Biogeochemistry (2011) 106:117–133
DOI 10.1007/s10533-010-9481-y

Pesticide desorption from soils facilitated by dissolved organic matter coming from composts: experimental data and modelling approach

Enrique Barriuso · Maria-Soledad Andrades · Pierre Benoit · Sabine Houot

Received: 29 May 2009 / Accepted: 27 May 2010 / Published online: 16 June 2010

Abstract Dissolved organic matter (DOM) interaction with pesticides was examined studying the ability of DOM to desorb 8 pesticides previously sorbed to soil. DOM was originating from municipal waste composts at two maturity degrees, recovered at 20°C and by hot-pressurised subcritical water. Pesticide desorption depended on their previous sorption on soil. When sorption was low ($K_{OC} \leq 50$, sulcotrione, metalaxyl), water was more efficient than DOM for desorption. On the contrary, when sorption was high ($K_{OC} \geq 2000$, trifluraline), little effect of DOM was observed. For the moderately sorbed pesticides, DOM favoured pesticide desorption compared to water. For the lowest sorbed pesticides ($K_{OC} \leq 100$), hysteresis was increased with larger proportions of DOM extracted with subcritical-water. Dissolved organic matter extracted from fresh-immature compost had larger capacity to mobilize the sorbed pesticides than the DOM from the mature compost. The pesticide desorption resulted from the positive and competitive interactions between pesticide, DOM and soil surfaces. These interactions were modelled considering separate partitioning coefficients. A general equation allowed the deduction of specific coefficients describing interactions in solution between pesticides and the non-sorbed fraction of DOM remaining in solution. This fraction was supposed to contain the most hydrophilic fraction of DOM and was able to interact with the most polar pesticide (amitrol). When pesticide hydrophobicity increased, the partitioning between pesticide and DOM decreased. Modelling the three-phase system (liquid, DOM and solid phases) pointed out that the solid phase played the most important role on pesticide behaviour through the sorption process of DOM and pesticides.

Keywords Desorption · Dissolved organic carbon · Compost · Herbicide · Pesticide · Sorption

Introduction

Soil organic matter drives pesticide behaviour in soils mainly through retention process. Thus, all practices modifying soil organic matter could modify the fate of pesticides in soils (Bellin et al. 1990; Barriuso et al. 1997; Businelli 1997; Celis et al. 1998a). The composting of municipal wastes (biowastes, green wastes and sewage sludges) produces organic amendments useable in agriculture, recycling organic matter to maintain soil organic matter and improving soil fertility and soil resistance to erosion (Houot et al. 2002; Annabi et al. 2007). The composts issued of

---

E. Barriuso (✉) · P. Benoit · S. Houot
INRA (Institut National de la Recherche Agronomique)-AgroParisTech, UMR 1091, Environnement et Grandes Cultures, 78850 Thiverval-Grignon, France
e-mail: barriuso@grignon.inra.fr

M.-S. Andrades
Universidad de La Rioja, 26006 Logroño, Spain

urban organic biodegradable wastes are often the only source of organic matter in suburban areas.

Compost application modifies both pesticide sorption and degradation in soils, depending on the pesticide nature, the maturity of the applied composts and the amounts added (Barriuso et al. 1997). Most often, only total organic matter content is considered when studying the effect of compost application on pesticide behaviour, and the nature of the organic constituents is poorly considered. Nevertheless, the origin of the composted materials and the maturity degree have a large influence on compost behaviour in soils, on their effects on soil properties and their capacity to interact with pollutants (Hartlieb et al. 2001).

A part of compost organic matter can easily become water soluble, either directly through leaching process, or indirectly after microbial degradation (Gigliotti et al. 2002). The dissolved organic matter (DOM) concentration has been proposed as a parameter for compost maturity characterisation (Zmora-Nahum et al. 2005). The DOM from composts is a complex mixture of molecules with different compositions and molecular sizes (Gigliotti et al. 2002). DOM is composed of organic colloids maintained in solution in dispersed state because of their high surface charge. Different DOM structural models proposed in the literature have pointed out the relationship between the organic nature, the conformational organisation, such as macromolecules or pseudomicelle structures (Pignatello 1998; Clapp and Hayes 1999). The DOM has many ecological functions (Zsolnay 2003). Its reactivity can be very high, either biologically by activation of the soil microorganisms (Marschner and Kalbitz 2003) or physico-chemically by favouring the pollutant desorption and leaching (Jardine et al. 1989; Zhou and Wong 2001; Ertunç et al. 2002).

Due to its water-solubility or dispersed colloidal state, the DOM can be mobile in the soil profile, contributing to pesticide leaching in case of DOM-pesticides interactions (Worrall et al. 1999; Chantigny 2003). These interactions can directly occur in solution between DOM and the pesticide fraction present in the mobile soil solution, or indirectly through competitive sorption of DOM facilitating the pesticide desorption (Barriuso et al. 1992; Celis et al. 1998a). The DOM conformation directly acts on the interaction with chemicals in solution through the localisation of functional groups and the hydrophobic/hydrophilic domains at the colloidal surface or through the development of a colloidal microporosity (Pignatello 1998; Pan et al. 2008).

Various techniques are used to recover water extractable organic matter (Zsolnay 2003). Leaching or extraction with water is currently used to recover DOM fraction from solid materials. Other more drastic techniques using hot water recover large proportion of DOM. Recently sub-critical hot-pressurised water was used to extract dissolved and colloidal materials from composts (Dur et al. 2006). In all cases, the recovered materials are water-soluble although their real significance in soils remained to be studied in field conditions.

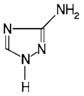
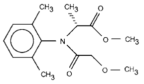
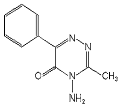
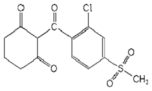
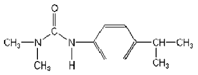
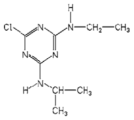
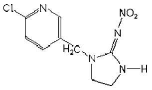
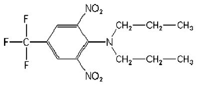
The aim of this work was to study the effect of compost DOM on sorption–desorption processes of different pesticides in soil. The DOM reactivity was characterized by the capacity to desorb different pesticides previously sorbed on soil. Then, sorption parameters used for risk assessment of pesticide mobility were calculated in presence of DOM and compared to the classical values obtained in only water. Two main factors were studied, (i) the maturity degree of the compost by working with a fresh compost and the same compost after 6 months of maturation, and (ii) the yields of DOM recovery when hot subcritical water was used for extraction. Eight pesticides were chosen covering a large variety of chemical structures and properties. A modelling approach considering separately the pesticide interactions between the different solid, liquid and colloidal-DOM phases is proposed to estimate the specific partitioning coefficients between DOM and pesticides.

Materials and methods

Pesticides

Eight pesticides were selected in relation to their chemical structures and physico-chemical properties (Table 1). Six pesticides were non-ionic in most environmental conditions: metalaxyl, metamitron, isoproturon, atrazine, imidacloprid, and trifluralin; two were weak acid or base: sulcotrione ($pK_a = 3.13$) and amitrole ($pK_a = 4.14$), respectively. The pesticide water-solubility varied from 0.18 mg l^{-1} to 280 g l^{-1}, and the octanol–water partition coefficient ($\log K_{ow}$)

Table 1 Characteristics of selected pesticides

Pesticide	Chemical name	Chemical structure	Water solubility[a] (mg l^{-1})	log K_{ow}[a]	Specific activity[b] (MBq $mmol^{-1}$)
Amitrole	1H-1,2,4-[^{14}C]triazol-3-amine		264,000	−0.97	68.7
Metalaxyl	Methyl *N*-(2,6-dimethyl-[^{14}C]phenyl)-*N*-(methosyacethyl)-DL-alaninate		7,100	1.65	143.7
Metamitron	4-Amino-3-methyl-6-[^{14}C]phenyl-1,2,4-triazin-5(4H)-one		1,700	0.83	184.1
Sulcotrione	2-[2-Chloro-4-(methylsulfonyl)[^{14}C]benzoyl]-1,3-cyclohexanedione		165	0.17	145.5
Isoproturon	*N*,*N*-dimethyl-*N*′[4-(1-methylethyl)[^{14}C]phenyl]urea		70	2.50	199.6
Atrazine	6-Chloro-*N*-ethyl-*N*′-(1-methylethyl)-1,3,5-[^{14}C]triazine-2,4-diamine		33	2.17	138.6
Imidacloprid	1-[(6-Chloro-3-[^{14}C]pyridinyl)methyl]-*N*-nitro-2-imidazolidinimine		510	0.57	327.1
Trifluralin	2,6-Dinitro-*N*,*N*-dipropyl-4(trifluoromethyl)-[^{14}C]benzenamine		0.32	4.83	347.5

[a] Data from Pesticide Properties Database (FOOTPRINT 2009)

[b] Origin of labelled ^{14}C-pesticides: Life Science Amersham (Little Chalfont, England) (amitrole, isoproturon and trifluralin), Sigma-Aldrich (Saint Louis, Missouri, USA) (atrazine), International Isotope (Munchen, Germany) (imidacloprid and metamitron), Novartis (Basel, Switzerland) (metalaxyl), and Izopot (Budapest, Hungary) (sulcotrione)

from −0.97 to 4.83. All pesticides were uniformly ^{14}C-labelled in the ring (radio-purity >95%). Non-labelled analytical standards were used to prepare pesticide solutions in water $CaCl_2$ (0.01 M) by isotopic dilution to reach concentration of 1 mg l^{-1} for each pesticide (0.1 mg l^{-1} for trifluralin), with radioactivity concentrations between 666 and 1036 kBq l^{-1}.

Composts

The composts were obtained from initial mixtures of green wastes and sewage sludge composted on an industrial plant. They were sampled during the fermentation phase after 1 month of composting (fresh immature compost) and during the maturation phase after 6 months of composting (mature composts). The green wastes came from municipal and private gardens, and sewage sludge from an urban area, recovered after dehydratation. Composting was conducted as follow: 6 weeks of indoor fermentation phase under enforced aeration, windrow screening at 40 mm then outdoor maturation up to 6 months. Compost samples were air dried, sieved at 10 mm then ground to 1 mm.

Soils

Soils were sampled in an experimental field located at Feucherolles, near Paris (France), initiated in 1998 to study the effects of different composts used in agronomic conditions. The soil is a Typic Hapludalf (Soil Taxonomy) developed on loess deposits, with an average content (g kg^{-1}) of 150, 783 and 67 of clay, silt and sand, respectively. The CEC was 9.4 $cmol^{+}$ kg^{-1} and pH (1:1 soil:water ratio) was 6.9. The ploughed layer (0–28 cm) was sampled in two plots: a control non-amended plot and an amended plot having received three times the mature compost since 1998 (every compost application was at an equivalent dose of 4 t C ha^{-1}). Soil samples were air-dried and sieved at 2 mm. Their organic C content was (g kg^{-1}) 10.6 and 12.8 for non-amended and amended soils, respectively.

DOM extraction from soils and composts

The reference water-extraction was done by rotary shaking at 20 ± 2°C during 24 h of 2 g dry matter of immature and mature composts or 50 g of non-amended and amended soils in 300 ml of MilliQ water (Millipore); water-extracts were then recovered by centrifugation at 1000×*g* for 10 min (Sorval RC5B centrifuge). Subcritical hot-pressurised water extraction of immature compost was done at 50, 125 and 175°C with a Dionex Accelerated Solvent Extractor (ASE 200). High pressure (107 Pa) allowed water to be maintained at liquid state when temperature was higher than boiling temperature. One gram (dry matter) of ground immature compost added to 25 g of calcinated sand were introduced in the extraction cells and were extracted at the different temperatures during two consecutive cycles of 20 min; the extracts were then filtered at 1 μm (Whatmann CF/C). All extractions were done in triplicate, then the extracts were pooled and organic C content was measured with a Shimadzu TOC-5050 analyzer. The DOM extracts were readily used or stored for only a few days at 4°C before sorption–desorption experiments.

Pesticide sorption and desorption studies

Pesticide sorption was done on non-amended soil using the batch equilibration procedure in 25 ml Corex glass centrifuge tubes with Teflon caps. Six grams of non-amended soil were dispersed in 10 ml of each water–$CaCl_2$ pesticide solution, shaken for 24 h at 20 ± 2°C, and then centrifuged at 1000×*g* for 30 min. The pesticide concentration was determined in the supernatants by liquid scintillation counting—LSC (Packard TRI CARB 2100 TR). The amount of sorbed pesticide was determined from the difference between the radioactivity measured in the supernatants and the initial pesticide water solution. All sorption experiments were run in duplicate. Sorption distribution coefficient (K_d, in l kg^{-1} dry soil) was calculated for each pesticide as:

$$K_d = C_s/C_e \tag{1}$$

where C_s (mg kg^{-1}) is the amount of pesticide sorbed corresponding to the solution concentration at equilibrium C_e (mg l^{-1}). When normalised by the organic C content (C_{org}, in mg C kg^{-1} of dry soil), this sorption coefficient gives the distribution coefficient K_{OC} (in l kg^{-1} C):

$$K_{OC} = K_d\ 1000/C_{org} \tag{2}$$

Pesticide desorption was measured after sorption by removing 6 ml of the sorption-supernatant replaced by 6 ml of MilliQ water or different DOM extracts coming from non-amended and amended soils and immature and mature composts extracted at 20°C, and from immature compost extracted at 50, 125 and 175°C. After shaking at 20 ± 2°C for 24 h, the suspensions were centrifuged and pesticide concentration determined in the supernatant by LSC. This desorption procedure was repeated five times. At each desorption step, the amounts of desorbed pesticide and of pesticide remaining sorbed were calculated. All desorption experiments were run in duplicate. Desorption isotherms were fitted to the Freundlich logarithmic equation:

$$\log C_S = \log K_F + n \log C_e \tag{3}$$

and the empirical Freundlich coefficients K_F and n were calculated.

In parallel, DOM sorption on non-amended soil was measured following similar procedure that described above for pesticides, but using DOM extracts instead of pesticide solutions. A blank was done in the same conditions using only water. After 24 h shacking and centrifugation, the organic C content in the supernatant was measured and the organic C sorbed was calculated from the difference of organic C concentration in the extract before and after sorption experiment. The dissolved organic C extracted from the non-amended soil and measured in the blank was systematically deducted. A sorption distribution coefficient for dissolved organic C (K_{DOM}) was calculated as:

$$K_{DOM} = C_{SOC}/C_{DOC} \tag{4}$$

where C_{SOC} (kg C kg^{-1} soil) is the amount of sorbed organic C on soil and C_{DOC} (kg C l^{-1}) is the concentration of dissolved organic C remaining in solution.

Description of sorption–desorption model

The measured desorption data result of multiple pesticide sorption–desorption interactions involving surfaces of solid constituents and dissolved organic constituents. Schematically, the desorption process can be considered as the resultant of competition between interactions at soil/solution interface, responsible for pesticide sorption, and interactions of pesticides in solution with the soluble materials (Fig. 1). Our approach was adapted from previous published works (Rav-Acha and Rebhun 1992; Celis et al. 1998b; Lee and Kuo 1999). In the studied case, when DOM is used for desorption, a part of DOM is sorbed, thus, it is necessary to consider the modification of soil/liquid interface caused by the DOM sorption. All these interactions can be described by the corresponding partial equilibriums. For simplification, only the system at equilibrium reached during the first desorption step was considered. We have assumed that the interactions defined in the Fig. 1 can be described by linear distribution coefficients. In these conditions, the desorbed pesticide present in the soil solution after the first desorption can be described by an apparent sorption/desorption distribution coefficient K_{des} (in l kg^{-1} soil) which is measured in the presence of the different DOM and which is calculated as following:

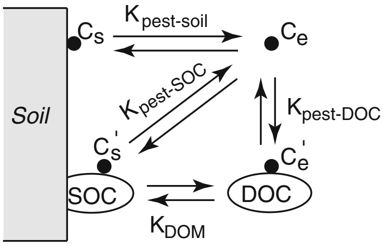


Fig. 1 Schematic representation of the separated interactions between pesticide, DOM and solid phases with identification of the corresponding partitioning coefficients (adapted from Celis et al. 1998b)

$$K_{des} = \frac{\text{Pesticide remaining sorbed (mg kg}^{-1}\text{ soil)}}{\text{Total pesticide in solution (mg l}^{-1}\text{)}} \tag{5}$$

Considering the model described in Fig. 1, K_{des} can be expressed as:

$$K_{des} = \frac{C_S + C_S' \cdot C_{SOC}}{C_e + C_e' \cdot C_{DOC}} \tag{6}$$

were C_S (mg kg^{-1} soil) is the amount of pesticide remaining sorbed on soil after the first desorption, C_S' (mg kg^{-1} C) is the amount of pesticide sorbed on DOM sorbed on soil (SOC), C_{SOC} (kg C kg^{-1} soil) is the amount of DOM sorbed on soil, C_e (mg l^{-1}) is the concentration of free-pesticide in solution, C_S' (mg kg^{-1} C) is the amount of pesticide associated to DOM remaining in solution (DOC), and C_{DOC} (kg C l^{-1}) is the concentration of DOM remaining in solution.

The different equilibria of Fig. 1 can be described by the following partial distribution coefficients:

$$K_{pest-soil} = \frac{C_S}{C_e} \tag{7}$$

corresponding to the sorption/desorption of the free pesticide in solution on soil surface, which corresponds to K_{des} when desorption was run with water, without DOM;

$$K_{pest-SOC} = \frac{C_S'}{C_e} \tag{8}$$

corresponding to the sorption of free pesticide in solution on sorbed DOM (SOC);

$$K_{pest-DOC} = \frac{C_e'}{C_e} \tag{9}$$

corresponding to the association of free-pesticide in solution with DOM remaining in solution, non-sorbed to the soil.

Thus K_{des} can be written as:

$$K_{des} = \frac{C_s + C_e \cdot K_{pest-SOC} \cdot C_{SOC}}{C_e + C_e K_{pest-DOC} \cdot C_{DOC}} = \frac{K_{pest-soil} + K_{pest-SOC} \cdot C_{SOC}}{1 + K_{pest-DOC} \cdot C_{DOC}}$$

hence:

$$K_{des} = \frac{K_{pest-soil} + K_{pest-SOC} \cdot K_{DOM} \cdot C_{DOC}}{1 + K_{pest-DOC} \cdot C_{DOC}} \tag{10}$$

This equation is similar to that proposed by Rav-Acha and Rebhun (1992), Celis et al. (1998b) or Lee and Kuo (1999) to describe pesticide or PAH sorption by clays or soils in presence of DOM coming from humic acids or liquid sewage sludge.

Using the Eq. 10, it is possible to estimate the value of $K_{pest-DOC}$ characterizing the interaction in solution between the DOM remaining in solution and the pesticides:

$$K_{pest-DOC} = \frac{K_{pest-soil} - K_{des} + K_{pest-SOC} \cdot C_{SOC}}{K_{des} \cdot C_{DOC}} \tag{11}$$

substituting C_{soc} by $K_{DOM}C_{DOC}$:

$$K_{pest-DOC} = \frac{K_{pest-soil}}{K_{des} \cdot C_{DOC}} - \frac{1}{C_{DOC}} + \frac{K_{pest-SOC} \cdot K_{DOM}}{K_{des}}$$

and reorganizing:

$$K_{pest-DOC} = K_{pest-SOC} \cdot \frac{K_{DOC}}{K_{des}} + \frac{1}{C_{DOC}} \cdot \left(\frac{K_{pest-soil}}{K_{des}} - 1\right) \tag{12}$$

This equation allows estimating $K_{pest-DOC}$ assuming a value of $K_{pest-SOC}$.

Results and discussion

Extractability and properties of dissolved organic matter

The proportion of organic C extracted at 20°C represented 0.6 and 0.8% of total soil organic C in non-amended and amended soils, respectively (Table 2). A larger proportion of total organic C was extracted in composts; this proportion decreased with compost maturation from 7.5 to 4% of total organic C in immature and mature composts, respectively (Table 2). Such decrease of water-soluble materials during composting corresponded to the biodegradation of labile organic fraction during composting (Liang et al. 1996; Grigatti et al. 2004). Dignac et al. (2005) examined the chemical nature of water extracts of composts using pyrolysis—GC–MS. They found that water extracts from the immature compost were formed by relatively more N-containing compounds, with an acetamide peak larger than in the water extracts from the mature compost. Acetamide is a tracer of non-degraded bacterial materials (peptidoglycanes) (Dignac et al. 2005). The chemical characteristics of water extracts quickly change during composting. Thus, more protein, phenolic and carboxylic C, have been detected in water extracts from composted materials than from the initial non-composted substrates that contain more carbohydrate C (Liang et al. 1996).

The increase of temperature and pressure during the water extraction allowed recovering additional DOM in water solution. Subcritical water extracted 14, 30 and 51% of total organic C of immature compost at 50, 125 and 175°C, respectively. Hot-pressurised water extracted supplementary organic compounds because their solubility in water and the water diffusivity increase with temperature, and because solvation properties of water are modified when temperature increases. Particularly, the water dielectric constant or water polarity decrease when the temperature increases; liquid hot-water can become a low-polar solvent if temperature is high enough (Yang et al. 1998). Thus, hot-pressurized water can extract additional organic colloids with increasing solubility for more hydrophobic compounds. However, additional chemical effects related to the hydrolytic properties of the water cannot be discarded (Lou et al. 2000).

In a previous work with the same soils and composts (Dur et al. 2006), we have shown that the size of the extracted colloids decreased when the extraction temperature increased. The largest proportion of the finest colloids was found when extractions were done at the highest temperature (175°C), with most extracted colloids having diameters smaller than 80 nm. Dignac et al. (2005) showed that with increasing water-extraction temperature, the relative amounts of polysaccharides increased in the water extracts. Lignin-derived products were also observed in the pyrolysates of DOM extracted at temperatures higher than 125°C. Hydrolytical properties of subcritical-water has been proposed as an hydrothermal treatment process for municipal organic wastes allowing solubilizing a large part of the solid materials and recovering large proportions of simple organic acids and glucose after hydrolysis of polysaccharides (Goto et al. 2004; Oomori et al. 2004). Subcritical water also provokes the hydrolysis of fatty acid esters (Khuwijitjaru et al. 2004).

Table 2 Total organic C in different DOM extracted from the non-amended soil (NAS) and the amended soil (AS), and from the mature compost (MC) and the fresh immature compost (FC)

	Soil DOM		Compost DOM		Subcritical DOM		
	NAS	AS	MC	FC	FC		
					50°C	125°C	175°C
Extracted DOM							
mg C l^{-1}	30	36	63	149	699	1184	2222
% of initial C	0.6	0.8	4.0	7.5	13.6	28.9	51.5
Non-sorbed DOM							
mg C l^{-1}	22	26	46	74	289	514	871
Sorbed DOM							
% of extracted DOM	27	27	27	50	59	57	61
K_{DOM} (l kg^{-1})	0.62	0.62	0.61	1.69	2.36	2.17	2.59

Sorption of different DOM using non-amended soil (NAS) as a reference, with calculation of the corresponding distribution coefficients K_{DOM} (in l Kg^{-1} C)

Sorption on soil of dissolved organic matter

DOM extracted from both soils were similarly sorbed on non-amended soil, representing 27% of the extracted organic C, corresponding to a distribution sorption coefficient K_{DOM} of 0.62 l kg^{-1} (Table 2).

The sorbed proportion of DOM extracted from the composts at 20°C decreased with the maturation degree: 50 and 27% for DOM extracted from immature and mature composts, respectively. The corresponding K_{DOM} increased from 0.61 to 1.69 l kg^{-1}. Both K_{DOM} values were larger than those found in the literature: Liang et al. (1996) and Janzen et al. (1996) found K_{DOM} of 0.3 and 0.4 l kg^{-1}, respectively for DOM from composted manures.

A larger proportion (59%) of DOM extracted from immature compost was sorbed to soil when temperature of water-extraction increased from 20 to 50°C, then remained rather constant even when temperature of DOM extraction increased to 175°C (maximum K_{DOM} was 2.59 l kg^{-1}). The increase of DOM-sorption was probably related to more hydrophobic properties of DOM extracted at high temperature. These values were larger than the sorption coefficients of 0.42 l kg^{-1} found by Janzen et al. (1996) for water extracts of composts obtained by autoclaving, but lower than sorption coefficients (around 4 l kg^{-1}) of hydrophobic fraction of DOM extracted from composts by Said-Pullicino et al. (2004).

The difference of sorption properties suggested differences in the reactivity and the nature of DOM depending on the maturity degree and the extraction temperature. Sorption on soil changes the particle size distribution in compost extracts (Dur et al. 2006). For DOM extracted either at 20°C or at 175°C, part of the coarsest organic fractions extracted from the compost disappeared from solution. Furthermore, after sorption of colloids extracted from compost at 175°C on soil, the smallest (55 nm) and coarsest particles (150 nm) disappeared. Soil-sorption can induce a selection of DOM, thus, the non-sorbed colloids remaining in solution may be less reactive against the soil surfaces than those that have disappeared from solution. When compost was added to a soil, a modification of the DOM extracted from the soil was pointed out by Gigliotti et al. (1997), with an increase of the polysaccharide content and a decrease of the alkenes in the DOM remaining in solution. This behaviour was attributed to the selective sorption of the hydrophobic compounds rather than the more hydrophilic which remained water-soluble (Jardine et al. 1989; Kaiser et al. 1996). Kaiser et al. (1997) showed that DOM sorption on soils causes a preferential removal of aromatic and carboxylic groups from solution, whereas alkyl-C estimated by ^{13}C-NMR accumulates in the solution. The selection of DOM constituents during sorption was pointed out by Wershaw et al. (1996) working with DOM from compost and alumina as sorbents. Contrastingly with the finding of Kaiser et al. (1997), Wershaw et al. (1996) observed an increase in the proportion of aliphatic components in the sorbed DOM compared to the initial DOM, suggesting that hydrophobic interactions also explained DOM sorption mechanism.

Pesticides sorption on soil

The sorption coefficients (K_d) on non-amended soil for the tested pesticides are in Table 3. The corresponding K_{OC} coefficients were calculated on basis of the organic C content of non-amended soil. All pesticides were moderately sorbed on soil except the most hydrophobic, trifluralin. The weak acid sulcotrione was the least sorbed, and the weak base amitrole had an intermediate K_{OC} of 104 l kg^{-1} despite its high water-solubility denoting its capacity to establish sorbing interactions through polar or ionic molecular forms. Both sulcotrione and amitrole were on their anionic and cationic forms respectively because the pH of water solution was larger than 6. The sorption of other non-ionic pesticides was in a narrow range of K_{OC} from 52, for the high hydrophilic metalaxyl, to 162 l kg^{-1} for imidacloprid. The calculated K_{OC} values corresponded to representative K_{OC} found in FOOTPRINT (2009) database (Table 3), although always in the lower ranges of K_{OC} values particularly for metalaxyl and metamitron, denoting a low pesticide sorption capacity of the non-amended soil.

Pesticide desorption by DOM

The Fig. 2 shows the desorption curves obtained for all pesticides and DOM extracts. The desorption of sorbed pesticides was progressive during the repeated desorption experiment reaching variable proportions of non-desorbed amount depending on pesticide and DOM extracts used for desorption. Trifluralin was the most hydrophobic pesticide and the most sorbed on soil; small desorption was observed in all cases. For the weak base amitrole, sorption probably involved ionic interactions with soil constituents, and these interactions were resistant to the desorption process with a low desorption rate; DOM from the immature compost was the most efficient at desorbing amitrole.

Apart from sulcotrione and metalaxyl, the two less sorbed pesticides, water was the less efficient solvent for desorption. DOM from the non-amended and amended soils had similar effect than water, except for sulcotrione and metalaxyl. For these two pesticides, desorption with DOM from non-amended and amended soils decreased after the second desorption step compared with water-desorption. This decrease of desorption rate can be related to pesticide sorption increase due to DOM sorption on soil that could contribute to increase the organic matter content in solid phase, favoring pesticide sorption. This effect was probably more important for the poorly sorbed pesticides. Ben-Hur et al. (2003) found that atrazine sorption in soils decreased with small DOM concentrations, because of formation of stable interactions in solution with DOM; however, when DOM concentration increased, atrazine sorption also increased through sorption of DOM–atrazine complex. Increase of pesticide sorption capacity was also found when soil was treated with hydrophobic fractions of DOM coming from compost (Said-Pullicino et al. 2004) or during co-sorption experiments of DOM and anilines (Flores-Cespedes et al. 2006).

In all cases, DOM extracted from immature compost recovered at 20°C had the largest capacity to mobilize the sorbed pesticide. Such result has been found for other compost and chemicals (Janzen et al. 1996). The desorbing capacity of DOM was partially lost for mature compost.

Increasing the organic C amount in DOM solutions when hot-pressurized water was used for DOM extraction decreased the desorption capacity of DOM compared to the DOM extracted at 20°C. This was always observed for the DOM extracts recovered at 50 and 125°C and the less sorbed pesticides ($K_{OC} \leq 100$) (sulcotrione, metalaxyl, atrazine, isoproturon and amitrole). The DOM extracted from

Table 3 Sorption coefficients, K_d and K_{OC}, for the different pesticides sorbed on non-amended soil

	K_d (l kg^{-1})	K_{OC} (l kg^{-1} C)	K_{OC}[a] (l kg^{-1} C)
Sulcotrione	0.42 ± 0.01	38 ± 1	90
Metalaxyl	0.57 ± 0.01	52 ± 1	165
Atrazine	1.04 ± 0.05	94 ± 4	100
Isoproturon	1.10 ± 0.01	100 ± 1	139
Amitrole	1.15 ± 0.02	104 ± 2	111
Metamitron	1.25 ± 0.03	114 ± 3	242
Imidacloprid	1.78 ± 0.01	162 ± 1	189
Trifluralin	27.4 ± 1.9	2490 ± 171	7200

[a] Data from the FOOTPRINT Pesticide Properties Database (FOOTPRINT 2009)

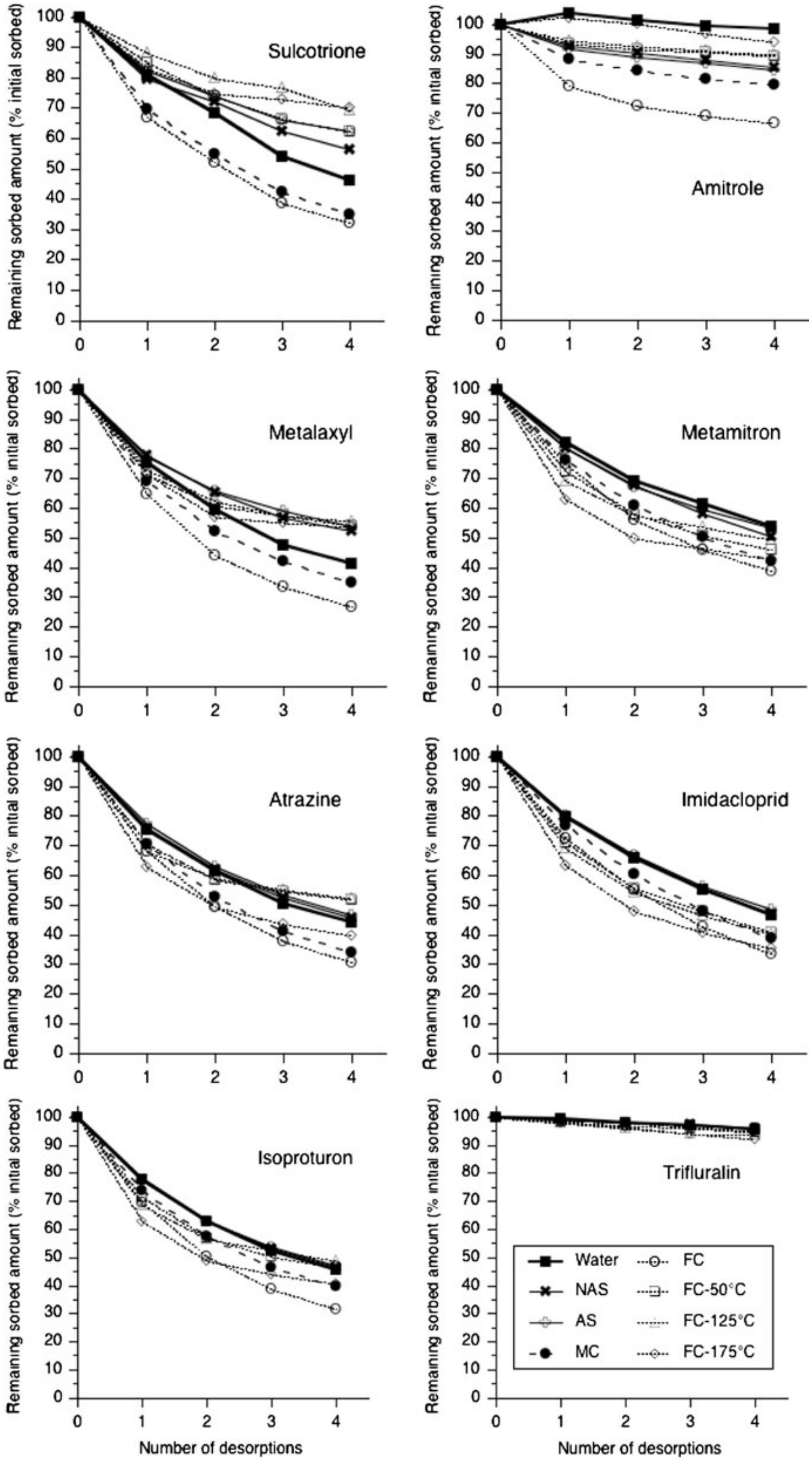


Fig. 2 Desorption curves for the different DOM of different pesticides previously sorbed to non-amended soil (NAS). DOM coming from non-amended soil (NAS) and amended soil (AS), and from the mature compost (MC) and the fresh immature compost (FC) extracted at different temperatures. Desorbed amount at each desorption step were expressed in percentage of the total amount of pesticide initially sorbed

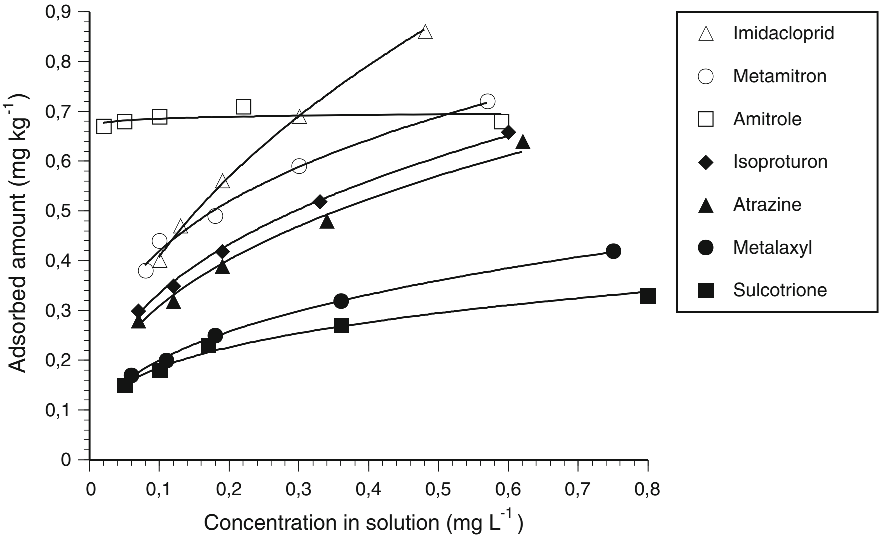


Fig. 3 Desorption isotherms of different pesticides. Example of the reference isotherms obtained with water. The amount of pesticide remaining sorbed is related to concentration of pesticide in solution; each point corresponding to each desorption step

immature compost at 175°C, containing the largest organic C amount, was able to desorb the largest amounts during the first desorption step for atrazine, isoproturon, metamitron and imidacloprid, which had $K_{OC} > 90$. However the rate of pesticide desorption with this DOM decreased during the following desorption step, denoting a competition between desorption and sorption caused by the increase of organic matter in the solid phase due to DOM sorption.

The pesticide desorption data can be represented as pseudo-desorption isotherms (an example is given in Fig. 3) that can be described by the classical Freundlich equation (Table 4). However, on the contrary to true desorption isotherms, the nature of the liquid phase differed during sorption and desorption. The K_F parameter gives indication on desorption capacity related to the isotherm slope at the origin; thus, the larger K_F is, the larger the desorbed amount at low pesticide concentration would be. For a given pesticide, the desorption capacity measured by the K_F slightly changed with the different DOM. The Freundlich exponent n gives indication on the isotherm curvature related to the desorption hysteresis. In all cases, the DOM extracted at 20°C from the immature and mature composts gave desorption isotherms with n values larger than the n values of the corresponding water desorption isotherms. Thus, DOM reduced the desorption hysteresis compared to water. Similar results have been found with other pesticides and DOM (Barriuso et al. 1992; Businelli 1997) explained by competition between DOM and pesticide sorption for the most energetic sorption sites, largely contributing to the hysteresis.

The desorption of the less sorbed pesticides ($K_{OC} \leq 100$) was more hysteretic with DOM extracted with subcritical-water compared to water. The n values were lower than n of the water desorption isotherms and the desorption intensity decreased, K_F being lower than K_F of the water desorption isotherms. A particular case was the imidacloprid behavior, which was the most sorbed pesticide (K_{OC} of 162) and showed significant desorption. For this pesticide, the curvature of desorption isotherms (n values) was not modified but the desorption capacity (K_F values) increased when the C content of the DOM increased. Flores-Cespedes et al. (2006) showed that imidacloprid sorption on soil was negatively affected by the presence of DOM which increased its desorption. That had consequences also on the increase of imidacloprid mobility in soil columns during percolation experiments with DOM solutions (Flores-Cespedes et al. 2002). Finally, desorption was negligible for trifluralin.

The sorption decrease in presence of DOM is attributed to the competition for the sorption sites between DOM and pesticides (Celis et al. 1998a) and/or the establishment of interactions in solution with DOM through mechanisms comparable to those implying surfactant. Quagliotto et al. (2006) estimated the critical micelle concentration (cmc) of polymeric

Table 4 Parameters of Freundlich isotherms of desorption, K_F and n, for all pesticides and DOM (desorption with water was used as a reference)

Pesticide	Water	Soil DOM		Compost DOM		Subcritical DOM		
		NAS	AS	MC	FC	FC		
						50°C	125°C	175°C
Sulcotrione								
K_F	0.36	0.37	0.35	0.36	0.34	0.32	0.33	0.32
n	0.288	0.202	0.157	0.381	0.395	0.160	0.115	0.107
r^2	0.986	0.973	0.971	0.988	0.983	0.968	0.979	0.906
Metalaxyl								
K_F	0.46	0.48	0.47	0.46	0.48	0.40	0.40	0.40
n	0.365	0.244	0.227	0.408	0.544	0.192	0.198	0.204
r^2	0.996	0.980	0.966	0.983	0.988	0.853	0.885	0.783
Atrazine								
K_F	0.74	0.77	0.80	0.80	0.80	0.61	0.62	0.64
n	0.382	0.355	0.360	0.529	0.586	0.241	0.229	0.369
r^2	0.990	0.989	0.988	0.990	0.992	0.844	0.808	0.860
Isoproturon								
K_F	0.79	0.85	0.82	0.82	0.86	0.73	0.68	0.67
n	0.372	0.384	0.355	0.466	0.577	0.324	0.263	0.351
r^2	0.997	0.996	0.988	0.996	0.991	0.909	0.845	0.843
Amitrole								
K_F	0.70	0.70	0.68	0.68	0.69	0.94	0.97	0.72
n	0.008	0.491	0.524	0.071	0.139	0.037	0.391	0.219
r^2	0.235	0.941	0.944	0.876	0.844	0.867	0.931	0.596
Metamitron								
K_F	0.85	1.05	0.88	0.91	0.91	0.76	0.73	0.71
n	0.309	0.353	0.298	0.448	0.493	0.333	0.272	0.333
r^2	0.985	0.999	0.985	0.998	0.992	0.937	0.856	0.817
Imidacloprid								
K_F	0.81	0.74	0.73	0.71	0.71	0.95	0.98	0.98
n	0.480	0.497	0.479	0.650	0.713	0.480	0.464	0.510
r^2	0.998	0.999	0.998	0.999	0.995	0.947	0.933	0.860
Trifluralin								
K_F	1.71	1.75	1.70	1.69	1.72	1.90	1.98	1.96
n	0.029	0.034	0.027	0.025	0.031	0.058	0.075	0.080
r^2	0.702	0.779	0.686	0.572	0.639	0.855	0.815	0.487

Desorption data were adjusted to the equation $C_s = K_F \cdot C_e^n$, where C_s is the pesticide remaining sorbed and C_e is the pesticide concentration in the desorption solution

extracts of composts around values of 400 mg C l^{-1}. Thus all water-subcritical extracts from immature compost in this work could be at a concentration above the cmc (Table 2), favoring a pesticide solubility increase by a like-surfactant effect of DOM extracts. The pseudo-micellar structure of DOM, favoring hydrophobic cores and hydrophilic regions, could explain the increases of pesticide desorption in presence of DOM solutions (Wanner et al. 2005).

Modelling approach

Pesticide desorption

The Table 5 summarizes the measured K_{des} for all pesticides and DOM calculated with Eq. 10. The initial values of sorption coefficients (K_d) for all pesticides (Table 3) were systematically lower than the corresponding distribution coefficient measured

Table 5 Distribution coefficients K_{des} (in l kg^{-1} soil) describing the first stage of desorption for different pesticides and DOM

Pesticide	Water[a]	Soil DOM		Compost DOM		Subcritical DOM		
		NAS	AS	MC	FC	FC		
						50°C	125°C	175°C
Sulcotrione	0.75 ± 0.05	0.79 ± 0.01	0.81 ± 0.01	0.62 ± 0.02	0.58 ± <0.01	0.77 ± 0.06	0.85 ± 0.06	0.78 ± 0.02
Metalaxyl	0.88 ± 0.02	1.01 ± 0.03	1.02 ± <0.01	0.78 ± 0.04	0.72 ± 0.02	0.82 ± 0.06	0.83 ± 0.02	0.82 ± 0.02
Atrazine	1.42 ± 0.04	1.52 ± 0.02	1.60 ± 0.02	1.27 ± 0.03	1.18 ± 0.04	1.22 ± 0.06	1.20 ± 0.01	1.04 ± 0.02
Isopro turon	1.57 ± 0.04	1.68 ± 0.05	1.64 ± 0.02	1.43 ± 0.04	1.30 ± 0.03	1.38 ± 0.01	1.29 ± 0.04	1.08 ± <0.01
Amitrole	3.20 ± 0.15	2.42 ± 0.06	2.28 ± 0.06	2.11 ± 0.11	1.70 ± 0.10	4.09 ± <0.01	4.43 ± 0.06	3.15 ± 0.14
Metamitron	1.93 ± 0.07	2.03 ± 0.01	1.99 ± 0.13	1.65 ± 0.03	1.59 ± <0.01	1.46 ± 0.02	1.38 ± 0.04	1.15 ± 0.02
Imidacloprid	2.31 ± 0.01	2.51 ± 0.10	2.58 ± 0.05	2.11 ± 0.07	1.85 ± 0.03	1.71 ± 0.09	1.64 ± 0.04	1.43 ± 0.05
Trifluralin	53.1 ± 5.5	52.3 ± 0.08	49.8 ± 0.7	54.7 ± 2.6	48.4 ± 1.5	49.8 ± 0.7	41.6 ± 1.0	39.7 ± 0.7

[a] The distribution coefficient for the desorption with water (water-K_{des}) was used to characterize the sorption/desorption equilibrium between the liquid phase and the soil in absence of DOM and it was noted in the text as $K_{pest-soil}$

with the water desorption ($K_{pest-soil}$). No-effect of DOM on pesticide desorption should be found when $K_{des} = K_{pest-soil}$. Following the Eq. 10, it is possible to write:

$$K_{des} - K_{pest-soil} = K_{pest-SOC} \cdot K_{DOM} \cdot C_{DOC} - K_{des} \cdot K_{pest-DOC} \cdot C_{DOC} \qquad (13)$$

Thus, if $K_{des} < K_{pest-soil}$, that is to say when DOM favors desorption compared to water, then:

$$K_{pest-SOC} \cdot K_{DOM} < K_{des} \cdot K_{pest-DOC} \qquad (14)$$

This inequality points out the role of pesticide interaction with the soluble (DOC) or sorbed (SOC) DOM, conditioning the DOM effect on the desorption process. The desorption with DOM would be larger than with water if pesticide interactions in solution with the non-sorbed fraction of DOM ($K_{pest-DOC}$) were large enough. Inversely, decreasing pesticide desorption in presence of DOM implies interactions with the DOM fraction sorbed on soil with high values of the corresponding $K_{pest-SOC}$.

Estimation of interactions in solution between pesticides and DOM

The Eq. 12 allowed testing different hypotheses on the extent of DOM-pesticide interaction. A first hypothesis is that pesticide has the same affinity for the sorbed DOM than for the DOM remaining in solution, then $K_{pest-DOC} = K_{pest-SOC}$, and the Eq. 9 becomes:

$$K_{pest-DOC} = \frac{1}{C_{DOC}} \cdot \frac{\left(\frac{K_{pest-soil}}{K_{des}} - 1\right)}{\left(1 - \frac{K_{DOM}}{K_{des}}\right)} \qquad (15)$$

However, when this equation was applied to the data set, only positive values of $K_{pest-DOC}$ were found when $K_{des} > K_{pest-soil}$. Thus the Eq. 15 only explained the increase of desorption when DOM was used but could not explain the decrease of desorption in presence of DOM. To explain that decrease, it was necessary to assume different affinities of sorbed and non-sorbed DOM against pesticides, thus $K_{pest-DOC} \neq K_{pest-SOC}$. $K_{pest-SOC}$ could not be experimentally calculated. However, it could be estimated assuming that the pesticide affinity by solid-organic matter (estimated by the K_{OC}) was similar for soil organic matter and for sorbed DOM, that is $K_{pest-soc} = K_{OC}$. With this last hypothesis, the corresponding $K_{pest-DOC}$ were calculated using Eq. 12 (Table 6).

For the DOM extracted at 20°C, $K_{pest-DOC}$ was in general larger on DOM from immature compost than from mature compost (Table 6). Thus, compost maturation reduced the affinity of the water-soluble organic matter to contract interactions with pesticides in solution. Amitrole and trifluraline gave the extreme values of the $K_{pest-DOC}$ for DOM extracted from composts at 20°C. The highest $K_{pest-DOC}$ was found for amitrole, ranging around 2000 l kg^{-1} C. These high values were related to the polarity of amitrole,

Table 6 Calculation of the coefficients $K_{pest-DOC}$ (in $l\ kg^{-1}$ C) describing the interactions in solution between the pesticides and the fraction of non-sorbed DOM, remaining in solution

Pesticide	Compost DOM		Subcritical DOM		
	MC	FC	FC		
			50°C	125°C	175°C
Sulcotrione	791	770	101	59	119
Metalaxyl	501	622	192	155	178
Atrazine	469	592	276	229	304
Isoproturon	394	597	250	239	327
Amitrole	1886	2088	nv	nv	89
Metamitron	652	602	370	308	387
Imidacloprid	387	707	426	347	411
Trifluralin	nv	305	156	220	227

The Eq. 12 was used assuming that $K_{pest-SOC} = K_{OC}$

nv negative values

denoting the existence of polar interactions in solution between this weak base and DOM. The lowest values of $K_{pest-DOC}$ were found for trifluralin, the most hydrophobic pesticide, and the least able to establish interactions with DOM remaining in solution, i.e. the most polar and hydrophilic fraction of DOM. The other pesticides ranged between these extreme comportments.

The $K_{pest-DOC}$ values were lower than values found in the literature for more hydrophobic compounds but were comparable to values shown by Ilani et al. (2005) for atrazine (40–846 $l\ kg^{-1}$) or ametryn (102–202 $l\ kg^{-1}$). The affinity to DOM tended to decrease when the pesticide hydrophobicity increased, as shown by the relation between the K_{ow} of the pesticides and the corresponding $K_{pest-DOC}$ from the water extracts at 20°C of immature and mature composts (Fig. 4). For the non-ionic pesticides, a general linear relationship can be calculated allowing the estimation of the coefficient describing the pesticide–DOM interaction in function of the pesticide K_{ow}:

for the immature compost: $K_{pest-DOC}$

$$= 760 - 85 \log K_{ow} \quad \left(R^2 = 0.871\right);$$

for the mature compost: $K_{pest-DOC}$

$$= 708 - 133 \log K_{ow} \quad \left(R^2 = 0.747\right).$$

These correlations contrasted with the general relations found in the literature, in which partitioning

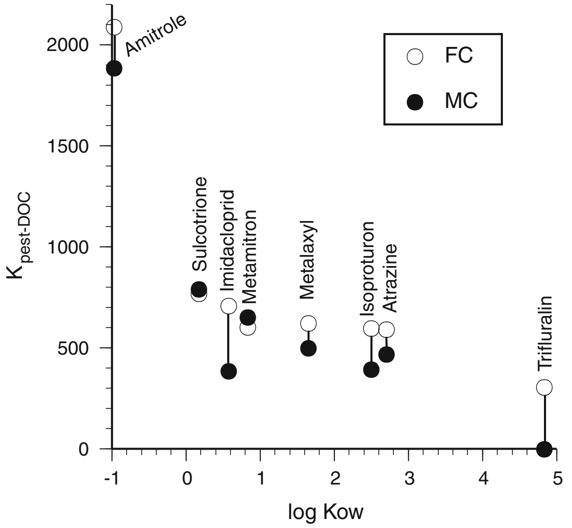


Fig. 4 Relationship between the calculated partitioning coefficients between pesticide and the non-sorbed fraction of DOM extracted from the composts at 20°C on soil ($K_{pest-DOC}$, in $l\ kg^{-1}$ C) and the pesticide partition coefficient between octanol and water (K_{ow})

coefficient with DOM are directly correlated to K_{ow} by linear (Jafvert et al. 1994) or logarithmic functions (McCarthy and Jimenez 1985; Rav-Acha and Rebhun 1992; Rebhun et al. 1996; Ohlenbusch and Frimmel, 2001). However, the data found in the literature mainly corresponded to more hydrophobic chemicals ($\log K_{ow} > 3$) and coefficients corresponded to non-specific hydrophobic interactions in solution without consideration of competitive sorption interactions between liquid and colloidal phases, and solid phase. The calculated $K_{pest-DOC}$ is an apparent partitioning coefficient taking into account the heterogeneous triphasic system induced by the presence of a solid phase. The Fig. 5 shows the distribution of partitioning coefficients related to the corresponding K_{ow} compiled by Rebhun et al. (1996). These data are representative of the data found in the literature, mostly for hydrophobic compounds, showing the increase of the partitioning coefficients to DOM when chemical hydrophobicity increased. Data obtained in this work concerned less hydrophobic chemicals ($\log K_{ow} < 3$, except trifluralin) and showed a break in the general trend found in the literature (Fig. 5). However, partitioning coefficients from the literature and the $K_{pest-DOC}$ calculated here can not be directly compared since literature data considered only two-phase system: colloidal-DOM and liquid phases. The

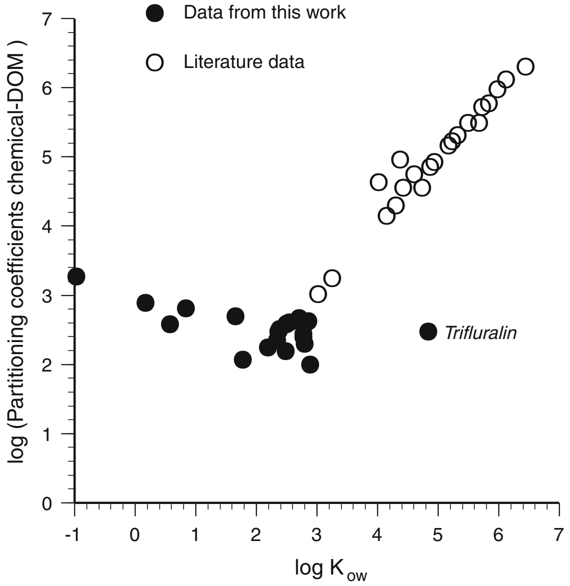


Fig. 5 Comparison of the chemical-DOM sorption partition coefficients calculated in the present work and those compiled by Rebhun et al. (1996), and their relation to octanol–water coefficients. Literature data corresponded to measurements in water solution, results from this work were obtained in presence of soil

proposed $K_{pest–DOC}$ is the resultant of the three-phase system, solid, colloidal-DOM and liquid phases. Only trifluralin had a K_{ow} comparable to the values compiled by Rebhun et al. (1996). However, the calculated $K_{pest–DOC}$ was out of the linear relationship published by these authors (Fig. 5). This pointed out the importance of the interactions with the solid phase and their implication in modulating the interaction in solution between DOM and pesticide.

The supplementary DOM extracted from immature compost by hot-pressurized water had a lower pesticide affinity than DOM extracted at 20°C from the immature compost. The values of $K_{pest–DOC}$ decreased when the extraction temperature increased from 50 to 125°C, then the $K_{pest–DOC}$ increased for the extracts at 175°C. These trends were observed for all pesticides. This suggested that the supplementary DOM extracted by subcritical water has a high proportion of hydrophobic materials and was preferentially sorbed on soil, thus facilitating pesticide sorption. In general, the partitioning coefficients of pesticide and DOM increase with the aromaticity degree of the DOM estimated by NMR analyses (Thomsen et al. 2002a).

The dependency of the partitioning coefficient to the DOM concentration was pointed out in simplified systems (Thomsen et al. 2002b). That can be explained by the heterogeneity of the DOM sites interacting with pesticides. Pesticide will show larger affinity towards the most energetically favourable sorption sites, then the interactions will concern sites with low sorption energy, which could explain a change in partitioning coefficient with change in the DOM concentration (Pan et al. 2008). Another proposed explanation is related to the modified colloid conformation in solution when the concentration increases. At low concentration, the system may be described as a true solution; however, at high concentration, the aggregation of the macromolecules leads to a two-phases system in solution with a modification of the available sorption sites in reason of the modification of the inter- and intra-molecular associations within and between the DOM macromolecules.

Finally, as an application, the estimated K_{des} and $K_{pest–DOC}$ can be used to propose an overall balance of pesticide sorption/desorption behavior, with identification of the proportion of free pesticide in solution and pesticide in solution associated to the DOM (Fig. 6). Thus for the pesticide with low or moderate sorption, the increase of DOM concentration slightly favored the pesticide desorption, but the largest effect was the decrease of the proportion of free pesticide in solution. For the most concentrated DOM, the proportion of pesticide associated to DOM represented between 26% (sulcotrione) and 40% (metamitron) of total pesticide. A particular behavior was found for amitrole (weak base) for which the proportion of free pesticide remained around 25% of the total, with the largest associations with DOM from water extracts of composts recovered at 20°C. The DOM effect on trifluralin was very low, between 2 and 3% of trifluralin remaining free in solution, but more than 96% remaining sorbed in all circumstances.

Conclusions

The indirect method used for $K_{pest–DOC}$ estimation through modelling gave realistic data for a heterogeneous three-phase system with liquid, DOM and solid phases. This method could be complementary to other direct methods allowing estimation of partitioning coefficients in solution, in absence of a solid

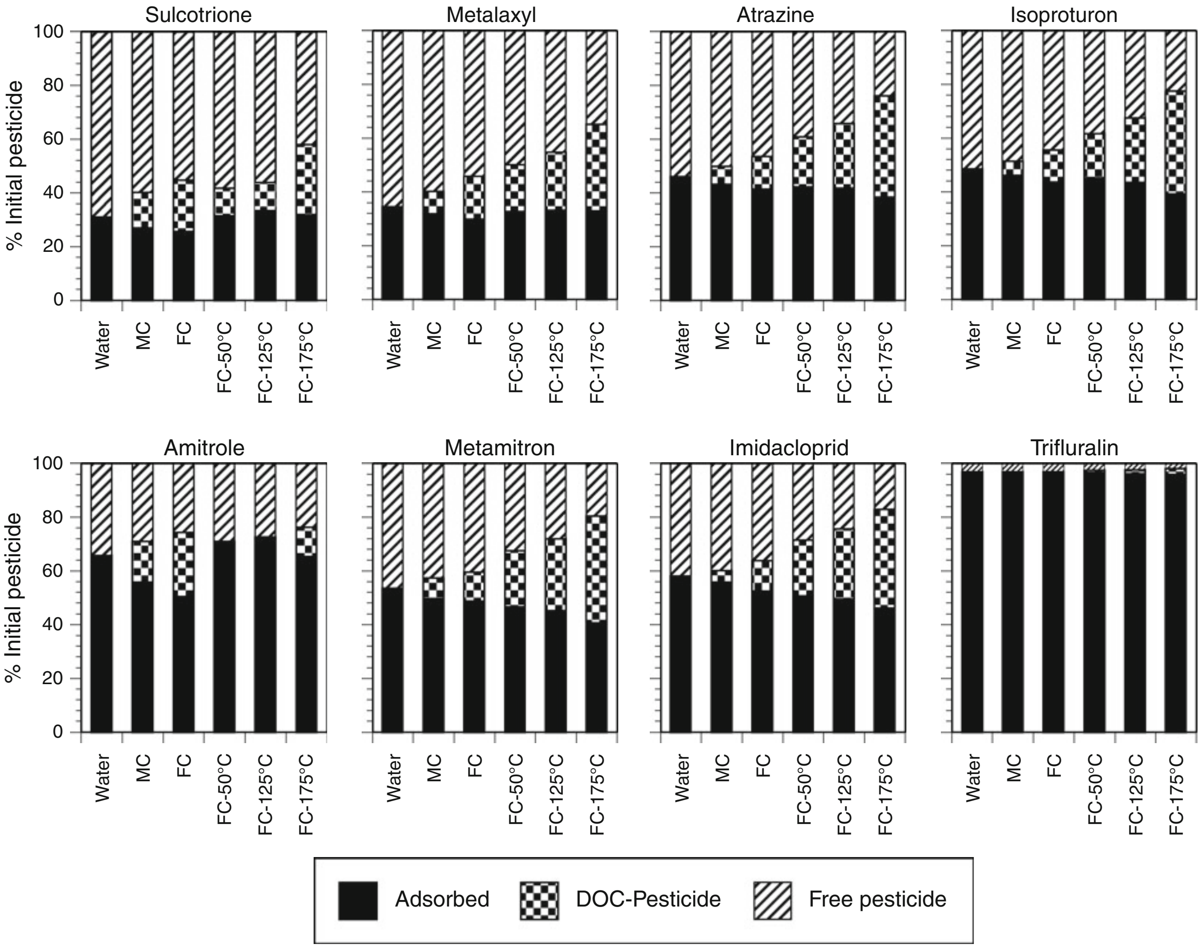


Fig. 6 Overall balance of the sorption/desorption behavior showing the distribution of pesticides between the solid and the pesticide in solution associated to the non-sorbed DOM (DOC) or free in the solution. Calculations combined the measured K_{des} (repartition of pesticide between solid and liquid phases) and the calculated $K_{pest-DOC}$ (repartition of pesticide in solution between DOM and the free solution)

phase. However, these methods, as equilibrium dialysis, fluorescence quenching or solubility enhancement, work well for compounds with low water solubility allowing high extent of interactions with DOM in solution. Hence, some values of interaction constants between some chemicals and DOM from compost are available, all larger than 30,000 l kg^{-1} C (Raber and Kogel-Knabner 1997), contrasting with the values found in this work with more hydrophilic pesticides. The low values of constants estimated in this work are in correspondence with some published data showing that for low hydrophobic pesticides, sorption is mainly governed by soil organic matter as a solid phase. In absence of solid phase, the interaction in solution between chemicals and DOM increases with pesticide hydrophobicity. However, in a triphasic system, taking into account the competitive interactions in the solid and liquid phases, shows that the solid phase was determinant on sorption process: the most hydrophobic part of DOM is removed from solution by sorption on solid phase, and pesticide sorption on this solid phase increases when their hydrophobicity increased.

The proposed model was too simple as it considers homogenous DOM, without taking into account fractions with different hydrophobicity and specific selection of DOM fractions during sorption onto soil. On the other hand, DOM is composed by amphiphatic flexible macromolecules, which have the possibility to modify their spatial conformation in solution with the formation of micelle-like aggregates if the concentration in solution is high enough. The external surfaces of these aggregates should be hydrophilic whereas the internal voids are considered as hydrophobic.

The DOM concentration levels used in this work were far from natural occurrence. This implies to be cautious in extrapolating our results to natural environment such as soils. Effectively, the interaction between DOM and pesticides can depend on the DOM concentration, and some works point out the non-linearity of sorption. DOM effects, mainly at the concentrations used in this work, are probably relevant at a local scale, conditioning the availability at short time–space scale, but it is more difficult to extrapolate consequences on co-transport of pollutant.

Acknowledgments This work was supported by the Department of Environment and Agronomy of the French National Institute for Agriculture Research (INRA) and by the French Science National Found through the National Program ECCO—Ecodynamic of pollutant substances. M. Andrades beneficed of a fellowship from the Secretary of Education and Universities of the Spanish Ministry of Education. The authors acknowledge the Research Center on Environment, Energy and Wastes (CRPE, Veolia group), for supplying composts and technical advice.

References

Annabi M, Houot S, Francou C, Poitrenaud M, le Bissonnais Y (2007) Soil aggregate stability improvement with urban composts of different maturities. Soil Sci Soc Am J 71: 413–423

Barriuso E, Baer U, Calvet R (1992) Dissolved organic matter and adsorption-desorption of dimefuon, atrazine, and carbetamide by soils. J Environ Qual 21:359–367

Barriuso E, Houot S, Serra-Wittling C (1997) Influence of compost addition to soil on the behaviour of herbicides. Pestic Sci 49:65–75

Bellin CA, O'Connor GA, Jin Y (1990) Sorption and degradation of pentachlorophenol in sludge-amended soils. J Environ Qual 19:603–608

Ben-Hur M, Letey J, Farmer WJ, Williams CF, Nelson SD (2003) Soluble and solid organic matter effects on atrazine adsorption in cultivated soils. Soil Sci Soc Am J 67: 1140–1146

Businelli D (1997) Pig slurry amendment and herbicide coapplication effects on s-triazine mobility in soil: an adsorption-desorption study. J Environ Qual 26:102–108

Celis R, Barriuso E, Houot S (1998a) Sorption and desorption of atrazine by sludge-amended soil: dissolved organic matter effects. J Environ Qual 27:1348–1356

Celis R, Barriuso E, Houot S (1998b) Effect of liquid sewage sludge addition on atrazine sorption and desorption by soil. Chemosphere 37:1091–1107

Chantigny MH (2003) Dissolved and water-extractable organic matter in soils: a review on the influence of land use and management practices. Geoderma 113:357–380

Clapp CE, Hayes MHB (1999) Sizes and shapes of humic substances. Soil Sci 164:777–789

Dignac MF, Andrades M, Houot S, Barriuso E (2005) Differences in the chemical composition of colloidal organic matter from various municipal solid waste composts as studied by pyrolisis/GC/MS. In: Bernal MP, Moral R, Clemente R, Paredes C (eds) Sustainable organic waste management for environmental protection and food safety. FAO and CSIC, Murcia, pp 67–70

Dur JC, Andrades M, Houot S, Tessier D, Barriuso E (2006) Characterization of colloids extracted from compost and soils by laser granulometry. Compost Sci Util 14:276–283

Ertunç T, Hartlieb N, Berns A, Klein W, Schaeffer A (2002) Investigations on the binding mechanism of the herbicide simazine to dissolved organic matter in leachates of compost. Chemosphere 49:597–604

Flores-Cespedes F, Gonzalez-Pradas E, Fernandez-Perez M, Villafranca-Sanchez M, Socias-Viciana M, Urena-Amate MD (2002) Effects of dissolved organic carbon on sorption and mobility of imidacloprid in soil. J Environ Qual 31:880–888

Flores-Cespedes F, Fernandez-Perez M, Villafranca-Sanchez M, Gonzalez-Pradas E (2006) Cosorption study of organic pollutants and dissolved organic matter in a soil. Environ Pollut 142:449–456

FOOTPRINT (2009) The FOOTPRINT pesticide properties database. University of Hertfordshire as part of the EU-funded FOOTPRINT project (FP6-SSP-022704). http://sitem.herts.ac.uk/aeru/footprint/. Accessed 30 June 2009

Gigliotti G, Giusquiani PL, Businelli D, Macchioni A (1997) Composition changes of dissolved organic matter in a soil amended with municipal waste compost. Soil Sci 162: 919–926

Gigliotti G, Kaiser K, Guggenberger G, Haumaier L (2002) Differences in the chemical composition of dissolved organic matter from waste material of different sources. Biol Fertil Soils 36:321–329

Goto M, Obuchi R, Hirose T, Sakaki T, Shibata M (2004) Hydrothermal conversion of municipal organic waste into resources. Bioresour Technol 93:279–284

Grigatti M, Ciavatta C, Gessa C (2004) Evolution of organic matter from sewage sludge and garden trimming during composting. Bioresour Technol 91:163–169

Hartlieb N, Marschner B, Klein W (2001) Transformation of dissolved organic matter (DOM) and 14C-labelled organic contaminants during composting of municipal biowaste. Sci Total Environ 278:1–10

Houot S, Clergeot D, Michelin J, Francou C, Bourgeois S, Caria G, Ciesielski H (2002) Agronomic value and environmental impacts of urban compost used in agriculture. In: Insam H, Riddech N, Klammer S (eds) Microbiology of composting. Spring-Verlag, Berlin, pp 457–472

Ilani T, Schulz E, Chefetz B (2005) Interactions of organic compounds with wastewater dissolved organic matter: role of hydrophobic fractions. J Environ Qual 34:552–562

Jafvert CT, Vanhoof PL, Heath JK (1994) Solubilization of non-polar compounds by non-ionic surfactant micelles. Water Res 28:1009–1017

Janzen RA, Xing B, Gomez CC, Salloum MJ, Drijber RA, McGill WB (1996) Compost extract enhances desorption of [alpha]-naphthol and naphthalene from pristine and contaminated soils. Soil Biol Biochem 28:1089–1098

Jardine PM, Weber NL, McCarthy JF (1989) Mechanisms of dissolved organic carbon adsorption on soil. Soil Sci Soc Am J 53:1378–1385

Kaiser K, Guggenberger G, Zech W (1996) Sorption of DOM and DOM fractions to forest soils. Geoderma 74:281–303

Kaiser K, Guggenberger G, Haumaier L, Zech W (1997) Dissolved organic matter sorption on subsoils and minerals studied by C-13-NMR and DRIFT spectroscopy. Eur J Soil Sci 48:301–310

Khuwijitjaru P, Fujii T, Adachi S, Kimura Y, Matsuno R (2004) Kinetics on the hydrolysis of fatty acid esters in subcritical water. Chem Eng J 99:1–4

Lee CL, Kuo LJ (1999) Quantification of the dissolved organic matter effect on the sorption of hydrophobic organic pollutant: application of an overall mechanistic sorption model. Chemosphere 38:807–821

Liang BC, Gregorich EG, Schnitzer M, Schulten HR (1996) Characterization of water extracts of two manures and their adsorption on soils. Soil Sci Soc Am J 60:1758–1763

Lou X, Miller DJ, Hawthorne SB (2000) Static subcritical water extraction combined with anion exchange disk sorption for determining chlorinated acid herbicides in soil. Anal Chem 72:481–488

Marschner B, Kalbitz K (2003) Controls of bioavailability and biodegradability of dissolved organic matter in soils. Geoderma 113:211–235

McCarthy JF, Jimenez BD (1985) Interactions between polycyclic aromatic hydrocarbons and dissolved humic materials: binding and dissociation. Environ Sci Technol 19:1072–1076

Ohlenbusch G, Frimmel FH (2001) Investigations on the sorption of phenols to dissolved organic matter by a QSAR study. Chemosphere 45:323–327

Oomori T, Khajavi SH, Kimura Y, Adachi S, Matsuno R (2004) Hydrolysis of disaccharides containing glucose residue in subcritical water. Biochem Eng J 18:143–147

Pan B, Ghosh S, Xing BS (2008) Dissolved organic matter conformation and its interaction with pyrene as affected by water chemistry and concentration. Environ Sci Technol 42:1594–1599

Pignatello JJ (1998) Soil organic matter as a nanoporous sorbent of organic pollutants. Adv Colloid Interface Sci 77: 445–467

Quagliotto P, Montoneri E, Tambone F, Adani F, Gobetto R, Viscardi G (2006) Chemicals from wastes: compost-derived humic acid-like matter as surfactant. Environ Sci Technol 40:1686–1692

Raber B, Kogel-Knabner I (1997) Influence of origin and properties of dissolved organic matter on the partition of polycyclic aromatic hydrocarbons (PAHs). Eur J Soil Sci 48:443–455

Rav-Acha Ch, Rebhun M (1992) Binding of organic solutes to dissolved humic substances and its effects on adsorption and transport in the aquatic environment. Water Res 26:1645–1654

Rebhun M, De Smedt F, Rwetabula J (1996) Dissolved humic substances for remediation of sites contaminated by organic pollutants. Binding-desorption model predictions. Water Res 30:2027–2038

Said-Pullicino D, Gigliotti G, Vella AJ (2004) Environmental fate of triasulfuron in soils amended with municipal waste compost. J Environ Qual 33:1743–1751

Thomsen M, Lassen P, Dobel S, Hansen PE, Carlsen L, Mogensen BB (2002a) Characterisation of humic materials of different origin: a multivariate approach for quantifying the latent properties of dissolved organic matter. Chemosphere 49:1327–1337

Thomsen M, Dobel S, Lassen P, Carlsen L, Mogensen BB, Hansen PE (2002b) Reverse quantitative structure-activity relationship for modelling the sorption of esfenvalerate to dissolved organic matter: a multivariate approach. Chemosphere 49:1317–1325

Wanner U, Fuhr F, Burauel P (2005) Influence of the amendment of corn straw on the degradation behaviour of the fungicide dithianon in soil. Environ Pollut 133:63–70

Wershaw RL, Llaguno EC, Leenheer JA (1996) Mechanism of formation of humus coatings on mineral surfaces 3 Composition of adsorbed organic acids from compost leachate on alumina by solid-state 13C NMR. Colloids Surf A108:213–223

Worrall F, Parker A, Rae JE, Johnson AC (1999) A study of suspended and colloidal matter in the leachate from lysimeters and its role in pesticide transport. J Environ Qual 28:595–604

Yang Y, Belghazi M, Lagadec A, Miller DJ, Hawthorne SB (1998) Elution of organic solutes from different polarity sorbents using subcritical water. J Chromatogr A810:149–159

Zhou LX, Wong JWC (2001) Effect of dissolved organic matter from sludge and sludge compost on soil copper sorption. J Environ Qual 30:878–883

Zmora-Nahum S, Markovitch O, Tarchitzky J, Chen Y (2005) Dissolved organic carbon (DOC) as a parameter of compost maturity. Soil Biol Biochem 37:2109–2116

Zsolnay A (2003) Dissolved organic matter: artefacts, definitions, and functions. Geoderma 113:187–209