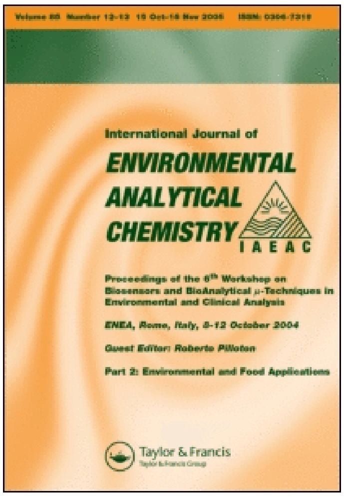

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TEFLUTHRIN SORPTION TO MINERAL PARTICLES: ROLE OF PARTICLE ORGANIC COATINGS

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The sorption of tefluthrin was studied on "pure" clay minerals and those that had been coated with aquatic humic substances over a mass percent carbon range of 0.02 to 2.15. Tefluthrin sorption onto humic-coated minerals was significantly greater than on to the clean minerals and increased with increasing quantities of sorbed humic substances. Humic acid, the most aromatic coating, was the strongest sorbent, followed by fulvic acid, hydrophilic macromolecular acid and natural coatings on estuarine suspended particles. This shows the significant impact of humic coatings on the sorptive capacity of mineral particles. The sorption was linear, also consistent with the operation of a partition process. The partition coefficient normalised to organic carbon (K_{OC}) after deduction of the contribution from the clean mineral, ranged from 120000 to 770000 and was highest for the most aromatic humic acid fraction.

KEY WORDS: Pyrethroids, tefluthrin, humic substances, clay minerals, sorption, suspended particles.

INTRODUCTION

Light-stable synthetic analogues of the natural pyrethrins, known collectively as 'pyrethroids', are widely used as household, public health and agricultural insecticides.[1,2]

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Their entry to natural water systems such as estuaries, directly via spraying over drainage or irrigation channels or indirectly as a result of spray drift or soil erosion is of particular environmental concern because of their extremely acute toxicity towards fish.[2,3] The pyrethroids are very hydrophobic and can penetrate biomembranes and organic coatings of suspended particles. They are thus easily sorbed to particulate surfaces because of their extremely low water solubility and high lipophilicity. Pyrethroids in the adsorbed state have been shown to be much less toxic because of reduced bioavailability.[2] However much remains to be discovered about how the pyrethroids become sorbed by suspended particles and how the sorbed pyrethroids are transported in the aquatic environments.

It has long been known that hydrophobic organic compounds, by virtue of their nature, tend to be easily adsorbed by sediment or soil particles. This is due mainly to the low water solubility of the organic compounds and to the presence of organic matter coated onto the particles.[4–6] Sorption of hydrophobic organic compounds is normally regarded as a partition process as linear adsorption isotherms are frequently observed and secondly, there is a good relationship between the carbon-normalised partition coefficient (K_{oc}) and the octanol/water partition coefficient of the chemicals (K_{ow}).[4–8] The mechanism of sorption can be considered as the transfer of solute from the aqueous phase to the organic phase in/on particle surfaces. However, the concept of partition as a mechanism has been questioned[9] so has the linearity of the isotherms as nonlinear isotherms have also been observed.[10,11] Adsorption and absorption could therefore both be present in the interactions between dissolved organic compounds and suspended particles, and the term sorption is used here loosely to refer to either process.

Previously it has been observed that K_{oc} for a given chemical is relatively constant and can be estimated from its physical properties such as octanol/water partition coefficient or water solubility.[5,6,12] However it is difficult to regard this as a universal rule bearing in mind the wide diversity in composition and structure of organic matter and the resulting sorptivities. Recent investigations[11,13–15] show that K_{oc} for a single organic compound may vary over an order of magnitude and such variations may be attributed to the fact that the composition of organic matter and the inorganic matrix is wide-ranging and secondly, not all organic matter is active in the sorption process.[16] Garbarini and Lion,[13] by using a multivariant regression analysis, found that the oxygen, sulphur and carbon content of a sorbent was a more accurate predictor of the sorptive capacity than carbon content alone; this is explained by the dependence of the ability of the organic matter to sorb organic pesticides on the relative hydrophilic/hydrophobic balance. Similarly it has been found that a good correlation exists between the K_{oc} and [H]/[O] ratio in organic matter, indicating a decrease in sorption with increasing proportions of oxygen-containing functional groups in natural organic substances.[15] The non-constant nature of K_{oc} has also been observed by Murphy *et al.*[11] who found the K_{oc} values could be higher or lower than those predicted from the K_{oc}-K_{ow} relationship. In summary the findings of these publications show that the K_{oc} for a particular organic compound is not a constant, rather, that it varies with the nature of organic coatings, nature of the inorganic phase, and the interactions between these two phases.

Although a lot of research has been carried out on the sorption of common hydrophobic organic compounds by sediments and soils, relatively little work has been done on the systematic analysis of the sorption of pyrethroids, especially by natural suspended particles.

This process has been found to be vital in reducing the aqueous concentrations of pyrethroids and hence limiting their availability to aquatic life.[2,3] Therefore it was the objective of the present research to investigate the adsorption of pyrethroids by "clean" mineral particles; to study the sorption of pyrethroids by mineral particles coated with natural humic material of varying polarity and aromaticity and to resolve the contribution from the organic coatings; to examine whether the K_{oc} for a specific pyrethroid is constant or quite possibly, dependent on the composition of organic coating, and finally to discuss the potential implications of this work by comparing the results for individual minerals to those results obtained for natural aquatic suspended particles isolated from estuarine waters.

EXPERIMENTAL PROCEDURES

Sorbents

Three clay minerals, *i.e.* montmorillonite (Fluka), aluminium oxide (γ-Al_2O_3, BDH) and kaolinite (Sigma) were obtained. The particle sizes were < 1μm, 0.015 μm and 0.1–4 μm respectively and specific surface areas were 286.8 m^2/g, 83.3 m^2/g and 25.1 m^2/g respectively, as measured by N_2 adsorption and BET isotherm method.[17] Before use in the sorption experiments, the clay minerals were treated with dilute alkaline solutions to remove any organic material. They were then centrifuged and rinsed with Milli-Q water to neutral pH. For estuarine axial surveys large volume water samples were collected in polyethylene carboys from several locations in the Tees Estuary, England. Suspended particles were obtained by continuous flow centrifugation and stored in 0.1M $NaHCO_3$ at 4°C.

Humic substances

Well-characterised aquatic humic substances were obtained from Dr M. H. B. Hayes, University of Birmingham, England. These were isolated from the River Dodder, Eire, Republic of Ireland by adsorption and cation exchange chromatography. H^+-saturated humic, fulvic and hydrophilic macromolecular acids were used in the experiments. Elemental compositions and aromatic carbon percentages have been reported previously.[18]

Pyrethroids

^{14}C labelled tefluthrin was supplied by Zeneca Agrochemicals and purified by radio-TLC on silica gel using hexane:diethyl ether (95:5). Purified tefluthrin (98% purity) was then

Table 1 Physical properties of tefluthrin.

MW	Solubility (mg/l)	mp, °C	K_{OW}	log K_{OW}
418.7	0.02	44.6	3160000	6.50

dissolved in hexane (HPLC grade) to prepare stock solutions of *ca.* 200 mg/l. The physical properties of tefluthrin were are shown in Table 1.

Sorption experiments

Sorption of pyrethroids by mineral particles was studied by a batch isotherm method using 30 ml Pyrex centrifuge tubes. A weighed quantity of clay minerals was introduced into each of a series of centrifuge tubes, to which was added 30 ml of a buffer solution (0.1M $NaHCO_3$, 0.1 g/l NaN_3, pH 7.6). Solution pH was then measured and adjusted to 7.6±0.1 with drops of HCl or NaOH solutions. Different volumes of tefluthrin stock solution in hexane were pipetted to the wall of each tube, which was later subjected to a N_2 purge for 2 min to remove the solvent. These tubes were carefully capped and shaken for 24 h to reach sorption equilibrium. The suspensions were then centrifuged at 3600 rev/min (1900g) for 1 h. Supernatant (4 ml aliquots) was then pipetted to 20 ml glass scintillation counting vials containing 16 ml of scintillation cocktail (Ultima Gold, Canberra Packard Ltd) and measured by liquid scintillation counting. The pyrethroid adsorbed by glassware and mineral particles was measured by decanting all the supernatant from the tube, adding 10 ml of dichloromethane (repeated twice) and measuring the radioactivity in the resulting desorption solution.

Control experiments in which only mineral particles in buffer solution and those in which pyrethroid in buffer only were also run in the same manner to determine the recovery of particles and adsorption of pyrethroids to glassware. Each experiment was repeated twice.

The amount of tefluthrin adsorbed by particles was calculated as the difference between ^{14}C activity desorbed from both clay minerals and the glass wall and that desorbed from the wall only. The percentage of recovery of the calculated sorbed tefluthrin was above 90%.

The sorption of pyrethroid by humic-coated particles was preceded by experiments on the adsorption of humic substances by clay minerals, which have already been described in detail.[18] After centrifugation, mineral particles with humic coatings were separated from humic solution; these were then washed once with organic-free 0.1M $NaHCO_3$ and centrifuged, and the amount of humic substances finally adsorbed was analysed by UV-visible spectrophotometry at 350 nm.[18] Tefluthrin stock solution in hexane was then added to each of these tubes by micropipette, with solvent evaporated under N_2 flow. Buffer solution was added to a total volume of 30 ml. These tubes were shaken for 24 h, centrifuged at 3600 rev/min for 1 h, with the supernatant measured for radioactivity, using the procedure described above. Control experiments were also run to check the adsorption of pyrethroids to glassware and possible desorption of humic material from particle surfaces.

Suspended particles collected from the Tees Estuary in Middlesbrough, England by continuous flow centrifugation, were studied in the same manner.

RESULTS AND DISCUSSION

Adsorption of tefluthrin by "clean" minerals

The adsorption of tefluthrin by montmorillonite, aluminium oxide and kaolinite, as shown in Figure 1, was well modelled by a linear regression equation:

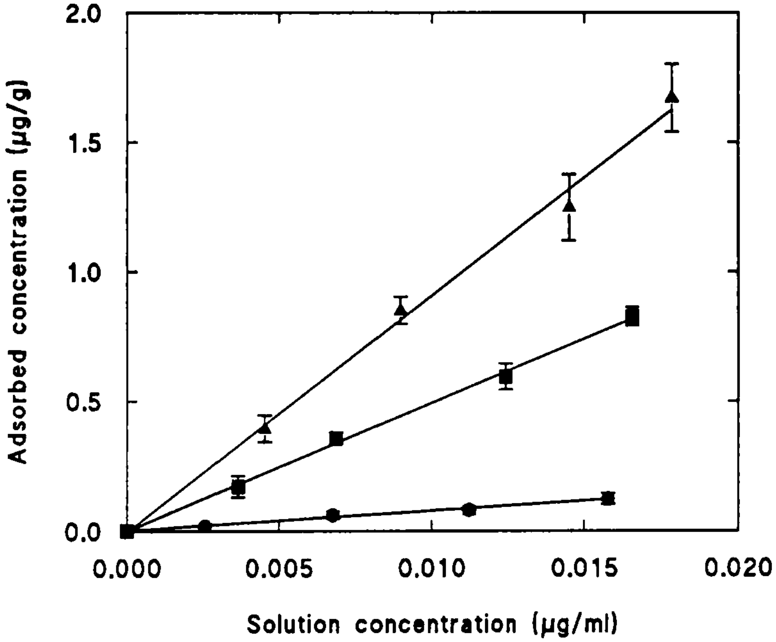

Figure 1 Sorption of tefluthrin by "clean" mineral particles. (▲) Montmorillonite, (■) aluminium oxide, (●) kaolinite.

$$Q_{min} = K_d \, C_{eq} \qquad (1)$$

Where Q_{min} is the amount of tefluthrin adsorbed by a gram of sorbent (µg/g), C_{eq} is the equilibrium concentration of tefluthrin in solution (µg/ml), K_d is the distribution coefficient of tefluthrin between particle and aqueous phases (ml/g). The linearity of the isotherms has been reported previously for the adsorption of fluoranthene, di- and trichlorobenzene and indole on Ca^{2+}-bentonite[19] and may be explained for the pyrethroids by the low concentrations used and hence low surface coverage of the mineral particles.

The adsorptive capacity per unit mass of minerals decreased in the order:

montmorillonite > aluminium oxide > kaolinite

for all the pyrethroids tested, an order coinciding with the order of specific surface area of the mineral particles. This is expected as adsorption is a surface phenomenon and increases with sorbent surface area. The distribution coefficients in terms of per unit surface area of sorbent (K_{min}) were also calculated and shown in Table 2. These can be compared

Table 2 Distribution coefficients for tefluthrin on "clean" minerals.

Montmorillonite		Aluminium Oxide		Kaolinite	
K_d(ml/g)	K_{min}(ml/m^2)	K_d(ml/g)	K_{min}(ml/m^2)	K_d(ml/g)	K_{min}(ml/m^2)
92	0.32	50	0.60	7.6	0.30

with literature values for other hydrophobic organic compounds. The amount of tefluthrin adsorbed by unit area of sorbents decreased in the order aluminium oxide > montmorillonite > kaolinite. This order is similar to the adsorption of chlorobenzenes to montmorillonite and kaolinite,[19] indicating the strong affinity of pyrethroids for the aluminium oxide surface.

Sorption of tefluthrin by minerals with humic coatings

Montmorillonite coated with different amounts of hydrophilic macromolecular acid was prepared as described previously and the sorption isotherms for tefluthrin are shown in Figure 2. A comparison of Figures 1 and 2 shows clearly a several-fold increase in the amount of tefluthrin sorbed by particles coated with hydrophilic macromolecular acid when compared to pure clay particles. The increase becomes more significant with the increase in the amount of hydrophilic macromolecular acid sorbed as represented by their f_{oc} values. f_{oc} is the mass fraction organic carbon of humic-coated particles, as calculated by the amount of

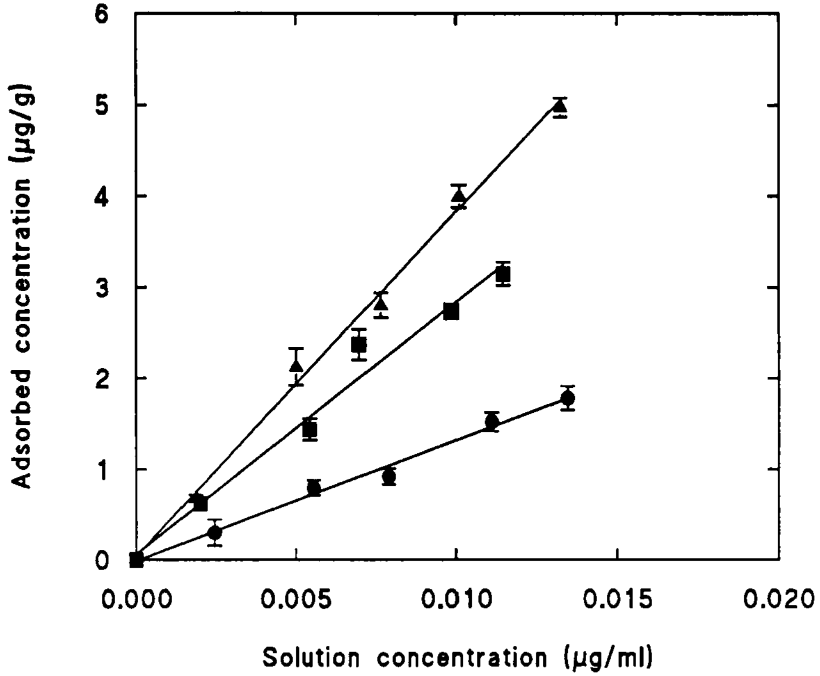

Figure 2 Sorption of tefluthrin by montmorillonite coated with hydrophilic macromolecular acid. f_{oc} values are (●) 0.0002, (■) 0.0007, (▲) 0.0012.

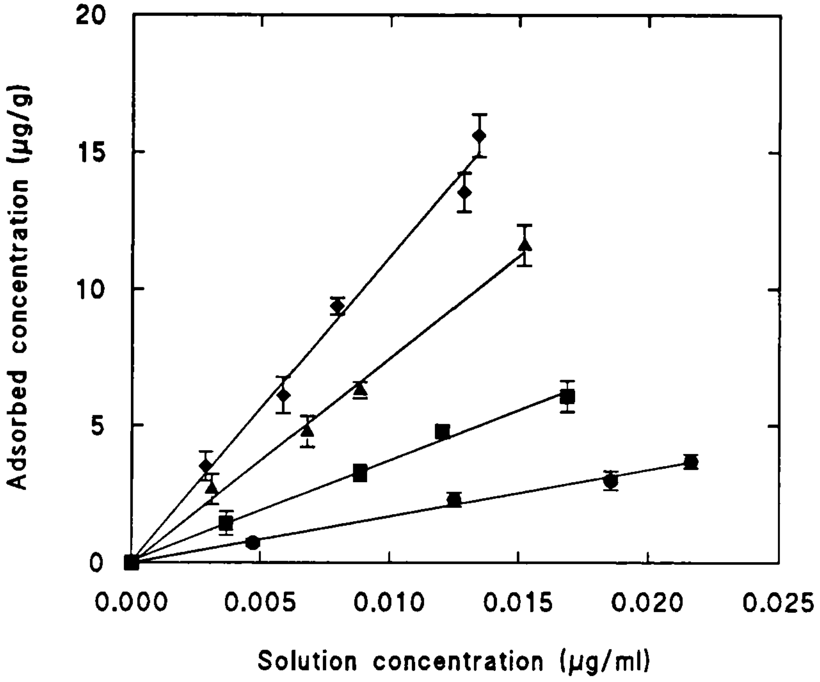

Figure 3 Sorption of tefluthrin by montmorillonite coated with fulvic acid. f_{oc} values are (●) 0.0002, (■) 0.0007, (▲) 0.0015, (♦) 0.0022.

hydrophilic macromolecular acid adsorbed by mineral particles and its elemental composition. This shows clearly the significant impact of particle humic coatings on the sorption of highly hydrophobic organic chemicals. As a result, hydrophobic bonding to the organic matter on particle surface seems to be the main mechanism of pyrethroid sorption.

The isotherms obtained were linear (r^2>0.98) and similar to the results reported by others for the sorption of other hydrophobic organic compounds to soils or sediments.[5,6,8,19,20] This suggests that organic pollutants partition into the organic phase of particles, a process similar to the partition of organic compounds to octanol from water.[8,19,20] However, nonlinear isotherms have were also been obtained by others.[10,11] Such non-linearity may be due to the low sorptive potential of organic coatings for some compounds.

A more pronounced increase in tefluthrin sorption was found for montmorillonite coated with fulvic acid (Figure 3), with even greater enhancement with humic acid coatings (Figure 4). As a result, humic acid coatings induced the highest increase in the sorptive capacity of montmorillonite for tefluthrin, followed by fulvic acid coatings then hydrophilic macromolecular acid coatings.

As it has been shown that organic coatings on clay particles have a significant impact on the sorptive capacity of particles towards hydrophobic organic pollutants, it is essential that the net effect of organic coatings be examined. This can be achieved by deduction from the total particle sorptivity of the mineral contribution followed by the calculation of K_{oc} (organic carbon normalised partition coefficients) according to the following formula:

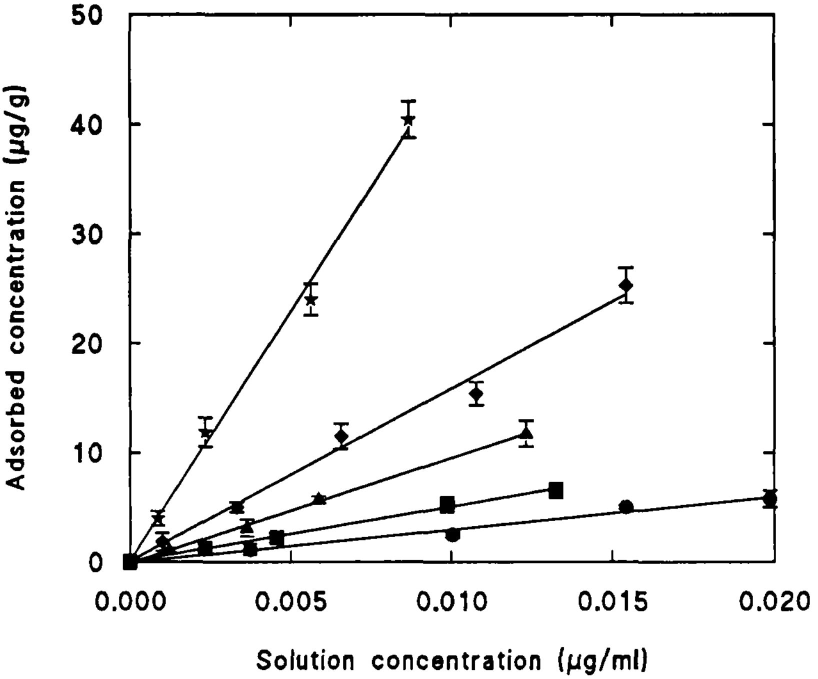

Figure 4 Sorption of tefluthrin by montmorillonite coated with humic acid. f_{oc} values are (●) 0.0003, (■) 0.0006, (▲) 0.0012, (♦) 0.0021, (★) 0.0065.

$$Q_{total} = Q_{min} + Q_{oc} \tag{2}$$

where Q_{total} is the total amount of tefluthrin sorbed by humic-coated particles (µg/g) while Q_{oc} is the amount sorbed by organic carbon (µg/g). As sorption isotherms for the humic-coated particles were also linear:

$$Q_{total} = K_t\, C_{eq} \tag{3}$$

where K_t is the slope of the isotherms for humic-coated particles. A substitution of equations (1) and (3) to equation (2) leads to:

$$K_t\, C_{eq} = K_{min}\, S\, C_{eq} + K_p\, C_{eq} \tag{4}$$

where K_{min} is the distribution coefficient of tefluthrin on "clean" minerals (ml/m^2), S is the exposed surface area of the clay (m^2/g) while K_p is the partition coefficient of tefluthrin in organic coatings (ml/g).

The exposed surface area of a clay was calculated as the difference between its total surface area and the area occupied by adsorbed humic molecules. The latter was calculated

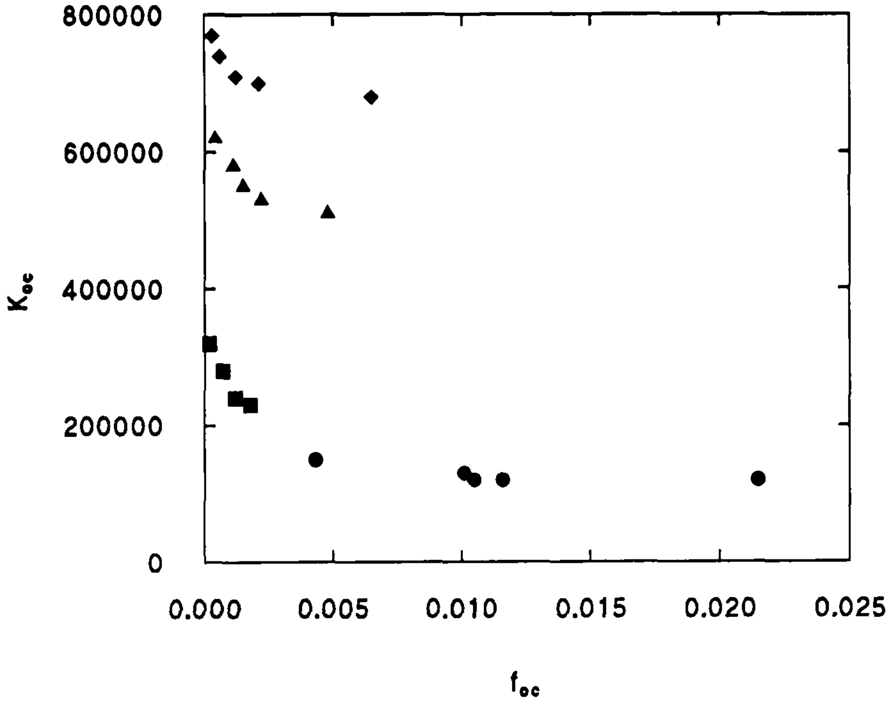

Figure 5 Variation of K_{oc} for tefluthrin with the degree and nature of organic coatings. (◆) humic acid, (▲) fulvic acid, (■) hydrophilic macromolecular acid, (●) Tees estuarine particulates.

taking into account the radius of gyration and molecular weight of the humic material and the amount adsorbed on clay particles. The organic carbon normalised partition coefficient can be calculated:

$$K_{oc} = \frac{K_t - K_{min} S}{f_{oc}} \tag{5}$$

As shown in Figure 5, the K_{oc} values for tefluthrin varied with the type and extent of organic coatings. The most aromatic coating, *i.e.* humic acid coating, produced the highest K_{oc}, followed by fulvic acid coating, hydrophilic macromolecular acid coating then natural coatings on the estuarine particles. This order also reflects decreasing aromaticity (indicated by ^{13}C-NMR results) and increasing polarity (indicated by O/C ratio)[18] and this is consistent with results found by others[11,13,15] who observed a decrease in sorption of hydrophobic compounds with increasing proportions of oxygen-containing functional groups in natural organic substances. This is also consistent with Gauthier *et al.*[21] who found the affinity of dissolved humic acid for pyrene increased with increasing aromaticity.

The K_{oc} values also decreased with increase in the extent of humic coatings (f_{oc} values), approaching a constant value at higher f_{oc} values. Such a trend has been reported previously[11] and indicates the non-proportional enhancement of pyrethroid sorption by humic coatings.

This may be explained by considering that at the lowest f_{oc} value all humic molecules on the particle surface; are active and fully accessible for pyrethroid sorption; when f_{oc} increases, humics sorbed to mineral surfaces adopt interfacial configurations that reduce sorption. The mineral surface apparently affects the structure of adsorbed humic molecules, possibly altering the size of hydrophobic domains on the humic molecules or their accessibility to pyrethroids.[11]

The results are however different from reports that K_{oc} values were relatively constant[5,12] for a single organic compound. The uniformity of K_{oc} values may be explained by the similarity in composition of organic matter used in those experiments.[5,12] This can therefore be considered as a special case for results reported in Figure 5, in which organic coating of the same composition would produce roughly constant K_{oc} values. Generally speaking however, K_{oc} values would not be constant as organic matter of different origins and with different degrees of humification and binding with the mineral phase will behave differently in sorbing hydrophobic organic pollutants.

CONCLUSIONS

Although a wide body of information describes the degradation of pyrethroids on plants and in soil, rather less is known about the fate of pyrethroids in natural waters. Given the acute toxicity of some of the compounds to aquatic life, it is important that such data are obtained. One mechanism which may influence the environmental fate of pyrethroids in water is sorption onto suspended particulates; especially particles containing a coating of lipophilic material such as the so-called 'humic substances' since pyrethroids are very hydrophobic. We have therefore allowed various fractions of aquatic humic substances to coat clean minerals and then studied the sorption behaviour of radio-labelled tefluthrin onto these particles and onto the clean minerals.

Tefluthrin sorption to both bare minerals and clay-humic complexes was linear. The role of the mineral and of the humic components was elucidated experimentally, and a model considering both fractions proposed.

The partition coefficients of tefluthrin on humic coatings (K_{oc}) were 1300–8300 times higher than the distribution coefficients on "clean" clay particles (K_d). This indicates that humic coatings are much stronger sorbents than bare mineral particles. This is consistent with the findings that dissolved humic material can complex strongly with organic chemicals and that humic coatings dominate particulate sorption of organic compounds. Results also show that K_{oc} for tefluthrin was not constant, rather it varied with the type of organic coatings, the type of mineral phase and the extent of organic coatings. This is because the complexation capacity of humic substances is dependent on their structure and chemical properties. Humic acid is the least polar (with the lowest O/C ratio) and the most hydrophobic (with the highest aromatic carbon content), and hence shows the greatest sorption enhancement. On the contrary, hydrophilic macromolecular acid is the most polar fraction of humic substances and therefore a much weaker sorbent than humic acid.

These results may have important implications for the fate of pyrethroids in water and suggest that sorption onto particulate matter may be a mechanism for the removal of pyrethroids from natural waters. Future studies should include investigations of possible desorption behaviour and of particulate-bound degradation pathways.

Acknowledgement

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