



The effects of organic matter–mineral interactions and organic matter chemistry on diuron sorption across a diverse range of soils



Ronald J. Smernik^{a,*}, Rai S. Kookana^{a,b}

^a Soils Group, School of Agriculture, Food and Wine and Waite Research Institute, The University of Adelaide, Waite Campus, Urrbrae, South Australia 5064, Australia

^b CSIRO, Land & Water, PMB 2, Glen Osmond SA 5064, Australia

HIGHLIGHTS

- Causes of variation in diuron K_{OC} for a diverse set of soils were investigated.
- HF-treatment increased K_{OC} for all but three soils, on average by a factor of 2.4.
- This showed organic matter–mineral interactions reduced K_{OC} of whole soils.
- There was no significant correlation between K_{OC} for the whole and HF-treated soils.
- K_{OC} of HF-treated soils increased with aryl C and decreased with O-alkyl C, alkyl C.

ARTICLE INFO

Article history:

Received 15 February 2014

Received in revised form 14 April 2014

Accepted 5 May 2014

Available online 24 June 2014

Handling Editor: X. Cao

Keywords:

Sorption

Diuron

NMR spectroscopy

Clay–organic matter interactions

Organo–mineral interactions

ABSTRACT

Sorption of non-ionic organic compounds to soil is usually expressed as the carbon-normalized partition coefficient (K_{OC}), because it is assumed that the main factor that influences the amount sorbed is the organic carbon content of the soil. However, K_{OC} can vary by a factor of at least ten across a range of soils. We investigated two potential causes of variation in diuron K_{OC} – organic matter–mineral interactions and organic matter chemistry – for a diverse set of 34 soils from Sri Lanka, representing a wide range of soil types. Treatment with hydrofluoric acid (HF-treatment) was used to concentrate soil organic matter. HF-treatment increased K_{OC} for the majority of soils (average factor 2.4). We attribute this increase to the blocking of organic matter sorption sites in the whole soils by minerals. There was no significant correlation between K_{OC} for the whole soils and K_{OC} for the HF-treated soils, indicating that the importance of organic matter–mineral interactions varied greatly amongst these soils. There was as much variation in K_{OC} across the HF-treated soils as there was across the whole soils, indicating that the nature of soil organic matter is also an important contributor to K_{OC} variability. Organic matter chemistry, determined by solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy, was correlated with K_{OC} for the HF-treated soils. In particular, K_{OC} increased with the aromatic C content ($R = 0.64$, $p = 1 \times 10^{-6}$), and decreased with O-alkyl C ($R = -0.32$, $p = 0.03$) and alkyl C ($R = -0.41$, $p = 0.004$) content.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Sorption of organic pollutants to soils is an environmentally important process that affects properties such as bioavailability, ecotoxicity, rate of degradation and their mobility. The affinity of a soil for a given molecule is usually expressed as a partition constant (K_d), which is simply the sorbed concentration divided by the solution concentration. In general, K_d increases with the organic C content of the soil, and hence K_d values are often normalized to the

soil C content by dividing by the organic C fraction (f_{OC}) to give K_{OC} . However, the relationship between K_d and f_{OC} is not an exact one, and hence K_{OC} for a given molecule can vary considerably between soils. In a review of published K_{OC} measurements, [Wauchope et al. \(2002\)](#) reported that where K_{OC} had been determined for a large number of soils, the coefficient of variation in K_{OC} was generally around 40–60% and that the ratio of maximum to minimum K_{OC} was generally around 3–10. They suggested variations in the nature of organic matter between soils may be a major contributor to this variation.

There is ample evidence that K_{OC} varies widely for different types of isolated organic matter such as different plant biopoly-

* Corresponding author. Tel.: +61 8 8303 7436; fax: +61 8 8303 6511.

E-mail address: ronald.smernik@adelaide.edu.au (R.J. Smernik).

mers (cellulose, lignin, cuticle), peat, coal and shale (Rutherford et al., 1992; Chen et al., 1996; Chefetz et al., 2000; Salloum et al., 2002). Isolated soil humic fractions also exhibit different K_{OC} values, with variation both between soils (Chen et al., 1996; Perminova et al., 1999; Salloum et al., 2001b) and between fractions isolated from the same soil (Perminova et al., 1999; Salloum et al., 2001b; Gunasekara and Xing, 2003; Kang and Xing, 2005). Amongst soil humic acids, K_{OC} generally increases with increasing aromaticity (Chen et al., 1996; Perminova et al., 1999; Salloum et al., 2001b). On the other hand, humin fractions, which are often more aliphatic (Salloum et al., 2001b; Kang and Xing, 2005), have been found to have higher K_{OC} values than corresponding humic acid fractions (Salloum et al., 2001b; Gunasekara and Xing, 2003; Kang and Xing, 2005).

It has proven harder to find a definitive link between K_{OC} and organic matter chemistry in whole soils, and few studies have found clear correlations between whole soil K_{OC} values and organic matter chemistry, as determined by solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Kile et al. (1999) reported that K_{OC} for carbon tetrachloride for 19 soils and 9 sediments was negatively correlated with the proportion of “polar organic carbon” (O-alkyl C + carbonyl C), and Ahmad et al. (2001) found a strong positive correlation of K_{OC} for two pesticides with aromatic C across 27 soils from Australia and Pakistan. Xing (1997) also reported a positive correlation between K_{OC} and aromaticity for a small set of four soils. Mitchell and Simpson (2013) reported a positive correlation between K_{OC} and aromatic C and a negative correlation between K_{OC} and O-alkyl C across a set of five soils for three compounds. Ahangar et al. (2008a) reported K_{OC} for diuron was positively correlated with aromatic C and negatively correlated with O-alkyl C for soils collected from a single paddock and noted that the consistency in mineralogy of their soils was likely to have contributed to their detection of a clear effect of organic matter chemistry on K_{OC} . Indeed, even for this restricted set of soils, there was no identifiable effect of organic matter chemistry on K_{OC} for another sorbate molecule, phenanthrene (Ahangar et al., 2008b).

Studies by Salloum and co-workers on 1-naphthol sorption provide a clear example of K_{OC} being correlated with organic matter chemistry for isolated organic samples (Salloum et al., 2001b) but not for the corresponding whole soils (Salloum et al., 2001a). They suggested that this difference may be caused by interactions between organic and mineral components that inhibit the accessibility of some organic matter domains, a mechanism which is consistent with the finding that the weighted average of K_{OC} for isolated humic fractions was greater than K_{OC} for the corresponding whole soils (Salloum et al., 2001b). Other research also suggests that organic matter–mineral interactions can decrease K_{OC} in whole soils and soil fractions (Njoroge et al., 1998; Celis et al., 2006). This was confirmed by Ahangar et al. (2008b), who found that removal of minerals by HF-treatment increased K_{OC} by a factor of 2–3, on a set of soils collected from one site. Furthermore, following HF-treatment, K_{OC} for phenanthrene showed strong correlations with organic matter chemistry that were absent for the whole soils.

In this study, we apply the approach of Ahangar et al. (2008b) of comparing K_{OC} for diuron before and after HF-treatment to a much larger and more diverse range of 34 soils selected to represent the diversity of soil and land-use systems in Sri Lanka. We have shown previously that diuron K_{OC} for this set of whole soils varies widely (Liyanaage et al., 2006). Our aim here is to test the influence of organic matter–mineral interactions (by comparing K_{OC} between corresponding whole and HF-treated soils) and the influence of the nature of organic matter (by linear regression of K_{OC} against NMR-derived measures of organic matter chemistry) across this diverse range of soils.

2. Materials and Methods

2.1. Selection and preparation of soils

The soils used in this study are a subset of the 43 soils described by Liyanaage et al. (2006). Nine soils from the previous study could not be included either because the C content was so low that HF-treatment was impractical or there was insufficient soil remaining to complete the analyses. Basic physical and chemical properties (pH, EC and clay, silt and sand contents), along with K_{OC} data for the whole soils for diuron and carbaryl can be found in Liyanaage et al. (2006).

The soils were HF-treated using the procedure of Skjemstad et al. (1994). Briefly, the HF-treatment consisted of nine successive treatments with 2% hydrofluoric acid solution. Each treatment involved shaking 3 g portions of soil in 50 mL of 2% hydrofluoric acid solution, end-over-end, for periods of 1 h (5 times), 16 h (3 times) and 64 h (once). Between treatments, samples were centrifuged, the supernatant discarded and replaced with fresh 2% hydrofluoric acid solution. Following the final treatment, the residue was rinsed 3 times with de-ionized water, then freeze-dried. Carbon contents of the HF-treated soils were measured on a LECO CR12 carbon analyzer.

Sorption Experiments: Diuron (>99% purity) was purchased from Sigma–Aldrich (Sydney, Australia). High performance liquid chromatography (HPLC) grade solvents and calcium chloride were obtained from Merck Pty Limited (Victoria, Australia). A stock solution of 1000 mg L⁻¹ diuron was prepared in methanol. Sorption experiments were carried out using a batch equilibration technique at ambient laboratory temperature (25 ± 3 °C), as reported previously (Liyanaage et al., 2006). For single point measurements on whole soil, an aliquot of soil (5 g) was equilibrated with 10 mL diuron solution (1.0 mg L⁻¹) by end-over-end shaking for 16 h, based on a preliminary kinetics experiment (Liyanaage et al., 2006). For HF-treated soils only 50 mg of the sorbent was equilibrated with 5 mL diuron solution (1.0 mg L⁻¹). At the end of the equilibration period, suspensions were centrifuged at 3000 × g for 20 min and 1 mL aliquots of the supernatant were filtered through 0.45 µm Teflon filters and analysed. Blanks without diuron and without sorbent were analysed and appropriate corrections were applied. Sorbed concentrations were calculated from the difference between the initial solution concentration and equilibrium solution concentration.

Diuron concentrations were determined using an Agilent 1100 series HPLC equipped with a diode array detector and C18 column. The operating conditions for diuron were: Apollo C18 cartridge (250 mm × 4.6 mm I.D., 5 µm particle size); isocratic elution at a flow rate of 1.0 mL min⁻¹; injection volume of 20 µL; mobile phase of acetonitrile: water 60: 40; UV detection at a wavelength of 220 nm. The retention time for diuron was noted to be 6.2 min with a minimum detection limit of 0.04 mg L⁻¹.

2.2. NMR analysis

Solid-state ^{13}C cross polarization (CP) NMR spectra were acquired with magic angle spinning (MAS) at a ^{13}C frequency of 50.3 MHz on a Varian Unity200 spectrometer. Samples were packed in a 7 mm diameter cylindrical zirconia rotor with Kel-F end-caps and spun at 5000 ± 100 Hz in a Doty Scientific MAS probe. A 1-ms contact time and a 1-s recycle delay were used, and 4000 transients were collected for each spectrum. Free induction decays were acquired with a sweep width of 40 kHz; 1216 data points were collected over an acquisition time of 15 ms. All spectra were zero-filled to 8192 data points and processed with a 50 Hz Lorentzian line broadening and a 0.005 s Gaussian broadening. Chemical

Download English Version:

<https://daneshyari.com/en/article/4408608>

Download Persian Version:

<https://daneshyari.com/article/4408608>

[Daneshyari.com](https://daneshyari.com)