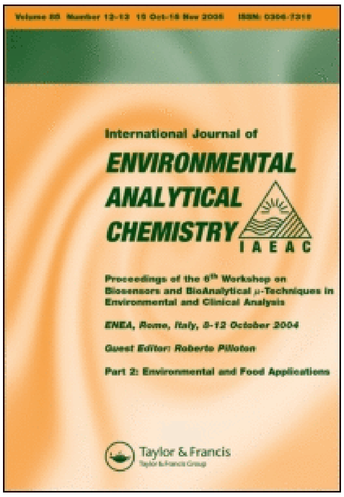

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SORPTION BEHAVIOUR OF CHLOROPHENOLS AND TRIAZINE HERBICIDES IN REFERENCE EURO-SOILS

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The influence of different soil sorption-controlling properties on sorption behaviour of chlorophenols (2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol) and triazine herbicides (chlorotriazines atrazine and simazine, and methylthiotriazines ametryn and prometryn) in natural sorbents was studied. Experiments were carried out with six European reference soils differing in soil organic matter content (SOM), grain size distribution, cation exchange capacity, and acidity, as well as in silt, clay, sand, iron oxide and aluminium oxide content. Freundlich isotherm coefficients K_f and $1/n$ as well as organic matter sorption coefficient and free energy change were calculated for all compounds in all sorbents. The sorption intensity for chlorophenols increased with increase of SOM, cation exchange capacity and sorbent sand content and decreased with increase of sorbent pH, silt and clay content. For chlorotriazines atrazine and simazine, statistically significant positive correlation between K_f sorption coefficients and SOM was obtained and the sorption was also favoured by lower content of coarse- and medium-grainy fractions of silt.

Keywords: Sorption; Chlorophenols; Triazine herbicides; EURO-Soil; Soil sorption-controlling properties

INTRODUCTION

The environmental fate of organic micropollutants is strongly influenced by their sorption in natural sorbents. Investigation of their sorption behaviour is fundamental to simulating and eventually predicting their transport in environmental compartments.

Chlorophenols are widely present as environmental pollutants. They belong to a class of polarizable hydrophobic compounds with relatively high *n*-octanol/water (K_{ow}) coefficients. They are weak organic acids, (pK_a 5–9). At typical ambient pH values, chlorophenols, in particular tetrachlorophenols and pentachlorophenol, are present in the aqueous environment predominantly as phenolate anions. The sorption of such partially ionised but still highly hydrophobic compounds comprises both molecular and ionic forms [1–3]. A strong dependence of phenolate sorption on the organic carbon of the sorbent has been reported [1] but the sorption mechanism for

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these compounds is presumed to be more complex [1,2]. Processes such as ion exchange, ligand exchange, formation of ion pairs and ion complexes in the sorbent surface have to be considered in addition to partitioning. The presence of some charged species in the sorbent material (Ca^{2+} and Mg^{2+} ions) [4] or other factors controlling the stability of more hydrophilic phenolate forms in the aqueous phase, such as pH and ionic strength [1–3] are expected to influence the sorption of chlorophenols.

Symmetric triazines are used world-wide as selective pre- and post-emergence herbicides for the control of weeds in many agricultural crops [5]. Owing to their extensive use and high persistence they contaminate the aquatic environment through agricultural run-off and leaching. The adsorptivity of triazine herbicides is supposed to be weak because of their high water solubility [6] which is dependent on the substitution in the 2-position [7]. They are weakly basic compounds (pK_a 2–4) [8] while the hydroxylated atrazine degradation products are stronger bases [9]. The sorption of s-triazines to clays and soil organic matter is related to the pK_a of the compound. Triazines with higher pK_a values show greater sorption because of mixed-mode binding to soils, while the primary binding mechanism of triazines with pK_a near 2 are hydrophobic interactions [10].

In this work we examined the sorption behaviour of three chlorophenols 2,4,6-trichlorophenol (TCP), 2,3,4,6-tetrachlorophenol (TeCP) and pentachlorophenol (PCP) as well as four triazine herbicides atrazine, simazine, prometryn and ametryn in six well-characterised reference EURO-Soils differing in soil organic matter content (SOM), grain size distribution and mineral composition, cation exchange capacity (CEC) and acidity, as well as in silt, clay, sand, iron oxide and aluminium oxide content [11]. The objective was to examine the sorption intensity of these compounds in relation to the chemical–physical characteristics of sorbates and sorbents.

EXPERIMENTAL

Chemicals

2,4,6-Trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol, all of them p.a. purity, were purchased from H.P. Chem. Service, West Chester, PA, USA. Acetic anhydride p.a., was the product of Fluka A.G., Buchs, Switzerland. Atrazine, 99.0%, simazine, 99.2%, prometryn, 99.7%, and ametryn, 98%, were purchased from Riedel de Haën, Seelze, Germany. *n*-Hexane for organic trace analysis p.a., was supplied from Merck, Darmstadt, Germany. Sep-Pak C_{18} silica cartridges were purchased from Waters Associates, Milford, USA. All other chemicals were products of p.a. purity of Kemika, Zagreb, Croatia. Sorbate stock solutions were prepared in $0.01\,mol\,L^{-1}$ solution of $CaCl_2$ in deionised water and stored in glass stoppered bottles. Methanol and acetone were redistilled before use. All solvents and reagents were tested for purity in blank procedures.

Soils

Five samples of reference surface EURO-Soils [11]: EURO-Soil 1 (Vertic Cambisol, A-horizon, Sicily, Italy), EURO-Soil 2 (Rendzina, A-horizon, Peloponnesos, Greece), EURO-Soil 3 (Dystric Cambisol, A-horizon, Wales, Great Britain), EURO-Soil 4

TABLE I Pedological characteristics of EURO-Soils (ES 1–ES 6)

	ES 1 *clay*	*ES 2* *silt loam*	*ES 3* *loam*	*ES 4* *silt*	*ES 5* *loamy sand*	*ES 6* *silt loam*
Sand (%)	3.3	13.4	46.4	4.1	81.6	1.7
Silt (%) total	21.9	64.1	36.8	75.7	12.6	82.4
coarse	4.0	21.3	19.4	52.2	7.4	62.5
medium	9.7	23.1	11.6	9.4	4.3	17.3
fine	8.2	19.7	5.8	4.1	1.0	2.6
Clay (%)	75.0	22.6	17.0	20.3	6.0	16.0
Organic carbon (%)	1.30	3.70	3.45	1.55	9.25	0.25
Organic matter (%)	2.65	6.40	6.45	2.85	15.90	0.80
CEC (mval/100 g)	29.9	28.3	18.3	17.5	32.7	11.4
Al_2O_3 (%)	23.92	8.66	11.92	12.07	3.85	12.64
Fe_2O_3 (%)	10.76	1.66	4.14	2.71	0.05	2.83
pH (in water)	5.9	8.0	5.8	7.0	4.6	8.3

Data from [11].

(Orthic Luvisol, A-horizon, Normandy, France) and EURO-Soil 5 (Orthic Podzol, A-horizon, Schleswig-Holstein, Germany), and one sample of terrestrial sediment EURO-Soil 6 (Orthic Luvisol, BC-horizon, Normandy, France) were obtained by courtesy of Dr. H. Muntau from the European Commission Joint Research Centre, Environment Institute, Ispra, Italy. The type and some pedological characteristics of EURO-Soils – organic matter and organic carbon content, pH, cation exchange capacity, sand, silt and clay content as well as content of Fe_2O_3 and Al_2O_3 – are shown in Table I.

Sorption Experiments

Portions of 0.5 g of dry soil with particle size < 1 mm were equilibrated overnight with 3 mL of deionised water. After centrifugation at 425 G for 10 min the aqueous phase was separated and 10.5 mL of sorbate solution, prepared in 0.01 mol L^{-1} $CaCl_2$ to maintain the constant ionic strength, was added to water-saturated sorbent. The suspension was agitated for 24 h on a mechanical shaker. The samples were centrifuged and the supernatant was carefully separated.

Sorption experiments were run for each sorbent in duplicate at five sorbate concentrations: from 0.02 to 0.45 nmol mL^{-1} for chlorophenols and from 3.97 to 231.33 nmol mL^{-1} for triazine herbicides. Two blank samples containing the sorbent and 10.5 mL of 0.01 mol L^{-1} $CaCl_2$ were prepared for each sorbent and handled identically to the samples. Two control samples prepared without sorbent at each concentration were used as reference solutions for quantitative analysis.

Analytical Procedures

After achieving sorption equilibrium, chlorophenols were accumulated from 5.0 mL of aqueous phase by C_{18} solid-phase extraction on a Sep-Pak C_{18} cartridge [12]. The cartridge was eluted with 1.5 mL of acetone. A solution of 2,4,6-tribromophenol (internal standard) in acetone, 3.0 mL of 0.1 mol L^{-1} Na_2CO_3, 2.0 mL of *n*-hexane and 50.0 μL of acetic acid anhydride were added to the eluate. After shaking for 1 min the *n*-hexane extract was separated, dried over anhydrous Na_2SO_4 and analysed by gas chromatography. The equilibrium concentrations of non-sorbed chlorophenols were determined with a Varian Aerograph Series 1400 gas chromatograph equipped with Sc ^{3}H electron capture detector. A glass chromatographic column, 1.8 m × 2 mm i.d., packed with 1.3% Silicone GE SF 96 + 5.3% QF 1 on 0.13–0.16 mm Supelcoport was used, operating at 160°C and 30 mL min^{-1} of nitrogen carrier gas flow. Injector and detector temperatures were 240 and 270°C, respectively.

The equilibrium concentrations of investigated triazine herbicides in the aqueous phase were determined spectrophotometrically (UV/VIS Spectrophotometer, Cecil Instruments Ltd., 9000 Series) by measuring the absorbance directly in the sorption equilibrium solution at wavelengths of characteristic absorption maxima: 222.8 nm for atrazine, 223.4 nm for simazine and ametryn, and 224.0 nm for prometryn [12].

RESULTS AND DISCUSSION

The concept of reference EURO-Soils was developed with the aim of harmonisation of testing adsorption/desorption behaviour of new chemicals in the European Union [11]. For this purpose five surface soils (EURO-Soils 1–5), representative for the respective territory, have been selected. In addition, one subsoil sample (EURO-Soil 6) was collected to represent material that is very poor in organic matter content.

EURO-Soils cover a wide range of sorption-controlling properties, e.g. grain size distribution, pH values, organic matter content and content of iron and aluminium oxides. Table I shows some pedological characteristics of EURO-Soil samples. It has to be emphasised that within the complete set of EURO-Soils there are often different pairs which show identical or similar values for an important sorption-controlling property (ES 1 and ES 3 for pH, ES 3 and ES 6 for clay content, ES 1 and ES 4 as well as ES 2 and ES 3 for organic matter content, ES 1 and ES 2 as well as ES 3 and ES 4 for CEC), but which totally differ with respect to other parameters. The EURO-Soils perfectly meet the requirements for testing and interpreting the behaviour of chemicals in the soil environment [11].

Some characteristics of the investigated chlorophenols and triazine herbicides are shown in Table II. For example, in a group of chlorophenols an increase in the number of chlorine substituents leads to an increase in the acidity and hydrophobicity [1]; the chlorotriazine pK_a values are lower than values for methylthiotriazines [8]; the $\log K_{\mathrm{ow}}$ values for simazine, ametryn, atrazine and prometryn are lower than values published for chlorophenols [13].

The extent of ionisation and hence the sorption behaviour of polar and easily ionisable compounds, like chlorophenols, are strongly influenced by water-phase

TABLE II Characteristics of investigated compounds

Compound	pK_a	$\log K_{ow}$
TCP	6.15	3.72
TeCP	5.40	4.42
PCP	5.25	5.24
Atrazine	1.7	2.53
Simazine	1.7	1.50
Prometryn	4.1	3.05
Ametryn	4.0	2.50

Data from [1,8,13].

acidity [1,2]. According to the sorbent acidities (Table I), ionised forms of all three investigated chlorophenols dominate in EURO-Soils 2, 4 and 6. In EURO-Soil 5 neutral chlorophenols are dominant. Both fractions – neutral molecules and chlorophenolate anions – of all three chlorophenols are present in EURO-Soils 1 and 3.

The results of sorption experiments obtained for sorption of investigated chlorophenols and triazine herbicides in EURO-Soils are shown in Tables III–V. To evaluate the sorption results the difference between the initial and equilibrium aqueous concentration of these compounds was calculated and ascribed to soil sorption. Experimental data sets were fitted to the sorption isotherm curve by non-linear regression for each pair of sorbate and sorbent. The relationship between the amount of sorbates sorbed per unit mass of soil (x/m in nmol g^{-1}) and their equilibrium aqueous concentration (C_e in nmol mL^{-1}) was calculated with respect to the Freundlich sorption isotherm, $x/m = K_f\ C_e{}^{1/n}$, where K_f is the sorption coefficient indicating sorption intensity and $1/n$ is constant for a given compound and sorbent, reflecting isotherm linearity.

TABLE III Sorption of chlorophenols in EURO-Soils: Freundlich isotherm coefficients and log K_{om}

Soil	*K_f*			*1/n*			*log K_{om}*		
	TCP	*TeCP*	*PCP*	*TCP*	*TeCP*	*PCP*	*TCP*	*TeCP*	*PCP*
ES 1	6.33	12.02	37.02	0.45	0.43	0.66	2.38	2.66	3.15
ES 2	2.16	2.07	5.32	0.62	0.55	0.49	1.53	1.51	1.92
ES 3	5.38	11.57	29.45	0.45	0.52	0.67	1.92	2.26	2.66
ES 4	0.84	1.12	3.97	0.22	0.41	0.55	1.47	1.59	2.14
ES 5	169.72	404.30	555.43	0.86	0.83	0.69	3.03	3.41	3.54
ES 6	0.40	0.10	0.13	0.39	0.42	0.06	1.71	1.12	1.24

TABLE IV Sorption of triazine herbicides in EURO-Soils: Freundlich isotherm coefficients and log K_{om}

Soil	*Atrazine*			*Simazine*			*Prometryn*			*Ametryn*		
	K_f	*1/n*	*log K_{om}*	*K_f*	*1/n*	*log K_{om}*	*K_f*	*1/n*	*log K_{om}*	*K_f*	*1/n*	*log K_{om}*
ES 1	4.30	1.07	2.21	20.62	0.67	2.89	164.73	0.57	3.79	194.59	0.60	3.87
ES 2	5.35	0.94	1.92	4.59	0.79	1.86	6.75	0.97	2.02	12.51	0.75	2.29
ES 3	2.22	1.00	1.54	19.19	0.33	2.47	4.22	1.18	1.82	1.35	1.22	1.32
ES 4	1.91	1.07	1.83	1.59	0.94	1.75	13.16	0.65	2.66	8.06	0.61	2.45
ES 5	24.54	0.95	2.19	48.85	0.72	2.49	130.23	0.79	2.91	238.92	0.66	3.18
ES 6	1.21	0.75	2.18	0.45	1.13	1.75	0.44	1.01	1.74	5.44	0.49	2.83

TABLE V Free energy change for sorption of chlorophenols and triazine herbicides in EURO-Soils

Soil	$-\Delta_r G$ (kJ mol^{-1})[a]						
	TCP	*TeCP*	*PCP*	*Atrazine*	*Simazine*	*Prometryn*	*Ametryn*
ES 1	13.43	15.03	17.76	12.40	16.21	21.26	21.71
ES 2	8.63	8.51	10.84	10.77	10.43	11.33	12.85
ES 3	10.85	12.72	15.02	8.64	13.85	10.21	7.40
ES 4	8.30	8.99	12.47	10.27	9.82	14.92	13.74
ES 5	17.10	19.23	20.01	12.28	13.97	16.32	17.84
ES 6	9.66	6.34	2.80	12.23	9.82	9.76	15.87

[a] $\Delta_r G = -RT \ln K_{\text{om}}$.

Organic matter sorption coefficients K_{om} were calculated by normalisation of K_f values for SOM in each sorbent. Coefficients K_{om} were used for calculation of free energy changes of sorption, according to the equation

$$\Delta_r G = -RT \ln K_{\mathrm{om}}$$

where R is the gas constant and T the absolute temperature.

The sorption intensity, indicated by the Freundlich sorption coefficients K_f and the organic matter sorption coefficients K_{om}, does not always follow the usual sequence of sorbate hydrophobicities (Tables III and IV). More hydrophobic TeCP was sorbed less than the least hydrophobic TCP in EURO-Soils 2 and 6 (Table III). The sorption of the most hydrophobic PCP in EURO-Soil 6 was also lower than the sorption of TCP. The sorption intensities of the most hydrophobic triazine, prometryn, in four out of six sorbents were lower than those of the less hydrophobic ametryn (Table IV). In three EURO-Soils the least hydrophobic simazine was sorbed considerably more strongly than more hydrophobic atrazine. The K_f coefficients in EURO-Soil 1 were significantly higher for all compounds than the coefficients in EURO-Soil 4 despite those two soils containing very similar amounts of organic matter. EURO-Soil 1 is characterised by the highest amount of clay and iron and aluminium oxides. However, a significant dependence of triazine and chlorophenol sorption intensities on the content of metal oxides in EURO-Soils was not found.

The intensities of chlorophenol sorption ($\log \mathrm{K}_f$ values) followed the changes in the total SOM content (Fig. 1A), as has been reported [1]. Regression lines linearly increased with the increase of SOM for all three chlorophenols and $r^2 > 0.869$ proving the compatibility of sorbates with SOM in investigated soils. The sorption intensity of triazine herbicides also increased with an increase of SOM, but the increase was statistically significant only for chlorotriazines (Fig. 2A). This result was consistent with the reported increase of the sorption intensity of atrazine with the increase of the organic carbon content of the intensively cultivated soils of the Po Valley, Italy [14].

The $\log K_{\mathrm{om}}$ values of chlorophenols increased linearly with an increase of sorbent CEC ($r^2 = 0.794$–0.899) (Fig. 1B) and exponentially decreased with an increase of sorbent pH ($r^2 = 0.874$–0.949) (Fig. 1C). The fraction of dissociated molecules (chlorophenolates) increases with an increase of sorbent acidity above the pK_a values of chlorophenol, and sorption of chlorophenolates is lower than sorption of neutral molecules. In a study of the sorption behaviour of 2,4-dichlorophenol, 2,3,4,5-tetrachlorophenol, TCP, and PCP in lake aquatic humic matter, Peuravuori *et al.* also observed a decrease of sorption intensity with an increase of aqueous-phase pH [15]. PCP equilibrium sorption coefficients normalised to organic carbon content were 3.20, 2.99 and 2.71 at pH 3, 5.5 and 7, respectively. Calculated distribution ratios between aqueous phase and sediment sample collected in the midwestern United States was also higher for the neutral PCP than for pentachlorophenolate anion [16]. The nature of the organic covering the clay surface also may have been affected by pH [16].

A sorbent's mineral surface, bearing polar functional groups and cationic species, may attract by mechanisms which either favour more hydrophilic molecules or are sterically controlled, favouring the sorption of species of smaller size and more appropriate shape. The intensities of chlorophenol sorption followed the changes in sorbent sand,

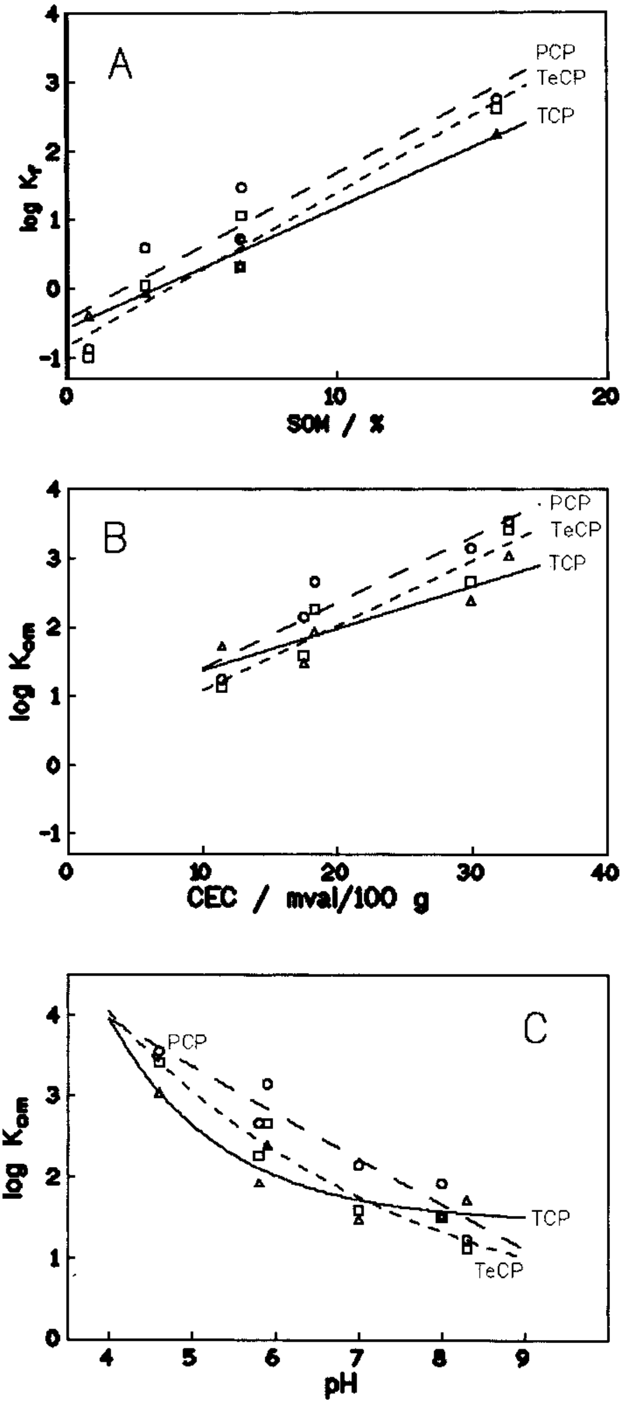

FIGURE 1 The correlation between (A) log K_f and soil organic matter content (SOM), (B) log K_{om} and soil cation exchange capacity (CEC) and (C) log K_{om} and pH for TCP (Δ—), TeCP (□- - -) and PCP (○– – –).

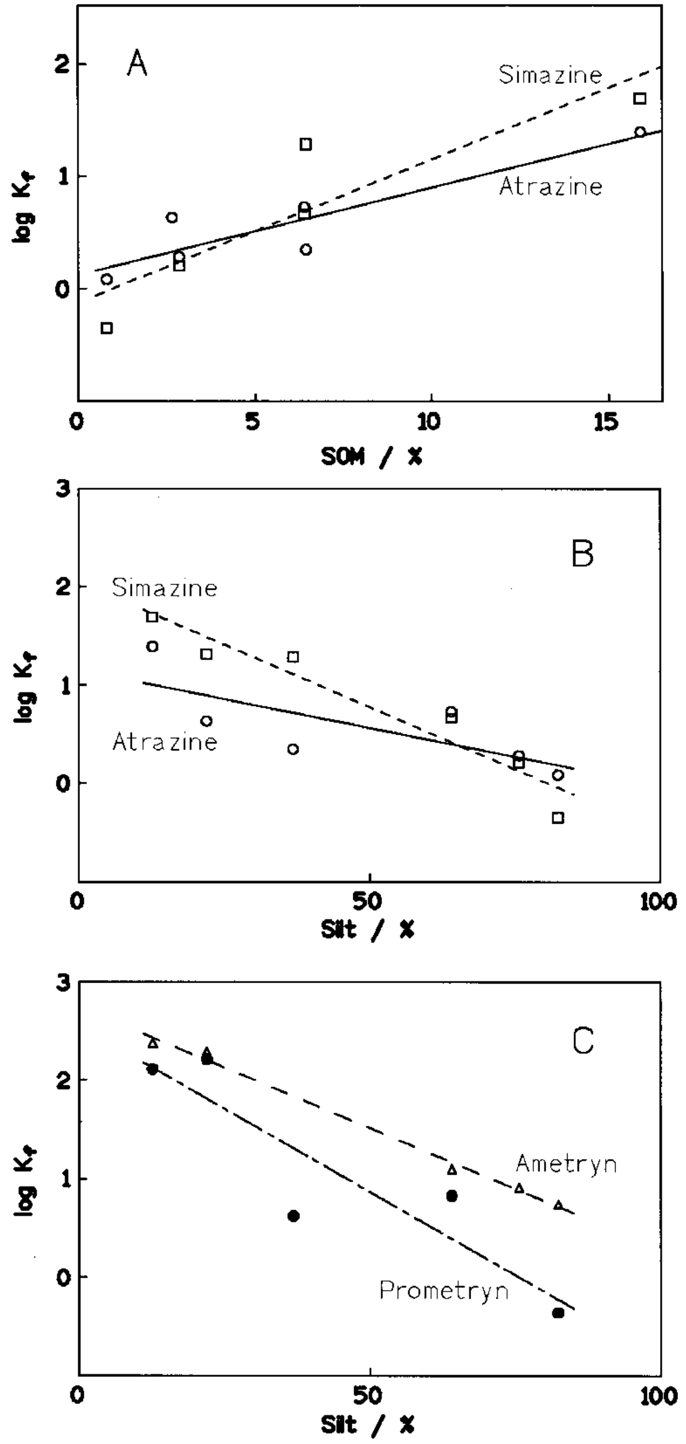

FIGURE 2 The correlation between sorption intensity (log K_f) and (A) soil organic matter (SOM) and (B) and (C) silt content for atrazine (○—), simazine (□- - -), ametryn (Δ– – –) and prometryn (●— - —).

silt and clay content (Fig. 3). The $\log K_{\mathrm{om}}$ values increased with an increase of sand content and decreased with an increase of silt and clay content. An increase of the total silt portion in EURO-Soils decreased the sorption intensity of triazine herbicides, but was statistically significant ($P < 0.05$) only for simazine and prometryn (Fig. 2B and C). The greatest negative impact on $\log K_f$ was from the soil coarse-grainy silt portion followed by medium-grainy silt, while fine-grainy silt did not influence the sorption. The sorption intensity of triazine herbicides was not influenced by the EURO-Soils' clay content.

The results obtained for sorption intensities of chlorophenols in EURO-Soils are lower than those for sorption of chlorophenols in natural sediments and aquifer materials [1] but the majority are within the extensive range of values reported in the literature [17]. The intensity of atrazine sorption is in good agreement with values of the sorption coefficients obtained for non-labelled atrazine after 16 h equilibration in EURO-Soils 1, 3, 4 and 5 [11]. The greater sorption constants obtained in the present study for atrazine in EURO-Soils 2 and 6 compared to the literature values are a consequence of differences in applied extraction procedures and/or in the initial compound concentration. The magnitude of sorption intensity could be somewhat greater for the lower concentration ranges [15].

As shown in Tables III and IV the Freundlich sorption coefficient $1/n$, reflecting the isotherm linearity, is considerably lower than unity for all sorbates in almost all EURO-Soils. The values of the $1/n$ coefficient were considerably less than 1 (≤ 0.8) in 16 out of 18 Freundlich equations for chlorophenols, and in 13 out of 24 Freundlich equations for triazine herbicides. The lack of isotherm linearity pointed to limited soil/sediment sorption capacity and indicated that sorption of sorbates was governed in different sorbents by different mechanisms and not only by simple partition. A similar conclusion can be drawn by comparing the values of changes in Gibbs energy during the sorption of investigated compounds in EURO-Soils (Table V). Negative $\Delta_r G$ values indicate a spontaneous sorption process and greater sorption intensities are followed by greater absolute values of $\Delta_r G$. The greatest values for all chlorophenols are obtained in EURO-Soil 5 ($-\Delta_r G = 17.1-20.0\,\mathrm{kJ\,mol^{-1}}$), while the lowest are in EURO-Soil 6 ($-\Delta_r G = 2.8-9.7\,\mathrm{kJ\,mol^{-1}}$). The majority of $\Delta_r G$ values obtained for sorption in EURO-Soils show the ability of chlorophenols to develop polar interactions with the polar sorbent groups. Hydrogen bonding could be one of the interaction mechanisms ($-\Delta_r G = 4-40\,\mathrm{kJ\,mol^{-1}}$) [18]. The average free energy changes during the sorption of ametryn ($-14.1 \pm 4.5\,\mathrm{kJ\,mol^{-1}}$) and prometryn ($-15.0 \pm 4.9\,\mathrm{kJ\,mol^{-1}}$) are comparable despite differences in their hydrophobicity and significantly different ($P < 0.05$) from those of atrazine ($-11.1 \pm 1.5\,\mathrm{kJ\,mol^{-1}}$) and simazine ($-12.4 \pm 2.7\,\mathrm{kJ\,mol^{-1}}$). Prometryn and ametryn are structurally related, both having a methylthio substituent, while atrazine and simazine belong to the chloro-s-triazine herbicides. Differences in $\Delta_r G$ values are indications of different sorption mechanisms for the two groups of triazine herbicides.

CONCLUSIONS

Sorption of the investigated compounds in EURO-Soils is a complex process that includes not only simple hydrophobic partition but also specific interactions depending on the characteristics of both sorbate and sorbent. The sorption

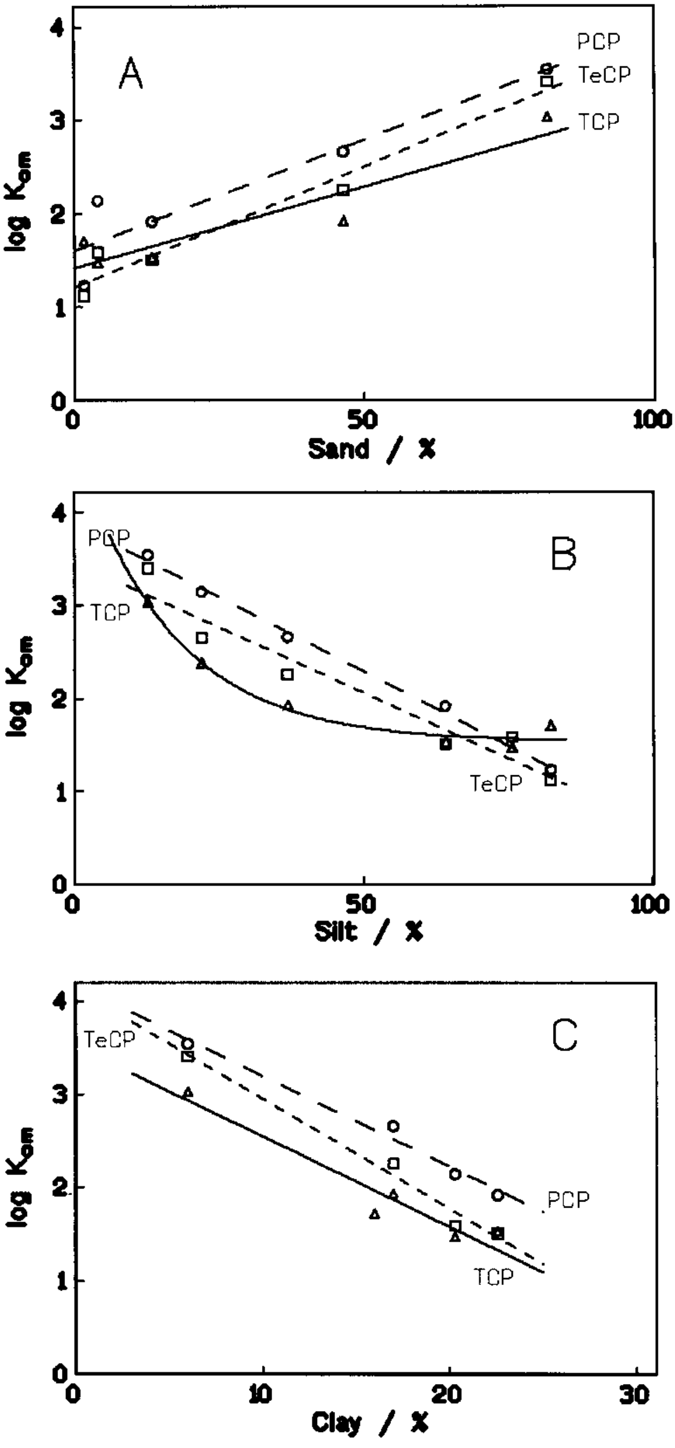

FIGURE 3 The correlation between sorption intensity (log K_{om}) and soil content of (A) sand, (B) silt and (C) clay for TCP (Δ—), TeCP (□---) and PCP (○———).

intensity of chlorophenols increased with increase of sorbent organic matter content, cation exchange capacity, and sorbent sand content, while a decrease of sorption intensity was observed with increase of sorbent pH, silt, and clay content. Statistically significant positive correlation between K_f sorption coefficients and sorbent organic matter content was also obtained for the chlorotriazines atrazine and simazine. Chlorotriazine sorption was favoured by lower content of coarse- and medium-grainy fractions of silt.

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