Extremely Small Amounts of B[a]P Residues Remobilised in Long-term Contaminated Soils: A Strong Case for Greater Focus on Readily Available and not Total-extractable Fractions in Risk Assessment

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ABSTRACT

There is a lack of understanding about the potential for remobilisation of polycyclic aromatic hydrocarbons (PAHs) residues in soils, specifically after the removal of readily available fractions, and the likelihood to cause harm to human and environmental health. Sequential solvent extractions, using butanol (BuOH), dichloromethane/acetone, and methanolic saponification were used to investigate the time-dependent remobilisation of B[a]P residues in aged soils, after removal of readily available or total-extractable fractions. After 120 d of aging, BuOH-remobilised B[a]P were small or extremely small ranging from 2.3 ± 0.1 mg/kg to 4.5 ± 0.5 mg/kg and from 0.9 ± 0.0 mg/kg to 1.0 ± 0.1 mg/kg, after removal of readily available and total-extractable fractions, respectively. After removal of readily available fractions, the remobilisation rates of B[a]P residues were constant over 5 re-equilibration times, as shown by first-order kinetics. The amounts of B[a]P remobilised significantly ($p < 0.05$) decreased with aging, particularly in hard organic carbon-rich soils. After 4 years of aging, BuOH- and total-remobilised B[a]P were generally < 5% of the initially spiked 50 mg/kg. Based on the findings of this study, the potential or significant potential for B[a]P NERs in soils to cause significant harm to human and environmental health are minimal.

Keywords: Polycyclic aromatic hydrocarbons, B[a]P, Nonextractable residues, Small Remobilisation, Release, Risk assessment

1. Introduction

The impacts and significance of nonextractable residues (NERs) of hydrophobic organic contaminants (HOCs), such as polycyclic aromatic hydrocarbons (PAHs), to human and environmental health risk assessments of contaminated land are gaining increasing attention within the scientific and regulatory communities [1-4]. Specifically, whether NERs will be remobilised in soil and pose unacceptable levels of risks to human and environmental health remain uncertain.

Sixteen priority PAHs are of global concern as they are ubiquitous and persistent in soils, and are potentially toxic and/or carcinogenic. Benzo[a]pyrene (B[a]P) is classified as a Group 1 carcinogen and is a key risk-driver for many PAH-contaminated sites [5, 6]. The potential for B[a]P to persist in soils is predictable given its high Log K_{ow}, very low aqueous solubility and volatility, as well as recalcitrance to biodegradation [5, 7]. The persistence and sequestration of PAHs are key features governing their fate in soils and may affect the biological functions and productivity of soils. PAHs are subjected to various physical, biological, environmental loss and sequestration processes [8], making it difficult to determine total PAH concentrations in soils, particularly for retrospective risk assessments. Non-exhaustive extractions of PAHs aged in soils often reveal that PAH desorption may be bi- or tri-phasic comprising a rapid initial loss phase, and then slow and/or very slow phases that remains constant over time under undisturbed environmental conditions [9]. Slow desorption of PAHs in soil is attributed to mass-transfer limitations resulting from PAH sequestration onto and into rubbery or glassy soil organic matter, clay-organic matter matrices and carbonaceous materials (such as black carbon), as well as diffusion into micro- and nano-pores [10, 11]. Detailed sequestration mechanisms are described elsewhere [12, 13].

Highly sequestered PAH fractions in soils may result in the failure of remediation objectives, particularly where associated concentrations exceed regulatory guideline values [14, 15]. Regulatory concerns regarding the potential risks of these sequestered residues to biological receptors may be justified [16, 17]. The highly sequestered PAH fraction is usually defined as that which is not extractable by exhaustive solvents [18]; hence, the term 'NERs'. Previous studies have reported that a fraction of PAH NERs may be extractable by methanolic saponification of pre-extracted soils [19]. Methanolic saponification cleaves ester or ether linkages within the soil matrix, thereby partially releasing entrapped or occluded PAH NERs [20]. According to Kastner et al. [18], entrapped or occluded NERs (parent compounds and metabolites), referred to as Type I NERs, are non-covalently bound to the soil matrix. This implies that although Type I NERs have low to high stability, they may be released or remobilisable at slow rates and small extents [21]. Type II NERs are covalently bound in soils, very stable, and less likely to be released. For PAHs, potential covalent binding of metabolites to the soil matrix may result in the formation of new compounds that are physico-chemically different from the original compound. Since Type II PAH NERs may be distinguishable from their parent compounds, their classification as NERs of original parent compounds may be arguable. Type III NERs are biogenic residues and bear no environmental relevance [18]. Biodegradation is not a substantial loss mechanism for hydrophobic and persistent high molecular weight (HMW) PAHs, such as B[a]P; hence, the bulk of total NER in soils from HMW PAHs may be Type I. A lack of understanding of soil-PAH interactions and the nature of PAH NERs in soil is a major uncertainty constraining risk-based approaches to contaminated land management, and may lead to over- or under-estimation of potential health risks that may be associated with exposure to PAH NERs in soils.

Many researchers regard highly sequestered HOC-fractions in soil as unimportant in risk assessments [22], because associated desorption rates are slow or very slow and soil half-lives may last for decades [21, 23]. In contrast, a few studies have showed potential for release of PAH NERs [19, 24]; however, amounts released and associated implications for risk assessment are not usually considered [21]. In these previous studies, highly sequestered PAH NERs are often considered as residues following exhaustive extraction of soils. Exhaustive extractions of PAH contaminated soils, a common technique in traditional risk assessment approaches, yield total-extractable PAH concentrations considered to be overestimative of risks to human and ecological health [22, 25]. Risk-based approaches, which are based on bioavailability or bioaccessibility concepts, focus on the fractions that are readily available to pose risks to human and ecological health [25, 26]. Till date, there are no published studies on the potential remobilisation of PAH residues in soils resulting from treatments that remove only readily available fractions, rather than those that remove total-extractable fractions. Such studies are required to minimise the uncertainties associated with risk-based approaches to contaminated land management.

The objectives of this study are to investigate: the time-dependent remobilisation of B[a]P residues in soils aged for up to 4 years after the removal of readily available fractions (partial removal); the remobilisation kinetics after equilibrating soils from which readily available fractions have been removed; and to compare the amounts of PAHs remobilised after partial removal and the removal of total-extractable fractions (complete removal) in soils.

2. Experimental

2.1. *Chemicals*

Analytical grade B[a]P (> 96% purity) was obtained as crystalline solid from Sigma Aldrich Pty Ltd., Sydney, Australia. Also sourced from the same supplier were p-Terphenyl-d14, analytical grade acetone (Ace), acetonitrile (ACN), 1-butanol (BuOH, density = 0.81 g/mL, ≥ 99.4%), dichloromethane (DCM), methanol (MeOH, HPLC Grade), toluene (Tol, 99.8%), potassium hydroxide (KOH) and silica sand. Hexane (Hex, HPLC grade) was purchased from Fisher Scientific, Loughborough, UK.

2.2. *Design*

Three air-dried soils I (Kurosol), M (Ferrosol) and B (Black Vertosol) were collected from a depth of 5 – 20 cm from the Adelaide Hills, South Australia, Mount Tamborine and Beaudesert, Queensland respectively. Soils properties were presented previously [27]. Soil I is sandy loam (10.7% Clay, 4.3% TOC), soil M is sandy-clay-loam (21.2% Clay, 7.4% TOC) and soil B is sandy-clay-loam (30.9% Clay, 3.5% TOC) (USDA textural classification). The contents (%) of soft- and hard-organic carbon (OC), and black carbon (BC)-rich materials were determined [21]. Air-dried soils were sieved through a 2 mm sieve, spiked with 50 mg/kg B[a]P, and wetted to their field moisture contents (25% to 40% on dry weight basis) [27]. Only B[a]P spiked soils aged in the dark for 120 d and 4 years were used. Silica sand was concurrently spiked and used as a reference material to monitor spike recovery after aging. Soil subsamples (n = 18 or n = 8) were collected and dried at 37.5 ^{o}C after each aging time. For the removal of readily available B[a]P fractions (A in Fig. 1), subsamples of soils (n = 18) were subjected to a mild BuOH extraction following quality control and quality assurance procedures described previously [27]. The resulting soil residues were then divided into 6 batches (n = 3) according to the design in Fig. 1.

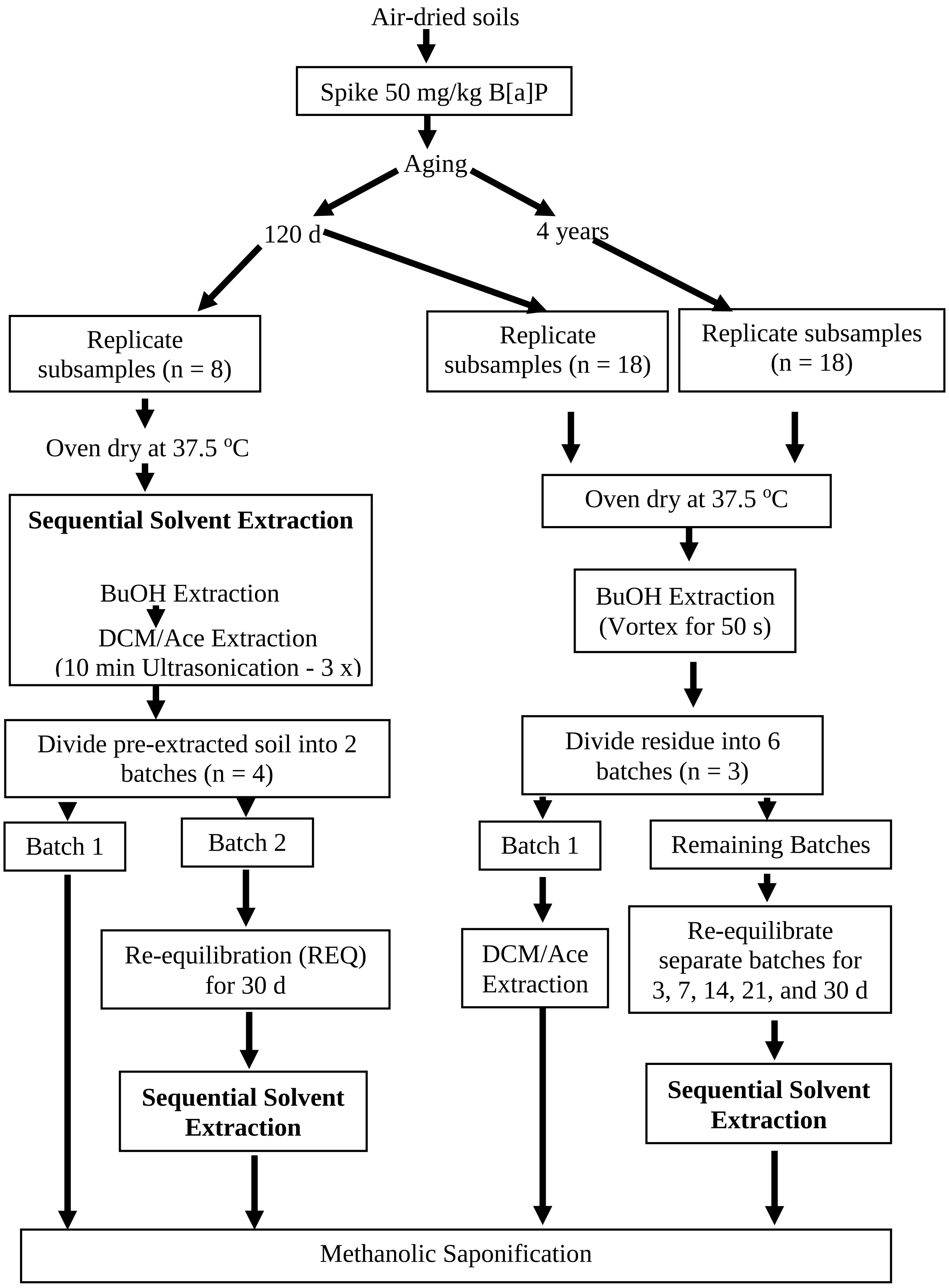

Fig. 1. Experimental design

The replicates did not show significant between-batch differences ($p > 0.05$) in their BuOH extractabilities (data not shown).

The first batch (n = 3) of the BuOH-extracted soil samples was subsequently extracted with DCM/Ace to remove B[a]P fractions that were not extractable by BuOH. The pre-extracted soils (NERs after DCM/Ace extraction) were further subjected to methanolic saponification (MeKOH). The remaining batches, i.e. 2, 3, 4, 5 and 6 (Fig. 1), were then kept in the dark to re-equilibrate at 25.5 ± 1.0 ^{o}C for 3, 7, 14, 21, and 30 d, respectively, for modelling of remobilisation kinetics.

For the removal of total-extractable B[a]P fractions (B in Fig. 1), only soils aged for 120 d were used. Subsamples (n = 8) were sequentially extracted with BuOH and DCM/Ace [27]. The pre-extracted soils were each divided into 2 batches (n = 4). The first batches of soils were extracted with MeKOH, while the second batches of soils were kept in the fume hood overnight and rewetted to field moisture contents, and re-equilibrated in the dark for 30 d.

After re-equilibration (REQ) of soils (A and B in Fig. 1), soils were again sequentially extracted with BuOH and DCM/Ace, and MeKOH. Blank soils were also treated in a similar manner. All percentage extractability calculations were based on the initial amounts of B[a]P spiked into the soil (50 mg/kg), unless otherwise specified.

$$\text{Extractability (\%)} = \left(\frac{\text{Amount of B[a]P Extracted by Solvent (mg)}}{\text{Amount of B[a]P Spiked into Soil (mg)}}\right) \text{X } 100\% \quad (1)$$

Remobilisation refers to the additional amounts of B[a]P extractable by BuOH, or by a combination of BuOH and DCM/Ace (total remobilisation), after REQ. The amounts of B[a]P released after the removal of readily available fractions were fitted to a first-order exponential decrease model as described previously [21].

2.3. Determination of Butanol-, Total-, and MeKOH-extractable B[a]P.

Soils were extracted with 1-BuOH following a previously described procedure with some modifications [27]. In the modified procedure, the butanolic supernatant was not decanted following centrifugation. Instead, a 2 mL aliquot of the supernatant was transferred into a clean glass vial, vacuum-concentrated, redissolved in ACN, and filtered through 0.45 µm PTFE syringe filters before transfer into 2 mL amber HPLC vials for analysis. After BuOH extraction, soils were extracted with 3 mL DCM/Ace (1:1, *v/v*) [27]. Total-extractable B[a]P is the sum of BuOH- and DCM/Ace- extractable B[a]P. The other operational definitions are presented in the SI. After the sequential solvent extractions, NERs were then subjected to MeKOH by extracting soils with 10 mL MeOH/2 M KOH (14:1, *v/v*) [27].

2.4. HPLC Analysis of B[a]P

The concentrations of B[a]P were determined with an Agilent 1100 Series HPLC equipped with a fluorescence detector (excitation wavelength = 230 nm and emission wavelength = 460 nm) as in described previously [27].

2.5. Data analysis

Extractability data were statistically analysed with SPSS (IBM Corporation, version 24) and graphing was by Origin (Microcal Software Inc., Northampton, MA, USA, version 6). No data transformation was applied. There were 3 independent and 2 or more outcome variables. The independent variables included: soil type (3 nominal categories); aging time (2 nominal categories); and the procedures for removing extractable fractions (i.e. partial or complete). The outcome variables were BuOH, DCM/Ace, total, and MeKOH extractability (mg/kg or %). A 95% significance level was used. One-way ANOVA was used to test between-group differences with Tukey’s post hoc test where equal variance is assumed and

Games Howell's test where equal variance is not assumed [28]. Student's *t* test was used for pairwise comparisons of independent samples.

3. Results and discussion

3.1. Spike recovery and data variability

Spike recovery of B[a]P from silica sand was > 95% throughout the study, showing that B[a]P losses during laboratory procedures were minimal. Total extractability (i.e. BuOH+ DCM/Ace extractability) of B[a]P 2 d (day 0) after spiking ranged from 78.5% (soil B) to 95.9% (soil M) and agreed with a previous study that used same soils [27, 29]. After MeKOH, complete mass balance (≥ 100%) was obtained, except in soil B where the mass balance was 88.9 ± 8.5%. At 120 d of aging, total extractability ranged from 53.2 ± 2.2% (soil B) to 80.0 ± 9.9% (soil M), whereas it ranged from 63% (soil B) to 86% (soil M) after MeKOH. Average standard deviation in B[a]P extractability was generally below 5%. Decreases in the recovery of PAHs due to the effects of aging and sequestration in soils, and variations due to soil properties, are well known [29-31]. Other studies have reported comparable decreases in total extractability from 100 to 80% over 200 d of aging using Soxhlet extraction [32], and 83 to 73% after 170 d of aging using a DCM-soxtec extraction technique [20]. In sterile conditions, ^{14}C-B[a]P in aged soil was not completely recovered [20]. The decrease in B[a]P extractability with aging was attributed to sequestration effects, although minimal losses from biodegradation may not be disregarded.

3.2. Extractability and aging of B[a]P in soils prior to re-equilibration

All soils showed substantial decrease ($p < 0.05$) in B[a]P extractability after aging. Butanol extractability has been used to assess PAH bioaccessibility in soils for human and ecological health risk assessments [29, 33-35]. Prior to REQ (day 0), BuOH extractability ranged from 16.2 ± 0.8 mg/kg (soil B) to 26.4 ± 1.0 mg/kg (soil I) at 120 d of aging (Fig. 2A), and 0.28 ± 0.03 mg/kg (soil B), 2.97 ± 0.38 mg/kg (soil I) and 3.02 ± 0.21 mg/kg (soil M) at 4 years of aging. Soil B had significantly lower ($p < 0.05$) B[a]P extractability than the other soils whose extractabilities were similar ($p > 0.05$). The decreases in B[a]P extractability through aging indicate that B[a]P became progressively sequestered in the soil matrix [36, 37]. Hard OC and clay-sized particle fractions in soils can sequester PAHs [29, 32, 38-40], through physical adsorption of PAHs to surfaces and occlusion or entrapment in pores [10, 13, 29, 41]. In this study, the fractions of hard OC relative to TOC (hard OC/TOC) in soils (0.45 – 0.58), as well as the contents of very fine-textured particles (10.7 – 30.9%) may account for the differences in B[a]P extractability by BuOH. This is indicated by the strong negative relationships between BuOH-extractable B[a]P and hard OC/TOC, and with clay content of soils ($R^2 > 0.9$) at 120 d and 4 years of aging in agreement with previous studies [21]. These strong relationships need to be validated using a wider range of soils.

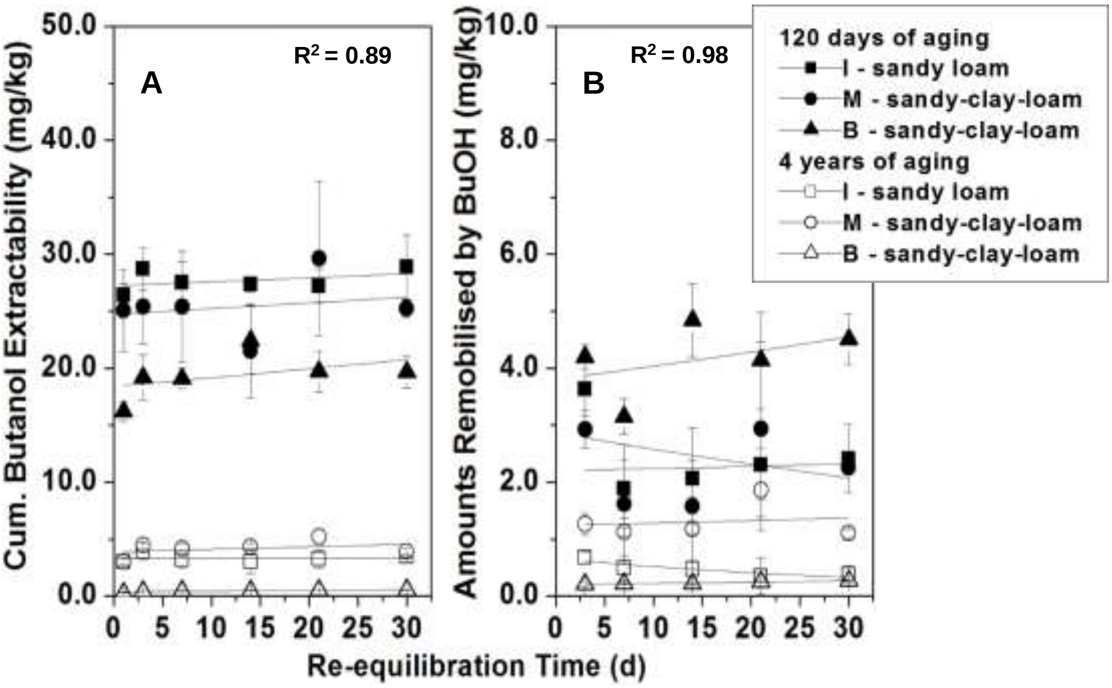

Fig. 2. Exponential curve-fitting of the cumulative amounts of butanol-extractable B[a]P following re-equilibration (A) and the amounts of butanol-remobilised B[a]P after each re-equilibration time (B). Values are means (n = 3) ± standard deviations. Values are means (n = 3) ± standard deviations. Note the differences in the Y-axis.

As with BuOH extractability, DCM/Ace-extractable B[a]P and total extractability (BuOH + DCM/Ace) decreased significantly ($p < 0.05$) after fresh spiking to 120 d of aging, and to 4 years of aging (Fig. 3), whereas B[a]P NERs increased (Fig. 3). The 4 year aged soils had a decrease in the cumulative total extractability of B[a]P ranging from 81% (soil M) to 97% (soil B) of the total-extractable B[a]P at 0 d of aging (Fig. 3). Methanolic saponification released detectable amounts of highly sequestered B[a]P NERs in the pre-extracted soils (Fig. 3). Although soil B contained the largest amount of B[a]P NERs after aging (Fig. 3), the fraction (%) of B[a]P NERs in pre-extracted soils released by MeKOH was consistently smaller in Soil B than in the other soils (Fig. 3), indicating stronger B[a]P sequestration by soil B. Soil B had large amounts of hard OC/TOC fractions and clay, and may be expected to strongly sequester B[a]P compared to the other soils [10, 42]. Strong sequestration of PAHs in soils lead to very low PAH extractability [20, 30], particularly in long-term aged soils [23]. The low total extractability from soil B, 2 d after spiking, further indicates rapid B[a]P sequestration and that the extents of sequestration is dependent on soil properties [29, 32, 43].

3.3. *Remobilisation of B[a]P after the removal of readily available fractions in soils*

The aim of BuOH extraction in the sequential extraction scheme was to partially, rather than completely, remove the extractable B[a]P fractions as in risk-based approaches to contaminated land management [22, 26, 44]. The amounts of B[a]P that were then re-extractable or remobilised after the removal of readily available fractions in soils are illustrated in Fig. 2. Cumulative BuOH extractability of B[a]P slightly increased after 2 d of REQ at 120 d and 4 years of aging (Fig. 2A), however, the increases were generally not significant ($p > 0.05$). Cumulative total extractability of B[a]P after 2 d of REQ were not significantly different ($p > 0.05$) from total extractability prior to REQ (Fig. 3). After 2 d of REQ (Fig. 2), cumulative BuOH extractability of B[a]P also remained unchanged ($p > 0.05$), indicating that the amounts of B[a]P remobilised by BuOH plateaued quickly. The constancy of BuOH-remobilised B[a]P after 2 d of REQ was reflected by the curves fitted with the first-order kinetic model (Fig. 2). The constancy in B[a]P remobilisation further showed that the rates and extents of decrease in the amounts of B[a]P remobilised were unchanged from 2 to 30 d of REQ, further reflecting the stability of the sequestered B[a]P.

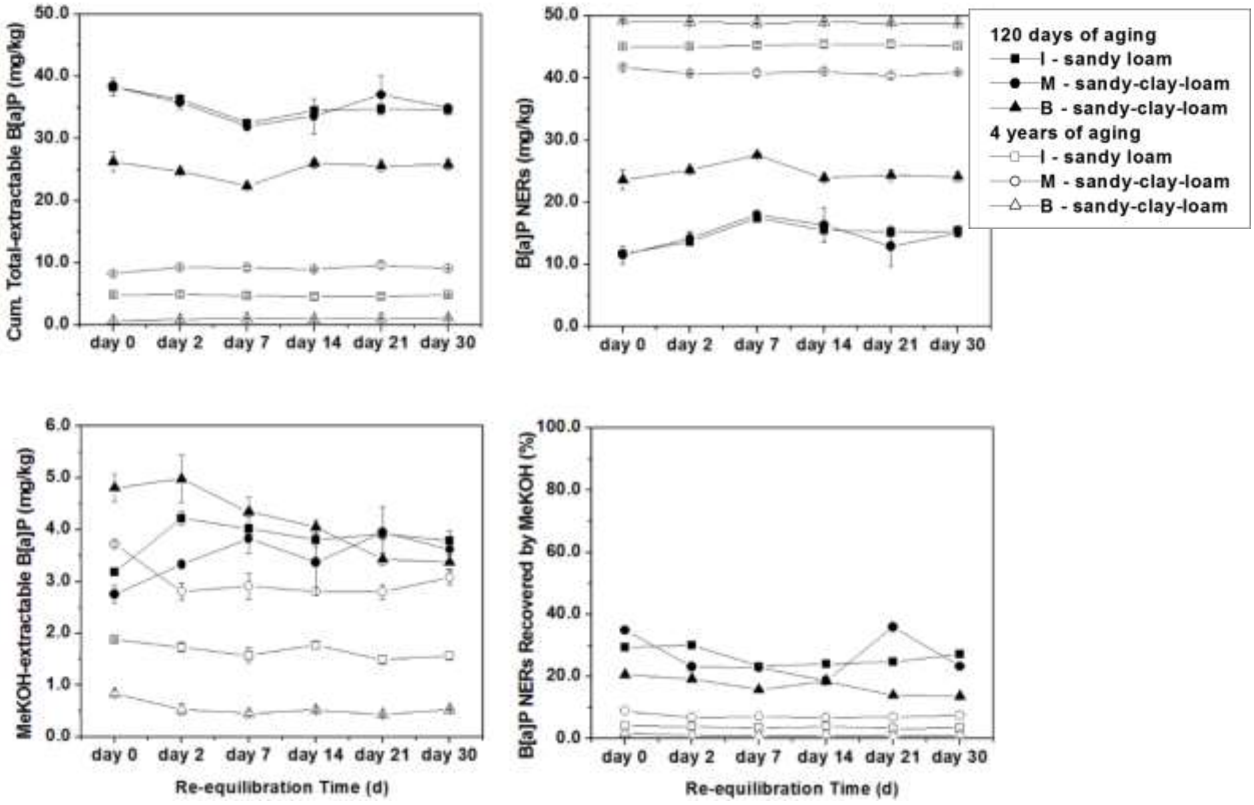

Fig. 3. Temporal changes in B[a]P extractability and sequestration before and after re-equilibration. Cum. is cumulative. NER is nonextractable. MeKOH is methanolic saponification. Values are means (n = 3) ± standard deviations. Note the differences in the Y-axis.

Specifically, BuOH-remobilised B[a]P after 30 d of REQ in soils at 120 d of aging were 4.5 ± 0.5 mg/kg, 2.4 ± 0.6 mg/kg and 2.3 ± 0.1 mg/kg in soils B, I and M, respectively (Fig. 2B). Although the amounts of B[a]P remobilised by BuOH after 120 d in soils were below 9% of the initially spiked concentrations (50 mg/kg) or below 13% of the residue after BuOH extraction prior to REQ, the effects of hard OC fractions and clay content on B[a]P remobilisation appear anomalously obscured. This anomaly may not be attributed to changes in hard OC- or clay-induced interactions on B[a]P extractability given that hard OC/TOC fractions and clay contents of soils showed negative relationships with B[a]P extractability by BuOH before REQ. Rather, the anomaly may be attributed to the non-exhaustive nature of the BuOH extraction [20] as it may underestimate the rapidly desorbing or readily available B[a]P fractions in soils [45]. The extent to which the readily available B[a]P fractions in soil B (16.2 ± 0.8 mg/kg) were removed by BuOH prior to REQ may be less efficient than the extents in the other soils (25.1 ± 3.6, and 26.4 ± 1.0 mg/kg in soils M and I, respectively). After REQ from 2 to 30 d, the readily available B[a]P fractions in all soils had equilibrated in the residual butanolic solvent (1 mL). Hence, subsequent re-extraction of soil B with BuOH after REQ efficiently captured both the readily available B[a]P that was not extractable prior to REQ and remobilised B[a]P, which may have resulted in the greater B[a]P extractability (remobilisation).

Sorption and desorption of PAHs may be underestimated during extraction of soils that may have not been equilibrated efficiently [46]. In this study, the subsequent DCM/Ace-extractable B[a]P after 30 d of REQ was smaller ($p < 0.05$) in soil B (5.5 ± 0.4 mg/kg) compared to soils I (6.6 ± 0.3 mg/kg) and M (9.2 ± 0.7 mg/kg). Hence, total-remobilised B[a]P after 30 d of REQ ranged from 29 (soil B) – 43% (soil M) of the residues after BuOH extraction prior to REQ. Cumulative BuOH extractability and total B[a]P extractability after REQ at 120 d of aging were also significantly smaller ($p < 0.05$) in soil B than in soils I and M (Figures 2 and 3). In addition, B[a]P NERs in soils recovered by MeKOH before and after REQ at 120 d of aging was smaller ($p < 0.05$) in soil B than in the other soils (Fig. 3), further reflecting stronger B[a]P sequestration of B[a]P in soil B. Further, the fraction of DCM-Ace extractable B[a]P relative to the residues obtained following BuOH extraction was again smaller in soil B (13.6%) than in soils I (28.9%) and M (35.4%) prior to REQ. This suggested that the potential for B[a]P remobilisation in the sandy-clay-loam soil B was low compared to the other soils. Although the sandy-clay-loam soil M had the largest TOC contents, its fraction of soft OC relative to TOC content (0.58) was larger than in soils I (0.55) and B (0.42). Considering that B[a]P sequestration in soils with large amounts of soft OC are weak [10, 13, 32], the large amounts of extractable B[a]P before REQ and potentially remobilisable B[a]P after REQ in soil M were reasonable. Soils B and I also contain expandable clays (i.e. montmorillonite) [29]; this may contribute to stronger B[a]P sequestration resulting in reduced B[a]P extractability and potential for remobilisation [47]. Hence, the influence of the quantity and quality of TOC, and clay, in soils should be considered towards understanding the extractability and potential for remobilisation of B[a]P NERs.

At 4 years of aging, the amounts of B[a]P remobilised by BuOH in soils were extremely small ($p < 0.01$) compared to the amounts remobilised after 120 d of aging (Fig. 2). Butanol-remobilised B[a]P were 1.1 ± 0.1 (soil M), 0.4 ± 0.2 (soil I), and 0.3 ± 0.0 mg/kg (soil B). This suggests that only 3% or less of initially spiked B[a]P (50 mg/kg), or of residues after BuOH extraction before REQ, was again re-extractable by BuOH. Total-remobilised B[a]P after 30 d of REQ were 6.0 ± 0.2 mg/kg, 1.9 ± 0.2 mg/kg, and 0.9 ± 0.07 mg/kg in soils M, I and B, respectively. This further suggests that approximately 2 to 13% of initially spiked B[a]P (50 mg/kg), or of residues after BuOH extraction conducted before REQ, was re-extractable. In addition, the fractions of B[a]P NERs recovered by MeKOH after 30 d REQ were again smaller in soil B (1.1%) than in soils I (3.5%) or M (7.5%), as with before REQ (Fig. 3). The extremely small amounts of extractable- and remobilised-B[a]P observed in all 3 soils after 4 years of aging, particularly in soil B, reflect the influence of aging and soil properties on B[a]P sequestration and remobilisation in soils. Slow repartitioning of sequestered B[a]P residues during the re-equilibration periods could explain the small amounts of B[a]P NERs remobilised in the soils, and further described below. The extents of potential remobilisation of B[a]P may be expected to further decrease or remain constant in soils after extended aging periods [30].

3.4. Comparison of B[a]P remobilisation in soils after the removal of the readily available and total-extractable fractions

The results obtained after 30 d of REQ at 120 d of aging are presented in Fig. 4. Our recent investigations revealed that B[a]P remobilised in soils at 200 d of aging, after removing total-extractable fractions, were very small (0.7 ± 0.0 to 3.3 ± 0.2 mg/kg) and decreased at very fast rates over time [21]. In this study, the extractable amounts of B[a]P in soils after 4 years of aging before REQ remained very small (Figures 2 and 3), reinforcing the effects of aging on B[a]P extractability [21]. Investigating the potential remobilisation of B[a]P after removing total-extractable fractions in soils aged for 4 years was not justified; hence, only the results for 120 d of aging and at 30 d of REQ are presented (Fig. 4).

Clearly, the amounts of B[a]P remobilised after the removal of the readily available fractions in soils were greater than those remobilised after the complete removal of extractable fractions (Fig. 4), particularly total-remobilisable B[a]P. This is reasonable since more highly sequestered fractions were removed by the exhaustive extraction prior to REQ, compared to the mild extraction.

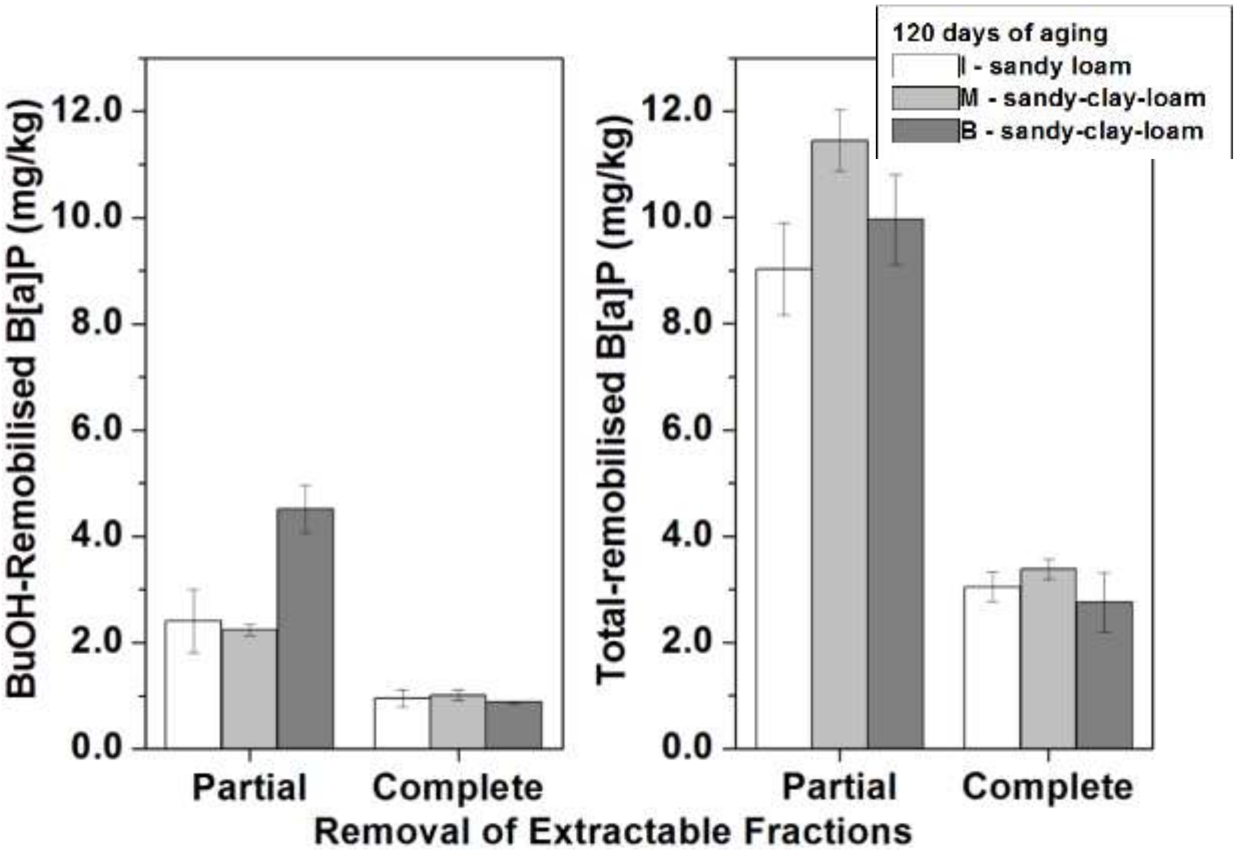

Fig. 4. Amounts of B[a]P remobilised following the removal of readily available and total-extractable B[a]P fractions in soils. Values are means (n = 3) ± standard deviations.

However, the amounts of BuOH-remobilised B[a]P after the removal of readily available fractions in soils at 4 years of aging were similar ($p > 0.05$) to the amounts remobilised after removal of total-extractable fractions in soils at 120 d of aging.

Therefore, these results show that it is realistic to assess the risks of potential B[a]P remobilisation from long-term contaminated soils based on laboratory measurements of readily available concentrations as measured in this study, or the use of other non-exhaustive extractions [44, 48]. Overall, structured monitoring for potential release of sequestered B[a]P from B[a]P-contaminated sites that are managed by risk-based approaches is suggested as good practice [49]. This is important because the impacts of changing exposure scenarios and changes in environmental conditions, such as pH, temperature, drying and wetting, freezing and thawing, and changes in land-uses on PAH remobilisation in long-term contaminated soils are not understood.

3.5. Proposed slow repartitioning of B[a]P residues following the removal of the readily available fractions

As illustrated in Fig. 5, B[a]P is weakly sequestered within easily accessible sites in soils (a), such as on clay surfaces and soft OC [20], during initial soil-B[a]P contact time and prior to aging and REQ (‘I’). Hence, large amounts of B[a]P may be solvent-extractable (‘b’, ‘c’, and ‘d’ in ‘I’). Over time (‘a’ in ‘II’), B[a]P accesses more sequestration sites, diffusing into soft OC or may be adsorbed strongly to clay or organo-clay surfaces, and may be entrapped in pores or cracks and adsorbed to flat surfaces of (or collapsed pores within) hard OC or BC-rich materials through π–π interactions [13]. Hence, a mild BuOH extraction of soil removes only weakly sequestered B[a]P [50], whereas subsequent DCM/Ace extraction of soil (‘b’ in ‘II’) removes highly sequestered B[a]P. Harsh solvents penetrate soil pores causing them to swell, and may competitively displace sequestered B[a]P [51]. Harsh solvent mixtures, such as DCM/Ace, possess greater pore swelling and stronger competitive displacement capacities than BuOH [51]. Hence, total extractability will be greater than BuOH-extractable B[a]P [27]. Methanolic saponification (‘c’ in II) partially releases more highly sequestered B[a]P from sites where they are physically entrapped [18]. The resulting residue after MeKOH extraction contain B[a]P that is very highly sequestered; this may be more associated with BC-rich materials in soils [10, 12]. We have previously reported a strong positive relationship between hard OC fractions and BC-rich fractions of these soils (r = 0.98, p = 0.02, n = 4), as well as between clay and hard OC/TOC (r = 0.87 and p = 0.13) [21]; however, contents of clay and hard OC were not multicollinear (R^2 = 0.26).

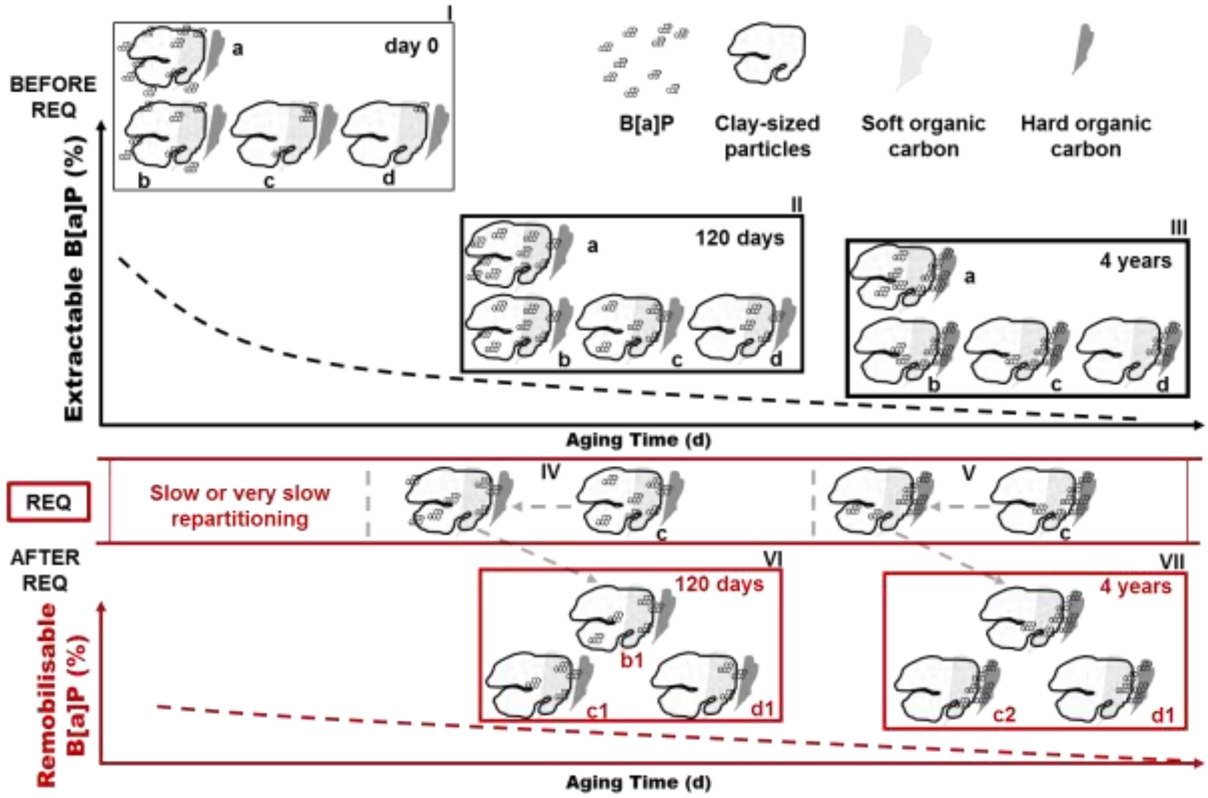

Fig. 5. Proposed slow repartitioning of B[a]P after the removal of readily available fractions. a is B[a]P-contaminated soil before aging; b is soil residue after mild BuOH extraction that removes the readily available fractions; c is NER after DCM/Ace extraction; and d is NER after methanolic saponification of soil.

These observations therefore support the strong B[a]P sequestration in soil B with large amounts of clay and hard OC/TOC fractions. Overall, the amounts of B[a]P extractable by each of the solvents decreased, whereas the non-extractable fraction increased over time due to increasing soil-B[a]P interactions (III).

Following the re-equilibration (IV and V) of the BuOH-extracted soil (‘c’ in ‘II’ and ‘III’), sequestered B[a]P may repartition slowly into more readily available compartments in soils due to the concentration gradient between sequestered and readily available compartments [21]. Highly sequestered B[a]P repartition at slow rates (V) [52]. After REQ (VI and VII), small amounts of B[a]P residues become re-extractable by BuOH (i.e. readily remobilisable B[a]P). Subsequently, DCM/Ace extraction of soil (‘b1’ in VI and VII) recovers B[a]P that is not readily remobilisable. Very small amounts of B[a]P residues (‘c1’ in VI and VII) may be further released by MeKOH, resulting in residues unlikely to be remobilised [18].

After aging of 120 d and 4 years, strong positive relationships were observed between BuOH-remobilised B[a]P after REQ and DCM/Ace-extractable B[a]P prior to REQ (r = 0.88, $p = 0.02$), as well as with MeKOH-extractable B[a]P ($r = 0.78$, p = 0.07) (Fig. S1). Hence, total-remobilised B[a]P showed a stronger relationship with MeKOH-extractable B[a]P after REQ than before REQ (Fig. S2). These relationships suggest that B[a]P remobilisation may be due to repartitioning of sequestered B[a]P during REQ. Overall, the extremely small amounts of B[a]P remobilised, particularly following extended aging (4 years), indicates a likelihood for very low remobilisation extents in long-term aged soils.

3.6. Implications for contaminated land decision-making

Risk-based approaches to contaminated land management is gaining ground in a number of countries [22, 53, 54]. However, not all regulators of contaminated lands agree to adopting risk-based approaches that rely on contaminant bioavailability or bioaccessibility due to associated uncertainties [55], such as the fate of contaminant residues in soils [4]. In this study, B[a]P remobilisation occurred in soils after 4 years of aging, but the amounts remobilised were extremely small (generally < 5% of initially spiked concentration, i.e. 50 mg/kg) and may be insignificant from a risk assessment perspective. For instance, considering the Australian health investigation levels (HILs) of at least 3 mg/kg B[a]P in soils [56], all contaminated soils used in this study passed the criteria based on the amounts of BuOH-remobilised B[a]P from soils after 4 years of aging. Generally, the HIL criteria was also passed where total-remobilised B[a]P was used in the soils. In this regard, the potential risks to human and environmental health are minimal and acceptable. These observations are a strong case for greater focus on readily available B[a]P fractions, rather than total-extractable fractions, in the risk assessment of long-term B[a]P-contaminated soils.

4. Conclusions

To the best of our knowledge, this study is the first report of the extremely small remobilisation of B[a]P residues after the removal of readily available fractions in long-term aged soils, including associated remobilisation kinetics and associated implications for contaminated land decision-making. After removal of readily available B[a]P fractions, only small amounts of B[a]P residues were remobilised through slow intercompartmental repartitioning of sequestered fractions into readily available fractions. However, amounts of B[a]P that were remobilised decreased significantly over time. At each aging time, remobilisation kinetics of B[a]P residues through the re-equilibration times investigated remained unchanged indicating that the small amounts of B[a]P residues which were remobilised remained stable with time. After extended periods of aging, the amounts of B[a]P remobilised in soils after prior removal of readily available or total-extractable fractions were generally extremely small, indicating no significant potential to pose risks to human and environmental health. Therefore, it is reasonable to consider readily available fractions of B[a]P in the risk assessment of long-term contaminated soils, rather than total-extractable fractions.

Conflict of Interests

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary material to this article can be found online.

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