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Review article

Residual hydrophobic organic contaminants in soil: Are they a barrier to risk-based approaches for managing contaminated land?

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ABSTRACT

Risk-based approaches to managing contaminated land, rather than approaches based on complete contaminant removal, have gained acceptance as they are likely to be more feasible and cost effective. Risk-based approaches aim to minimise risks of exposure of a specified contaminant to humans. However, adopting a risk-based approach over alternative overly-conservative approaches requires that associated uncertainties in decision making are understood and minimised. Irrespective of the nature of contaminants, a critical uncertainty is whether there are potential risks associated with exposure to the residual contaminant fractions in soil to humans and other ecological receptors, and how they should be considered in the risk assessment process. This review focusing on hydrophobic organic contaminants (HOCs), especially polycyclic aromatic hydrocarbons (PAHs), suggests that there is significant uncertainty on the residual fractions of contaminants from risk perspectives. This is because very few studies have focused on understanding the desorption behaviour of HOCs, with few or no studies considering the influence of exposure-specific factors. In particular, it is not clear whether the exposure of soil-associated HOCs to gastrointestinal fluids and enzyme processes release bound residues. Although, *in vitro* models have been used to predict PAH bioaccessibility, and chemical extractions have been used to determine residual fractions in various soils, there are still doubts about what is actually being measured. Therefore it is not certain which bioaccessibility method currently represents the best choice, or provides the best estimate, of *in vivo* PAH bioavailability. It is suggested that the fate and behaviour of HOCs in a wide range of soils, and that consider exposure-specific scenarios, be investigated. Exposure-specific scenarios are important for validation purposes, which may be useful for the development of standardised methods and procedures for HOC bioaccessibility determinations. Research is needed to propose the most appropriate testing methods and for assessing potential risks posed by residual fractions of HOCs. Such investigations may be useful for minimising uncertainties associated with a risk-based approach, so that consideration may then be given to its adoption on a global scale. This review critically appraises existing information on the bioavailability of HOC residues in soil to establish whether there may be risks from highly sequestered contaminant residues.

Contents

Abbreviations: BR, Bound Residue; CSM, Conceptual Site Model; DCM, Dichloromethane; DCM/ACE, Dichloromethane/Acetone; ECETOC, European Centre for Ecotoxicology and Toxicology of Chemicals; EET, Exhaustive Extraction Technique; EHRA, Ecological Health Risk Assessment; ER, Extractable Residue; EVA, Ethylene Vinyl Acetate; GI, Gastrointestinal; HHRA, Human Health Risk Assessment; HOC, Hydrophobic Organic Contaminant; HPCD, Hydroxypropyl-β-Cyclodextrin; HPLC-FD, High-performance Liquid Chromatography with Fluorescence Detection; MGP, Manufactured Gas Plant; NEET, Non-exhaustive Extraction Technique; NEPM, National Environment Protection Measure; NER, Non-extractable Residue; OC, Organic Carbon; PDMS, Polydimethylsiloxane; PED, Polyethylene devices; POM, Polyoxymethylene; RA, Risk Assessment; RBA, Relative Bioavailability; RBLM, Risk-based Land Management; SARA, Soil-sediment Availability Ratio; SBE, Silicon-based Extraction; SFE, Supercritical Fluid Extraction; SGV, Soil Guideline Value; SOP, Standard Operating Procedure; SPE, Solid Phase Extraction; SPMD, Semipermeable Membrane Devices; SPME, Solid Phase Micro-extraction; TR, Total Residue; USEPA, United States Environmental Protection Agency.

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1. Introduction

"To forget how to tend soils is to forget ourselves".

[(Mahatma Gandhi)]

Chemical contamination of soils is a global problem (FAO and ITPS, 2015) and is arguably of similar significance as other major environmental challenges such as climate change and biodiversity loss (Rockstrom et al., 2009). Sustainable soil management has a vital role for addressing the challenge of widespread contamination, especially with regard to attaining the United Nations 'Sustainable Development Goals' (UN, 2016). Among the anthropogenic contaminants of soils, hydrophobic organic contaminants (HOCs) require attention as they are persistent, they bioaccumulate, and are toxic and potentially carcinogenic (IARC, 1983; USEPA, 2008; Jones and de Voogt, 1999). Examples of important HOCs include PAHs, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), dichloro-diphenyl-trichloroethane (DDT) and other chlorinated pesticides. The risk of soil contamination by HOCs is a matter of great concern for human and ecological health (enHealth, 2012). Human exposure to HOCs in soils may be by oral ingestion, inhalation, and/or dermal routes (enHealth, 2012; Khan et al., 2008). Ingestion has been regarded as very important for HOCs, such as the PAHs (enHealth, 2012; Ramesh et al., 2004).

Assessment of HOC contamination in soils is currently based on the measurement of total concentrations and the assumption that the measured HOCs are 100% bioavailable (Ortega-Calvo et al., 2015; NRC, 2003; Semple et al., 2003; Naidu, 2008). It has been reported that total contaminant concentrations in ingested soil or food do not provide a good measure of the contaminant's absorption *via* the organism's gut membrane or that absorbed into its systemic circulation (NRC, 2003; Lu et al., 2010; Semple et al., 2004; Siciliano et al., 2010; Versantvoort et al., 2005; Cave et al., 2010). This may be due to the interactions between the contaminant and the soil. Wide variations in soil and HOC properties may significantly affect bioaccessibility (bioavailability + potential bioavailability) of HOCs in humans (Lu et al., 2010; Duan et al., 2014; Nathanail and Ogden, 2013; Semple et al., 2013). For example, when HOCs enter soil, sequestration processes such as diffusion of molecules into inaccessible micro- and nano-pores, as well as sorption to soil components, are known to affect bioavailability and bioaccessibility (Duan et al., 2014; Alexander, 2000; Luo et al., 2012; Ma et al., 2012; Northcott and Jones, 2001a; Cornelissen et al., 1997a; Luthy et al., 1997). Consequently, varying soil-organism-HOC interactions may influence the significance of potential harm that may result from exposure. Hence, the bioaccessible contaminant concentration rather than the total concentration in soil is more important for realistic risk assessment (RA) purposes.

Risk-based approaches to contaminant management and remediation offer feasible remediation practices in that they recognise that complete removal of a contaminant is likely to be technically very difficult, expensive, and sometimes unnecessary (Naidu et al., 2008; Duan et al., 2015a; Thavamani et al., 2015; Das et al., 2013). Risk-based approaches need to be underpinned by a thorough understanding of the chemical behaviour of HOCs in soils, and in particular definition of the fraction of the total concentration that is relevant to biological or environmental impacts, *i.e.* bioaccessibility. Adoption and application of risk-based approaches face a significant hurdle due to the lack of regulatory recognition of the bioavailability concept which underpins the approach, although it is perceived as an important concept for RA within certain sections of the regulatory (Latawiec et al., 2011) and scientific (NRC, 2003; Semple et al., 2003; Naidu, 2008; Semple et al., 2004; Ng et al., 2010) communities. This is related to the lack of standard operating procedures (SOPs) for measuring the bioavailable fractions of HOCs in soil, as such measurements are still in their infancy. Although validated SOPs for bioavailability of thoroughly studied inorganic contaminants such as lead in soil have gained regulatory approval and are currently in use in the USA (USEPA, 2012a), there is no generally accepted SOPs for determining HOC bioavailability in soil. In addition, information on the bioavailability and risks associated with 'residual' HOCs in soil is limited.

Although bioavailable fractions of HOCs are by definition of most concern in assessing their environmental and health risks in soil, it is yet to be demonstrated conclusively whether residues that remain following removal of the bioavailable fractions pose ongoing risk from long-term exposure, especially in historically contaminated soils (Duan et al., 2015a; ECETOC, 2010; ECETOC, 2013b; Rhodes et al., 2008a; Kastner et al., 2014; Barraclough et al., 2005). In the absence of conclusive evidence regarding potential risk arising from long-term exposure to residual fractions, the adoption of the risk-based approach for HOCs is often challenged. There have been arguments regarding the significance of non-extractable residual (NER) fractions, defined in this review as highly sequestered residues, to ongoing risks in the long term (ECETOC, 2010; ECETOC, 2013b; Barraclough et al., 2005; Barriuso et al., 2008; Craven, 2000; Craven and Hoy, 2005; Gevao et al., 2003; Gevao et al., 2000; Richnow et al., 1999), because changes in environmental or exposure conditions may mobilise residual pools in soil (Thavamani et al., 2015; Gevao et al., 2003; Birdwell and Thibodeaux, 2009; Juhasz et al., 2010; Calderbank, 1989). A number of papers have argued that long-term exposure to NER fractions in soil poses little or no risk because of the strong interactions between HOCs and soil components especially organic matter (OM), resulting in very slow remobilisation HOCs, mainly through desorption (Northcott and Jones, 2001a; Cornelissen et al., 1997a; Thavamani et al., 2015; Das et al., 2013; Gevao et al., 2003; Rhodes et al., 2010; Doick et al., 2005a; Mayer et al., 2016). Desorption rates of HOCs from historically contaminated soils and sediments have been reported to be slow or very slow