge stabilization by composting has been used for many years, with wastewater treatment plants in Poland using this method in adjacent fields until 1990 [22]. The compost from municipal or industrial sewage sludge is very rich in nutrients and organic compounds and may be applied especially to poor sandy soils to improve their properties. However because of the complex chemical composition of compost it is very difficult to predict all the consequences of using it. Introduction of the compost obtained from sewage sludge into the soil changes its sorption properties according to the various xenobiotics found in soils.

The objectives of this study were:

- (i) to model sorption of linuron by soil horizons with different amounts of organic carbon;
- (ii) to compare sorption of linuron by soil and by soil amended by compost from sewage sludge.

## Reagents and Instruments

Soil samples (podzolic soil) were collected from the barren area. They were collected from the following depths: 0-15 cm A horizon, 15-30 cm A-Bv horizon, 30-40 cm Bv horizon. Organic matter content was determined as mass loss on combustion at 550°C. The amount of humic and fulvic acid carbon was obtained by 0.1M NaOH extraction and 0.5M H<sub>2</sub>SO<sub>4</sub> precipitation (humic acids) according to simplified Turin's method.

The compost sample was taken from Torun's Wastewater Treatment Plant, where it was prepared from sewage sludge. The sludge was first fermented and then mixed with structural material (mixed wooden cuttings and straw) at a ratio of 1:1. The prepared mixture matured four months. The organic matter content was determined as mass loss on combustion at 550°C. The organic carbon was measured in the TOC analyser Shimadzu TOC-SSM-5000A (Kyoto, Japan). Total nitrogen was obtained according to the Kiehl Dahl method. The dissolved organic carbon was extracted at the solid to water ratio 1:100 and the concentration of carbon was measured using the TOC analyser. The extractants were air dried at room temperature. UV-Vis and <sup>13</sup>C CP/MAS NMR spectra were taken to describe properties and composition of the water extracts of the compost. The UniCam Helios a UV-Vis Spectrometer (Cambridge, UK) and Bruker NMR Spectrometer (Germany) at 75.47MHz were used in this study.

The concentration of linuron in the sorption experiments was measured by high performance liquid chromatography using UV-Vis detector (HP 1050 series)

In this study a C-18 LichroCART column and acetonitrile/water (80/20) were used as the stationary and the mobile phase, respectively. The injection volume was 20 µl, the flow was 1 cm<sup>3</sup>/min and the detection wavelength 250 nm. Deionized water was used and all chemicals were of HPLC analytical grade.

## Experimental Procedures

**Sorption kinetics.** Five grams (air-dried) of soil, passed through a 0.43 mm sieve to obtain better homogeneity, were put together with 40 cm<sup>3</sup> 6.3 mg/dm<sup>3</sup> linuron solution in 0.01M CaCl<sub>2</sub> to 330 cm<sup>3</sup> glass bottles and shaken for various times (up to 12 h). After that the suspensions were centrifuged (25 min, 4000 rpm) and linuron was determined.

**Batch Experiments.** Sorption of linuron by soil was carried out using the batch equilibrium method. Five grams (air-dried) of soil passed through a 0.43 mm sieve and were shaken for 8 h with 40 cm<sup>3</sup> solution of linuron ranging from 0.6 to 25 mg/dm<sup>3</sup>. After this time the suspensions were centrifuged and linuron was determined.

**Sorption modelling.** Two sorption equations were used in this study; Freundlich and Dual Reactive Domain Model (DRDM).

The Freundlich equation is

$$q = K_f \cdot C^n, n < 1 \quad (1)$$

where:  $q$  is the amount of the sorbed chemical in equilibrium,  $C$  stands for the concentration of the chemical in solution,  $K$  and  $n$  are empirical constants,  $K$  is called a sorption coefficient.

The recently developed DRDM includes a linear phase-partitioning component and a single limited-site Langmuir-type isotherm component [14-17]:

$$q = K_d \cdot C + M \cdot \frac{k \cdot C}{1 + k \cdot C} \quad (2)$$

where  $K_d$  is called the partition coefficient,  $M$  is the sorption maximum capacity,  $k$  is the equilibrium constant.

To test the goodness-of-fit the model to the experimental data the residual root mean square error (RMSE) was used. In this study it is defined according to [23] as:

$$RMSE = \left( \frac{SSE}{m - p} \right)^{1/2} \quad (3)$$

In this equation  $m$  stands for the number of observations,  $p$  is the number of parameters in the model and SSE is the residual sum of squares computed with all weights set to unity.

**Calculations.** In all measurements we assumed that independent variable,  $C$  - concentration of chemical in solution, is free of errors. For all calculations we used the Curve Expert 1.37 freeware program. In our study we used weighting by unity.

## Results and Discussion

The parameters describing the physicochemical properties of soil samples studied are collected in Table 1. They differ from each other not only in organic matter content but also in the fractions of humic substances and clay content. In order to obtain sorption equilibrium a kinetic study was performed. The equilibrium exists after about 2-4 hours of shaking for A soil horizon and A-Bv soil horizon. For the Bv horizon the equilibrium conditions were obtained even within 2-4 hours. This may indicate some differences in interactions between linuron and various soils with different organic content [24].

The parameters of the sorption models of linuron in soil are gathered in Table 2.

For the cases studied here K<sub>f</sub> parameter in the Freundlich Model increases when the amount of SOM in soil increases, which is a general rule for hydrophobic chemicals like linuron [2]. The second parameter n varies from 0.69 to 0.97. The goodness-of-fit parameter, RMSE, shows that the Freundlich Model provides the best fit for Bv soil horizon; however, correlation coefficient does not say that. This is probably due to the smaller number of observation points in this case (RMSE value depends on number of observations).

The isotherms obtained for A and A-Bv horizon are almost C type [25], whereas the sorption in Bv horizon displays L - shape. Type C isotherm indicates a constant partition of the solute between the solution and the adsorbent. The type L shape is indicative of a gradual decrease in sites available for sorption as the concentration of the solute in the solution increases. Some authors reported that L - shape isotherms for sorption of substituted phenylureas by humic acids are due to specific interactions through charge transfer, mainly with free radical quinone structures [26].

The DRD Model also describes sorption at good accuracy. The RMSE values are similar to those obtained for the Freundlich model (see the Table 2). This model, in contrast to the Freundlich one, gives some physical meaning of the adjustable parameters. The results in Table 2 show that the partitioning process rather than adsorption (high K<sub>d</sub> value) is dominant for the topsoil (A horizon). Maximum sorption capacity is much smaller here than for Bv soil horizon. The partitioning process is rather weak (small K<sub>d</sub> value) for Bv soil horizon. The third soil sample from A-Bv horizon has the smallest sorption capacity whereas the partition coefficient K<sub>d</sub> takes a value between those for A and Bv horizon. The

Table 1. Physicochemical soil parameters.

	Soil horizons		
	A	A-Bv	Bv
Organic Matter content [%]	6.3	4.0	2.1
Humic Acid carbon content [%]	49.27	21.39	6.20
Fulvic Acid carbon content [%]	42.28	21.06	12.01
pH (KCl)	3.94	4.23	4.46
Ca content [mg/kg]	6.67	8.40	3.60
sand [%]	66.29	66.85	72.23
silt [%]	28.82	26.25	20.30
clay [%]	4.89	6.90	7.47

Table 2. Parameters of the Freundlich and DRD Models.

	Soil horizons		
	A	A-Bv	Bv
<b>Freundlich Model</b>			
K <sub>f</sub> [dm <sup>3</sup> kg <sup>-1</sup> ]	14.31	6.83	2.50
n	0.938	0.968	0.686
r	0.9994	0.9975	0.9822
RMSE	1.544	2.319	1.390
<b>DRD Model</b>			
K <sub>d</sub> [dm <sup>3</sup> kg <sup>-1</sup> ]	12.09	6.20	0.25
M [mg kg <sup>-1</sup> ]	3.764	1.976	24.86
k [dm <sup>3</sup> mg <sup>-1</sup> ]	5.108	15.402	0.066
r	0.9996	0.9989	0.9919
RMSE	1.438	2.370	1.493

equilibrium constant k is much higher in this case than for the two other horizons.

The compost from fermented sewage sludge from Torun's Wastewater Treatment Plant is very rich in organic matter as shown in Table 3.

The UV-Vis analysis of Dissolved Organic Matter (DOM) presented in Table 4 show rather high absorbency at 280 and 472 nm, which corresponds to relatively high amounts of lignin-like structures and the material at the beginning stage of humification. Low A value at 664 nm corresponds to a low amount of highly humified material. However, the studied compost has relatively high amounts of lignin-like structures; the Q<sub>d/6</sub> value, absorbency ratio at 472 to 664 nm, is very close to the value

Table 3. Basic characteristics of compost organic matter and dissolved-in-water compost organic matter.

Sample	Loss in combustion [%]	Humidity [%]	Organic Carbon [%]	Total nitrogen [%]
Compost	45.37	6.89	25.06	1.52
Dissolved organic matter	-	-	3.56	0.044

generally obtained for humic acids, reported to be below 5. The results obtained for dissolved organic matter also show relatively high amounts of the material at the beginning stage of humification.

Table 4. Optical characteristics of the dissolved organic matter (DOM).  $Q_{2/4}$  - absorbency ratio at 280 to 472 nm,  $Q_{2/6}$  - absorbency ratio at 280 to 664 nm,  $Q_{4/6}$  - absorbency ratio at 472 to 664 nm.

Absorbency	value
$A_{664}$	0.0233
$A_{472}$	0.1197
$A_{280}$	2.71
$Q_{2/4}$	22.63
$Q_{2/6}$	116.22
$Q_{4/6}$	5.14

The  $^{13}\text{C}$  CP/MAS NMR spectrum of natural samples may be divided into four spectral areas as follows:  $\delta = 0\text{--}45$  ppm chemical shift range which corresponds to alkyls;  $\text{CH}_2$  and  $\text{CH}_3$  in aliphatic alkanes, fatty acids and waxes,  $\delta = 45\text{--}110$  ppm chemical shift range corresponds to O-alkyls; methoxyl C in lignin, alkyl-amino C, oxygenated C in carbohydrate and di-oxygenated C in cellulose,  $\delta = 110\text{--}160$  ppm chemical shift range - aromatic C, e.g. phenolic C (150-160 ppm),  $\delta = 160\text{--}220$  ppm chemical shift range - carbonyl C, carboxyl groups in aliphatic acids and benzene-carboxylic acids, C in amide and ester structures and C=O groups of quinones. The spectrum is presented in Figure 1 and the shift ranges are gathered in Table 4. The results suggest that the DOM of compost sample is much more rich in alkyl carbon than the aromatic one. The water soluble organic matter from compost is at the beginning stage of humification.

Compost from sewage sludge has a great ability to modify sorption properties of soil, especially with regard to hydrophobic compounds like linuron. Carbon-rich materials provide soluble and insoluble organic matter that may alter pesticide sorption. Additionally, the later evol-

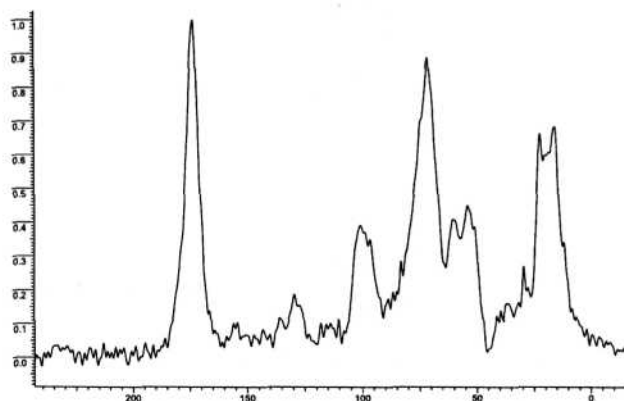


Fig. 1.  $^{13}\text{C}$  CP/MAS NMR spectrum of DOM.

Table 5. The chemical shifts ( $\delta$ ) and percent of the spectrum of DOM attributed to the group of chemicals.

$\delta$ [ppm]	Forms of carbon	Percent of the spectrum
0-45	alkyls	24.75
45-110	O-alkyls	47.23
110-160	aromatics	8.90
160-220	carbonyl	19.13

ution of these materials in soil may lead to important changes as regards their reactivity with hydrophobic chemicals owing to an increase in the degree of polycondensation of the humic-like molecules provided by these materials and the incorporation of a variety of functional groups with different reactivity [27]. The humification of organic macromolecules from compost origin in soil might develop a specific surface area and hence sorption capacity increases. The structural characteristics and properties of the humic-like compounds of the materials like compost from sewage sludge are, moreover, different from native soil humic substances and their evolution could also alter pesticide sorption. Regarding surfactants, owing to their specific properties they are able to increase the apparent solubility of hydrophobic organic compounds, especially at concentrations above their critical micellar concentration [27].

E. Barriuso et. al. [7] studied sorption of three pesticides characterized by various water solubility: dimefuron, atrazine and carbetamide in soil amended with water-soluble organic matter (Dissolved Organic Matter - DOM) from different origin. He carried out the experiments in two ways:

- (i) treating the soil with the DOM before adding the herbicide,
- (ii) (ii) mixing the herbicide and DOM before adding the soil.

The result of the adsorption experiments was a large increase of adsorption for the three herbicides in the presence of dissolved organics from fermented straw (STRF), when the soil was pre-treated with DOM before adding herbicides. In contrast, in all cases, liquid sludge (LS) when added to soil decreased herbicide adsorption. The adsorption of atrazine was favoured when soil was pre-treated with DOM from all studied origins except from LS. In contrast, the adsorption decreased when DOM was pre-incubated with herbicide. The reverse effect was found for carbetamide, which is the most water-soluble of the three herbicides. Tendencies shown by atrazine were observed with dimefuron, but the adsorption modifications were smaller. In general, the DOM - herbicide pre-incubation caused a decrease of the atrazine and dimefuron adsorption [7].

E. Iglesias-Jimenez et. al. [27] carried out a study on sorption of two sparingly water-soluble pesticides: linuron and diazinon in soil and in amended soil with organic materials like city refuse compost (CRC), commercial humic acid (HA), anionic surfactant sodium dodecyl sulphate (SDS) or cationic surfactant tetradecyltrimethylammonium bromide (TDTMA). The soil with organic material was incubated for various periods of

time. In all cases the increase in sorption of linuron and diazinon was found as incubation time increased. Incubation might enhance the colloidal properties of the organic materials introduced to soil, the degree of polymerization, and the incorporation of a variety of functional groups with different reactivities [27]. The exogenous organic matter also enhances the physicochemical properties of soil (water retention, granulation, soil structure) and organic-mineral particle properties in particular [20]. On the basis of the results obtained for the compost studied and for the literature data the behaviour of linuron and other hydrophobic chemicals in amended soil by the compost could be very diverse. Generally, linuron should be retained in amended soil. The effect of dissolved organic matter from compost might be important.

### Conclusions

The sorption of linuron in soil and some aspects of adding exogenous organic material to soils were studied here. The Freundlich and DRD Models describe accurate data. In general, sorption of hydrophobic chemicals like linuron is controlled mainly by soil organic matter. Soil with more organic matter might retain more sparingly water-soluble chemicals.

Sewage sludge stabilisation by composting is currently used often in agriculture. Amendments like compost from sewage sludge might change soil characteristics and its sorption properties in particular. Depending on the origin of natural organic matter it increases or decreases the sorption of pesticides in soil. On the basis of this study the only rule that may be deduced is that more hydrophilic xenobiotics interact with dissolved organic matter stronger than hydrophobic ones.

To conclude: more intensive studies are needed to better recognise the possible interactions between xenobiotics and various forms and fractions of natural (compost or soil origin) organic matter.

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