

Effect of the Nature of Exogenous Organic Matter on Pesticide Sorption by the Soil

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Abstract. A study was carried out on the sorption of two sparingly water-soluble pesticides (diazinon and linuron) by a sandy loam soil modified with different exogenous organic materials (EOMs) containing humic-like substances: city refuse compost (CRC), peat (P), commercial “humic” acid (HA), liquid “humic” acid (LHA), and two (nonhumic) model compounds (surfactants), tetradecyltrimethylammonium bromide (TDTMA) and sodium dodecyl sulphate (SDS), before and after 2- and 8-month incubation periods with the soil. In all cases, the isotherms fitted the Freundlich sorption equation ($x/m = KC_e^n$), generally with r^2 values greater than 0.99. The value of the sorption constant K for the natural soil was 8.81 for diazinon and 2.29 for linuron. These values increased significantly for EOM modified soils with respect to natural soil, with the exception of the samples modified with SDS and LHA, in which cases they decreased, possibly due to the micellar properties of these compounds. Incubation of EOMs with soil increased their sorption capacity: the K_{oc} values were increased proportionally to the incubation time for both pesticides and for all treatments carried out. Accordingly, the sorption capacity of hydrophobic pesticides increases with the degree of evolution in the soil of EOMs with “humic”-type compounds, possibly due, among other causes, to the increase in the EOMs’ colloidal properties and the modifications occurring in the hydrophobic-hydrophilic characteristics of the soil surfaces. The main conclusion is that application to the soil of carbon-rich wastes, especially those with a high degree of maturity, may offer an important strategy for reducing pesticide leaching and for eliminating pesticide residues from soil with the use of anionic surfactants.

Pesticide residues are an important source of pollution both in soils and surface or ground waters. It is therefore necessary to carry out basic studies on the main processes governing the transport of such compounds, their sorption and mobility. The sorption of hydrophobic pesticides is intimately linked to the content of total organic carbon (TOC) of the soil (Chiou 1989; Calvet 1989; Arienzo *et al.* 1994). However, the TOC content (amount) should not be understood as the only criterion for assessing the sorption capacity of a pesticide; both the nature

and the evolution of the organic matter (quality) also play a very important role. In general, retention increases with the degree of humification of soil organic matter (Kozak *et al.* 1983; Gaillardon *et al.* 1983; Payá-Pérez *et al.* 1992), although increases in the solubility of hydrophobic organic compounds due to dissolved organic matter have also been described (Wershaw *et al.* 1969; Chiou *et al.* 1986; Lee and Farmer 1989; Santos-Buelga *et al.* 1992). Thus, these two sorption processes may either prevent or favor pesticide leaching.

There are few references to the effect of exogenous organic matter (EOM) on pesticide sorption, especially with respect to the effect on this process of the nature of the organic matter applied and the evolution of this in the soil. Among the organic materials that may coincide with pesticides in the soil, the most important are solid or liquid organic amendments, such as manure, city refuse compost, peat, sewage sludge, liquid “humic” acids, and surfactants, which are used as adjuvants in pesticide formulations and also are present in irrigation water and sewage sludge. Carbon-rich materials provide soluble and insoluble organic matter that may alter pesticide sorption. Additionally, the later evolution of these materials in the soil may lead to important changes as regards their reactivity with hydrophobic organic compounds owing to an increase in the degree of polycondensation of the “humic” molecules provided by these materials and the incorporation of a variety of functional groups with different reactivities (Martínez-Iñigo and Almendros 1992; Almendros 1995). In particular, the most humified organic matter may develop important specific surface areas and hence have a high sorption capacity. The structural characteristics and properties of the “humic” compounds of some of these materials, such as city refuse compost, are moreover different from native soil humic substances (González-Vila and Martín 1985). Accordingly, their evolution in the soil could alter the pesticide sorption. Regarding surfactants, owing to their specific properties, these are able to increase the apparent solubility of hydrophobic organic compounds, especially at concentrations above their critical micellar concentration (Singer and Tjeerdema 1993; Di Cesari and Smith 1994; Sun *et al.* 1995).

In the present work, we studied the sorption of two sparingly water-soluble pesticides—diazinon and linuron—in a soil amended with different EOMs as a function of their nature and degree of evolution after a 240-day period of incubation. Diazinon (0,0-diethyl-0-2-isopropyl-6-methylpyrimidin-yl phosphorothioate) is an organophosphorus insecticide and linuron

(3(3,4-dichlorophenyl)-1-methoxy-1-methyl-urea) is a herbicide belonging to the urea group. Both compounds are very persistent in the soil (Maier-Bode and Härtel 1981; Sattar 1990) and their residues have been detected in surface and ground waters (Hallberg 1989; Croll 1991).

Materials and Methods

Soil Sample

The soil material used was from the surface horizon (0–10 cm) of a Eutric Cambisol from a northwestern area of the province of Salamanca (Spain). The characteristics of the soil were as follows: pH, 7.5; TOC, 4.5 g kg⁻¹; clay, 18.1%; silt, 15.5%; sand, 64%; and cation-exchange capacity, 9.4 cmol/kg⁻¹. The mineralogical composition of the clay fraction was illite, kaolinite, and montmorillonite.

Pesticides

¹⁴C-labeled diazinon with a specific activity of 610 MBq g⁻¹ and 97% purity was purchased from International Isotope (Munich, Germany). Unlabeled diazinon of technical purity (98%) was supplied by Riedel de Haen (Hannover, Germany). The chemical is a liquid with a water solubility of 40 mg L⁻¹ (Tomlin 1994).

¹⁴C-labeled linuron with a specific activity of 1310 MBq g⁻¹ and 98% purity was obtained from Hoechst AG (Frankfurt, Germany). Unlabeled linuron of technical purity (99%) was supplied by Promochem GmbH (Wesel, Germany). The chemical is a solid with a water solubility of 81 mg L⁻¹ (Tomlin 1994).

Organic Materials

The organic materials employed were the following: city refuse compost (CRC) from the MSW treatment plant at Valdemingómez (Madrid, Spain); *Grün Garant* peat (P) (Deutsche Torfgesellschaft GmbH, Saterland Scharrel, Germany); *Humimag* liquid amendment (LHA) (Braker Laboratories, S.L., Valencia, Spain); commercial humic acid (HA) (Fluka AG, Busch, Switzerland); sodium dodecyl sulphate (SDS) anionic surfactant (Aldrich Chemical Co., Milwaukee, WI, USA), and tetradecyltrimethylammonium bromide (TDTMA) cationic surfactant (Aldrich Chemical Co., Milwaukee, WI, USA).

The TOC contents of the amendments were as follows: 281 g kg⁻¹ for CRC, 347 for P, 221 for LHA, and 470 for HA (on a dry-weight basis).

Preparation of Amended Soils

Soil mixtures (<2 mm fraction) were prepared with amounts of the different EOMs equivalent to a dose of 9.08 mg/C/g soil⁻¹ (20 t/C/ha⁻¹ equivalent-rate), except LHA, which was applied at a dose of 4.54 mg/C/g soil⁻¹, referred to as dry-weight. The mixtures were homogenized in an orbital shaker. Part of the mixture was separated for use with no further treatment while the other part was incubated over 240 days (soil humidity equivalent to 80% of the field capacity at 28°C). An intermediate sample was collected after 60 days of incubation. Table 1 shows the TOC content of the soil amended with the different treatments before and after incubation of the material.

Sorption Experiments

Sorption isotherms were determined using a batch equilibrium method. Five grams of air-dried soil (<2 mm) were mixed with 10 ml of

Table 1. Total Organic Carbon contents (g kg⁻¹) of natural soil and soil treated with organic materials before and after 2- and 8-months incubation periods

	0 Days	60 Days	240 Days
Soil	4.3	3.8	3.8
CRC	12.5	9.8	8.3
P	17.3	17.2	17.3
HA	15.2	15.4	13.6
LHA	6.2	4.5	3.6
TDTMA	16.2	14.6	14.8
SDS	17.7	16.2	16.2

solution containing 5, 10, 15, 20, or 25 µg ml⁻¹ of the pesticide and a solution activity of 100 Bq ml⁻¹ in 30-ml stoppered centrifuge tubes. Samples were equilibrated by shaking for 19 h in a mechanical shaker thermostatted at 20°C; this time had previously been confirmed to be sufficient for equilibrium to be reached. Following equilibration, the suspensions were centrifuged for 30 min at 3300 r.p.m. To determine the pesticide concentration in equilibrium, a 1.0-ml aliquot of clear supernatant solution was mixed in minivials with 4.5 ml of scintillation liquid (Ecoscint A, National Diagnostics, Atlanta, GA, USA), and ¹⁴C activity (disintegrations per minute) was determined on a Beckman LS 1800 scintillation counter (Beckman Instruments Inc., Fullerton, CA, USA). All measurements were carried out in duplicate. The equilibrium solute concentration in the solid phase was calculated as the difference between the initial pesticide concentration and the equilibrium concentration, according to the following equation:

$$x/m = (C_0 - C_e) v/w$$

where x/m is the concentration in soil (µg g⁻¹), C_0 is the initial concentration in solution (µg ml⁻¹), C_e is the final concentration in solution (µg ml⁻¹), v is the solution volume, and w is the weight of the soil.

Results and Discussion

In all cases, the pesticide sorption isotherms fit the Freundlich equation ($x/m = KC_e^n$), generally with r^2 values greater than 0.99. In this equation, the K constant represents the amount sorbed for an equilibrium concentration of 1 µg ml⁻¹ and n reflects the degree to which the pesticide sorption extent is dependent upon concentration. The K and K_{oc} values for the sorption of both pesticides by natural soil and modified soils before and after incubation of the EOMs are shown in Tables 2 and 3. K_{oc} is the K value normalized to 100% total organic carbon ($K_{oc} = 100 K/\%TOC$). Figure 1 shows the sorption isotherms for diazinon and linuron corresponding to nonincubated samples.

The isotherms obtained for diazinon are in general of type C ($n = 1$), according to the classification of Giles *et al.* (1960), although some do display a slight "L" nature at high equilibrium concentrations ($n < 1$). According to Giles *et al.* (1960), type C isotherms indicate a constant partition of the solute between the solution and the adsorbent, and are characteristic of the sorption of hydrophobic organic compounds by the organic matter of soils or sediments.

The isotherms obtained for linuron are in general of type L ($n < 1$), with the exception of that corresponding to TDTMA, which has an n value close to unity (C isotherm). The type L shape is indicative of a gradual decrease in sites available for

Table 2. *K* and *K*_{oc} values for the adsorption of diazinon by natural and EOM-treated soils before and after 2- and 8-months incubation periods

	0 Days		60 Days		240 Days	
	<i>K</i>	<i>K</i> _{oc}	<i>K</i>	<i>K</i> _{oc}	<i>K</i>	<i>K</i> _{oc}
Soil	8.81	2049	8.54	2247	7.93	2087
CRC	10.84	867	10.14	1035	9.28	1118
P	12.09	699	13.00	751	13.34	771
HA	88.31	5810	88.05	5718	92.17	6777
LHA	7.34	1184	7.54	1676	7.55	2097
TDTMA	21.93	1354	22.81	1562	22.23	1502
SDS	0.07		0.33		0.43	

Table 3. *K* and *K*_{oc} values for the adsorption of linuron by natural and EOM-treated soils before and after 2- and 8-months incubation periods

	0 Days		60 Days		240 Days	
	<i>K</i>	<i>K</i> _{oc}	<i>K</i>	<i>K</i> _{oc}	<i>K</i>	<i>K</i> _{oc}
Soil	2.29	533	2.62	689	2.42	637
CRC	4.70	376	4.10	418	5.16	622
P	16.02	926	18.43	1065	18.55	1072
HA	19.70	1296	22.36	1452	22.10	1625
LHA	2.66	429	1.84	409	1.70	472
TDTMA	72.70	4488	69.18	4738	78.55	5307
SDS	0.42		0.35		0.30	

sorption as the concentration of solute in solution increases; that is, the sorption of new molecules would occur with greater difficulty, possibly involving some kind of bond or a specific type of binding mechanism to the humic material. Spurlock (1995) indicated the presence of specific sorbed phase interactions for substituted phenylureas in soils, particularly at low sorbed concentrations. In this sense, as Spurlock and Biggar (1994) reported, relatively polar nonionic compounds like linuron sorb nonlinearly, possibly due to unsuppressed mineral adsorption, particularly at low concentrations relative to solubility. Reports have been made of the existence of a kind of specific interaction of substituted phenylureas and humic acids through charge transfer, mainly with free radical quinone structures (Senesi and Testini 1984; Senesi and Miano 1995). Despite this, it should be noted that the degree of curvature of the isotherms is in fact very small (the *n* value varies between 0.8 and 0.9) and some even display a "C" character at high equilibrium concentrations. Accordingly, in general it is possible to assume a partition mechanism (hydrophobic interaction) to explain the sorption of linuron, at least at higher equilibrium concentrations. Indeed, hydrophobic interaction as a predominant mechanism in the sorption of linuron by humic acid was already described in 1974 by Khan and Marzurkevich (1974).

The value of the sorption constant *K* for the natural soil before incubation was 8.81 for diazinon and 2.29 for linuron. These values varied considerably in the sorption of both pesticides by the modified soils as a function of the EOM added, ranging from 0.07 to 88.31 for diazinon and from 0.42 to 72.70 for linuron (see Tables 2 and 3, respectively). In general, these values increased significantly with respect to natural soil, with the exception of the samples modified with SDS, in which

case they decreased. The values of the *K* constant followed an order of: HA > TDTMA > P > CRC > soil > LHA > SDS for diazinon and TDTMA > HA > P > CRC > LHA > soil > SDS for linuron. These sequences in the order of sorption do not vary appreciably after 2 and 8 months of incubation of the EOMs with the soil.

Regarding the two surfactants employed, TDTMA (a cationic surfactant) is strongly retained by soil colloids, the sorption of the pesticide increasing noticeably. By contrast, SDS (an anionic surfactant) drastically reduces the sorption of diazinon and linuron by the soil. Surfactants are amphiphilic substances characterized by having two different moieties, one polar and the other nonpolar, at opposite ends of a single molecule. The polar moiety is hydrophilic and the nonpolar one is hydrophobic. The nonpolar end is generally a long-chain hydrocarbon, which may be linear, branched, or aromatic (Singer and Tjeerdema 1993). Above the critical micellar concentration (cmc), surfactants form self-aggregates (micelles) with the hydrophobic groups inside and with the hydrophilic groups in contact with the aqueous phase. Such micelles act as colloids and can strongly enhance the apparent solubility of hydrophobic organic compounds, especially anionic and nonionic surfactants, extracting them from soils and sediments (Kile and Chiou 1989; Liu *et al.* 1991; Edwards *et al.* 1991; Singer and Tjeerdema 1993). By contrast, cationic surfactants may be retained by soil colloids via a cation-exchange mechanism, to form structures known as *hemimicelles*, and may strongly enhance pesticide sorption through hydrophobic bonds (Wagner *et al.* 1994). The strong sorbent power of the organic matter derived from quaternary ammonium cations has been reported in studies carried out on the sorption of hydrophobic organic compounds in general (Boyd *et al.* 1988a, 1988b) and hydrophobic pesticides in particular (Hermosín and Cornejo 1992; Sánchez-Camazano and Sánchez-Martín 1994) using clays and soils saturated with these organic cations. According to our findings, TDTMA should increase the sorption of diazinon and linuron with respect to natural soil through hydrophobic interaction with the hydrocarbon chains of hemimicelles. However, the sorption of linuron by TDTMA is much greater than that of diazinon (*K*: 72.70 and 21.93, respectively), indicating a greater affinity of linuron for the TDTMA sorbed by the soil with respect to the TDTMA remaining in solution in the form of micellar structures (under the experimental conditions used here to obtain the isotherms, the dose provided was 74.9 times above the cmc of TDTMA: 100 mg L⁻¹). The fact that TDTMA-modified soil sorbs linuron more strongly than diazinon (despite solubilities that would predict otherwise) may be due to different sorption mechanisms (Spurlock and Biggar 1994). This is consistent with a recent work (Iglesias-Jiménez *et al.* 1996) where the authors compare the sorption of diazinon with that of ethofumesate, a pesticide with a water-solubility of 110 mg L⁻¹, which is closer to that of linuron. At concentrations above the cmc, ethofumesate (more soluble) is sorbed more than diazinon by the TDTMA retained by the soil. These findings point to the importance of the degree of hydrophobicity of the pesticide molecule, of the clay fraction, of the surfactant concentration employed, that is, above or below the cmc, and of the cationic or anionic nature of the surfactant; the anionic surfactant is not—or only slightly—retained by the soil, and hence SDS retains the molecules of both pesticides in solution in the hydrophobic interior of the micelles, thus avoiding their

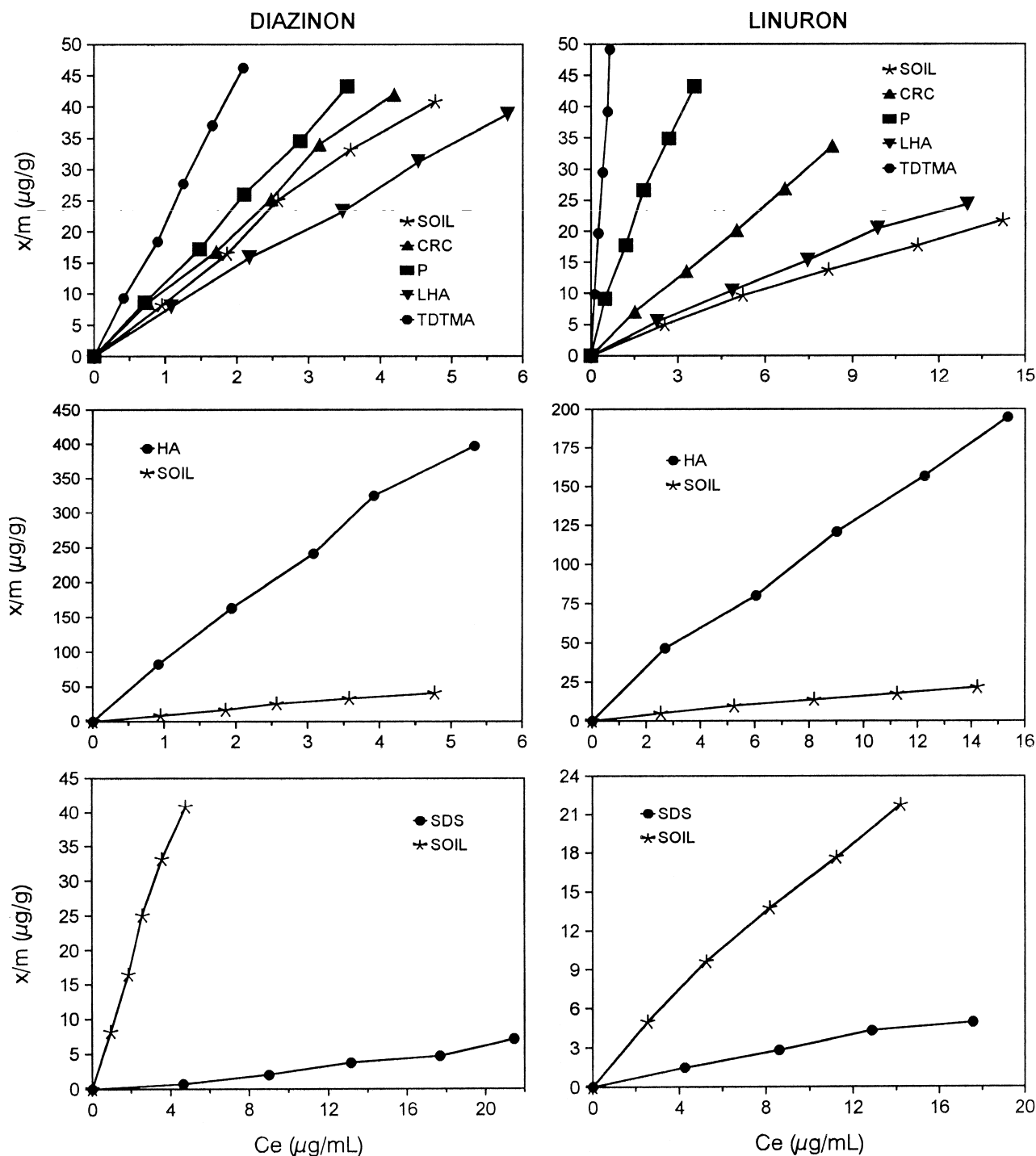


Fig. 1. Adsorption isotherms of diazinon and linuron (nonincubated samples)

sorption by the soil. This kind of behavior persists even after 8 months of incubation (Tables 2 and 3), implying a low rate of microbial degradation of SDS; additionally, the amount of unmineralized compound must be sufficient to maintain a concentration above the cmc.

Application of solid carbon-rich materials with humic-type compounds (HA, P, CRC) to the soil increased the K values, although the degree of sorption varied considerably depending on the nature of the EOM, the same relative order ($HA > P >$

CRC) being maintained for both diazinon and linuron. This increase was very important in the case of solid “humic” acid (HA), where the Freundlich K constant rose from 8.81 to 88.3 for diazinon and from 2.29 to 19.70 for linuron. In the case of CRC and P, despite the relatively high load of carbon incorporated into the soil, the increase in the K constant with respect to the natural soil was lower than that observed in the treatment with HA. These results are in agreement with the notion that the sorption of nonionic pesticides is increased with the degree of

maturity or the “humification” state of the material (Guo *et al.* 1991).

By contrast, the application of liquid “humic” acid (LHA) to the soil decreased K values. Like other liquid amendments, LHA contains one part of “humified” organic matter in solution and another part in suspension. When this substance is added to the soil, one fraction is incorporated into the adsorbent complex and the other remains in soluble form. According to Wershaw’s micellar model (Wershaw 1986), dissolved organic matter may enhance the apparent solubility of hydrophobic organic compounds in a similar way to the mode of action of surfactants under supra-micellar conditions. According to this model, the humic material in solution would be formed from amphiphilic humic polycondensates that would interact to form micelle-like or pseudomicelle structures in solution, with a polar hydrophilic exterior surface and a hydrophobic interior. This micellar configuration displays the property of being able to retain nonpolar molecules inside it through hydrophobic interaction.

Effect of Incubation on the Sorption of Diazinon and Linuron

Incubation of EOM with the soil causes the most labile organic matter to become mineralized, giving rise to a reduction in soil TOC contents. Figure 2 shows the loss of TOC with respect to the nonincubated samples, expressed in percent form. CRC and LHA show the strongest degree of mineralization—34 and 42% after 8 months, respectively (the TOC content in soil treated with LHA is approximately equivalent to that of unamended incubated soil). By contrast, no appreciable changes are seen with P throughout the incubation period, possibly due to its high content in lignin, and HA is only slightly mineralized as from 2 months of incubation, pointing to the high biological stability of the “humic” molecules present in this material.

The reduction observed in the TOC is reflected in a decrease in the K values of some treated soils, this reduction being important in the case of diazinon with CRC and for linuron with LHA (Figure 3). However, the incubation process of EOM in soil increases the sorption capacity of the nonmineralized organic matter in all cases: K_{oc} values were increased for both pesticides and for all treatments carried out; the increases were in general proportional to the incubation time (Figure 4). Accordingly, the nonmineralized organic matter (more evolved and stabilized) shows a greater sorption capacity than fresh organic matter applied to soil. The order of increase in K_{oc} after 8 months was LHA (77%) > CRC (29%) > HA (17%) > TDTMA (11%) > P (9%) for diazinon and CRC (65%) > HA (25%) > TDTMA (18%) > P (16%) > LHA (10%) for linuron.

The slight increase in K_{oc} for both pesticides observed with the cationic surfactant TDTMA (which is slightly mineralized—10%) suggests an increase in the size of the hemimicelles at the adsorbent surface owing to the effect of incubation. This is possibly due to the incorporation of new alkyl-ammonium molecules that would interact with previously sorbed alkyl chains via hydrophobic or van der Waals’ interactions between the alkyl chains themselves (Boyd *et al.* 1988b). This therefore makes the adsorbent surface more hydrophobic.

Incubation of P only slightly increases the K_{oc} values (10% for diazinon and 16% for linuron). Since this material does not undergo any important mineralization during incubation, this

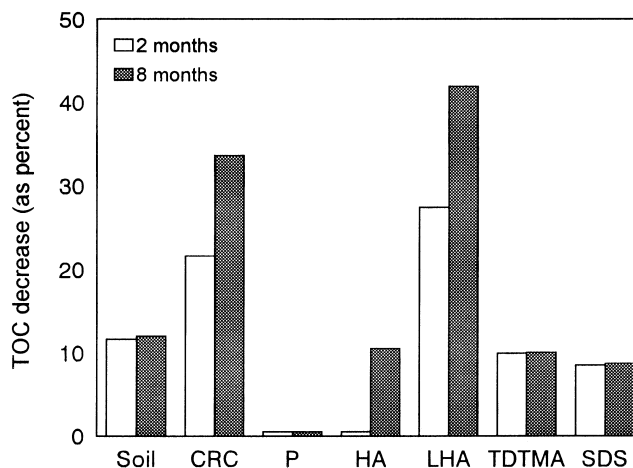


Fig. 2. Decrease in TOC content following incubation of the organic materials with the soil

small increase points to a slight evolution of the humic fraction of the peat toward more polycondensed forms, with greater sorbent power, due to the incorporation of phenolic or prehumic polyphenolic structures during incubation. The increase in the degree of polycondensation and in the specific surface area of humic-like macromolecules could also account for the slight increase in K_{oc} observed with HA treatment for both pesticides. An increase in the degree of polycondensation during soil organic matter humification is an important factor in the retention of organic compounds (Benoit 1994). However, in the case of the peat, the variation in the K_{oc} values after incubation could also be explained in terms of an increase in the reactive surface area of the lignin fraction due to a slight degradation of other associated materials. In this sense, the rapid increase observed in the retention of hydrophobic pesticides by fresh sparingly humified plant residues is due to a progressive increase in the proportion of recalcitrant constituents, such as lignin, with a greater sorption capacity, consecutive to the degradation of more labile materials, especially the hemicellulose and cellulose fractions (Benoit 1994). It is possible both processes (increase in reactivity due to a proportional increase in lignin and polycondensation of carbon-rich prehumic molecules) might contribute together to the increase in the sorption capacity.

The increase in K_{oc} with CRC (65% for linuron and 29% for diazinon) after 8 months was striking. The humic acid-like substances of CRC are highly aliphatic in nature and different in structure than the soil humic compounds, with an elevated presence of *n*-alkanes and fatty acids (González-Vila and Martín 1985). Natural soil humic acids have polyphenolic structures with a greater degree of polycondensation and aromaticity (Andreux 1979; Stevenson 1982); hydrophobic active sites of these include some aliphatic side chains or lipid portions together with aromatic lignin-derived moieties with high carbon contents and bearing a small number of polar groups (Senesi and Miano 1995). Accordingly, the high degree of hydrophobicity of the humic-type compounds of CRC implies that their evolution in the soil and their reactivity with hydrophobic pesticides must be different from that of soil humic compounds; *i.e.*, the application of CRC as an organic amendment could alter soil pesticide sorption properties. An

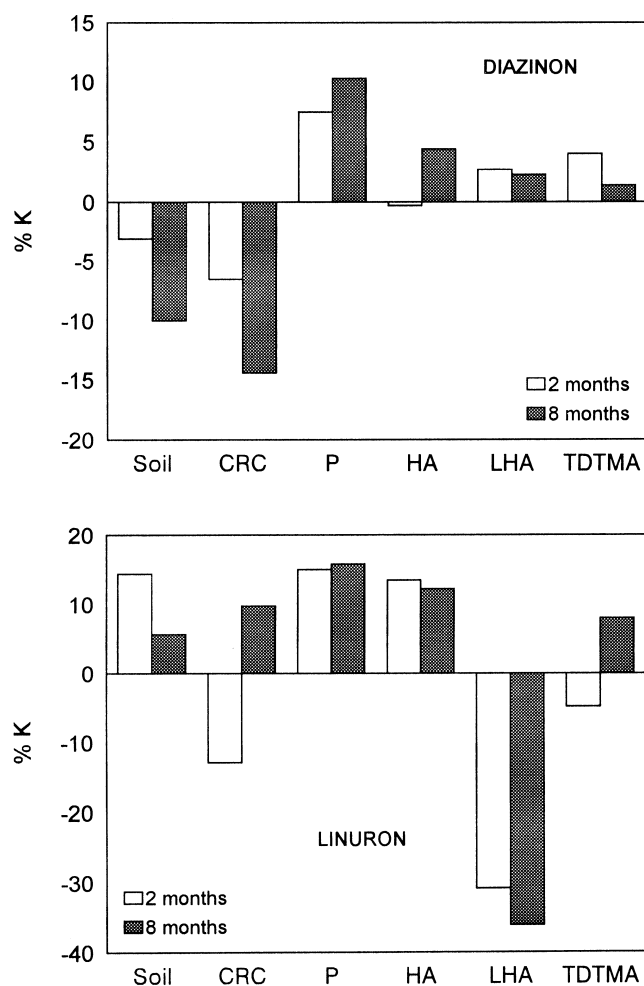


Fig. 3. Variations in the Freundlich K values of diazinon and linuron due to the effect of incubation of organic materials with the soil (expressed in percentage form with respect to nonincubated samples)

increase in the degree of hydrophobicity of the adsorbent surfaces after incubation, owing to the accumulation of aliphatic structures from the CRC, could account for the increase in the K_{oc} for both hydrophobic pesticides. In this sense, González-Vila *et al.* (1985) have reported important increases in the soil of *n*-alkanes and fatty acids bound to the organic-mineral complex following the application of CRC. Nevertheless, K_{oc} values of diazinon and linuron for the CRC-treated soil after incubation were lower than K_{oc} values for nontreated soils; this indicated a higher sorption capacity of the organic matter of natural soil than organic matter from compost.

An important fact is that the increase with time in K_{oc} values, expressed as a percentage, was higher in the case of linuron (more water-soluble than diazinon). This greater sorption capacity for linuron of the organic matter from CRC after incubation could be explained, apart from nonspecific hydrophobic or partitioning interaction, in the sense that the incubation of CRC would elicit an increase in the formation of reactive structures or groups for the formation of more specific bonds with linuron, especially free radical quinone structures (electron-acceptor molecules). Electron donor-acceptor mechanisms and the formation of charge-transfer complexes may be possible

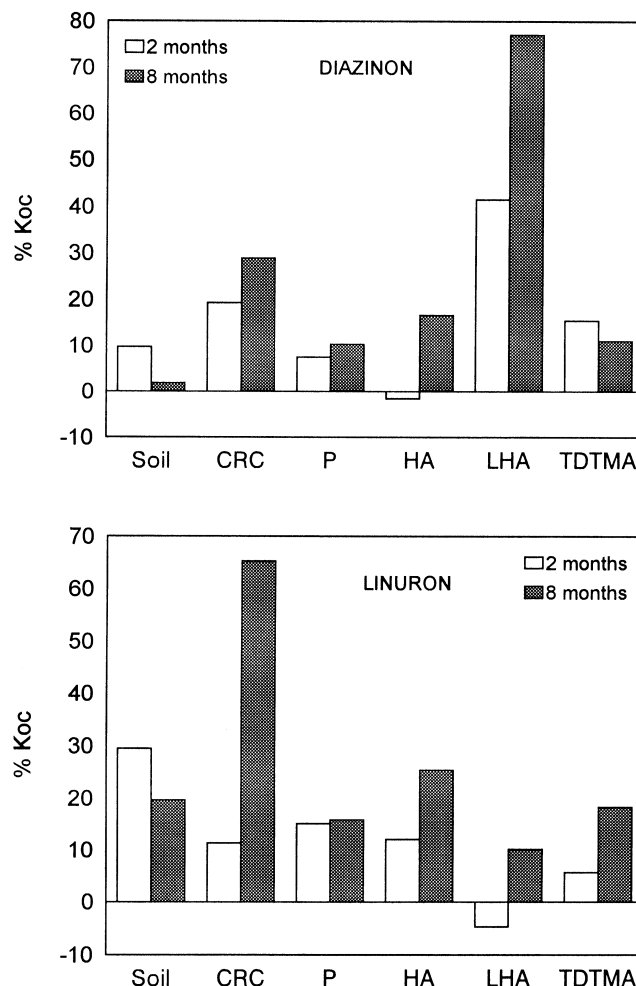


Fig. 4. Variation in K_{oc} values (K 100%/TOC) of diazinon and linuron due to the effect of incubation of organic materials with the soil (expressed in percentage form with respect to nonincubated samples)

between quinone structures and substituted phenylurea herbicides (Senesi and Testini 1984; Senesi 1992; Senesi and Miano 1995). Even Senesi (1990, 1992) suggests that important parallels exist between chemical reactions that these herbicides undergo with soil humic substances (formation of organic donor-acceptor complexes) and their herbicidal action in plants (phytotoxicity), *i.e.*, the photosynthesis inhibition by interference with single-electron transfers in the Hill reaction in chloroplasts. Charge-transfer interactions between substituted phenylureas and humic acid materials in soil were also indicated by Briggs (1969).

Accordingly, the evolution of certain aromatic compounds furnished by CRC toward permanent free radicals, semiquinone-type or quinone-like structures, would occur during incubation, in a way similar to the humification process of soil organic matter (Andreux 1979; Stevenson 1982). Senesi (1989) reported that electron spin resonance spectra of "humic" acid from various organic waste materials as compost and sewage sludge as well as sludge-amended soils indicated the presence of free radical species of the same chemical nature as those of native soil humic acids. The increase in concentration of quinone-like compounds with an increasing degree of humifica-

tion has been reported for some carbon-rich materials, such as peat samples (Senesi 1990). The increase in quinone-like structures would possibly give rise to a greater degree of adsorption of the phenylurea herbicide linuron by specific interaction through a charge-transfer mechanism (Senesi and Miano 1995). The joint occurrence of charge-transfer bonds on well-humified, highly aromatic humic acids, and hydrophobic bonding on low-humified, highly aliphatic humic acids, has been described by Senesi *et al.* (1994) for the herbicide alachlor.

The increase in K_{oc} was noteworthy for LHA with diazinon (77%), the K_{oc} of natural soil being reached. The increase for linuron was 10%. As reported above, in the case of LHA, the original organic matter is strongly mineralized. The important increase in K_{oc} with diazinon could be explained partly in terms of an increase in the degree of hydrophobicity of the adsorbent surface due to the incorporation into the soil of the more hydrophobic "humic" material. In this sense, Barriuso *et al.* (1992) have reported that the interaction of dissolved organic matter with the soil during incubation could modify the hydrophobic-hydrophilic characteristics of soil surfaces, increasing the number of sites available for the less water-soluble pesticides and decreasing the number of sites available for the more hydrophilic compounds. Despite this, the Freundlich K values after 8 months of incubation were in both cases lower than the respective K value for incubated natural soil. Thus, the K value was 7.93 for the sorption of diazinon by soil and 7.55 for the sorption of this pesticide by LHA-treated soil; for linuron, these K values were 2.42 and 1.70, respectively. Therefore, even after 8 months of incubation LHA slightly reduces the sorption capacity of the soil for both pesticides, implying that both of them have a high affinity for the still dissolved, nonmineralized organic matter.

Conclusions

The sorption capacity of hydrophobic pesticides by soils amended with EOMs containing humic-type compounds increases with the degree of evolution of EOM, possibly due to the increase in its colloidal properties, the degree of polymerization, and the incorporation of a variety of functional groups with different reactivities. In particular, the interaction of EOMs with the soil during incubation could modify the hydrophobic-hydrophilic characteristics of soil surfaces.

In sum, the addition of EOM to soils may alter the sorption and mobility of hydrophobic pesticides, the degree of modification depending on the nature, the degree of "humification" (evolution), the residence time of the EOM, and, especially, on the presence of soluble fractions. Additionally, depending on their cationic or anionic nature, the coexistence of surfactants with pesticides in the soil may decrease or increase sorption to a considerable extent.

The results suggest the possibility of using organic materials and surfactants to develop physicochemical methods for preventing the pollution of soils and waters by pesticides, and for eliminating pesticide residues from these media.

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