

A model assessing bioavailability of persistent organic pollutants in soil

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Abstract

In this paper a model is proposed for describing persistent organic pollutants (POPs) bioavailability in soil. The model is written in Fortran 90 and describes POPs' behaviour as resulting from four different processes: sorption-desorption equilibrium, slow diffusion (aged fraction), fast irreversible sorption (bound residues) and biodegradation of the bioavailable fraction.

The POP sorption to soil surfaces is described assuming a rapid rate of sorption-desorption to and from soil surfaces and a slower rate of diffusion into the internal matrix (aging). Biodegradation is described as resulting from bacterial growth using sigmoidal Monod kinetics for the contaminant dissolved in soil solution (for non-hydrophobic compounds) and first order kinetics for the degradation of the sorbed-available fraction. In the case of hydrophobic compounds, first-order kinetics is employed to describe also the degradation from the soil solution. Sorption and diffusion are approximated by first order kinetics. Finally, the formation of bound residues is described using an exponential saturation equation. The rate constants for the different processes are estimated using linear and non linear first order kinetics approaches. The rate constants of the irreversible processes are estimated from experimental data. Model evaluation was performed using data from previous experiments with phenanthrene as test compound.

Keywords

Modelling; Bioavailability

Introduction

Persistent organic pollutants (POPs), because of their high toxicity, long environmental persistence and high bioaccumulation factors, are considered serious pollutants. In the last twenty years their potential impact to the environment has been analysed and described extensively.

The fate and behaviour of organic pollutants in soil is governed by many factors, including soil characteristics, compound properties and environmental factors (Reid et al. 2000a, Chung and Alexander 2002, Nam et al. 2003). Polycyclic Aromatic Hydrocarbons (PAHs) represent one of the most widespread organic pollutants in the environment. PAHs are formed as by-products of incomplete combustion of organic materials and are emitted in the environment mainly from anthropogenic sources. A great environmental concern is associated with their presence, as some of them were demonstrated to be carcinogenic. They are highly hydrophobic, recalcitrant to degradation and due to their affinity for fatty tissues they tend to be bioaccumulated within food-chains.

Organic pollutants have traditionally been studied with exhaustive extraction techniques and these results are often coupled to risk assessment models to add a biological interpretation. However, this approach does not take into account two important processes, bioavailability and aging (Hatzinger et al. 1995, Laor et al. 1996). Bioavailability is a dynamic rather than a static process. Time-dependent losses in bioavailability have been demonstrated for several organic and inorganic chemicals. Upon entering a soil system, pollutants first contaminate the macropores and the particle surfaces containing relatively few bacteria. They then diffuse into smaller pores where biotransformation may take place, given that the environmental conditions are in favour of microbial activity. Pollutants also diffuse into extremely small pores of the mineral or organic soil fraction. The result of the slow entrapment of chemicals into sites within the soil matrix that are not accessible to the microbial biomass is called aging (Alexander 2000). As POPs persist within a soil or sediment matrix, they become increasingly resistant to desorption and thus less bioavailable (Gevao et al. 2000). The nature and extent of aging processes depends on soil and compound properties as a result of physical, chemical and biological inter-

actions (Chung and Alexander 1998, Northcott et al. 2001). Pollutants become unavailable when the rate mass transfer is zero (i.e. the case of aged and bound residues).

Reliable and representative techniques for the assessment of the bioavailable fraction of organic contaminants are still lacking. The problem is complicated by the fact that this fraction varies depending on the physico-chemical properties of the molecule; for the same contaminant the type of soil and target organisms have also to be considered (Chung and Alexander 1998).

Since only very recently the concept of bioavailability has been introduced in the literature and the mechanisms of aging and bound residues formation are not yet fully understood, few bioavailability models exist by now. Scow and Hutson (1992) presented the DSB-Model using terms for linear sorption to particulate surfaces, diffusion within soil aggregates and biodegradation using Monod kinetics. Shelton and Doherty (1997) proposed a conceptual model that describes pesticide biodegradation rates, accounting for bioavailability and microbial growth using Monod kinetics. Cornelissen et al. (1998) used a first-order, two-compartment model to describe desorption. Altfelder et al. (2000) described the role of slow kinetics in non-singular sorption of organic compounds in soil, using a non-linear two-stage sorption model. A more sophisticated model coupling intraparticle diffusion/sorption, non-linear sorption, and biodegradation was suggested by Karapanagioti et al. (2001). However, the focus of the latter model is on predicting the magnitude of natural attenuation of solutes undergoing transport and mobile-immobile domain mass transfer in porous media, rather on describing the patterns of bioavailability.

The model proposed in this paper is a conceptual five compartment one, which describes the soluble, sorbed (bioavailable), aged (non bioavailable), bound (non bioavailable) and degraded fraction of a contaminant entering a soil system. This model can be used along with innovative non-exhaustive extraction techniques, such as cyclodextrins and hydrophobic resins, in order to assess the bioavailability of hydrophobic organic compounds in soils.

Processes described

Adsorption-desorption-aging kinetics

The sorption is composed of two distinct processes: a rapid rate of adsorption to soil surfaces, which is in rapid equilibrium with the soluble fraction and remains readily bioavailable, and a slower rate of diffusion into soil aggregates-organic matter particles, which is not readily available for degradation. The latter is the aged fraction of the pollutant and is described with the first order rate constant k_2 . The rapid rate of sorption-desorption to and from soil surfaces is described by first order kinetics. The ratio of the pollutant concentration sorbed to soil surfaces to pollutant in soil solution is estimated by the equation: $K_d = f_{om} K_{oc}$. An initial estimation is required for the first order rate constant for sorption to soil surface (k_1); given this estimate, the first order rate constant for desorption from the soil (k_3) can be obtained from the equation: $K_d = k_1 / k_3$. If known, the K_{oc} is used directly to estimate the K_d . In the case that K_{oc} is not known, the value of the K_{ow} is used to estimate it, by solving the following equation: $\log K_{oc} = 0.92 \log(K_{ow}) - 0.23$.

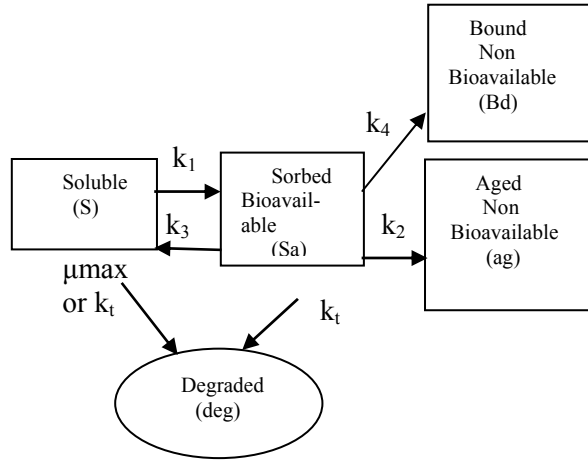
Bound Residues

When the rate of mass transfer to the degrading microorganisms is zero, pollutants form bound residues, thus becoming unavailable. The formation of bound residues is described using an exponential saturation equation: $\text{bound} = \text{boundF}(1 - e^{-k_4 t})$ where k_4 is the rate constant for formation of bound residues and boundF is the highest relative concentration that bound residues can reach and it is proportional to the initial sorbed concentration.

Biodegradation

Rates of contaminants degradation have traditionally been described using first order kinetics where the rate is assumed to be dependent only on the pesticide concentration. However, in cases where contaminants are used as growth substrates by soil microorganisms, accelerated biodegradation is observed that is best described by sigmoidal kinetics. When growth linked processes are observed (bacterial growth), Monod kinetics is more appro-

priate; on the other hand Michaelis-Menten kinetics is mostly used to describe non-growth linked biodegradation. In this model only in the case of non-hydrophobic substances Monod kinetics is used to describe the degradation from the substrates in soil solution. In the case of sorption dependent degradation the biodegradation can occur also from the sorbed part of the substrate (as in the case of phenanthrene), and first order kinetics are used to describe the degradation from the sorbed and the soluble phase. The first order degradation rate constant is estimated from the equation: $k_t = \ln(2)/DT50$, where DT50 is the pollutant's half life in days. In figure 1 is given the box diagram and the equations that govern the conceptual model.



$$\frac{\partial S}{\partial t} = -k_1 S + k_3 Sa - \frac{\mu_{\max} S B}{K_s + S} \text{ or } \frac{\partial S}{\partial t} = -(k_1 + k_t) S + k_3 Sa$$

$$\frac{\partial Sa}{\partial t} = k_1 S - (k_3 + k_2 + k_t + k_4) Sa$$

$$\frac{\partial ag}{\partial t} = k_2 Sa \quad Bd = boundF (1 - e^{-k_4 t})$$

$$\frac{\partial deg}{\partial t} = k_t Sa + \frac{\mu_{\max} S B}{K_s + S} \text{ or } \frac{\partial deg}{\partial t} = k_t (Sa + S)$$

Fig. 1. Box diagram and model equations ($\partial S/\partial t$ =time variation of substrate concentration in soil solution, $\partial Sa/\partial t$ = time variation of substrate sorbed concentration, $\partial ag/\partial t$ = time variation of substrate aged concentration, $\partial Bd/\partial t$ = time variation of substrate bound concentration, $\partial deg/\partial t$ = time variation of substrate degraded concentration, μ_{\max} =maximum contaminant utilization/mass of micro-

organisms (1/h), B =total microbial concentration (mg/Kg), K_s =contaminant half-saturation constant (mg/L), k_1 =first order rate constant for sorption to soil om (1/day), k_2 =first order rate constant for aging (1/day), k_3 =first order rate constant for desorption from the soil om (1/day), k_4 =first order rate constant for bound residues (1/day) k_t =first order rate constant for degradation, boundF=maximum allowed bound residues concentration).

Materials and Methods

Model compound

In the present study phenanthrene ($C_{14}H_{10}$), a neutral organic compound that contains three aromatic rings, was selected as a representative PAH. It has environmental properties such as aqueous solubility, octanol–water partition coefficient (K_{ow}), and vapor pressure that are similar to other PAHs, such as acenaphthene, fluoranthene, and fluorene. The parent structure of the phenanthrene is similar to the structure of higher molecular weight and more carcinogenic PAHs, such as benzo(a)pyrene, so it is hypothesised that phenanthrene is an adequate representative compound that would give a general indication of PAH behaviour (Khodadoust et al. 2004). All PAHs are hydrophobic, and phenanthrene has an aqueous solubility of 1.1 mg/L at 25°C.

Chemical assessment of the bioavailable fraction

The bioavailable fraction of chemicals has usually been associated with the quantity which is easily desorbed; in turn such quantity is determined by extraction of the aqueous phase. With hydrophobic organic compounds such as PAHs, poorly soluble and with a strong affinity towards the organic matter, this method has great limitations, since very low amounts of these compounds will be in the soil solution, while a large labile and potentially bioavailable pool remains on the solid phase. To address this problem some authors (Wang and Brusseau 1993, Reid et al. 2000b, Puglisi et al. 2003) have proposed to enhance the solubility of this contaminants with cyclodextrins solutions. Cyclodextrins are cyclic oligomers of α -D-glucose formed by the action of enzymes on starch. They present a hydrophilic surface and an internal hydrophobic cavity. Although fairly soluble in water, they are at the same time able to entrap hydrophobic

molecules inside their cavity, enhancing their solubility. When internal cavity is substituted with functional groups, such as in hydroxypropyl- β -cyclodextrins (HPCD) the solubilization effect towards hydrophobic compounds is furthered. Cyclodextrine extractions follow an equilibrium kinetics and the quantity extracted is strongly correlated to the bioavailable fraction (Reid et al. 2000b).

Experimental Section

Soil Spiking

Soil samples were collected in South Italy, in the Province of Bari (località Terra Ripagnola). Soils in this area are loamy, 25 cm deep, with a red colour due to high content of iron oxides, hence the denomination “red soils”. Soil samples were passed through a 2 mm sieve to remove roots and other vascular materials. Samples were spiked with a dilution mixing method with acetone as a carrier solvent and then divided in separate microcosms of 20 g each. Sterilisation was then carried out on treatment 1 and 2 by means of γ -irradiation (5 Mrads). The experiment was carried out on both sterilised and non sterilised samples, and 3 treatments (5 replicates each) were compared:

1. sterilised soil contaminated with 10 ppm of phenanthrene
2. sterilised soil contaminated with 100 ppm of phenanthrene
3. non sterilised soil contaminated with 100 ppm of phenanthrene

Phenanthrene extractions from soil

HPCD and methanol extractions were carried out in sterilised and non sterilised soil in different time-steps. The quantity extracted with HPCD represents the bioavailable fraction of the contaminant. The quantity extracted with methanol represents the sum of the bioavailable, and the aged fraction, while the total initial compound concentration minus the quantity extracted with methanol (bioavailable+aged) at the sterilised soil gives the bound fraction. Finally, the total initial compound concentration minus the quantities extracted with methanol, minus the bound fraction at the non-sterilised soil, gives the biodegraded fraction of the chemical at each time-step.

Regarding the HPCD extraction, samples of 1 g of soil were weighted in centrifuge polycarbonate tubes and added with 20 mL of HPCD 50 mM. The tubes were sealed, placed on an orbital shaker at 180 revertants/min for 12 hours and then centrifuged at 4000 revertants/min for 1 hour. Then

the supernatant was re-centrifuged for 10min, filtered and finally injected in HPLC for phenanthrene quantification.

Regarding the methanol extraction, samples of 1 g of soil were weighted in centrifuge polycarbonate tubes and added with 20 mL of methanol. The tubes were sealed, placed on an orbital shaker at 180 revertants/min for 12 hours and then centrifuged at 4000 revertants/min for 1 hour. After centrifugation the supernatant was filtered and injected in HPLC for phenanthrene quantification.

Results

In the case of phenanthrene, because of its hydrophobicity, the biodegradation can occur not only from the concentration in the soil solution but also from the sorbed fraction of the substrate (sorbed/bioavailable). For this reason first order kinetics are used to describe the degradation from the sorbed and the soluble phase. Since in the experimental results the extraction with HPCD represents the bioavailable fraction of the phenanthrene (soluble+sorbed/bioavailable) the first order degradation constant k_t for the soluble and the sorbed fraction is the same. The first order rate constant for bound residues, k_d , was estimated from the experiment with the sterilised soil. The experimental results, with the non-sterilised soil, showed that the degradation of the phenanthrene started after 50 days of the contamination. On this account a lag-phase time of 50 days was predicted before biodegradation to start. The half-life of the phenanthrene was estimated in 30 days.

Table 1. Sorption-desorption, diffusion, degradation and bound residues formation kinetic constants

initial concentration = 10 and 100		{mg/kg}
dt50 = 30		{days}
t _{lag} = 50		{days}
kt = 0	ig 0 < t < t _{lag}	
kt = ln(2)/dt50	if t > t _{lag}	{1/day}
logK _{ow} = 4.2		
log(K _{oc}) = 0.92*log(K _{ow}) – 0.23		
om = 0.01		{kg/kg}
K _d = om*K _{oc}		
k ₁ = 0.02		{1/day}
k ₂ = 0.003		{1/day}
k ₃ = k ₁ /k _d		{1/day}
k ₄ = 0.1		{1/day}
boundf = 15 % initial concentration		{mg/kg}

Table 1 summarises the first order rate constants for sorption-desorption, degradation, aging and bound residues formation for the non-sterilised soil.

Figure 2 shows the predicted concentrations, as a percentage of the initial applied concentration, of bioavailable (soluble+sorbed), non bioavailable (soluble+sorbed), non bioavailable (aged+bound) and degraded fractions of phenanthrene in the non-sterilised soil. Figure 3 compares modelled and measured concentrations of phenanthrene in the non-sterilised soil. The model was run with initial phenanthrene concentrations of 10 and 100 ppm with similar results. The model accounts for the water solubility of the substrate and does not allow the concentration in the soil solution to exceed it.

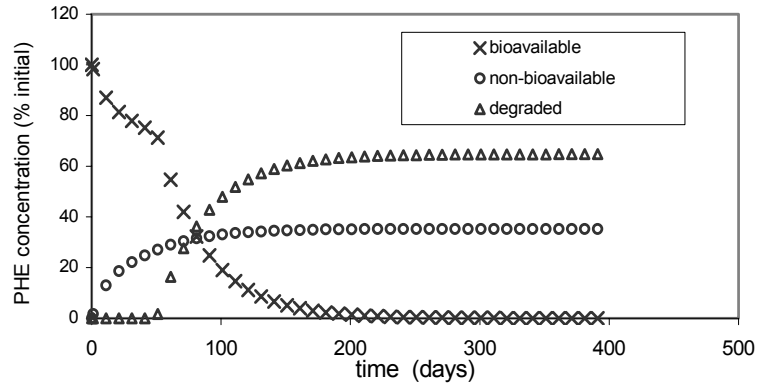


Fig. 2. Model predictions for bioavailable, non bioavailable and degraded phenanthrene

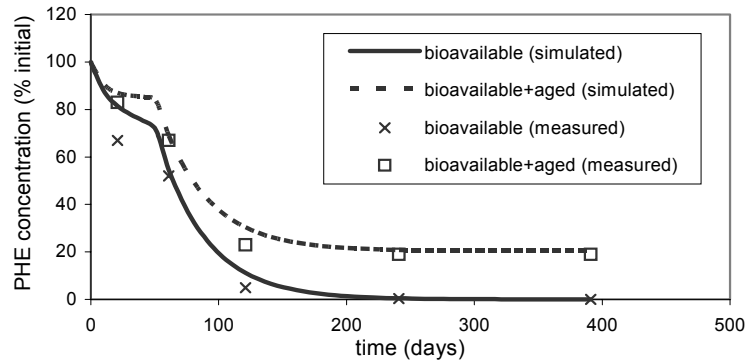


Fig. 3 Comparison between model predictions and measured concentrations of phenanthrene.

Conclusions

The proposed five compartment model can be used along with experimental data to predict the organic contaminants bioavailability in the course of time. Non-exhaustive extraction techniques, for bioavailability assessment of hydrophobic organic compounds in soils, such as cyclodextrins and hydrophobic resins, can provide the necessary data to calibrate and evaluate the model. The bioavailable fraction of the substance is the fraction in the soil solution and, in the case of hydrophobic organic compounds, also the fraction sorbed to the soil surfaces. First order kinetics are used to describe the degradation of the sorbed fraction, while sigmoidal Monod kinetics describe the degradation of the substrate in soil solution, if data are available. First order kinetics are used for the slow diffusion into soil aggregates-organic matter particles (aged fraction) and an exponential equation describes the formation of bound non-available residues. The model, after being calibrated using experimental data, described satisfyingly the phenanthrene sorption-desorption, aging, degradation and formation of bound residues for the range of 10-100ppm of initial phenanthrene concentration.

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