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Assessing bioavailability of complex chemical mixtures in contaminated soils: progress made and research needs

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Abstract: Understanding the distribution, behaviour and interactions of complex chemical mixtures is key for providing the evidence necessary to make informed decisions and implement robust remediation strategies. Much of the current risk assessment frameworks applied to manage land contamination are based on total contaminant concentrations and the exposure assessments embedded within them do not explicitly address the partitioning and bioavailability of chemical mixtures. These oversights may contribute to an overestimation of both the eco-toxicological effects of the fractions and the mobility of contaminants. In turn, this may limit the efficacy of risk frameworks to inform targeted and proportionate remediation strategies. In this review we analyse the science surrounding bioavailability, its regulatory inclusion and the challenges of incorporating bioavailability in decision making process. While a number of physical and chemical techniques have proven to be valuable tools for estimating bioavailability of organic and inorganic contaminants in soils, doubts have been cast on its implementation into risk management soil frameworks mainly due to a general disagreement on the interchangeable use of bioavailability and bioaccessibility, and the associated methods which are still not standardised.

This review focuses on the role of biotic and abiotic factors affecting bioavailability along with soil pysicochemical properties and contaminant composition. We also included advantages and disadvantages of different extraction techniques and their implications for bioavailability quantitative estimation. In order to move forward the integration of bioavailability into site-specific risk assessments we should (1) account for soil and contaminant physicochemical characteristics and their effect on bioavailability; (2) evaluate receptor's potential exposure and uptake based on mild-extraction; (3) adopt a combined approach where chemical-techniques are used along with biological methods; (4) consider a simplified and cost-effective methodology to apply at regulatory and industry setting; (5) use single-contaminant exposure assessments to inform and predict complex chemical mixture behaviour and bioavailability.

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KEYWORDS: bioavailability, partitioning, contaminated land, risk assessment, sorption, ageing

1 Introduction

Contaminated sites are often impacted by a wide range of organic and inorganic chemical mixtures, for example, heavy metals, polycyclic aromatic hydrocarbons (PAHs), phenols or chlorinated hydrocarbons (CHC) (European Environment Agency, 2012). These contaminants will often form complex mixtures in soil that complicate the assessment of risk and the achievement of site-specific remediation objectives (Renoux et al. 2013). Unlike single contaminants, the physico-chemical interactions of mixed contaminants are not well understood as the additive, synergistic or antagonistic effects of mixtures will often yield bioavailability values that differ from those of individual contaminants (Ramakrishnan et al. 2011). Poor understanding about the fate and behaviour of contaminant mixtures in soil limits the effectiveness of risk-based contaminated land management decisions.

Risk assessment is an established methodology that is employed to assess the potential impacts of contaminants on human and ecological health (Vegter et al. 2002). Reflecting regional legislation, expertise, and socio-economic issues, several risk-based contaminated land management frameworks have been published to support environmental management decisions (Brassington et al., 2010, Kabari et al., 2016). Typically, these frameworks use tiered assessment approaches. A limitation of such frameworks, similar to that of exposure assessment methods, is the inability to assess the risk posed by complex chemical mixtures. In fact, these frameworks are based on conservative risk screening levels and therefore tend to overestimate the risk, as they do not take into account the amounts of chemicals potentially bioavailable in soil and bioaccessible to organisms. Determining appropriate site specific measures and remedial objectives depends on our understanding of contaminant partitioning and interaction with the soil matrix over time. Measuring the total concentration of contaminants in soil does not provide a useful basis for the evaluation of the potential risks to humans and the environment. The variety of physical–chemical properties, and thus differences in the migration and fate of individual compounds, as well as the toxicity of different fractions and compounds must be taken into account in risk assessments.

Over the last 30 years, accounting for the bioavailable nature of soil contaminants has received increasing attention. As a result, a great amount of scientific literatures have reported on the development of methods to estimate the bioavailable fraction of these contaminants. Despite this progress, implementation of these methods into contaminated land decision-making processes has not yet been statutorily defined, and uncertainties remain on how bioavailability should be assessed and integrated into existing risk based management frameworks (Ortega-Calvo et al. 2015; Wu et al., 2013; Harmsen & Naidu 2013; Naidu et al. 2015)

In this review we will highlight the factors that influence the bioavailability of chemical in soil and will discuss the challenges that complex chemical mixtures pose. We will critically review the extant literature to assess the use of bioavailability in contaminated land risk assessments. Finally, we will offer suggestions for how bioavailability could be integrated into existing contaminated land risk assessment frameworks.

2 Bioavailability concept

Defined from a chemical perspective, bioavailability is the fraction of freely available (not sorbed or sequestrated) contaminant in the environment that is mobile and thus most likely to lead to human exposure (Dean and Scott, 2004; Ruby et al., 1996). Similarly, Semple et al. (2004) defined bioavailability as the contaminant fraction "freely available" in a medium and able to reach the cellular membrane of an organism over a given time. Thus, for a contaminant to be bioavailable it must be mobile and there must be a likelihood for exposure with a biological membrane.

2.1 Factors affecting bioavailability

Managing risk associated with chemical mixture in the environment requires an understanding of how contaminants are released, transported, and taken up by a target receptor. The different transportation and uptake pathways that affect the quantitative estimation of bioavailable fractions of metals and oil-derived products in soil depends on both the physicochemical characteristics (Table 1), the receptors (Table 2), and other additional factors (Table 3). Among the physicochemical factors, soil characteristics (pH, soil composition, organic carbon percentage, and salinity), compound properties (hydrophobicity, aqueous solubility, and acid dissociation constant) and transformation/degradation processes are generally responsible for interactions occurring between the soil matrix and the chemical compounds (Table 1). Biological processes (e.g. bioaccumulation, biotransformation) whereby contaminants are transported into an organism, are highly dependent on the type of organism and its biology (Table 2). It is important to recognize that any combination of individual physicochemical and biological processes will affect contaminant bioavailability and exposure of receptors.

Soil matrix heterogeneity will also affect bioavailabilty (Farmer 1997). Among physicochemical factors, sorption is the main factor influencing the biotic and abiotic transformations happening over time (i.e ageing) in solid environmental matrices, which normally yield to a more stable solid-associated compound and therefore a decrease in bioavailability (Zhang et al., 2014; Moyo et al., 2014; Dube et al., 2001; Kleber et al., 2007) .

Sorption, which includes absorption and adsorption, is the process whereby a chemical compound adheres (reversibly or otherwise) to the surface of a soil particle (Olu-Owolabi et al., 2014).
The sorbed substance is referred to as the *sorbate* (compound) and the material that it is sorbed to is referred to as the *sorbent* (solid phase). When contaminants are released in the soil, the chemistry of the particles and the equilibrium between phases will influence the pathways and interactions between sorbate and sorbent.

Contaminants will interact with both the mineral and organic content of soil, either sorbing to surfaces, or migrating within the porous structure of soil compartments (Reid et al. 2000). Contaminants can also dissolve into the pore water of a soil matrix, making it available for biodegradation **Figure 1**(). The interaction between contaminant and soil particle will lead to different degrees of desorption (1) rapid — compounds can easily desorb and return to the pore water; (2) slow — reversible but over a longer timeframe(Ren et al. 2018); (3) non reversible — rate of contaminant removal is low and compounds are bound (sequestrated) to the soil (Kuppusamy et al. 2017). The non-reversible fraction is generally believed not to be relevant for bioavailability assessment.

Partitioning of a contaminant at the solid-water interface will depend on the chemical structure of the contaminant. For example, small organic contaminants and low molecular weight PAHs could dissolve into the soil pore water, or could be rapidly sorbed onto the particle surface (Vicent et al. 2013; Abdel-Shafy & Mansour 2016). PAHs with high molecular and larger organic molecules with non-polar structures, on the other hand, tend to sorb onto the non-polar, condensed organic domains of soils (Loibner et al., 2000). These fraction resist degradation and will persistent. However, even small molecules can become persistent environmental pollutants, for example, chloro-organic compounds show a great stability and recalcitrance due to their C–Cl bond (Nikel et al., 2013). Metals also sorb to soil particles, particularly iron hydroxides, clays, and carbonate minerals, and can form solid stable compounds with oxygen and sulphur, becoming irreversibly enclosed and thus, not bioavailable.

Table 1 : Physicochemical factors influencing bioavailability of metals and oil-derived products in soil (similarities and differences)

Factors	Metals	Implication for element behaviour and bioavailability	Reference of special interest	Oil derived product	Implication for oil compounds behaviour and bioavailability	Reference of special interest
Contaminant characteristics	Present in different elemental forms (metal speciation)	Metals' bioavailability can increase or decreased depending on the chemical form. Formation of sulphide cause low solubility (low bioavailability).	(Violante et al. 2010) (Rinklebe et al. 2016) (Liu et al. 2016) (Shahid et al. 2017)	Molecular weight , polarity hydrophobicity , solubility octanol partitioning coefficient (K_{OW}) sorption coefficients ($K_{OC,}$ K_d), acid dissociation constant (pK_a)	Highly complex chemical mixture and concentration constantly changing due to transformation and interactions with environmental media over time	(Duan & Naidu 2013) (National Research Council 2014) (Trellu et al. 2017)
Soil characteristic and Sorption Desorption	Influenced by both geochemical processes (e.g., redox/pH) and soil characteristics (e.g particle size, organic content).	High pH form insoluble metal (decrease in bioavailability), low pH form free ionic species or organo-metals (increase in bioavailability). The presence of mineral phosphates and carbonates decreases bioavailability.	(Lomaglio et al. 2017) (Wang et al. 2016) (Pauget et al. 2011) (Pan et al. 2016) (Tahervand & Jalali 2016)	Quantity and type/quality of organic carbon, clay content, organic content (condensed humic material, soot particles), and soil organic matter can influence bioavailability.	Binding of PAHs to condensed organic domains rend these compounds less bioavailable. Adsorption can be also influenced by pH, depending on the presence or absence of intrinsic positive or negative charges on the compounds functional groups.	(Cecchin et al. 2016) (Lukić et al. 2016) (M. Zhang et al. 2014) (Sabljic & Nakagawa 2014) (Wu et al. 2013) (Chen et al. 2017) (Yu et al. 2018)
Transformation Degradation (biological/chemical)	No degradation	Metal cannot be degraded; inorganic contaminants can only be bio accumulated or sequestrated (Olaniran et al., 2013). Their bioavailability depends on the partitioning and distribution across soil substrates. However presence of metals (if bioavailable) can inhibit organic compound	(H.-Y. Yu et al. 2016) (Palleiro et al. 2016) (Young 2013)	Both biotic (microbial degradation), and abiotic degradation (volatilisation leaching, photodegradation) can lead to transformation and degradation of organic compounds in soil.	Bioavailability of organic compounds over time tends to decrease due to diffusion into soil particles, formation of stabile complexes, and to microbial degradation.	(Sihag et al. 2014) (Vila et al. 2015) (Ghosal et al. 2016) (Marquès et al. 2016) (Alegbeleye et al. 2017)

		degradation interfering with microbial processes.				
Oxidation/Reduction Cation exchange capacity, and soil pH	Influenced by the presence of organo-mineral colloids (adsorption). Complexation with humus, precipitation in presence of clay mineral and Fe, Mn, Al oxides and carbonates.	Reducing conditions due to a high content of organic carbon and/or sulphide can cause formation of less soluble species e.g Cr(III)	(Ashraf et al. 2012) (H. Y. Yu et al. 2016) (An et al. 2015) (Schneider et al. 2016) (Kunhikrishnan et al. 2016)	Changes in pH can influence mostly ionizable organic compounds, impacting sorption and removal of organic solutes from solution (Naidu, 2011). Changes in redox potential and pH can accelerate oxidation of organic contaminants (Eggleton and Thomas, 2004).	Both mineral and humic substances can impact bioavailability of organic pollutants via oxidative and reductive transformation processes.	(Ling et al. 2015) (Xiao et al. 2014) (Zhang & Fan 2016) (Zhang et al. 2015)

Table 2 : Biological factors influencing bioavailability of metals and oil-derived products in soil (similarities and differences)

Factors	Metals	Implication for element behaviour and bioavailability	Reference of special interest	Oil derived product	Implication for oil compounds behaviour and bioavailability	Reference of special interest
Uptake	Metals uptake is typically based upon bioassay exposures to a dissolved chemical, therefore highly dependent on the metals solubility in solution, and oxidation states.	Highly dependent on the system considered for example in plants the bioavailability of a certain metal in the water phase, depends on root structure, but also presence/absence of organic acids exudate (such as citrate and oxalate). For aquatic species bioavailability depends on both ingestion of metal-enriched sediment during feeding, and uptake of metal suspended particles from solution (du Bray 1995).	(Wyszkowska et al. 2012) (Seshadri et al. 2015) (Tangahu et al. 2011) (Rüdel et al. 2015)	Depend on multiple factors such as concentration in soil, its chemical form, soil pH, biological species, and uptake pathways of specific species.	Depend on where and how an organism lives and feeds in the soil or sediment.	(Peters et al. 2016) (Juhasz et al. 2014) (Beriro et al. 2016) (Lal et al. 2015) (Rostami & Juhasz 2011)
Bio concentration, bioaccumulation, and biotransformation	Metal bioaccumulation (in bacteria, fungi, and plants) can happend throught biosorprion or absorption and uptake. Metal can potentially interact and affect funtion of enzymes involved in biodegradation of chlorinated organic compounds.	Depend on uptake, levels of fats (lipids) within the organism, metabolism, age, growth life stage, and gender.	(Berthelot et al. 2008) (Jaishankar et al. 2014) (Tchounwou et al. 2012) (Khan et al. 2015)	Strong correlations between the bio-concentration factor, bioaccumulation factor and the octanol: water partition coefficient (K_{OW})	Depend on uptake, levels of fats (lipids) within the organism, metabolism, age, growth life stage, and gender.	(Fantke et al. 2016) (McLachlan et al. 2011) (Pampanin 2017) (Vasseur & Bonnard 2014)

Table 3 : Additional factors influencing bioavailability of metals and oil-derived products in soil (similarities and differences)

Factors	Metals	Implication for element behaviour and bioavailability	Reference of special interest	Oil derived product	Implication for oil compounds behaviour and bioavailability	Reference of special interest
Ageing	A rapid uptake via electrostatic adsorption is usually followed by a secondary transformation that form a more stable complex.	Ageing can have an effect on inorganic contaminant, where metal precipitation can occur rapidly causing a decrease in bioavailability and toxicity. However is less clear how stable/reversible is the process (Hamon, McLaughlin, and Lombi 2006).	(Wijayawardena et al. 2015) (Liang et al. 2014) (Wang et al. 2017) (Romero-Freire et al. 2017) (Jiang et al. 2017)	Different processes might occur: incorporation into natural organic matter (absorption), slow diffusion into small pores (soil intraparticle).	Overall a decrease in bioavailability has been observed during time due to different factors (dilution, dispersion biodegradation, volatilisation, and irreversible sorption).	(Duan et al. 2014) (Duan et al. 2015) (An et al. 2017) (An et al. 2017) (Smith et al. 2011) (Liu & Haderlein 2013)
Co-contaminant interaction	Metal-metal interaction is mostly competitive affecting affinity for soil-surface and sorption. For instance Zn is a competitor for Cd and Pb sorption sites . Metal-organic joint interaction such as: Cu-pyrene (Chigbo et al. 2013) can significantly henance heavy metals concentration in shoot and roots. Heavy metals transport can be henanced by the presence of organic contaminants due to : association with mobile colloids, formation of metal-organic	Metals that compete for the same sorption sites can trigger the release of the competitor metal, enhancing its bioavailability. Necessity of addressing contaminant as a mixture	(Sun & Zhou 2010) (Van Genderen et al. 2015) (Meyer et al. 2015) (Zhao et al. 2016) (Chigbo et al. 2013)	Organic-metal interaction: high concentration of inorganic might influence mobility of PAHs. Organic-organic interaction: competitive displacement, co-solvency. Molecules with similar structure are highly competitive for sorption sites because of their interchangeability.	As for metals, the organic-organic interactions might challenge bioavailability predication. The sorption/desorption rate can be altered by competitive displacement processes and therefore manifest a non-linear behaviour. In addition some natural compounds might also share a similar structure and therefore displace anthropogenic compounds increasing their bioavailability. Necessity of addressing contaminant as a mixture	(Olaniran et al. 2013) (Gauthier et al. 2014) (Biswas et al. 2015) (Wuana et al. 2014)

	complexes that are not sorbed onto the surface (competitive sorption).

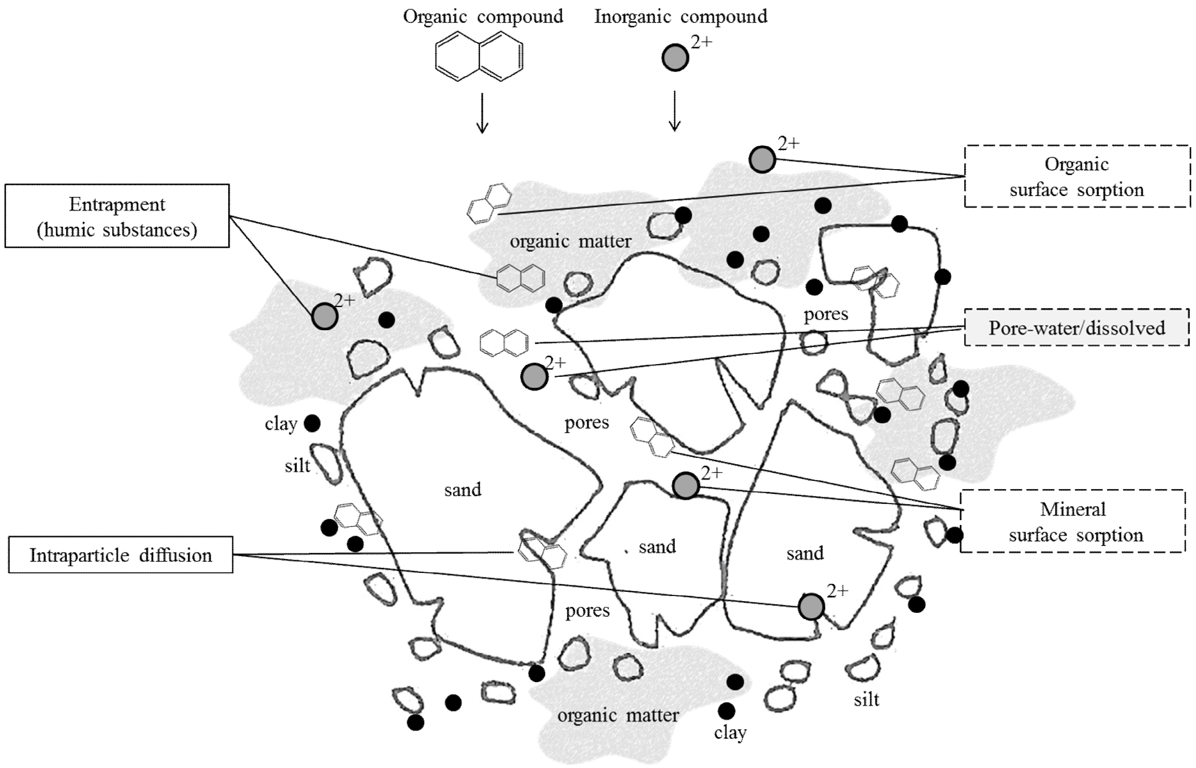

Figure 1: Process of sequestration of the compounds in soil, adapted from (Reid et al., 2000), bold textbox indicates the non-desorbing fraction (irreversible processes), dashed textbox indicates the rapidly-desorbing fraction (reversible processes), and the highlighted textbox represent the dissolved fraction (bioavailable).

Contaminant retention is largely regulated by soil particle size distribution (Table 1). Smaller particle sizes provide a greater surface for interactions with hydrophobic organic chemicals (Capri et al., 2004). Clays and fine-grained sediments have the greatest surface area and therefore a high capacity to retain organic and inorganic compounds. Further to this, the presence of oxides (Fe and Al oxides, hydroxides, and oxyhydroxides) along with reactive calcium carbonate ($CaCO_3$) can enhance organic and inorganic contaminants retention (Loibner et al., 2006) and therefore favour the biological stabilization of organic carbon (encapsulation) (Heng et al., 2010). Such mechanisms will however hinder microbial degradation of the compounds of concern due to reduced accessibility (Krull et al., 2001).

Hard- and soft-organic matter are also associated with retention and ageing processes (Table 3). Soil organic matter (SOM) is formed from natural organic matter (e.g. vegetal decomposed material), animal residues at various stages of decomposition, fulvic acids, and humic acids (Sharma et al., 2010). Generally, SOM is thought to be composed of “soft carbon” (amorphous or hydrolysable carbon), and “hard carbon” (condensed or non-hydrolysable carbon) constitute of kerogen, black carbon, and lignin (Weber et al., 1992). Black carbon and kerogen, in particular, can bind tightly the organic contaminants reducing their solubility and/or dissolution rate, and thus bioavailability (Stroud et al. 2007; van Elsas et al. 2006; Berkowitz et al. 2008). Large amounts of organic matter in the soil have also been shown to effect the residence time of organic matter-associated metals. For example, when organic matter is oxidized, the associated metals are likely to be released, becoming more bioavailable. Conversely, soil with low organic matter content will often accumulate oxide minerals (e.g. clay) that favour the complexation of both metals and metalloids, thus reducing the bioavailable fraction (John & Leventhal 1995). Soil properties are site specific and will vary from one site to another, therefore, if two sites contain equivalent amounts of a certain contaminant, their bioavailability may still vary significantly, depending on how tightly the chemical is bound to the soil.

The ratio between bioavailable and non-bioavailable fractions is shown in Figure 2. Over time, the proportion of bioavailable contaminant will decrease, relative to the non-bioavailable fraction. Pollutants in soil and sediment do not disperse quickly and the desorption and remobilization of metals and oil-derived products in soil are considered long-term processes. For example, heavy metals associated with fluvial sediments can display a residence time from days to years, on the order of 100 – 1000 years (depending on stream-flow dynamics) (Ciszewski & Grygar 2016; Coulthard & Macklin 2003). Heavy metals also have a long residence time in soil (Sayadi et al. 2017), ranging from 500 to 3000 years (Lepp 2012; Jørgensen 2000; Ayres 1992; Alloway 1995). The process of aging can enhance the amount of absorbed heavy metals in soil, where a redistribution from weakly bound fractions to more strongly bound fractions can be observed (Settimio et al. 2014; Wang et al. 2015). Recent metal contamination tends to be more reactive and prone to dissolution compared to older contamination where the elements might be in crystalline forms (Lynch et al. 2014), which presents a lower environmental risk (Baran et al. 2015; Environmental Agency 2008).

Sediment and soil-bound organic contaminants can persist over decades without significant concentration reductions. Chlorinated or hydrophobic contaminants, in particular, tend to desorb very slowly over time with a desorption rate on the order of years, due to their ydrophobicity (Eggleton & Thomas 2004). Though oil derived products tend to persist in soil, the PAH bioavailable fraction will decline exponentially over time (Yang et al. 2016). Weathered hydrocarbon residues pose negligible risks to human health, and this is reflected in post-treatment remedial objectives (Coulon et al., 2010; Jiang et al., 2016). When bioavailable fractions are high (despite being below risk-based clean-up levels) further treatment and more stringent clean-up levels should be mandated to reduce the elevated risk of exposure that is present (Cipullo et al., 2017).

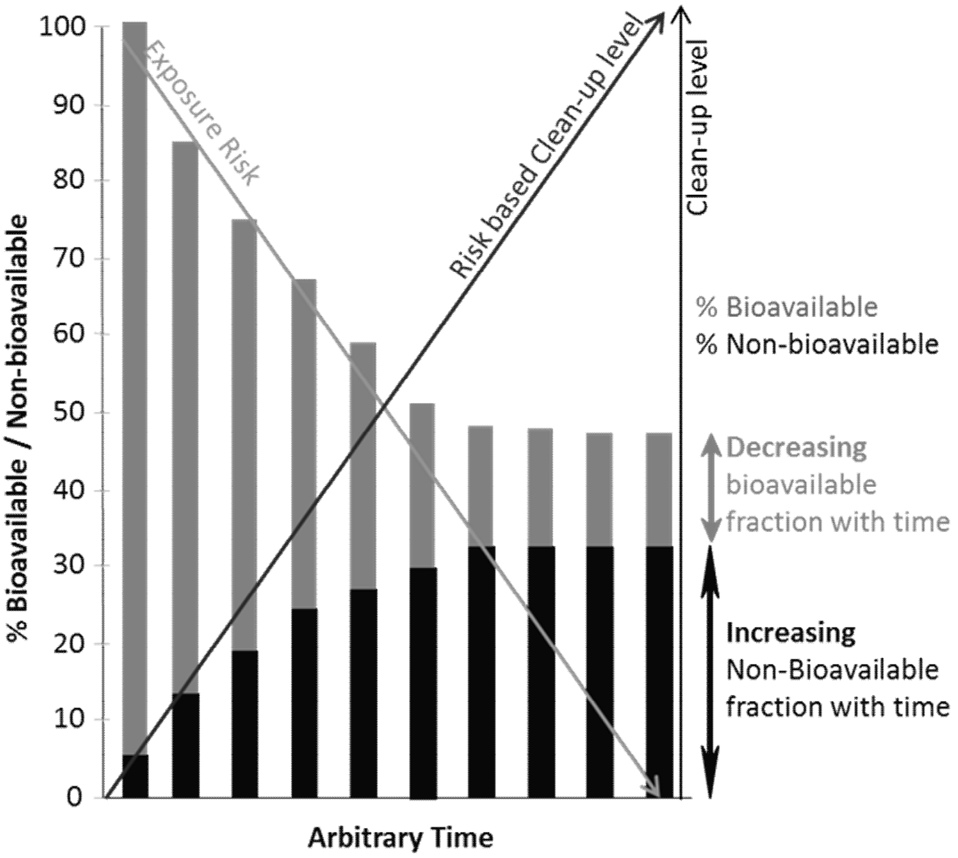

Figure 2: Relationship between the percentage of bioavailable and non-bioavailable contaminants in soil, exposure risks and risk based clean-up level (adapted from Reid et al., 2000; Tri-Service Ecological Risk Assessment Workgroup, 2003).

The necessity of collecting case-specific parameters can challenge the development of a unified methodology to assess the bioavailable fraction, and to determine the risks to human and environment in a straightforward way. A number of analytical methods to assess readily (bio) available compounds in soil and sediments are available, and we discuss these in the following sections.

2.2 Methods for estimating bioavailability of heavy metals

Metals can be present in soil as either free metal ions, forming various soluble complexes with inorganic or organic ligands; or associated with colloidal and mineral materials (McLean and Bledsoe, 1992) becoming strongly incorporated with the soil matrix (inert). Most of the divalent

heavy metal cations (e.g., Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) share a relatively similar structure and therefore display similar behaviour in soil (Olaniran et al., 2013).
Total metal concentration estimated with acid digestion (e.g aqua regia) mobilizes all forms of metal in soils and sediment. This measure refers to both metal content in particulate (sorbed + precipitated), and dissolved (inorganic complexes + organic complexes + free ionic forms) fractions. Particulate metals do not contribute to the solid-solution distribution (potentially bioavailable), and may only become available through very slow desorption processes. This fraction does not provide appropriate basis for expressing metal bioavailable (labile) concentration in soil, thus presumably not readily available for receptor uptake.

Several approaches are used to determine the pool of labile metals (concentration and distribution) in soils and sediments; including exchange resins, diffusive gradient in thin films (DGT), conventional single-step extractions, and sequential extractions (Table 4). Passive samplers (e.g exchange resins) act as ion sinks and are used to quantify free ion activities, solution fractions, and labile pool concentrations of metals in soils (Qian and Schoenau, 2002; Ge et al., 2005). Free ion activity in solution represents the most relevant parameter for assessing bioavailability and toxicity of metals in contaminated soils. The use of exchange resins has been successfully applied to predict uptake of metal in the environment (e.g. in plants (Peijnenburg et al., 2007)).
To date, no standard technique has been validated. Diffusive gradients in thin films (DGT), is a relatively cost-effective technique, based on a layer of hydrogel and resin gel. The DGT devices allow for the passive accumulation of labile species from a solution (in real time), and have been used to assess in situ the fraction of metals dissolved in water (Zhang 1998; Hooda et al., 1999; Parker et al., 2016).

As an in situ sampling technique, DGT can be also used in soil to determine the labile (bioavailable) fraction of elements, and to understand how this fraction changes in the environment. However, continuous depletion of metals from pore water can limit the diffusion of analytes to the DGT sampler, affecting the estimation of the available pool of metals (Peijnenburg et al. 2014). In addition, development and validation of a DGT method to establish accumulation in biological endpoints remains a challenge, due to the complexity of the uptake by model organisms and inconsistent results (Menegário et al. 2017).

Single-step extraction (Table 4) uses a wide range of extractants including: salt solutions ($CaCl_2$, $NaNO_3$, NH_4NO_3, $Ca(NO_3)_2$, $AlCl_3$, $MgCl_2$), acid solutions (HNO_3, CH_3COOH , HCl) and chelating agents (EDTA, DTPA). These tests were initially designed to predict nutrient deficiency in soil, and generally contain organic chelates and acids in order to mimic plant metals uptake (National Research Council 2003). Single-step extraction were lately adapted to measure the labile concentration of metals in soil and sediments, potentially available for ecological receptors uptake (Alvarez et al. 2011).

Table 4 : Methods to characterize labile fraction and bioavailability of metals in contaminated soils

Method	Advantages	Disadvantages		Reference
Passive sampler	• Passive samplers are relatively low-cost, can be used for insitu measurements (Menegário et al. 2017), can achieve low detection limits (Peijnenburg et al. 2014), and allow long-term trends assessments. • DGT was found to be a good tool for measuring in situ metal bioavailability in sediments (Ren et al. 2015). • DMG is a relevant tool for *in situ* assessment of environmental risks posed by metals (Perez et al. 2016) • Passive sampler measurement can be translated into fugacity models and equilibrium studies to understand chemical potential acrivity and estimate potential risk (Amiard-Triquet et al. 2015).	• Little attention is given to the effects that water chemistry and method of field deployment may have on uptake kinetics (Mills et al. 2014). • In some cases require a time-consuming elution step, with acids, in order to retrieve the analyte from the solid sorbent phase (Almeida et al. 2014). • DGT and DMT not yet considered suitable for routine analysis due to poor detection limit, time-consuming procedures, and a lack of validatation (Brand et al. 2009) • Deployment of DGT samplers where nanoparticles are high may result in an overestimation of dissolved metal concentrations (Pham et al. 2015)	Exchange resins	(Cantwell et al. 1982) (Holm et al. 1995) (Lorenz et al. 1997) (Christensen & Christensen 1999)
			Diffusive gradient thin film (DGT) and Donnan membrane technique (DMT) Diffusive Milli-Gels (DMG)	(Davlson & Zhang 1994) (Agbenin & Welp 2012) (Koopmans et al. 2008) (Pampura et al. 2006) (Weng et al. 2005) (Perez et al. 2015)
Stripping voltammetry	• High sensitivity, higih reproducibility, and mainly used for the detection of trace levels of heavy metal ions (Almeida et al. 2014). • Found to be suitable for assessment of heavy metals bioavailability to plants (Dytrtova et al. 2008).	• Limitations for on field measurements, sample perturbations due to sample handling and storage (Rurikova & Kudrava 2006) • Adsorption effects of humic and fulvic acids in soil accompanied by the metal complexation can limit the successo of this method (Rurikova & Kudrava 2006)	Anodic (or cathodic) stripping voltammetry	(Sauvé et al. 1997) (Zima & van den Berg 1994) (Davidson & Smyth 1979)
Competitive chelation	• Method has good sensitivity and can provides reliable estimates of ion activities (Amacher 1984)	• Equilibrium between chelate and soil can be take a long time to be attained (Norvell & Lindsay 1972; Norvell & Lindsay 1969) • The success of the metod depend on abundancy of metal of interest and the selected competing metal(Workman & Lindsay 1990)		(Xue et al. 1995)
Ion exchange	• Ion exchange results were comparable to ion selective electrode, and anodic stripping voltammetry (Ge et al. 2005). • Simple, cost-effective, relatively easy to	• Requires a characterization of the resin adsorption properties (Weng et al. 2005). • Soil solution composition need to be	Cation exchange resin	(Sunda 1984) (Apte & Batley 1995) (Qian & Schoenau 2002) (Ge et al. 2005)

	use, and applicable to different soil type (Qian & Schoenau 2002) • Possibility of simultaneous multimetal • measurement (Weng et al. 2005)	considered during speciation analysis (Fotovat & Naidu 1997)		
Single extraction salt solutions	• Single extractions can be used to perform fast screening analysis of the labile pool of elements in soils and sediments (Sakan et al. 2016). • Significant positive correlations between the single extractions methods results and lettuce shoot content were obtained for several metals (Pinto et al. 2015). • $CaCl_2$ extraction has been reported as being a good proxy for bioavailabilityof metals in soils to plants (Houben et al. 2013) and was correlated with concentrations of potential harmful element in plant (Qasim et al. 2015) • Leaching test employing a neutral salt solution ($CaCl_2$ or NH_4NO_3) is considered to be sufficient to measure the bioavailable fraction of mobile metals (in particular Cd, Ni, and Zn) (Kim et al. 2015). • The single extraction method involving EDTA presented good precision (Sahito et al. 2015). • Using the single-step extraction (EDTA or acetic acid) allows to predict metal extractable content (bioavailable) in vineyard soil-grapevine system (Vázquez Vázquez et al. 2016)	• Chemical extractions can hardly account for the complex processes involved in metals uptake by plants therefore not sufficient for estimating soil metal bioavailability to plants (Krishnamurti et al. 2015). • Complexing and chelating extractants (EDTA and DTPA) showed poor colrelation with phes concentrations in plant (Qasim et al. 2015) • No consensus on best single step extraction conditions to extract maintain integrity of arsenic species (Sun et al. 2015) • At low reactive element to organic matter ratios, dilute nitric acid extraction (0.43 M) can underestimates concentration of geochemically reactive elements with a particularly high affinity for organic matter or oxides (Groenenberg et al. 2017)	0.01-1 M $CaCl_2$	(Houba et al. 2000) (Young et al. 2000) (Novozamsky et al. 1993) (Ure 1996)
			0.1 M $NaNO_3$	(Gupta & Aten 1993)
			NH_4NO_3	(Novozamsky et al. 1993)
			0.1 M $Ca(NO_3)_2$	(Meers et al. 2007)
			0.3M $AlCl_3$	(Hughes & Noble 1991)
			0.02-0.1 M $MgCl_2$	(Makino et al. 2006)
Single extraction acid solutions			different concentrations of HNO_3	(Tipping et al. 2003) (Almås et al. 2007) (Novozamsky et al. 1993)
			CH_3COOH	(Ure 1996)
			HCl	(Novozamsky et al. 1993)
Single extraction Chelating agents:			EDTA	(Ure 1996) (Cappuyns 2012)
			DTPA	(Leggett & Argyle 1983) (Lindsay & Norvell 1978)
Sequential extractions	• These methods are simple, low cost, applicable to different soil type, and results are often comparable (Rosado et al. 2016). • BCR method provide relevant information on the relationships between soil characteristics and metal potential fractions for uptake by the plant (Sungur et al. 2014).	• Sequential extraction are inadequate for determining the extraction kinetics, and subjected to high risk of bias due to re-adsorption processes (Rosas-Castor et al. 2015) • BCR method drawbacks includes lacks of specificity and difficulty in interpreting results (Huang et al. 2014), • BCR method results tedious and time-	BCR extraction	(Ure et al. 1993)
			modified BCR extraction	(Rauret, López-Sánchez, Sahuquillo, Barahona, et al. 2000)
			four-step chemical fractionation procedure	(Tessier et al. 1979)
			four-step chemical fractionation	(Elliott et al. 1990)

	• BCR method showed correlations between available metal and the plant uptake (Fernández-Ondoño et al. 2017). • The modified version of the three-step procedure proposed and validated by the BCR (Community Bureau of Reference) could potentially be accepted as the standard method(Ahmadipour et al. 2014) • CISED method can provide a powerful tool for understanding metal fractionation in soils (Cave et al. 2015) • CISED is a valuable methodology for srudying the solid-phase fractionation of potential harmful element in soil and potential bioavailability (Reis et al. 2014; Palumbo-Roe et al. 2013; Cox et al. 2013) • Sequential leaching studies can help understanding leachability, solubility, and mobility of heavy metal;,therefore allowing to make assumptions on metal bioavailability for risk assessment (Kaakinen et al. 2015)	consuming due to long shaking time and filtration requirements (Matong et al. 2016). • Interpretation of data from the CISED extraction may more challenging than selective chemical extractions (Reis et al. 2014) • Main limitation associated with sequential extraction procedures is the long time associated extraction (Khan et al. 2013). • Limitations associated with sequential extraction methods includes; redistribution of analytes among phases, incomplete extraction, non-selectivity of reagents, and precipitation of other minerals (Selim 2015) • Laborious and time-consuming techniques, results often of difficult interpretation (Domini et al., 2011). •	procedure	
			five-step chemical fractionation procedure	(Mclaren and Crawford 1973)
			six-step chemical fractionation procedure	(Miller et al. 1986)
			seven-step chemical fractionation procedure	(Krishnamurti et al. 1995)
			non-specific sequential extraction (CISED)	(Cave et al. 2004)

Complex organic reagents (EDTA, DPTA) are also used to mimic the organic exudates produced by plants, and have been positively correlated with metal concentration found in plants (Domínguez 2008) and further exploited to mimic the bioavailable fraction. Chelating agents, due to their high affinity for metal ions, are used to enhance the solubilization of metal(loids) through the formation of soluble chelates (Bolan et al. 2014). Caution is needed, however, because studies have shown that results are not consistent and robust across different types of soil (National Research Council 2003), and are highly dependent on extraction conditions and trace elements speciation (Cappuyns 2012).

Single-step extraction techniques widely vary in type of extractant used, its concentration, soil: solution ratio, and extraction time. They can partially dissolve trace elements associated with different fractions (e.g pore water and exchangeable), which provides useful information about metals behaviour (Alvarez et al. 2011).Though relatively simple to use (minor sample handling), in single-step extraction mode the non-labile metal fraction might also become solubilized, which might cause an overestimation of the labile pool of several metals (Moreno et al. 2005; Qasim et al., 2015).

While passive samplers and single-step sequential extraction have been used to measure labile metals, these methods do not provide information on the fate and behaviour of contaminants over time. Sequential extraction, however, can be used to quantify the distribution of metals and assess the mobility of potentially harmful elements over time (Sungur et al. 2015). The procedure involves leaching successive fractions of metal by increasing the strength of an acid solution (HNO_3, HF-$HClO_4$, $HClO_4$, HCl, CH_3COOH) or other reagents (such as $Na_4P_2O_7$, NH_2OH) used for each phase association (Zimmerman and Weindorf, 2010). The number of step may vary from 3 to 7 (Table 4). Sequential extraction has been used for over 30 years (Tessier et al., 1979) and has been modified to create the community Bureau of reference method (BCR) (Rauret, López-Sánchez, Sahuquillo, Muntau, et al. 2000) and the Chemometric Identification of Substrates and Element Distribution (CISED) method (Cave, et al., 2004), which overcome non-selectivity and redistribution of trace elements. The BCR method has been validated against a sediment reference material (BCR-701) and provides extractable concentrations for several metals (Rodgers et al, 2015). The non-specific sequential extraction CISED has been validated against a sediment reference material (BGS-102) and uses chemometric data processing to provide mechanistic information about metal-soil phase associations (Gál et al., 2006). Results from CISED could be a powerful tool to understand how mineralogical forms might affect bioavailability, yet considerably more chemometric and geochemistry information need to be applied (Giacomino et al., 2011).

Despite the large amount of information that sequential approaches can provide the standardisation and application of these technique in commercial laboratories is limited because of the laborious and time-consuming nature of these techniques and the difficulty of interpreting the results (Alvarez et al., 2011).

2.3 Methods for estimating bioavailability of oil-derived products

Estimating the bioavailability of organic compounds and integration into decision processes remains a scientific and regulatory challenge. Research into the bioavailability of oil-derived contaminants has received considerable attention in the last 20 years (Thompson 2016). In the context of implementing bioavailability into regulatory frameworks it is important to both quantify the (potentially) bioavailable fraction, but to also understand the mobility and behaviour of contaminants in soil in order to assess potential effects of complex contaminations on receptors. Empirical approaches are often used to predict contaminant toxicity or assess the effectiveness of remediation treatments (Environment Agency 2006; Environment Agency 2010) Computational methods to integrate the multitude of compounds and molecular structures has proven most challenging, for example, crude oil and its composition of several hundred different organic compounds, each of which possesses chemical characteristics that influence the rate and efficacy of degradation (Weng et al., 2015). Molecular weights have been shown to most strongly affect a compound's persistence in soil (Atlas, 1995). Moreover, complex physico-chemical interactions between different compounds can lead to unexpected or poorly understood reactions (e.g. co-solvency), which might alter the bioavailable nature of a compound in mixture.

A wide range of analytical procedures have been used to estimate the bioavailable fractions of organic contaminants in mixtures (e.g. oil constituents) (see for review Brand et al., 2012; Ortega-Calvo et al., 2015). These procedures can measure different fractions: freely dissolved fraction (passive samplers), which measure the dissolved (actual) concentration in a matrix, and rapidly desorbed fraction (non-exhaustive techniques), which uses extractants to recover compounds from soil (Table 5).

Table 5 : Extraction methods in relation to bioavailability of organic compounds

Type	Method	advantages	disadvantages
Passive sampler (solid phase)	- Polydimethylsiloxane(PDMS) - Solid-Phase Microextraction (SPME) - Polyoxymethylene solid phase extraction (POM-SPE) - Triolein embedded cellulose acetate membrane (TECAM) - C18 membrane disks - Diffusive gradients in thin films (DGT) - Semipermeable membrane devices	- Consistent relationship between chlorobenzenes levels in biota and in the PDMS-SPME fibers (van der Wal et al., 2004) - SPME can accurately measure freely dissolved pore water concentrations to estimates earthworms uptake (Van Der Wal et al. 2004) - PDMS is very sensitive and able to detect PAHs freely dissolved pore water concentrations (ng/L) (Laak et al., 2006). - SPME shows good correlation between bioaccumulation of organic contaminants on a wide range of organisms (You and Landrum, 2006) - SPME and POM-SPE generally are able to predict PAHs concentrations in earthworms (Gomez-Eyles et al., 2011)	- SPME and POM-SPE tended to under predict PAHs root concentrations (Gomez-Eyles et al., 2011) - SPME measures truly dissolved concentrations but it is not able to measure compounds associated with dissolved organic matter (ECETOC, 2014). - Poor correlation between availability of PAHs in soil and bio concentration factors in earthworms (Bergknut et al., 2007)
Fluid-phase extractions	- Subcritical Water Extraction (SWE), superheated water technique (SWAT) - supercritical fluid extraction (SFE) , sequential supercritical fluid extraction (SSFE)	- Good correlation between SWE extraction of 14C-activity fraction mineralized by catabolically active Pseudomonas (Latawiec et al., 2008) - Successfully used to predict rates of long-term release of organic compounds (Weber, 2001; Hawthorne et al., 2000; Miller and Hawthorne, 1998) - SWE selectively extracts the PAHs relative to the readily extracted fraction (Smith 2002) - SFE recoveries of the ‘‘mobile’’fraction of PAHs were greater than 90% (Librando and Aresta, 2004) - The amount of PCBs extracted by SFE was very close to the estimated bioavailable fraction in earthworms (Hallgren et al., 2006)	- Potential degradation of analytes subjected to high temperatures. - Lack of significant correlation between the amounts desorbed/amount assimilated by earthworms (Weber et al., 2002). - Contaminants with high molecular weight ((in decreasing polarity and increasing Kaw-coefficients) showed reduced recoveries when applying SSFE (Loibner et al., 2000) - Mild SFE was not able to differentiate pyrene availability in unaged soils (Sun and Li, 2005). - using SFE for predicting bioavailability can be limited due to great variability of soil matrix (Cajthaml and Väclav, 2005)
non-exhaustive extraction techniques	- Mild solvent (butanol, methanol, n-propanol, or ethyl acetate) - combination of solvent and CaCl2 solution - surfactants (Triton X-100)	- Methanol-water and n-butanol extraction of chemical mixtures were correlated with uptake by earthworms (Elsey and Lexander, 1997) - Good correlation between extractable fraction/ uptake earthworms (Kelsey et al., 1997; Tang et al., 1999) - Good correlations between extractable fractions/ bacterial genotoxicity assay (Alexander and Alexander 2000; Tang et al., 2002)	- Little consistency among different soils (Chung and Alexander, 1998). - High variability in technical operation (type of mixture, shaking time) limit the comparability of data (Cachada et al., 2014). - PAHs extracted by mild solvent extraction show a similar composition to the total soil PAHs (Bergknut et al., 2007) - Mild solvent extractions consistently over predicted

			PAHs biotic concentrations (Gomez-Eyles et al., 2011) • PAHs bioavailability (estimated with butanol) and earthworm bioavailability were found to be non-related (Johnson et al., 2002). • Triton X-100 failed to predict PAHs bioavailability in contaminated sediments because extracted both readily and poorly bioavailable PAHs (Cuypers et al., 2002).
	• Tenax	• Tenax was found to be a matrix-independent, cheap and less time-consuming chemical method of estimating bioavailable fraction in PCB-contaminated field sediments (Trimble et al., 2008) • Successfully used to assess the bioavailability of aromatic compounds in sediment (Morrison et al., 2000; Cal et al., 2008; Harwood et al., 2012). • good correlation between "bioavailable" fraction in the sediment and quantity measured by Tenax extraction (You and Pehkonen, 2007) • Rapidly desorbing fractions of PAHs measured by Tenax have been linked to biodegradation rate (Braida et al., 2004; Shor et al., 2003; Cornelissen et al., 1998) • Tenax extraction of PAHs, PCBs and organochlorine pesticides were correlated to bioavailability to worms (Hulscher et al., 2003) • The Tenax extraction is a good technique to predict bioavailability to earthworms of aged PAHs in soil (Lu et al., 2011)	• The process involves a lot of steps in order to estimate the rapidly desorbing fraction (Xing et al., 2011) • Contaminant desorbing fractions in river sediments extracted by Tenax overestimated the bioavailable fraction of benthic invertebrates (Leppanen et al., 2003) • Few studies where correlations between Tenax extractable amount and biota-sediment accumulation were not related (Sormunen et al., 2008 and 2009; Leppa and Kukkonen, 2006) • The Tenax measure of rapidly desorbing fraction is not the only factor contributing to the bioavailability. A number of ecological factors (species and feeding habits) can affect the bioavailable fraction in model organisms, and remain undetected by Tenax extractions (Akkanen et al, 2007)
	• Aqueous hydroxypropyl-B-cyclodextrin (HPCD)	• 1:1correlation phenantrene extracted/degraded by microorganisms (Reid et al. 2000a) • HPCD was successfully used to predict PAHs bioavailability in contaminated sediments (Cuypers et al. 2002). • HPCD was successfully used to predict the microbial bioaccessibility and mineralisation rate of aliphatic hydrocarbon (Stroud et al., 2008) • A significant relationship ($p < 0.01$) between HPCD extractability /mineralization (Rhodes et al., 2008) • HPCD β was found to be a good estimation of bioavailable fraction in both single, and multiple contaminants conditions (Stroud et al., 2009) • HPCD ease in sample handling and that no additional device is needed (Cui et al., 2013)	• Predictability of HPCD extraction decreased for higher organisms such as earthworms (Barthe and Pelletier 2007; Hartnik et al., 2008) • Poor indicator of PAH accumulation in benthic invertebrates (Barthe & Pelletier 2007). • Cyclodextrin size and structure can limit the complexation of some PAHs (size dependent) (Villaverde and Pe 2012; Stokes et al., 2005) • Cyclodextrin extractions consistently over predicted PAHs biotic concentrations (Gomez-Eyles et al., 2011)

2.3.1 Passive sampler methods (PSMs)

Passive sampler methods (PSMs) (Table 5), commonly defined as biomimetic extractions (ECETOC 2014), are used to measure the freely dissolved concentration (Cfree) of contaminants (Parkerton et al., 2012) in equilibrium with the rapidly desorbing fraction. These techniques are based on the molecular diffusion principle, and often use polymer materials such as polydimethylsiloxane, polyethylene, polyoxymethylene, and ethylvinylacetate (Parkerton et al., 2012). Passive sampler methods have been used to predict PAH bioavailability, and have been shown to correlate well with model organism PAH uptake and bioaccumulation (Jonker et al., 2007; Gomez-Eyles et al., 2011; Muijs and Jonker, 2011). Although PSMs are valuable tools for providing weight of evidence and informing regulatory decision-making, there exists a lack of consensus about its implementation and standardization. The following issues were identified and need to be overcome in order to further develop and implement these techniques: (1) PSM has been applied to only a limited number of target compounds; (2) the complexity of the equilibrium sampling methods requires better characterization of potential errors when applied in situ; (3) adoption of robust quality assurance and control strategies are needed (Mayer et al. 2014).

Correlation with in-vivo measurements and bioaccessibility data are not fully validated, and the complexity of (bio)accumulation mechanisms (Cachada et al., 2014) that govern toxicity responses are not yet fully understood. More information and guidance on the application of passive sampling for the management contaminated sediment sites can be found in the SERDP and ESTCP national guidance documents (Burgess and Driscoll, 2016; Driscoll and Thompson, 2016).

Supercritical Fluid Extraction (SFE) (Table 5) uses supercritical fluids (e.g. CO_2, combination with solvents) to extract a compound from a soil matrix. This technique used to study sorption/desorption processes and to estimate bioavailability of organic pollutants in sediment. Data obtained from SFE can be can be fit to a prediction model to obtain information about the bioavailable fraction for PAHs (bioavailable). Different experiments found the amount of organic compounds (PCBs) extracted by SFE to represent the readily extracted fraction (Smith, 2002) and the bioavailable fraction uptake by earthworms (Hallgren et al. 2006). SFE was also found to recover over 90% of the mobile fraction of PAHs from soil and sediments samples (Librando and Aresta, 2004).

Though SPE can measure the freely dissolved fraction, it is likely to underestimate the concentration/uptake in benthic organisms (with other uptake routes) and its use can be limited due to great variability of soil matrix (Cajthaml and Väclav, 2005). In addition, SFE was found to be able to predict degradation for low molecular weigh PAHs (three and four ring), with a good correlation between biodegradability and bioavailability (Naidu 2011), but often overestimated bioavailability of high molecular weight PAHs due to their different extractability.

2.3.2 Non-exhaustive techniques

Non-exhaustive techniques to assess the bioavailability of organic compounds in soil (Table 5) include mild solvent extraction (Kelsey et al., 1997; Liste and Alexander 2002), solid sorbents (e.g. Tenax) (Cornelissen et al., 2001; Hulscher et al., 2003 ,Lydy et al. 2015) and hydroxypropyl-β-cyclodextrin (HPCD) (Reid et al., 2000; Cuypers et al., 2002; Stokes et al., 2005).

Mild solvent extraction consists of adding a polar solvent or mixture of solvent and water (e.g. butanol, ethanol, methanol, methanol-water) to a sediment or soil sample, agitating the mixture, and then analysing the extract for contaminants (Cui et al., 2013). This technique has shown good correlation between extractable fraction and uptake in earthworms (Kelsey et al., 1997) and bacterial genotoxicity assay (Alexander and Alexander 2000; Liste and Alexander 2002). Mild solvent extraction could also be used as a proxy to estimate the contaminant bioaccessible fraction, however it shows little consistency between different soil types (Chung & Alexander 1998).

Tenax is a polymer resin that, when mixed with contamianted sediment, will recover target compounds. Sorbed compunds are eluted from the resin with a solvent and fresh polymeric beads can be added several times (multiple steps) and harvested to measure the recoverable hydrocarbons (Cui et al., 2013). Tenax has been used to assess the bioavailability of aromatic compounds in sediment (Morrison et al. 2000; de la Cal et al. 2008; Harwood et al. 2012).

Hydroxypropyl-cyclodextrin (HPCD) is a cyclic oligosaccaride formed by α-D-glucopyranoside units linked 1-4 and bound together in a ring (Riding et al. 2013). This structure is highly soluble (hydrophilic outside), and creates a hydrophilic cavity, capable of forming inclusion complexes with hydrophobic compounds such as organic contaminants (Bardi et al. 2000). In these inclusion complex formations, water molecules are released from the HPCD cavity through displacement by a more hydrophobic molecule in solution (Del Valle 2004). HPCD vary in size (α , β, γ) depending on the number of glucose monomers (generally six to eight units) present in the ring. Generally, an aqueous solution of HPCD is mixed with soil or sediment (1:20 ratio) and then the aqueous phase recovered via centrifugation and the supernatant is analysed for the presence of target contaminants

(Cui et al., 2013). Alternatively, the supernatant is discarded and the soil pellet resuspended and extracted using exhaustive solvents (total extraction), and cyclodextrin uptake measured by substraction (comparing the sum totals of PAHs extracted by HPCD against the total amount extracted by exhaustive solvent) (Papadopoulos et al. 2007). Reid et al. (2000b) showed a reliable prediction of the microbial available concentration of PAHs in soil compared to classical methods based on Soxhlet extraction. Positive correlation has been observed between the amount of HPCD extracted and microbial mineralization in activated carbon-amended soils (Rhodes et al. 2008). Potential of HPCD for indicating bioavailable organic contaminant has been recognized, but no clean-up thresholds for CD-extractable PAHs have been implemented yet (CCME, 2006). Main limitations associated with of HPCD extraction are the reduction of potential for indicating bioavailable fraction in higher organisms (earthworms, benthic invertebrates) (Barthe and Pelletier 2007; Hartnik et al., 2008) and the size of the HPCD cavity that might prevent PAHs complexation, owing to steric constraints, which would result in poor extraction efficiencies (Stokes et al., 2005).

In summary, while passive samplers can be used to estimate the readily-available (pore water concentration) for most soil organisms (Brand et al. 2013), bioavailable concentrations measured by Tenax and HPCD correspond to the sum of the fraction dissolved in pore water and the concentration that could become available on a longer term (i.e. rapid and slow desorbing fraction). Methods to estimate potential bioavailable concentrations can be considered more conservative; therefore we believe that both Tenax and HPCD could be more suitable compared to PSMs for the evaluation of receptor's potential exposure and implementation into the risk assessment. Overall the number of laboratory studies and publications on less exhaustive techniques is promising but they require further efforts to obtain an optimised and enhanced procedure that can be applied across different soil samples and a wider range of contaminants. Such methods could assist in evaluating exposure of ecological receptors and facilitate a more proportionate definition of risk. In addition, these measurements may have implication when establishing remediation endpoints.

3 Challenges in assessing complex chemical mixtures bioavailability

Methods to assess bioavailability predominantly focus on assessments carried out on individual substances, or a limited number of substances. Humans and ecological receptors, however, are exposed to a wide variety of chemicals and therefore understanding the potential adverse effects of interactions between these chemicals in mixture is fundamental to assessing risk. We can summarise the challenges of assessing the bioavailability of complex chemical mixtures in three key points (1) standards for mixed-pollutants are absent; (2) combination effects studies on complex chemical mixtures are limited; (3) bioavailability is often neglected.

In co-contaminated sites, the presence of both inorganic and oil-derived products, in mixture compositions of near infinite character can produce unpredictable effects (Borgert 2004). Uncertainty in the behaviour of these mixtures reflects not only the complexity of the soil matrix, but also the heterogeneous nature of contaminants in soil, as well as temporal variations in chemical structure and concentration. Conventional risk assessments apply risk-based criteria (guideline values) to deterministic models to make decisions about soil remediation, and establish clean-up standards. However, exposure-risk relationships are established on specific quantitative values (maximum acceptable risk), which can largely vary among different countries (Aqeel et al. 2014), depending on the assumption made when modelling exposure. Whereas conventional exposure assessment relied on the measurable effects of individual chemical species, (de Zwart & Posthuma 2005), predictive models for exposure assessment, are unlikely to account for (and interpreted) the combatorial effects of chemical mixtures (Cornelis et al., 2010). Regulatory frameworks address chemical mixtures based on the contribution of each individual compound present in the mixture, if individual compound toxicity does not exceed the threshold, the overall mixture is considered non-toxic (Heys et al. 2016). Over the last decade, the increasing interest in complex chemical mixtures has been reflected by legislative developments and scientific improvement in understanding of the role of bioavailability of single (Elgh-Dalgren, 2009; Bradham et al., 2015; Chen et al., 2015; Fadaei et al., 2015; Henry et al., 2015; Juhasz et al., 2015; Ortega-Calvo et al., 2015; Stegemeier et al., 2015; Tao et al., 2015) and multiple contaminants (Allan et al., 2012; Gouliarmou and Mayer, 2012; Cain et al., 2013; Liu et al., 2013; Kuhn & Maurice., 2014; Amato et al., 2014; Jia et al., 2014; Arp et al., 2014) however, to date, potential risks of combined chemicals are rarely examined in risk assessment (Kienzler et al. 2016).

Only a few laboratory based studies have attempted at studying complex chemical mixtures toxic effect on in vitro or biological systems (Environment 2002) more data are required on synergistic and antagonistic interactions of these compounds. While the concepts of mixture toxicity have been discussed for decades, their use has been limited by the absence of toxicological data associated with specific substances, the lack of bioavailability data, and generally the uncertainty associated with knowledge on mixtures of compound. The greatest knowledge gap at the present time is the lack of understanding regarding the mode of action of mixture of compounds which limits the definition of a set of criteria, and therefore requires a careful case-by case approach (EU 2011).

Cumulative risk assessment (CRA) is a relatively new approach that aims to quantify the health or environmental risk by estimating the level of exposure to multiple contaminants (U.S. Environmental Protection Agency (EPA) 2003). CRA represents a conceptual innovation in the decision making process by moving from a single effect approach to a multiple ecological and human approach to the effects caused by multiple exposure of contaminants (Fox, 2002). Although cumulative risk assessment appear to be pragmatic, few ecotoxicological specific guidelines (e.g. pesticides regulations) account for it (European Environment Agency, 2012). At present, CRA may be the best way to add a health dimension to basic contaminant concentration evaluation. It also might support the decision making process creating a more comprehensive understanding of chemicals behaviour in the environment. Further development and additional studies to verify if CRA is a fair representation of the combine risk for compounds that might not be equal in toxicity, ecotoxicity and chemical behaviour are needed. Ultimately, CRA should not be the only measure of risk, but a valuable support to other analytical tools for investigating environmental risk.

Bioavailability is often not well understood and therefore neglected in the risk assessment process. Bioavailability is influenced by a wide range of physicochemical (including both soil and nature of contaminant) (Table 1) and biological factors (Table 2) and it can greatly differ among different organisms, therefore designing suitable one-fit-all extraction approach can be challenging. In order to estimating the bioavailable fraction we should question which of these method provide a good representation for the specific species we intend to protect. Several chemical analytical methods have been developed to assess the bioavailability of inorganic and organic compounds, yet few of them were found to correlate with uptake in model organisms. As such, none of these techniques have been applied to complex chemical mixtures (Muijs and Jonker, 2011a).

4 Conclusions

Given the multiple variables affecting the availability of chemicals in soil, we should look at bioavailability not as a fixed value (concentration), but as a dynamic process between an organism and the chemical-uptake over time (ageing). Methods to estimate bioavailability are still not sufficiently cost-effective and standardised. While a great deal of studies and results have been achieved in regards to estimating bioavailability of inorganic contaminants, there are still more work to be done for organic contaminants. Bioavailability and bioaccessibility estimations are seen as useful means to inform human health risk assessment and improving cost-effective management of contaminated land. For instance, when the exceedance of the guideline values is minor, bioaccessibility become the main driver on large site investigations where costs associated with soil removal are considerably high. Nevertheless, lack of information regarding other potential routes of exposure (dermal contact and inhalation) contributes in limiting our confidence in integrating these findings into risk assessment. Similarly, bioavaliability is still not fully understood and implemented in existing frameworks, because of both multiple definition across different disciplines and lack of standardised test to measure it. Also, a large number of studies and chemical methods have shown that bioavailable fractions can be positively correlated with uptakes in model organisms and microbial mineralization; obtained data are however inconsistent among different type of contaminants and across different receptors tested. An approach based on weigh of evidence should apply chemical-techniques to measure the bioavailable and bioaccessible fraction, along with biological methods (bioassays) to better understand effects of contaminants uptake and related bioavailability in humans. Bioassays provide a direct measure of contaminant's (bioavailable) concentration for a specific organism over time and are able to quantify and detect a wide range of toxins at relatively low cost.

Understanding and implementing site-specific bioaccessibility and bioavailability data mean being able to represent more realistically the on-site conditions. Implementation of bioavailability can help the revision of exposure estimate, reducing the cost of remediation, and bringing a greater degree of judgment when assessing risk, and allowing greater levels of contamination left safely in soil. However, in order to provide increased confidence in using bioavailability, further investigation is needed on how to incorporate it into risk assessment. Moreover new approaches are required to tackle the complexity of chemical mixtures and the likely effect of exposure. The challenges are understanding the potential risk connected to a complex chemical mixture, and assessing how the physico-chemical interactions, such as co-solvency, sorption, desorption, and saturation, can affect the potential toxicological response. Understanding which chemicals are effectively bioavailable may be the key for future risk assessment.

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