Characterising the exchangeability of phenanthrene associated with naturally occurring soil colloids using an isotopic dilution technique

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ABSTRACT

The association of polycyclic aromatic hydrocarbons (PAHs) with inorganic and organic colloids is an important factor influencing their bioavailability, mobility and degradation in the environment. Despite this, our understanding of the exchangeability and potential bioavailability of PAHs associated with colloids is limited. The objective of this study was to use phenanthrene as a model PAH compound and develop a technique using ^{14}C phenanthrene to quantify the isotopically exchangeable and non-exchangeable forms of phenanthrene in filtered soil water or sodium tetraborate extracts. The study was also designed to investigate the exchangeability of colloidal phenanthrene as a function of particle size. Our findings suggest that the exchangeability of phenanthrene in sodium tetraborate is controlled by both inorganic and organic colloids, while in aqueous solutions inorganic colloids play the dominant role (even though coating of these by organic matter cannot be excluded). Filter pore size did not have a significant effect on phenanthrene exchangeability.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are environmental contaminants released from a variety of anthropogenic and natural sources (Hawthorne et al., 2002) which have toxic, mutagenic, and carcinogenic properties (ATSDR, 1995; Juhasz and Naidu, 2000; Mumtaz et al., 1996). PAHs are relatively immobile in soil matrices because of their low aqueous solubilities and high organic carbon (C) -water (K_{OC}) partitioning coefficients (Martens et al., 1997). However, several studies have shown that the presence of water-dispersible naturally occurring colloids (henceforth referred to as colloids) may enhance their mobility (MacKay and Gschwend, 2001; Zhou et al., 1999). Colloids are operationally defined as particles between 1 and 1000 nm in diameter, which encompasses natural nanoparticles (<100 nm), and include particles of layered silicates and sesquioxides (Fe- and Al-oxyhyroxides), organic macromolecules, bacteria and viruses (Lead and Wilkinson, 2006).

Their high specific surface area means that colloids have a high sorptive capacity and can be effective sorbents of low solubility and hydrophobic contaminants.

When defining the partitioning of contaminants between dissolved and particulate fractions, a widely accepted approach is to use filtration through 0.45 or 0.2 μm pore size filters. Filter pore size also plays a role in standardised procedures such as the Toxicity Characteristic Leaching Procedure (TCLP) and the Australian Standard Leaching Procedure (ASLP) (ASLP, 1997; TCLP, 1992). However, these approaches may overestimate the dissolved/leachable fraction as the filters used (0.6–0.8 μm) may be unable to completely remove all the colloidal material present in soil extracts, leachates and natural waters. For example, Gounaris et al. (1993) demonstrated that up to 60% of the 'dissolved' PAH fraction in groundwater from an abandoned landfill was associated with the >0.1 μm colloids. Similarly pore-water colloids from a heavily contaminated site was shown to bind pyrene and phenanthrene (Chin and Gschwend, 1992). Bergendahl (Bergendahl, 2005) investigated the leachability of phenanthrene and naphthalene from coal-tar contaminated soil using the EPA's TCLP test and used a mathematical model to predicted that a significant fraction of the total phenanthrene was associated with the colloidal phase. Colloid generation may also be exacerbated during ASLP assessment due to the elevated pH of the sodium tetraborate extractant (pH 9.2) and

vigorous shaking during the batch extraction process. Colloid-facilitated transport of PAHs has previously been observed (Villholth, 1999) but it is still unclear which type of leaching test and solid/liquid separation method provides the best simulation of this process. Standardised tests that better reflect the release of PAHs to the aqueous environment and their potential for transport and/or uptake by biota are needed to underpin risk assessment.

The goal of this study was to develop an isotopic dilution method to determine the phenanthrene pool in equilibrium (over the time period investigated) with truly dissolved phenanthrene in soil extracts to quantify the fraction that may be considered chemically and biologically active. This method is used to quantify the isotopically exchangeable pool (E-value) and a 'fixed' or unreactive (over the course of the equilibration period) pool (Hamon et al., 2008). The isotopic dilution principle was originally developed, and is well established, for inorganic nutrients and contaminants and has been be extended to studies of organic contaminants by using labelled compounds (e.g. ^{14}C). However, only few examples using this approach to assess organic contaminant exchangeability in soil have been reported. Celis and Koskinen (1999) characterised the irreversibility of pesticide sorption-desorption by soil in batch experiments and Sander and Pignatello (2005) used ^{14}C-naphthalene to assess the sorption hysteresis of this compound to organic matter. Williams and Kookana (2010) also used an isotopic dilution technique to measure isotopically exchangeable carbamazepine (CBZ), in river sediments and showed that the isotopically exchangeable fraction of CBZ decreased by 82.5% over a 28 day period following amendment with black carbon. Recently, Delgado-Moreno and Gan (2013) described a method using stable isotope labelled pyrene and bifenthrin to measure their bioavailability in sediments and showed a significant relationship between the derived E-values and bioaccumulation into Chironomus tentans.

In contrast to the aforementioned studies which focussed on whole soil or sediments, the objectives of this research were to a) develop a radioisotopic dilution technique to assess the lability/exchangeability of PAHs associated with colloids in contaminated soil:water and sodium tetraborate extracts and b) to determine the relationship between colloid size (0.7, 0.5, 0.3 μm) and isotopic exchangeability. Phenanthrene was used as a model compound as it is a USEPA priority pollutant, ubiquitous at PAH-contaminated sites and has been commonly used in sorption − desorption studies (Chefetz and Xing, 2009; Huang et al., 2003; Young and Weber, 1997). It was hypothesised that a) the removal of colloidal fractions with decreasing filter pore size would decrease the total concentration of phenanthrene in the extract; b) the relative exchangeability of phenanthrene (as percentage of the total) would be inversely related to the size of the colloids in the extracts and c) phenanthrene exchangeability would be reduced in soil:tetraborate extracts compared to soil:water as a result of enhanced colloid generation during ASLP.

2. Materials and methods

2.1. Isotope dilution principle

The isotopic dilution technique in this study used ^{14}C-phenanthrene. In a colloid-water system the total mass of phenanthrene (m_{tot}) is distributed among different pools:

$$m_{tot} = m_w + m_{LC} + m_{NC} \qquad (1)$$

Where the subscripts w, LC and NC indicate the truly-dissolved aqueous, labile (or exchangeable) and non-labile phenanthrene associated with colloids, respectively. The sum of the truly-dissolved and labile phenanthrene associated with colloids is defined as the exchangeable pool (E-value). The principle of isotopic dilution is based on the premise that, when a small amount of ^{14}C phenanthrene is introduced into a colloid-water system, it will readily (and reversibly) redistribute itself among the truly-dissolved and colloidal exchangeable phases in the same way as other molecules of phenanthrene (non-labelled) (Hamon et al., 2008; Lombi et al., 2003):

$$\alpha_w/\alpha_{LC} = m_w/m_{LC} \qquad (2)$$

Where α is the activity of ^{14}C-phenanthrene and the subscripts have the same meaning as above. This means that the specific activity (Bq/mg) of the dissolved and exchangeable phenanthrene bound to colloids is the same:

$$m_w/\alpha_w = m_{LC}/\alpha_{LC} \qquad (3)$$

As the isotopic ratio in these two fractions is equal then the isotopic ratio of the overall exchangeable pool is also the same:

$$m_w/\alpha_w = m_{LC}/\alpha_{LC} = \text{E-value}/A \qquad (4)$$

Where A is the total activity of the labelled phenanthrene introduced into the system, which can be measured based on the ^{14}C activity in a spiked blank solution. Therefore, based on the equations above, the E-value may be written as (Hamon et al., 2008):

$$\text{Phenanthrene E-value} = (m_w/\alpha_w) \times A \qquad (5)$$

In a system where colloids are present, separation of the truly-dissolved fraction is not a simple task. In this case, as suggested by Lombi et al. (2003), a resin can be introduced in the system to sample the exchangeable pool and the E-value calculated as follows:

$$\text{Phenanthrene E-value} = (m_r/\alpha_r) \times A \qquad (6)$$

Where the subscript r indicates the mass and activity of phenanthrene in the resin. It should be noted that not all the exchangeable phenanthrene needs to be removed from the resin. The amount extracted simply needs to be large enough to allow a precise quantification of the isotopic ratio. Finally, it should be kept in mind that the dilution of the introduced ^{14}C-phenanthrene within the pre-existing phenanthrene pool is time-dependent. In theory, at infinite equilibration time and assuming no degradation, the introduced labelled compound would mix uniformly with the entire phenanthrene pool (Hamon et al., 2008). It should also be noted that this method assumes that the resin does not extract phenanthrene from the non-exchangeable pool.

2.2. Soils used

Four Australian soils (referred to as S1–S4) were used in this study. S1 and S2 were collected from former gas manufacturing plant sites in Victoria, whereas S3 and S4 were collected from a former tram maintenance facility and a former wood preservation (creosote) site in South Australia, respectively. All samples were air-dried and sieved (<2 mm). Soil pH ranged from 5.9 to 8.1 (1:5 soil:water), TOC (2.3–7.7 %) and total concentration of phenanthrene in S1–S4 was 180, 52, 93 and 21 mg kg^{-1} respectively. Soil characterisation methods and results are reported in Supporting information (SI, Table S1).