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

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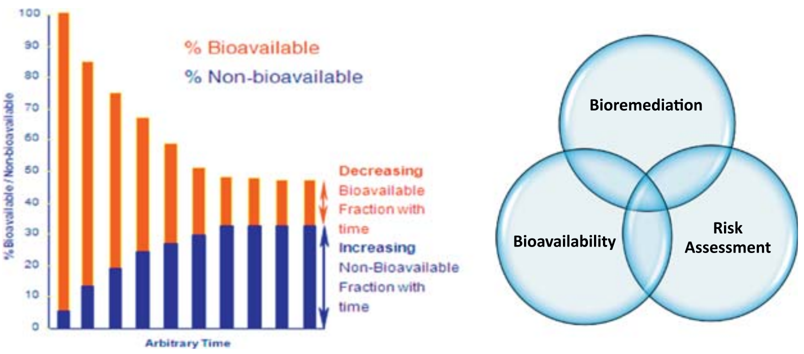
HIGHLIGHTS

- Soil and contaminant physicochemical characteristics affect bioavailability.
- Mild-extraction is suitable to evaluate receptor's potential exposure and uptake.
- Chemical estimation of bioavailability should be supported by bioassays.
- Single-contaminant exposure assessments can be used to inform mixed bioavailability.

GRAPHICAL ABSTRACT



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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 ecotoxicological 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 physicochemical 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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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 physicochemical 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, Sam 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 (D. Zhang et al., 2014; M. 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., 2000a, 2000b, 2000c). Contaminants can also dissolve into the pore water of a soil matrix, making it available for biodegradation Fig. 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 and 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, 2006). 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.

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