

Fate of anthropogenic organic pollutants in soils with emphasis on adsorption/desorption processes of endocrine disruptor compounds*

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Abstract: After providing a brief overview of the various phenomena that anthropogenic organic pollutants (AOPs) of various nature and origin are subjected to in soil, the paper focuses on an important class of these, the endocrine disruptor compounds (EDCs), which are hormone-like substances able to alter (i.e.) disrupt, the normal endocrine functions in animals and humans. EDCs may enter the soil through current agricultural practices and/or disposal of urban and industrial effluents, sludges, and wastes. The estrogenic risk of EDCs is generally related to their distribution and speciation in the various soil phases, in which adsorption/desorption processes play a very important role. Adsorption kinetics and adsorption/desorption isotherms of the EDCs: bisphenol A (BPA), octylphenol (OP), 17- α -ethynylestradiol (EED), and 17- β -estradiol (17ED), onto four samples collected from the surface (depth 0–30 cm) and deep (depth 30–90 cm) horizons of two acidic sandy soils in Portugal (P) and Germany (G) (P30 and G30, and P90 and G90, respectively) were determined using a batch equilibrium method and the high-performance liquid chromatography (HPLC) technique. Adsorption of EDCs onto all soils examined occurs in two phases, a rapid one in less than 10 h of contact, and corresponding to more than 90 % of total adsorption, and a slow one that may need several hours until attainment of equilibrium. Experimental adsorption data fit best in a linear isotherm for BPA, in a nonlinear, L-shaped Freundlich isotherm for EED, in either a linear or a nonlinear Freundlich isotherm for OP, and in a Langmuir isotherm for 17ED. Thus, no limiting adsorption is observed for soils examined over the concentration range tested for BPA, OP, and EED, whereas a maximum adsorption (i.e., saturation) is reached only by 17ED. In general, the values of the Freundlich constant, K , and of the distribution coefficient, K_d , calculated from the experimental isotherms of the four EDCs onto soils examined follow the same trend, that is: G30 > P30 > P90 \geq G90. Further, the K and K_d values of any EDC are positively correlated with the soil organic carbon (OC) content, which is larger for surface horizon soils than deep horizon soils. Adsorption of BPA is generally reversible, and its desorption occurs quickly and completely, thus, it is expected to move down the soil profile, and possibly contaminate the groundwater. On the contrary, OP and EED are adsorbed almost irreversibly, and are slowly and only limitedly desorbed, thus are expected to accumulate, especially in the top soil layer, and cause soil contamination.

Keywords: anthropogenic organic pollutants; soil; endocrine disruptor compounds; adsorption kinetics; adsorption/desorption isotherms.

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ANTHROPOGENIC ORGANIC POLLUTANTS AND THEIR FATE IN SOIL

An anthropogenic organic pollutant (AOP) may be defined as any organic chemical that is foreign to the natural ecosystem and may adversely affect, either directly or indirectly, the natural physical, chemical and biological equilibria and processes in the global environment or a portion of it (e.g., the soil). Potential AOPs that can reach the soil by purpose include various types of pesticides (e.g., herbicides, insecticides, fungicides, etc.) and other organic chemicals that are currently used in agricultural practices and as agricultural product conservation. Further, AOPs can reach the soil incidentally, that is, by wet and dry atmospheric deposition of volatile chemicals originated from a variety of sources, including industrial emissions and solid waste incineration; by discharge of municipal and industrial wastes, refuses, sludges, and effluents; and by soil amendment. These AOPs include chemical substances of widely differing classes and properties such as: (a) polynuclear aromatic hydrocarbons (PAHs) contained in waste streams originated from various industrial processes such as combustion of fossil fuels, chemical manufacturing, petroleum refining, metallurgical processes, and some coal, oilshale, and tar sand conversion systems; (b) phthalic acid diesters (PAEs) used mainly as plasticizers, but also as pesticide carriers and insect repellents, in dyes, cosmetics, and lubricants; (c) endocrine disruptor compounds (EDCs) (see below); and (d) alkanes, organic solvents, detergents, and surfactants.

Once on the soil surface, AOPs may undergo volatilization, photodecomposition, or be transported by soil runoff and/or erosion to surface waters. In particular, the photochemical decomposition of AOPs is induced by sunlight [1], and can be either direct or indirect. Direct photolysis is initiated through absorption of sunlight by the AOP molecule that becomes energetically excited, and can then be transformed to photoproducts. In indirect photolysis, sunlight is initially absorbed by organic or inorganic chromophore compounds present in soil, other than the AOP molecule. These compounds, which include several clay minerals, metal oxides and hydroxides, transition-metal ions, and various fractions of soil organic matter (SOM), especially humic substances (HSs), may then either transfer the energy to the AOP molecule (photosensitization) or produce specific, greatly reactive, short-lived photoreactants such as the solvated electron, singlet oxygen, superoxide radical anion, peroxy and hydroxy radicals, hydrogen peroxide, and various oxireductive species, which may then react with the target AOP (photoinduction) [2].

The parent AOPs, and possibly their photodecomposition products, can enter the soil, where their behavior and performance is controlled by several factors, including the physical and chemical properties of the AOP; the thickness, hydrological status, composition, and nature of the soil; and the type and extent of interactions of the AOP with the various soil constituents. In the soil, AOPs can be leached, eventually reaching the groundwater table, and/or be subjected to various phenomena including physical and chemical adsorption/desorption processes onto/from soil inorganic and organic solid and colloidal components, partial or total chemical decomposition and/or biological degradation, and uptake by plant roots.

Biodegradation operated by soil microorganisms is considered to be one of the primary factors that determine the fate of AOPs in soil [3]. The major microbial processes that AOPs may be subjected to in soil include: hydrolysis, oxidative coupling, hydroxylation, β -oxidation, epoxidation, N-dealkylation, decarboxylation, ether cleavage, aromatic ring cleavage, heterocyclic ring cleavage, sulfoxidation, and several synthetic reactions [4]. All these processes are mediated by various intracellular and extracellular enzymes, including hydrolases, esterases, amidases, phosphatases, proteases, lyases, various phenoloxidases, oxidoreductases, monooxygenases, and various mixed function oxidases [4]. The AOPs having a chemical structure similar to that of natural organic compounds are usually more susceptible to biodegradation than those having little structural resemblance to natural organic matter (OM) [5]. However, several AOPs cannot be degraded before the microorganism populations manage to develop novel specific enzymes through genetic mutation and natural selection [6,7].

Soil mineral colloids, which include clay minerals, metal oxides, carbonates, and other minerals with large surface area and relatively high charge density, are extensively involved both in the abiotic

transformation of AOPs in soil, and in their immobilization/accumulation by surface and interlayer adsorption [8]. These processes vary with the structural and surface properties of the minerals; the saturating cations and their hydration status; the molecular structures of AOPs; and environmental factors such as pH, available water, redox conditions, and ionic strength of the medium [9]. Thanks to their large specific surface areas and lattice imperfections [8], most soil minerals, including Mn(IV) and Fe(III) oxides, Al hydroxides, aluminosilicates such as allophane, various clay-size layer silicates, and even primary minerals common in soil environments, possess catalytic properties and are able to mediate several AOP transformations. For example, the surfaces of mineral colloids behave as Brønsted acids and have the ability to protonate many uncharged AOPs, and thus favor their degradation reactions by surface acid catalysis. Mineral phases also contribute markedly to the complexity of biodegradation processes by surface adsorption of microorganisms, thus altering, and often drastically reducing, their biological activity and mobility.

Numerous studies have demonstrated that AOPs have a greater affinity for soil organic colloids than that for mineral colloids [10]. Thus, the content and nature of SOM, and especially of its most abundant and reactive fraction, i.e., HS, play a major role in determining the fate of AOPs in soil. The HS fraction of SOM consists of a physically and chemically heterogeneous mixture of relatively high-molecular-mass, yellow-to-black colored organic compounds of mixed aliphatic and aromatic nature, formed by secondary synthesis reactions (i.e., humification) between microbial and chemical decay and transformation products and recalcitrant residues of biomolecules originated from organisms during life and after death [10]. The HS macromolecules consist of aromatic, phenolic, quinonic, and heterocyclic "building blocks" that are randomly condensed or linked by aliphatic, oxygen, nitrogen, and sulfur bridges, and bear aliphatic, glucidic, amino acidic, and lipidic surface chains as well as chemically reactive functional groups of various nature, including carboxylic, phenolic, alcoholic, and carbonyl groups. Further, HS contain highly reactive organic free radical moieties of prevalent semiquinonic nature, and are rich in hydrophilic and hydrophobic sites, exhibit a polydispersed and polyelectrolytic character, possess surface activity, and present a relatively open, flexible, sponge-like structure rich of holes. All these properties qualify HS as privileged natural organic compounds in the interaction with AOPs.

The HS may interact with AOPs in several ways and thus influence AOP behavior, performance, and fate in soil with important implications in their persistence, immobilization and accumulation, mobility and transport, bioavailability and biotoxicity, degradability, volatilization and leaching, and residue monitoring in soil. In particular, HS are shown to be able to: (a) modify water solubility of relatively water-insoluble, nonionic AOPs such as PAHs, PAEs, PCBs, DDT, and *n*-alkanes, possibly by partitioning into HS or adsorption onto HS, or by an overall increase in solvency; (b) exert catalytic activity in some AOP transformations, e.g., acid hydrolysis of some chloro-*s*-triazines and alkaline hydrolysis of *n*-alkyl esters of 2,4-D (2,4-DOE); (c) act as photosensitizers in promoting the photodegradation of some AOPs; and, especially, (d) adsorb and partition AOPs [11–15].

Adsorption represents probably the most important mode of interaction of AOPs with HS. AOPs can be adsorbed to various extent by HS through specific physical and chemical binding mechanisms and forces with varying degrees and strengths. These include ionic, hydrogen, and covalent bonding, charge-transfer or electron donor-acceptor mechanisms, dipole-dipole and van der Waals forces, ligand exchange, and cation and water bridging. However, adsorption of nonpolar (hydrophobic) AOPs can be better described in terms of nonspecific, hydrophobic, or partitioning processes between soil, water, and the HS organic phase. The mechanism(s) and extent of adsorption depend on the amount, composition, and the physical and chemical nature and properties of both the AOP and the HS. Important properties that influence adsorption/desorption include: the molecular structure; the number and type of functional groups; the size, shape, and configuration; the polarity, polarizability, and charge distribution; solubility of both HS and AOP; and the acidic or basic or neutral, ionic or nonionic nature of the AOP. The conditions of the medium, such as pH, ionic strength, redox potential, and amount of water, will also greatly influence adsorption of AOPs onto HS in soil.

For any given AOP, several possible adsorption mechanisms may operate simultaneously and/or in sequence. Initially, the AOP molecule may be adsorbed by HS sites providing the strongest binding, followed by progressively weaker sites as the stronger sites become filled. Once adsorbed, the AOP may be subject to other processes (e.g., it may further react, becoming either covalently and irreversibly bound or only physically trapped into the HS matrix). Adsorption processes may thus vary from complete reversibility to total irreversibility (i.e., the adsorbed AOP may be easily desorbed, desorbed with various degrees of difficulty, or not at all). Further, the effect of adsorption on AOP migration in soil depends on whether the adsorption occurs on insoluble, immobile HS such as humic acids, or on dissolved or suspended, mobile fractions such as fulvic acids. Thus, HS can either “attenuate” or “facilitate” AOP movement and transport in soil.

ENDOCRINE DISRUPTOR COMPOUNDS

The EDCs comprise several organic compounds of natural and anthropogenic origin widely diffused in the environment which are suspected or known to interfere with the normal endocrine functions of animals and humans by acting as hormone-like substances in the organism [16,17]. These include natural and synthetic estrogens of human origin; different classes of herbicides, fungicides, insecticides, and nematicides; various industrial chemicals including PCBs, PAEs, dioxins, various products and by-products of paper, paint, plastic industries; and some pharmaceutical products, like estrogenic compounds [18,19]. These compounds may enter the soil through current agricultural practices and/or by application, discharge and/or disposal of urban and industrial effluents, sludges, and wastes.

Although research needs for risk assessment of health and environmental effects of EDCs have been recently stressed [20], and despite the increasing social concern for the actual exposure of animals and humans to EDCs, the attention on these issues has mainly focused on water contamination, whereas relatively little information is available on the impact and fate of EDCs introduced into soil. The risk assessment of potential environmental hazards associated with the presence of EDCs in soil, as well as the definition of possible remediation measures, require an accurate evaluation and quantification of the soil response to these compounds. The response of soil to the estrogenic risk of EDCs is generally related to the distribution and speciation of EDCs in the various soil phases. The EDCs can either be extensively and strongly bound to the solid soil fractions and accumulate in the top soil layer, or limitedly and weakly bound, and thus be moved down to deeper soil horizons and groundwater. Thus, the evaluation of the rate and extent of adsorption/desorption processes of EDCs onto/from different soil horizons represent a key factor for understanding their behavior, performance, and fate in soil, and assessing their potential environmental impact.

The objective of this work was thus to determine and interpret adsorption kinetics and adsorption/desorption isotherms of some representative EDCs in surface and deep horizons of two sandy soils. The soils and EDCs studied were chosen in the framework of a European Commission (EC)-supported research project aiming to evaluating the behavior and performance of some specific EDCs in surface and deep layers of acidic sandy soils of two different climatic areas of Europe. The addition of ethanol to water was necessary in a minimal amount capable of increasing the solubility of extremely low water-soluble EDCs up to an adequate analytical value. The concentrations of EDCs used for adsorption/desorption experiments were above those commonly found in the environment in order to obtain a more evident effect and better clarify the type and mechanism of adsorption/desorption. A conventional batch equilibrium method and a standard high-performance liquid chromatography (HPLC) procedure extensively described in the current pertinent literature were used to perform the experiments.

MATERIALS AND METHODS

Soils

The soil samples used in this work were collected from the surface (0–30 cm) and deep (30–90 cm) horizons of two acidic sandy soils originating from two areas near Lisbon in Portugal (P) and near Dresden in Germany (G), and are labelled, respectively, as P30 and G30 and P90 and G90. Before analysis and experiments with EDCs, each soil was air-dried, crushed, and passed through a 2-mm sieve.

Soil samples were analyzed by standard conventional procedures for their most relevant physical and chemical properties, and results obtained are shown in Table 1. Both soils have a sandy texture and are acidic. In particular, the surface horizons of both soils (samples P30 and G30) have much higher organic carbon (OC) and related OM contents than the corresponding deeper horizons (P90 and G90). Further, the surface horizon of the G soil (G30 sample) is much richer in OC and OM than the corresponding P horizon (P30 sample), whereas the opposite is true for the G90 sample with respect to the P90 sample.

Table 1 Some physical and chemical properties of soils examined.

Parameter	P30	P90	G30	G90
Sand %	93.0	93.9	94.9	94.8
Silt %	4.4	3.5	3.6	3.2
Clay %	2.6	2.6	1.5	2.0
pH (H ₂ O)	4.8	5.5	5.9	5.4
pH (KCl 1N)	4.5	4.8	5.5	4.6
Electrical conductivity at 25 °C (1:2) dS/m	0.050	0.040	0.095	0.092
Organic carbon g/kg	3.6	1.8	9.3	1.1
Organic matter g/kg	6.3	3.3	16.0	1.8
Total N g/kg	0.4	0.3	0.7	0.2
C/N ratio	9.1	6.0	12.6	5.3
Available P mg/kg	36	14	16	7
K mmol/kg	0.887	0.788	2.049	1.893
Ca mmol/kg	4.005	3.262	14.051	2.830
Na mmol/kg	0.962	1.024	1.081	0.796
Mg mmol/kg	0.531	0.429	1.997	0.456

Endocrine disruptor compounds

The EDCs investigated in this work were: (a) bisphenol A (BPA) [2,2-(4,4-dihydroxydiphenyl) propane]; (b) octylphenol (OP) [4-(1,1,3,3,-tetramethylbutyl)phenol]; (c) 17 α ethynilestradiol (EED) [17 α -ethynil-1,3,5(10)-estratriene-3,17 β -diol]; and (d) 17 β estradiol (17ED) [1,3,5(10)-estratriene-3,17 β -diol]. All compounds, 99 % purity, were obtained from Sigma Aldrich Chemie GmbH, Steinheim, Germany. Their molecular formulas are shown in Fig. 1.

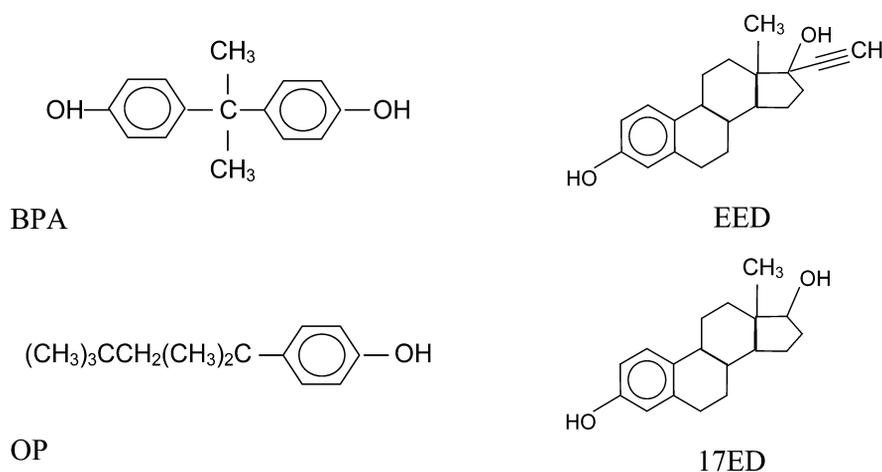


Fig. 1 Molecular formulas of EDCs examined.

BPA is a xenoestrogen formed as an intermediate compound in the preparation of epoxy resins and polycarbonates; it is also used in manufacturing adhesives, building materials, compact disks, and electrical and electronic parts, and in agriculture as a fungicide. OP is a xenoestrogen formed as a stable biodegradation metabolite from OP polyethoxylates that are widely used in the formulation and production of plastics, paints, pesticides, and detergents. EED is a synthetic estrogen used for medical purposes, often in combination with progestogen as an oral contraceptive. 17ED is the most potent mammalian estrogenic hormone.

Adsorption kinetics

Adsorption kinetics were measured for each EDC to evaluate the adsorption rates onto soil samples examined and to establish an adequate equilibration time to be used for measuring adsorption isotherms.

Ten aliquots of 5 g of soil (air-dried and 2-mm-sieved) were each suspended in 20 mL of either a water solution of BPA at a concentration of 10 mg L⁻¹ or a 20 % (v/v) ethanol/water solution of EED or 17ED at a concentration of 20 mg L⁻¹. For OP, 10 aliquots of 1 g of soil were each suspended in 25 mL of a 6 % (v/v) ethanol/water solution of OP at a concentration of 1 mg L⁻¹.

The mixtures were then mechanically shaken for each of 10 different time periods: 0.25, 0.5, 1, 2, 4, 8, 16, 24, 48, and 72 h. At the end of each time period, the suspensions were centrifuged, and the supernatants were analyzed by HPLC to determine the residual concentration of each EDC in solution, using the procedure adopted for obtaining adsorption isotherms as described in the following subsection. All experiments were conducted in triplicate at a temperature of 20 ± 2 °C.

Adsorption isotherms

Adsorption isotherms of each EDC onto each soil sample were obtained using a batch equilibrium (slurry-type) method. Aliquots of 5 g of soil were added in glass flasks with 20 mL of either water solutions of BPA at concentrations of 1, 2, 4, 8, 12, 20, and 40 mg L⁻¹ or 20 % (v/v) ethanol/water solutions of EED or 17ED at concentrations of 1, 2, 4, 8, 12, and 20 mg L⁻¹. For OP, aliquots of 2 g of soil were added to 15 mL of 10 % (v/v) ethanol/water solutions of OP at concentrations of 0.1, 0.2, 0.5, 1, 2, 4, and 5 mg L⁻¹. All experiments were conducted in triplicate.

Equilibration was achieved by mechanical shaking of mixtures for 24 h at 20 ± 2 °C in the dark. Suspensions were then centrifuged at 17 400 g for 15 min, and the supernatant solutions were removed

and analyzed for the equilibrium concentrations, C , of each EDC by HPLC using a Thermo Separation Products Liquid Chromatograph. For the determination of BPA, EED, and 17ED, a 15-cm Merck LiChrospher® 60 RP-Select B column and an ultraviolet detector operating at 280 nm were used. For the determination of OP, a SUPELCOSIL™ LC-18 column and a fluorescence detector operating at 230 nm excitation and 310 nm emission were used. In all cases, the mobile phase used was a solution of acetonitrile/water at a ratio of 40/60 (v/v) for BPA, 50/50 (v/v) for EED and 17ED, and 75/25 (v/v) for OP. The amount of each EDC adsorbed was calculated as the difference between the initial concentration and the equilibrium concentration of EDC in solution.

To construct adsorption isotherms, experimental adsorption data obtained for each EDC on each soil were tentatively fitted to both a linear and nonlinear Freundlich equation:

$$x/m = K C^{1/n} \quad (1)$$

and the Langmuir equation:

$$x/m = (KCb)/(1 + KC) \quad (2)$$

where x/m is the amount of each EDC adsorbed in mg kg^{-1} , C is the equilibrium concentration of EDC in solution in mg L^{-1} , $1/n$ indicates the degree of nonlinearity between solution concentration and amount adsorbed, and b is the Langmuir adsorption maximum.

The magnitude of adsorption (i.e., the adsorption capacity of the substrate) was estimated by the values of both the Freundlich constant, K , and the distribution coefficient, K_d , which is defined as the mean value of the ratios of the amount of EDC adsorbed, x/m , at each equilibrium concentration, C , according to:

$$K_d = [(x/m)/C]_{\text{mean}} \quad (3)$$

Further, the OC partition coefficient, K_{OC} , which provides the amount of EDC adsorbed per unit of OC present in the substrate, was calculated for all soil samples according to:

$$K_{OC} = (K \times 100)/OC \% \quad (4)$$

Desorption isotherms

Desorption isotherms of BPA, OP, and EED were obtained by measuring their sequential release immediately after adsorption onto the various soil substrates. To obtain previous adsorption of EDC, the substrates were equilibrated for 24 h with either an aqueous solution of BPA or a 20 % (v/v) ethanol/water solution of EED at concentrations of 20 mg L^{-1} , or a 10 % (v/v) ethanol/water solution of OP at a concentration of 5 mg L^{-1} , using the same solution/substrate ratios as above for adsorption experiment.

After 24-h equilibration, the mixtures were centrifuged, and the equilibrium solution was carefully removed and replaced with the same volume of bidistilled water or the appropriate ethanol/water solution. After each desorption step, the amount of dissolved EDC present in the equilibrium solution that remained entrapped in the substrate was duly calculated and subtracted from the total amount of EDC measured in the supernatant solution. The suspensions were then shaken mechanically for 24 h to obtain a new equilibrium condition and centrifuged. The desorption procedure was repeated a maximum of five times for BPA and OP and four times for EED or until the concentration of EDC in the supernatant solution reached the detection limit in the conditions used. After each desorption step, the concentrations of BPA, OP, and EED in the supernatant solutions were measured by HPLC using the same conditions described above for adsorption experiments. The amount of EDC that remained adsorbed was calculated by difference. All experiments were conducted in triplicate. Attempts made to measure desorption of 17ED from soils examined were unsuccessful, because 17ED apparently degraded during the experiments, as shown by the appearance of unquantifiable degradation products in HPLC analysis.

For comparative purposes, in all cases both the adsorption parameters, K_{ads} and $1/n_{\text{ads}}$, and desorption parameters, K_{des} and $1/n_{\text{des}}$, were calculated by using the nonlinear Freundlich equation (eq. 1) described above. The value of K_{des} vs. K_{ads} is considered to provide an indication of the degree of reversibility/irreversibility of the adsorption process [21], whereas the value of $1/n_{\text{des}}$ vs. $1/n_{\text{ads}}$ may be related to the rate of the desorption process [22].

RESULTS AND DISCUSSION

Adsorption kinetics

Representative adsorption kinetics curves measured for the four EDCs examined onto soil G-30 are shown in Fig. 2. Adsorption of any EDC onto any soil appears to occur in two consecutive phases, a rapid one occurring in the first few hours of contact (generally less than 10 h), which generally corresponds to more than 90 % of total adsorption, and a slow one that may need several hours until the attainment of the equilibrium. BPA appears to be the most quickly adsorbed EDC onto all substrates.

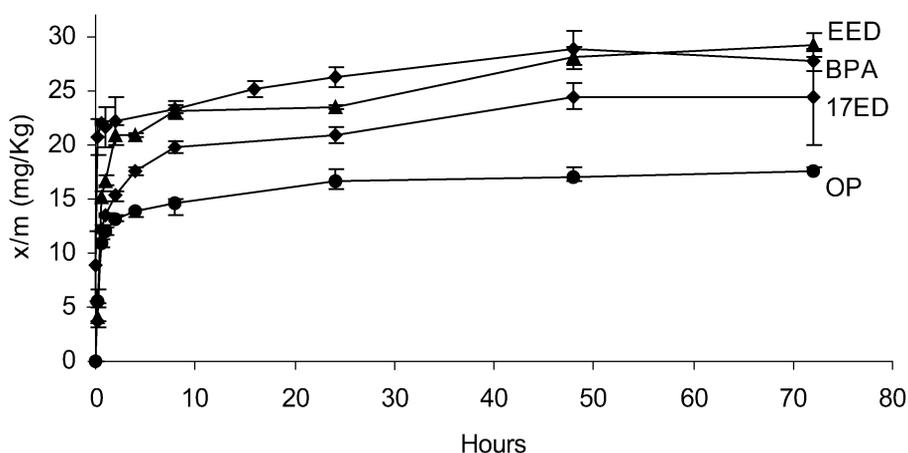


Fig. 2 Representative adsorption kinetics curves of EDCs onto soil G-30.

The rapid adsorption phase would occur on the most reactive and/or accessible sites of the substrate, whereas the slower adsorption may reflect the involvement of less reactive and/or more sterically hindered sites. In all cases, an equilibration time of 24 h was considered adequate and was used for the measurements of adsorption isotherms.

Adsorption isotherms

Experimental adsorption data for BPA onto all soils fit better in linear, C-type isotherms and for EED in nonlinear, L-shaped ($1/n < 1$) Freundlich isotherms (Fig. 3). Adsorption data of OP onto G-soils fit better in linear isotherms, and onto P-soils in nonlinear, Freundlich isotherms (Fig. 3). A linear, C-type isotherm indicates that a constant partition of the EDC occurs between the solution and the substrate, that is, adsorption is directly proportional to the solution concentration over the concentration range tested. A nonlinear, L-shaped isotherm indicates that the EDC has a moderately high affinity for the substrate in the initial stages of adsorption, which occurs with increasing difficulty as adsorption sites are filled. In both cases, no limiting adsorption (saturation) occurs over the whole concentration range considered for any EDC onto any substrate examined. For 17ED, the best fits of experimental adsorption data onto all soils examined are in a Langmuir-type isotherm (Fig. 3). This type of isotherm sug-

gests that 17ED has a moderately high affinity for the substrate in the initial stages of adsorption, whereas it has increasing difficulty in finding vacant sites as they are filled, finally reaching a maximum of adsorption (i.e., saturation).

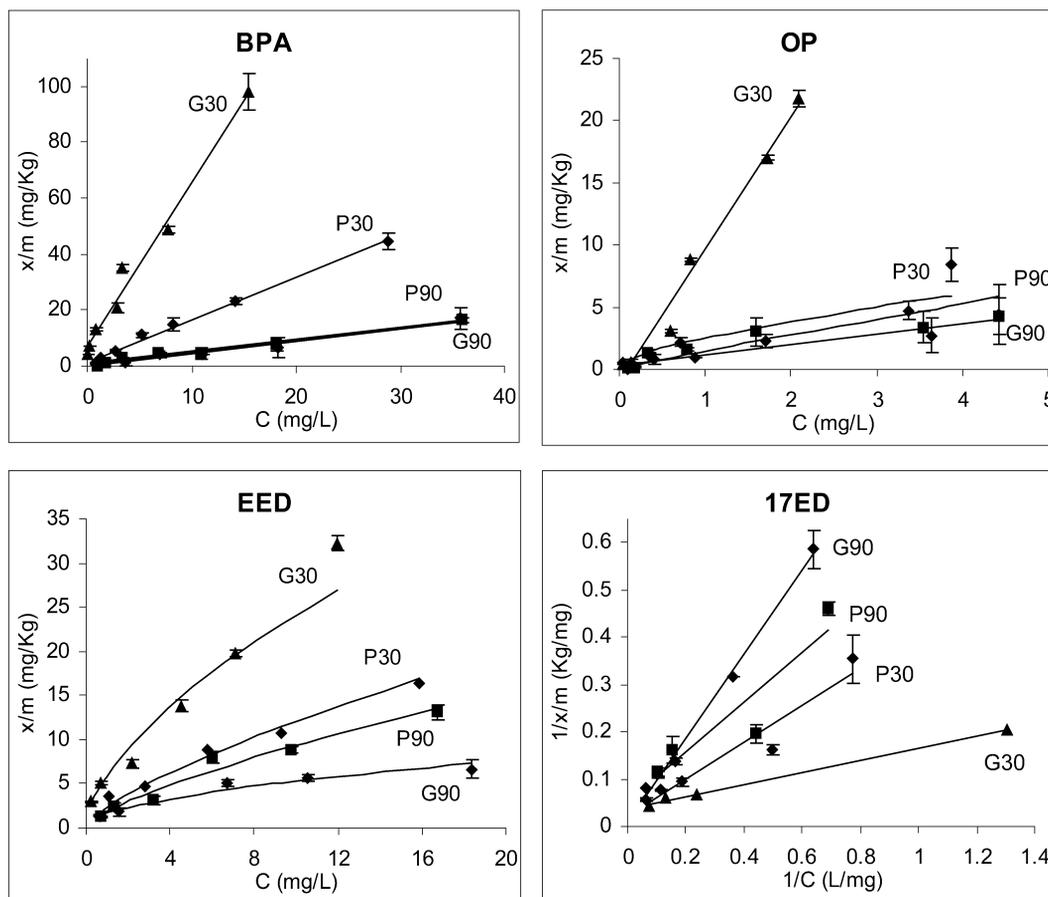


Fig. 3 Adsorption isotherms of EDCs onto soils examined.

The correlation coefficients, r , the Freundlich parameters, K and $1/n$ where applicable, the distribution coefficients, K_d , and the OC partition coefficient, K_{OC} , calculated from experimental data for BPA, OP, EED, and 17ED are shown in Table 2. The K and K_d values follow the same trend for adsorption of any EDC onto soils examined. In general, surface horizon soils, and especially soil G30, appear to have a much greater adsorption capacity for any EDC examined than the corresponding deep horizon soils. This effect appears to be related to the OC content of soil samples examined, as it is shown by the direct correlations ($P < 0.01$ and $P < 0.05$) found between K and K_d values of any EDC and soil OC % (Fig. 4).

Table 2 Correlation coefficients, r , adsorption parameters, K and $1/n$, distribution coefficients, K_d , and OC partition coefficients, K_{OC} , for adsorption of BPA, OP, EED, and 17ED onto soils examined.

Soil	r	K (L Kg ⁻¹)	$1/n$	K_d (L kg ⁻¹)	K_{OC} (L kg ⁻¹)
BPA					
P30	0.995	1.59	n.a. ^a	1.74	436
P90	0.980	0.61	n.a.	0.53	335
G30	0.977	6.54	n.a.	12.91	703
G90	0.974	0.45	n.a.	0.71	424
OP					
P30	0.960 ^b	2.60	0.60	4.76	713
P90	0.939 ^b	1.45	0.93	1.69	797
G30	0.988 ^c	10.03	n.a.	8.68	903
G90	0.955 ^c	0.94	n.a.	1.39	1023
EED					
P30	0.969	2.30	0.72	1.73	631
P90	0.982	1.73	0.73	1.17	953
G30	0.985	5.92	0.61	3.77	637
G90	0.987	1.66	0.51	0.70	1562
17ED					
P30	0.967	n.a.	n.a.	1.98	543
P90	0.922	n.a.	n.a.	1.40	768
G30	0.999	n.a.	n.a.	3.47	373
G90	0.997	n.a.	n.a.	1.02	960

^an.a.: not applicable.

^bFreundlich nonlinear isotherm.

^cLinear isotherm.

More or less extended differences are measured among K_{OC} values, i.e., the K values normalized to the content of soil OC, which is assumed to be the only factor that determines the extent of adsorption of each EDC by soil. In particular, for BPA the K_{OC} values follow the order: G30 > P30 > G90 > P90, whereas for OP the K_{OC} values are similar for the surface and deep horizons of the same soil but differ between the P-soils and G-soils. For EED and 17ED, similar K_{OC} values are obtained for surface soils, but they differ from K_{OC} of deep soils. These results suggest that the OC nature and properties, and not only its content, affect the adsorption capacity of OC for any EDC. Further, the different trends obtained for K_{OC} values, with respect to K and K_d values, would suggest that soil components other than OC, such as soil clay minerals, could be involved in the adsorption of EDCs. The comparison of either K or K_d values of the various EDCs examined shows that OP is generally the most adsorbed among the EDCs, whereas EED and 17ED show a similar extent of adsorption onto any soil examined.

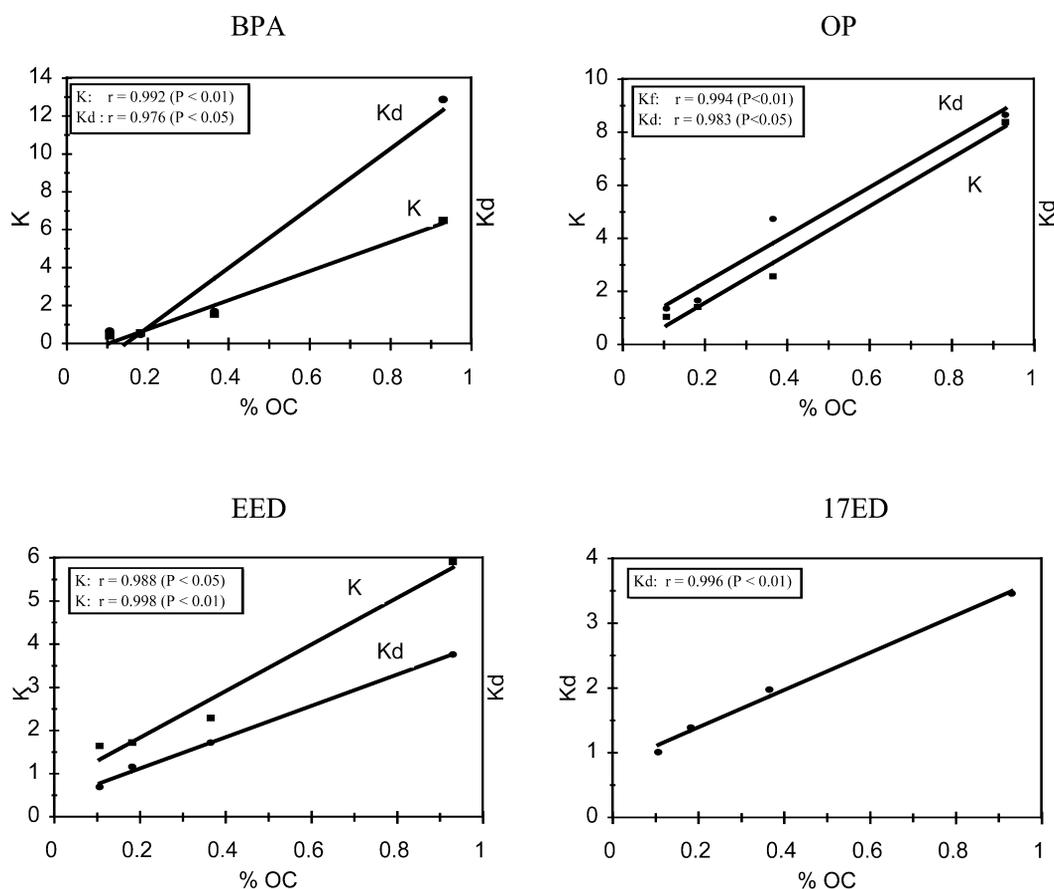


Fig. 4 Relationship between Freundlich K values and distribution coefficients, K_d , of EDCs and OC % of soils examined.

Adsorption/desorption studies

Even though adsorption data of EDCs onto the various substrates examined could be best fitted in one of the three equations described above, a nonlinear Freundlich equation was used in all cases to fit both experimental adsorption data and desorption data to obtain adsorption and desorption parameters comparable for any EDC and any substrate examined. This procedure can be assumed as valid on the basis of the generally good correlation coefficients obtained in all cases for a nonlinear Freundlich fitting of both adsorption data and desorption data.

Table 3 shows the correlation coefficients, r , Freundlich nonlinear adsorption/desorption parameters, and the percentages of initially adsorbed (100 %) (averages of three replicates) BPA, OP, and EED that are desorbed from each substrate at the end of the desorption experiment (number of steps are indicated between parentheses). The percentages of initially adsorbed (100 %) BPA, OP, and EED that remain adsorbed onto each substrate after each desorption step are shown in Table 4, and summarized graphically in Fig. 5.

Table 3 Correlation coefficients, r , for Freundlich nonlinear isotherms, Freundlich adsorption/desorption parameters, and total amounts desorbed after a number of desorption steps (indicated between parentheses in last column) for BPA, OP, and EED from soils examined.

Soil	Adsorption			Desorption			% desorbed
	r	K_{ads} (L kg ⁻¹)	$1/n_{\text{ads}}$	r	K_{des} (L kg ⁻¹)	$1/n_{\text{des}}$	
BPA							
P30	0.988	1.65	1.02	0.947	0.21	1.93	100 (4)
P90	0.937	0.35	1.22	0.978	0.06	1.94	100 (3)
G30	0.982	15.2	0.61	0.963	23.7	0.23	49.6 (5)
G90	0.893	1.00	0.69	0.996	1.19	0.84	100 (4)
OP							
P30	0.960	2.60	0.60	0.923	8.36	0.006	4.5 (5)
P90	0.939	1.45	0.93	0.930	2.32	0.36	84 (5)
G30	0.965	8.40	1.05	0.992	26.96	0.003	2.3 (5)
G90	0.879	1.08	1.02	0.962	2.56	0.30	79 (5)
EED							
P30	0.969	2.30	0.72	0.940	11.03	0.15	41.3 (4)
P90	0.982	1.73	0.73	0.966	10.18	0.08	32.3 (4)
G30	0.985	5.92	0.61	0.886	30.26	0.03	11.4 (4)
G90	0.987	1.66	0.51	0.915	4.91	0.08	37.3 (4)

Table 4 Percentages (%) of initially adsorbed (100 %) BPA, OP, and EED that remain adsorbed onto each soil examined after each desorption step.

Soil	1	2	3	4	5
BPA					
P30	41.8	17.9	1.6	0	–
P90	28.6	2.0	0	–	–
G30	79.4	67.2	56.1	53.5	50.4
G90	43.0	21.2	8.3	0	–
OP					
P30	97.8	97.2	96.6	96.0	95.5
P90	48	28	19	15	16
G30	98.3	98.2	98.0	97.8	97.7
G90	42	35	25	21	21
EED					
P30	92.5	66.5	64.0	58.7	n.d. ^a
P90	81.4	72.1	71.8	67.7	n.d.
G30	99.4	94.0	90.4	88.6	n.d.
G90	75.7	73.1	71.6	62.7	n.d.

^an.d.: not determined.

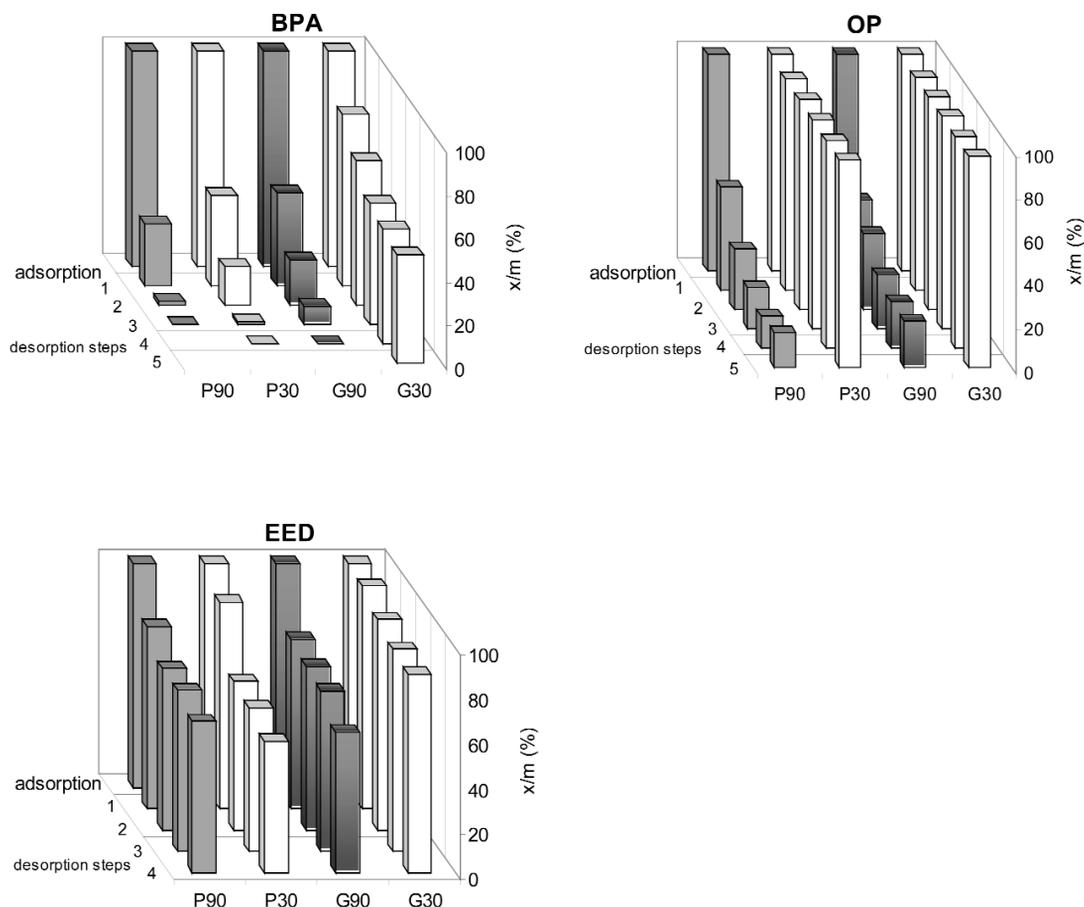


Fig. 5 Percentages (%) of initially adsorbed (100 %) EDCs that remain adsorbed onto each soil examined after each desorption step.

For P-soils, the K_{des} values of BPA are much smaller than the corresponding K_{ads} values, which suggests the occurrence of a largely reversible adsorption of BPA. On the contrary, G-soils show a K_{des} value slightly larger than the corresponding K_{ads} value, thus suggesting a moderate irreversibility for BPA adsorption. With the exception of soil G30, the values of $1/n_{\text{des}}$ are generally greater than those of $1/n_{\text{ads}}$, thus indicating a fast rate of desorption of BPA from most substrates. Desorption of BPA from most soils is completed (100 %) after three or four desorption steps, with the only exception of sample G30, which still retains half of the amount of adsorbed BPA at the end of the desorption experiment.

The K_{des} values of OP and EED for all samples examined are larger (up to five times) than the corresponding K_{ads} values, and $1/n_{\text{des}}$ values are much smaller (up to three orders of magnitude) than the corresponding $1/n_{\text{ads}}$ values. These results suggest for all the substrates a marked irreversibility of adsorption of OP and EED, and a rate of desorption much slower than the rate of adsorption. Although total (100 %) desorption of OP and EED never occurs, the amount of OP desorbed from soils P90 and G90 after five desorption steps reaches values of 84 and 79 %, respectively. However, only a few percent of OP are desorbed from samples P30 and G30, and a high amount of EED is retained by all samples at the end of the experiment.

SUMMARY AND CONCLUSIONS

AOPs introduced into soil by various means, either by purpose or incidentally, and their partial breakdown products, can be subjected to several phenomena. To date, extensive studies have been carried out on the distinct roles of microbial degradation, effect of minerals, and interaction with SOM fractions on the fate of AOPs in soil. However, relatively little has been done to integrate/interrelate the information about the combined action of microorganisms, extracellular enzymes, mineral colloids, and SOM/HS on the fate of AOPs in the multicomponent system soil. In the real soil, each of these four major components not only participates in the transformation of AOPs but also modifies the participation of the three other components. For example, HS and minerals can catalyze certain transformation reactions of AOPs, but at the same time they act as sorbents of AOPs, thus altering the impact of microorganisms, enzymes, and chemicals, generally reducing the bioavailability, and, in turn, the biodegradation of AOPs.

Among AOPs, EDCs may enter the soil through current agricultural practices and/or disposal of urban and industrial effluents, sludges, and wastes. Adsorption/desorption processes play a very important role in determining the distribution and speciation of EDCs in the various soil phases, and in turn their estrogenic risk in the environment. Adsorption of EDCs examined onto the sandy soil horizons studied is generally very fast, mainly occurring in the first few hours of contact. Adsorption isotherms indicate that no saturation occurs for adsorption of BPA, EED, and OP onto any soil, whereas a saturation state is reached for 17ED adsorption onto all substrates. The K and K_d coefficients follow the same trend for any EDC, thus suggesting that either one of them is useful for evaluating soil adsorption capacity for the various EDCs. Surface horizon soils, which are richer in OC content, exhibit a much greater adsorption capacity than deep horizon soils, thus EDCs tend to accumulate in surface horizons. The small differences in K_{OC} values measured among the various soils suggest that not only the content but also the nature and properties of OC affect the extent of adsorption, and that other soil components (e.g., clay minerals) might be involved in the adsorption process of EDCs. Among the various EDCs examined, OP appears to be the most adsorbed, and EED and 17ED show a similar extent of adsorption onto any soil. With the exception of one soil sample, adsorption of BPA is reversible, and desorption occurs quickly and is completed after few steps, thus BPA is expected to move down the soil profile and possibly contaminate the groundwater table. On the contrary, adsorption of OP and EED is mostly irreversible and partial desorption occurs slowly, thus resulting in the retention of most of the compound by soil solid phases, especially on the surface layer, with corresponding soil contamination.

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