Effect of ageing on benzo[a]pyrene extractability in contrasting soils

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HIGHLIGHTS

- In vitro assessment of B[a]P in contaminated soils using 4 different methods.
- An exponential kinetic model fits well with the extractability data.
- Fitting parameter and ^{14}C residue correlates with key soil properties.
- Fractionation of B[a]P was obtained based on extractability by extractants.

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ABSTRACT

Changes in benzo[a]pyrene (B[a]P) extractability over 160 days ageing in four contrasting soils varying in organic matter content and clay mineralogy were investigated using dichloromethane: acetone 1:1 (DCM/Ace), 60 mM hydroxypropyl-β-cyclodextrin (HPCD) solution, 1-butanol (BuOH) and Milli-Q water. The B[a]P extractability by the four methods decreased with ageing and a first-order exponential model could be used to describe the kinetics of release. Correlation of the kinetic rate constant with major soil properties showed a significant effect of clay and sand contents and pore volume fraction (<6 nm) on sequestration of the desorbable fraction (by HPCD) and the water-extractable fraction. Analysis of ^{14}C-B[a]P in soils after ageing showed a limited loss of B[a]P via degradation. Fractionation of B[a]P pools associated with the soil matrix was analysed according to extractability of B[a]P by the different extraction methods. A summary of the different fractions is proposed for the illustration of the effect of ageing on different B[a]P-bound fractions in soils. This study provides a better understanding of the B[a]P ageing process associated with different fractions and also emphasises the extraction capacity of the different methods employed.

1. Introduction

Benzo[a]pyrene (B[a]P) is a persistent organic contaminant that is present in soils at many contaminated sites. B[a]P contamination is of great concern as it has well-documented genotoxic effects on a broad range of prokaryotic and mammalian organisms and is carcinogenic to a variety of animals [1]. The classical clean-up technique for organic pollutants from contaminated soils is biodegradation which is a biphasic process with an initial phase of rapid degradation, followed by a phase with a much slower transformation rate. B[a]P does not always biodegrade because of its chemical structure which makes it resistant to microbial attack. Moreover, its strong hydrophobicity limits its concentration in aqueous solution [2]. However, as B[a]P persists and ages in soil, it may become less available for uptake by organisms and therefore have diminished toxicity [3].

Irrespective of the nature of chemical input into soils or sediments, increasing contact time between chemicals and soil/sediment reduces the magnitude of the bioavailable fraction, as a consequence, their biodegradation. An inverse relationship between the extractability of organic contaminants in aged soils and contact time has often been reported [4–6]. Whereas, a declining bioavailability with ageing has long been recognised, there are limited studies on the kinetics of desorption with ageing. Those studies that have been reported, has focused on high

extraction recovery using sequential extractions [7], rather than time-dependent release similar to that which may occur under the field conditions.

A recent review of the Australian National Environmental Protection Measure (NEPM) has made provisions for the inclusion of bioavailability for both human health and ecological health while conducting site-specific risk assessment [7,8]. However, the term bioavailability by its definition is organism- or receptor-dependent as well as being influenced by complex organism/contaminant interactions, and it is limited by chemical, biological or physical factors [9]. The receptors selected for evaluation of bioavailability in risk assessments range from microorganisms, lower animals such as earthworms and other invertebrates, to small mammals and even higher animals that better represent humans.

The determination of bioavailability is usually time consuming and costly. A variety of simple, empirical mild extraction tests have been used to estimate bioavailable pools, and some of them, e.g. hydroxypropyl-β-cyclodextrin (HPCD) and butanol extractions, were found to correlate well with microbial degradation and earthworm bioaccumulation of mid-molecular weight PAHs such as phenanthrene and pyrene in soils at different ageing periods [10–13], or pyrene bioavailability to earthworms [14]. For human health risk assessment, various extractants have been developed to mimic mammalian digestive processes. However, studies to validate biological measurements are sparse, except for in a recent study the BuOH and DCM/Ace extractability were found have significant correlation with the relative bioavailability using swine model and eight spiked soils [15].

Sorption of organic contaminants to soil is mainly influenced by the organic matter (SOM), and sometimes by the clay content of soil [16]. The decrease in extractability and bioavailability with ageing is thought to involve diffusional or reaction processes of the organic solute with solid phase and diagenetic processes that change the properties of the soil or sediment [17–19]. Therefore, both the nature of the chemicals and the soil properties are important. For non-polar hydrophobic contaminants such as PAHs, it has been shown that physical diffusion into micropores of soils and sediments can result in their inaccessibility even to the smallest microorganisms [20]. The presence of recalcitrant PAHs

in long-term contaminated field has also been found to be related to humin or the mineral phases associated with carbon materials in soils [21,22]. However, the mechanisms underlying the ageing processes including the slow but continuous release over time have yet to be fully understood in relation to bioavailability and the implications to potential risks arising from the more recalcitrant desorbing fraction.

Contaminant bioavailability depends on the properties of both the contaminant and the soil environment. Extraction approaches that take into account the contaminant physico-chemical interactions with soil could therefore provide useful information on their bioavailability, although further validation or mechanistic understanding of the interaction with ageing is required to fully understand the changes in bioavailability with time. Given the biphasic nature of contaminant desorption in aged soils, four extraction methods, ranging from an aqueous solution frequently used for screening PAH contamination, to mild extraction by HPCD and butanol and an exhaustive extractant in the form of dichloromethane: acetone (DCM/Ace at 1:1), were used to investigate the kinetics of B[a]P desorption with ageing using soils spiked with ^{14}C-labelled B[a]P over a 160-day period. We hypothesise that the biphasic nature of desorption will vary with the nature of extractant and, for an aggressive and exhaustive extractant such as DCM/acetone that is commonly used for total extraction, the release behaviour may not be biphasic. The objectives of this study were thus: (1) to study changes in B[a]P extractability over time in selected soil types of Australia, and (2) to explore the soil properties which control the B[a]P ageing process.

2. Materials and methods

2.1. Chemicals and solvents

Bezo[a]pyrene (analytical grade) was obtained from Sigma–Aldrich (Sigma–Aldrich Pty. Ltd., Sydney, Australia) for analysis. ^{14}C-Benzo[a]pyrene (54 mCi/mmol) was purchased from Amersham Life Science for soil spiking. Hydroxypropyl-β-cyclodextrin (HPCD) powder and other solvents including 1-butanol (BuOH), dichloromethane (DCM), acetone (Ace),

Table 1
Pertinent properties of the soils used in the experiments.

Soil properties		MTA	BDA	N	I
Classification		Ferrosol	Black Vertisol	Tenosol	Kurosol
TOC (%)		7.50	3.27	1.71	5.06
DOC (mg/L)		103.2	95.5	47.7	108.4
pH		5.1	6.0	7.1	5.1
EC (μS cm^{-1})		87	75.5	402	69.1
CEC$_b$[a] (cmol$_c$ kg^{-1})		6.37	38.70	9.44	7.91
Particle size fraction (%)	Sand	61.9	53.0	87.6	68.1
	Slit	16.8	16.1	6.7	21.2
	Clay	21.2	30.9	5.7	10.7
Soil texture		Sandy clay loam	Sandy clay loam	Loamy sand	Sandy loam
Surface area (m^2/g)		51.7	4.0	7.9	6.0
Mesopores volume (cm^3/g)[b]		0.097	0.008	0.008	0.012
Average pore diameter (Å)[c]		76.2	81.3	39.4	81.4
Clay mineralogy		Kaolinite, Gibbsite, Quartz	Montmorillonite, Kaolinite, Montmorillonite-Kaolinite interstratifications, Feldspar	Quartz, Illite, Kaolinite, Feldspar	Illite, Kaolinite, Quartz, Montmorillonite
Pore volume < 6 nm percentage (%)		24.4	22.8	51.0	24.7
Pore volume < 6 nm (cm^3/g)		0.020	0.002	0.004	0.003

[a] BaCl$_2$ Compulsive Exchange Method (Gillman and Sumpter, 1986).
[b] Single point adsorption total pore volume of pores (<424 Å diameter at P/P_0 = 0.95).
[c] Adsorption average pore width (4 V/A by BET).