Influences on the sorption affinity of soil organic matter for non-ionic organic pollutants

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ABSTRACT

Sorption of non-ionic organic compounds to organic matter is usually characterized as a partitioning interaction, which is quantified by K_{oc}, the organic-C normalized partitioning coefficient. However K_{oc} for any single compound varies considerably between soils, often by a factor of 3-10. This study addresses some of the potential causes of this variability.

Forty-four soil cores were collected from a 2 ha paddock. Ten of these cores were selected for sorption measurements. The chemical composition of the soil organic matter (SOM) was determined using ^{13}C NMR analysis. It was found that K_{oc} for diuron was positively correlated with aryl C ($r^2 = 0.59$) and negatively correlated with O-alkyl C ($r^2 = 0.84$). There were no such correlations for phenanthrene K_{oc}.

A second set of experiments was carried out to investigate the effects of SOM–mineral interactions on the sorption properties of a selection of the soils. It was found that HF-treatment increased K_{oc} for both phenanthrene and diuron. The HF treatment removes mineral matter leaving the organic phase unaffected by the treatment. The increase in K_{oc} on HF-treatment soils provides strong evidence that interactions between organic matter and soil minerals block organic matter sorption sites. Furthermore, following HF-treatment, there was a positive correlation between K_{oc} for phenanthrene and aryl C and carbonyl C and a negative correlation with O-alkyl C. This suggests that the non-constancy of the relationship between organic matter chemistry and K_{oc}, for whole soils in the case of phenanthrene, may be a consequence of variability of the effect of organic matter-mineral interactions on $K_{oc.}$

The influence of lipids on the sorption of diuron and phenanthrene to soils was also investigated. Lipids are known to cover the surfaces of organic matter in soil. K_{oc} for diuron and phenanthrene were consistently higher for the lipid-extracted soils than for the whole soils (average of 31% for diuron and 29% for phenanthrene), indicating that lipids block sorption sites on the organic matter. Sorption experiments on one pair of HF-treated soils indicated that the blocking effects of minerals and lipids are independent, because lipid extraction and HF-treatment combined increased K_{oc} by more than either treatment alone.

In the last experiment, the effect of solvent conditioning on the sorption of diuron and phenanthrene was investigated. The K_{oc} values for compounds were consistently higher for solvent-treated whole soil and lipid-extracted soil than corresponding soils before solvent treatment. Solid-state ^{13}C NMR spectra of the solvent-treated soils indicated that there were no significant changes in the chemical structure of SOM caused by solvent treatment. Solvent treatment changes the physical conformation of the SOM, increasing its sorption affinity.

The key findings from the research are:

- Variations in sorption affinity for diuron are related to differences in the soil organic matter chemistry.
- SOM-mineral interactions can have a substantial influence on K_{oc} for non-ionic compounds.
- Lipids may block the active sorption sites on the SOM thereby diminishing sorption overall.

- Solvent conditioning can change the physical conformation of SOM and lead to enhancement sorption of diuron and phenanthrene.

DECLARATION

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

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1) Ahangar, A. G., R. J. Smernik, R. S. Kookana and D. J. Chittleborough. 2008. Clear effects of soil organic matter chemistry, as determined by NMR spectroscopy, on the sorption of diuron. Chemosphere 70: 1153-1160.

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4) Ahangar, A. G., R. J. Smernik, R. S. Kookana and D. J. Chittleborough. The effect of solvent conditioning on soil organic matter sorption affinity for diuron and phenanthrene. Chemosphere: submitted.

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PUBLICATIONS ARISING FROM THIS THESIS

1) Ahangar, A. G., R. J. Smernik, R. S. Kookana and D. J. Chittleborough. 2008. Clear effects of soil organic matter chemistry, as determined by NMR spectroscopy, on the sorption of diuron. Chemosphere 70: 1153-1160.

2) Ahangar, A. G., R. J. Smernik, R. S. Kookana and D. J. Chittleborough. 2008. Separating the effects of organic matter-mineral interactions and organic matter chemistry on the sorption of diuron and phenanthrene. Chemosphere 72: 886-890.

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