Review

Mixed contaminant interactions in soil: Implications for bioavailability, risk assessment and remediation

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Majority of contaminated sites in the world contain complex mixtures of heavy metals and organic contaminants from diverse natural processes and anthropogenic activities. Mixed interactions of heavy metals and organic contaminants may affect their bioavailability and accumulation in soil and biota through synergistic or antagonistic processes. Evaluation of contaminant bioavailability is a necessary component of the overall site assessment process for establishing either bioavailability-based or risk-based, site-specific remedial options. However, contemporary approaches aimed at the effective characterisation of contaminated soils for risk assessment, remedial and regulatory purposes are frequently challenged by knowledge gaps in contaminant bioavailability, mixed contaminant effects and emerging contaminants. Understanding mixed contaminant interactions at the elemental and molecular levels is, therefore, imperative not only to explain the underlying mechanisms controlling the fate and transport of these contaminants in soils, but also predict their bioavailability, ecotoxicological effects on natural communities under realistic exposure conditions and remediation endpoints. In this paper, scattered literature is harnessed to review specific soil-contaminant interactions, inter-contaminant (metal-metal, organic-organic, metal-organic) interactions and their implications for bioavailability, risk assessment and soil remediation.

Key words: Heavy metals, organic contaminants, mixed contaminant interactions, co-contaminated soil, bioavailability, risk assessment, soil remediation.

INTRODUCTION

A majority of contaminated soils in the world contain complex mixtures of heavy metals (HMs) and organic contaminants (OCs) that originate from natural processes, to some extent, and anthropogenic activities, to a greater extent (Naidu et al., 2010; Megharaj et al., 2012). The co-occurrence of HMs and OCs in contaminated soils is an issue of great concern affecting human health and ecosystems in the world today

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(Mattson et al., 2009; Olaniran et al., 2013). Government, industry and the public are now much aware of the potential dangers that complex mixtures of xenobiotics such as HMs- mercury (Hg), cadmium (Cd), lead (Pb), nickel (Ni), copper (Cu), zinc (Zn), chromium (Cr), arsenic (As) and OCs-total petroleum hydrocarbons (TPHs), polychlorobiphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), dioxins and furans (PCDD/Fs), phthalic acid esters (PAEs), chlorinated solvents, pesticides, antibiotics and detergents pose to human health and the environment (Amor et al., 2001; Khan et al., 2004; Hoffman et al., 2005; Bardena et al., 2013; Yang et al., 2013). The co-occurrence of HMs and OCs in soil can adversely affect microbial processes with serious implications for biodegradation of OCs and negatively or positively affect the root growth of plants, thereby, disturbing the root enhanced dissipation of OCs (Lin et al., 2008; Couling et al., 2010; Thavamani et al., 2011a). Furthermore, mixed interactions among the HMs and OCs can synergistically or antagonistically affect their accumulation in the soil and biota (Chigbo et al., 2013). Concerns regarding the potential risks of persistent, bioaccumulative and toxic chemicals capable of long-range migration in the environment have necessitated international and national guidelines for the evaluation and control of risks posed by existing substances including HMs and OCs (Mackay and Fraser, 2000; McGrath and Semple, 2010).

The evaluation of contaminant mobility/bioavailability is a necessary component of the overall assessment of a site for establishing either mobility-/bioavailability-based or risk-based, site-specific remedial options (Nicholaidis and Shen, 2000; Ehlers and Luthy, 2003; Clothier et al., 2010). However, contemporary approaches aimed at the effective characterisation of contaminated soils for risk assessment, remedial and regulatory purposes are frequently challenged by knowledge gaps in contaminant bioavailability, mixed contaminant effects and emerging contaminants of concern (Posthuma et al., 2008; Clothier et al., 2010; Naidu et al., 2010; Pignatello et al., 2010; Clarke and Smith, 2011; Naidu and Wong, 2013). Ideas on the numerous interactions of HMs and OCs mixtures at the elemental and molecular levels are, therefore, imperative not only to explain the underlying mechanisms controlling the fate and transport of these contaminants in soils (Bertsch and Seaman, 1999), but also predict their bioavailability and ecotoxicological effects on natural communities under realistic exposure conditions (Chapman, 2002). Moreover, knowledge of mixed contaminant interactions and their antagonistic or synergistic effects in soil is required to boost soil ecotoxicological literature currently dominated by studies of single contaminant exposure (Naidu et al., 2010).

The use of models and computer simulations can significantly improve the understanding of chemical information and multi-dimensional data obtainable at contami-

nated sites (Dube et al., 2001). Despite these approaches and some investigations incorporating mixed contaminant interactions (Table 1), soil is a heterogeneous matrix whose equilibrium is shifting continually and mixed contaminant interactions are non-stereotyped and site-soil-specific. Consequently, investi-gations of mixed contaminant interactions continue to be necessary in tandem with global efforts to bridge the existing knowledge gaps in this aspect of environmental science. In this paper, scattered literature has been harnessed to review possible soil-contaminant and inter-contaminant (metal-metal, metal-organic, organic-orga-nic) interactions in relation to bioavailability, risk assessment and soil remediation.

HEAVY METAL INTERACTIONS IN SOIL

The behaviour of HMs is difficult to generalise, and so, understanding the chemistry of the particular HM and the environment of concern is necessary. However, the factors that control HM chemistry and the environmental characteristics used to produce estimates of HM fate and effects can be generalised. In natural soils, HMs exist mainly in relatively immobile forms in primary silicate minerals (for example, quartz, feldspars) and secondary clay minerals (for example, kaolinite, montmorillonite), but as a result of weathering, a fraction of the HMs content is gradually converted to mobile forms accessible to biota depending on the geological history of the area (Pierzynski et al., 2000). In contaminated soils, however, the input of HMs is mostly in non-silicate bound forms and contributes to the pool of environmentally available or bioaccessible metals the portion of total HMs in soil that is available for physical, chemical and biological modifying influences (McGeer et al., 2004). The intro-duction of HMs in soils through contamination eventually leads to changes in their chemical forms or phases and their multidimensional distribution, mobility and toxicity (Shiowatana et al., 2001; Buekers, 2007). The forms of HMs identifiable in soils are: (i) soil solution forms (ionic, molecular, chelated and colloidal forms) with high mobility, (ii) ions at the exchange interface, non-selec-tively sorbed, readily exchangeable ions in inorganic or organic fractions, (iii) ions specifically sorbed by inorganic colloids, more firmly bound ions with medium mobility, (iv) ions complexed or chelated by organic colloids, including elements present in decomposing organic materials and the soil biomass, medium to high mobility because of eventual decomposition of organic matter, (v) ions occluded by, or structural components of, secondary minerals and other inorganic compounds, medium metal mobility, (vi) elements incorporated in precipitated (hydr)oxides and insoluble salts, or fixed in crystal lattices of clay minerals, or present in the structure of primary minerals; low metal mobility, available after weathering or decomposition (Ure et al., 1993; Romić,

Table 1. Some studies incorporating mixed contaminant interactions in soil.

Contaminant	Soil texture (or type)	Location	Reference
Metal-Metal			
Cd, Cu, Ni, Pb, Zn	Sandy clay loam, Silty clay loam, Loam	Pamplona, Spain	Echeverría et al. (1998)
Cr, Ni, Cd	Clayey soils	Chicago, USA	Reddy et al. (2001)
Cd, Zn, Pb	Silty clay	Northern Taiwan	Lai and Chen (2005)
Cd, Cu, Cr, Pb, Zn	Sandy loam	Scotland, UK	Markiewicz-Patkowska et al.(2005)
Ni, Zn, Cu, Pb, Cd, Cr	Loamy sand, Silty loam	Olsztyn, Poland	Wyszkowska et al. (2007)
Cu, Pb, Ni, Zn		Santiago, Chile	Cazanga et al. (2008)
Cd, Pb, Ni, Cu, Zn, Co	Andisols	Agrinion, Greece	Kalavrouziotis et al. (2009)
Zn, Cd, Pb	-	Aligarh, India	Mohammad et al. (2009)
Cd, Cu, Ni, Pb, Zn	Cambisols	Makurdi, Nigeria	Wuana and Okieimen (2011)
Pb, Zn, Cd, Ni, Mn, Cu, Cr, Co, V	Sandy loam -	New Orleans, USA	Zahran et al. (2012)
Metal-organic			
As, Cd, Pb, Zn, Chlordane	-	New Haven, USA	Mattina et al. (2003)
As, DDT, DDD, DDE	Sand, Clay loam, Sandy clay loam	NSW, Australia	Van Zwieten et al. (2003)
Atrazine, chlorpyrifos,	Soil/Sediment	Mississipi, USA	Hwang et al. (2005)
MMA, methylmercury	Sandy clay loam	Shanghai, China	Shen et al. (2006)
Cd, Zn, Pb, PAHs	Loam	Zhejiang, China	Lin et al. (2008)
Cu, pyrene	-	Birmingham, UK	Chigbo et al. (2013)
Cd, Zn, Ni, TPHs	Loamy sand	Pretoria, SA	Atagana (2011)
Pb, Cd, Zn, Cr, Cu, As, Mn, Ni, PAHs	Sandy loam	Sydney, Australia	Thavamani et al. (2011a, b)
Cd, Pb, Zn, Cu, Mn, Co, humic acids	Fluvisol	Switzerland	Hajdu and Slaveykova (2012)
Tetracycline, Cd, Cu, Pb	Silty clays	Nanjing, China	Zhao et al. (2013)
Zn, Cu, Al, Fe, ^{14}C-phenanthrene	Sandy loam	Lancaster, UK	Obuekwe and Semple (2013)
Organic-organic			
TNT, pyrene	Silty loam, Loam	Maryland, USA	Chekol et al. (2002)
Phenanthrene, chrysene, dichlorobiphenyl	Sediment	The Netherlands	Morelis et al. (2007)
Surfactants, HOCs	-	-	Laha et al. (2009)
[14]C-PAHs	Clay loam	Lancashire, UK	Couling et al. (2010)
CBs, PAHs	-	California, USA	Faria and Young (2010)
PAHs	-	Chelsea, USA	Xiao and Huang (2011)
Fluoroquinolones, Sulfonamides	Brazilian soils	Piracicaba, Brazil	Leal et al. (2013)
Phthalate esters	Clay	Wuhan, China	Liu et al. (2013b)
TNT, RDX, HMX	Silty sand	Tennessee, USA	Sharma et al. (2013)
CBs, chloroethene	Silty sand, Silty clay	Guangzhou,China	Shu et al. (2013)
Sulfonamides	Silt loam, Clay	Hamilton, NZ	Srinivasan et al. (2013)
PAEs	Silty clay	Nanjing, China	Yang et al. (2013)

TNT = 2,4,6-trinitrotoulene ; RDX = hexahydro-1,3,5-triazine; HMX = octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine ; PAHs = polycyclic aromatic hydrocarbons; PAEs = phthalic acid esters ; POPs = persistent organic compounds; DDT = 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane; DDD = 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane; DDE = 1,1-dichloro-2,2-bis(4-chlorophenyl) ethylene; HOCs = hydrophobic organic compounds; MMA = monosodium acid methanearsonate; CBs = chlorobenzenes

2012). Evaluation of the chemical forms of HMs including free metal ions, other inorganic and organic complexes and their associations among the soil components is referred to as chemical speciation (Ure et al., 1993;
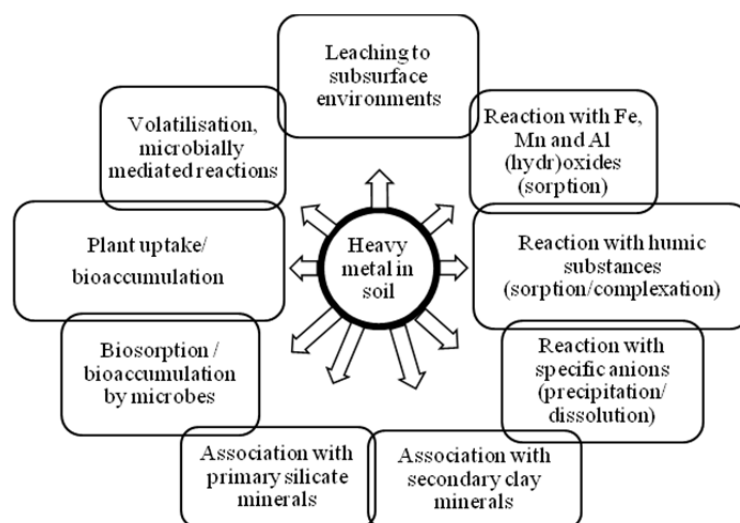
Figure 1. Summary of interrelated biotic and abiotic processes determining the fate and transport of heavy metals in soils.

Templeton et al., 2000; Janssen et al., 2003; Gismera et al., 2004; Hlavay et al., 2004). The level of exposure of organisms to the HMs relative to their speciation in the soil system is called bioavailability, considered as the fraction of the contaminant's total amount that is freely available to cross an organism's cellular membrane from the soil the organism inhabits at a given time (Semple et al., 2004, 2007). In the environmental field, chemical speciation analyses can be used to accurately determine the human health or ecological risks posed by the HM species discovered and quantified at a site and redirect this understanding into the design, selection, optimization and monitoring of remediation strategies applied for site cleanup (D'amore et al., 2005). The present discourse precludes the various methods used to evaluate the speciation of HMs in solid and solution phases of soils because they have been extensively dealt with elsewhere (Tessier et al., 1979; Lake et al., 1984; Ure et al., 1993; Ma and Rao, 1997; Salbu et al., 1998; Maiz et al., 2000; Kabala and Singh, 2001; Morera et al., 2001; Filgueiras et al., 2002; Voegelin et al., 2003; Hlavay et al., 2004; D'amore et al., 2005; Zhang and Young, 2006; Rao et al., 2008; Okoro et al., 2012; Romić, 2012; Wuana et al., 2013). It, however, suffices to highlight herein, the fundamental interactions that influence the fate of HMs in soil (Figure 1).

Interactions with clay minerals and Fe, Mn and Al (hydr)oxides

Soil-HMs interactions are essentially due to the presence of a highly dispersed colloidal fraction of the soil solid phase called 'soil sorption complex' (Dube et al., 2001). In soil, HMs are loosely sorbed on alumino-silicate and phyllosilicate clay minerals as a result of the prepon-

derance of competing cations (for example, Ca). The clay minerals, however, carry Fe, Mn and Al oxides which are more effective at the adsorption of HM cations than the silicates (Violante et al., 2010). Fe and Mn oxides have a much greater adsorption capacity relative to Al oxides and other clay minerals (Basta et al., 2005). The adsorption of HM cations (for example, Pb, Cu, Zn, Cd, Cr, Hg, Ni) and oxyanions (for example, AsO_4^{3-}, AsO_2^-, SeO_4^{2-}, SeO_3^{2-}, MoO_4^{2-}, WO_4^{2-}, VO_4^{2-} and CrO_4^{2-}) onto oxide surfaces is pH dependent. The selectivity sequence of HM cation adsorption has been reported for goethite, haematite and aluminium hydroxides as: Cu > Pb > Zn > Cd > Co > Ni > Mn; Pb > Cu > Zn > Cd > Co > Ni > Mn and Cu > Pb > Zn > Ni > Co > Cd, respectively. No correlations have, however, been found between the selectivity sequences and the sequence of ionic radii (Pb > Cd > Zn > Cu > Ni) nor between the selectivity sequences and those of electronegativity (Cu > Pb > Ni > Cd > Zn) (Abd-Elfattah and Wada, 1981). Additionally, spectroscopic techniques such as electron spin resonance (ESR) and extended x-ray absorption fine structure spectroscopy (EXAFS) have shown that the strong bonding of Pb, Cu, Co, Cr, Mn, Ni and Zn to these oxide surfaces is due to formation of inner-sphere metal surface complexes and formation of metal hydroxide precipitate phases (Lake et al., 1984; Hettiarachchi 2003; Basta et al., 2005; Violante et al., 2010). Adsorption processes in soils have historically been described using empirical isotherm equations such as the Freundlich Langmuir, Tempkin, Toth and Dubinin-Radushkevich models (Goldberg, 2005).

Interactions with soil organic matter

In addition to Fe, Al, Mn oxides, humic substances (HSs),

a fraction of soil organic matter, are another important category of sorbents for HMs in soils. Strong adsorption on HSs occurs through the formation of HM complexes, thereby, reducing HM solubility and mobility in soil (Adriano, 2003). Evidence from molecular-scale FTIR spectroscopy has revealed that HMs form strong bonds with specific functional groups of HSs: carboxylate (-COO^-), phenolic and sulphur-hydryl (-SH) functional groups (Zhou et al., 2005; Erdogan et al., 2007). Adsorption of HMs on HSs increases with pH because HMs preferentially binding with ionised functional groups formed with increasing pH. Metal sorption by HSs is reduced less at lower pH than metal sorption on Fe, Mn, Al oxides (Basta et al., 2005).

The tendency of HMs towards complexation by HS ligands in soils is rationalised by the Pearson's principle, commonly referred to as the hard, soft acid and base (HSAB) principle (Pearson, 1968; Smith, 2007). The HSAB principle categorises Lewis acids and bases such that H^+ and all of the metal cations of interest in soil solutions are Lewis acids, while the Lewis bases include H_2O, oxyanions (OH^-, COO^-, CO_2^-, SO_4^{2-}, PO_4^{3-}), and inorganic N, S and P electron donors. The HSAB principle indicates that hard acids (Fe^{3+}, Mn^{2+}) tend to form complexes with hard bases (OH^-, COO^-), while soft acids (Cd^{2+}, Hg^{2+}) prefer soft bases (-SH).

Borderline acids (Cu^{2+}, Zn^{2+}, Pb^{2+}) will form complexes with a weak or strong base (Pearson, 1968; Essington, 2004; Smith, 2007). After the HM-ligand complex formation, other ligands may compete to destabilise it and form new complexes with the HM cation (Sposito, 1994). The general order of affinity for metal cations complexed by organic matter has been reported as: Cu^{2+} > Cd^{2+} > Fe^{2+} > Pb^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Zn^{2+} (Adriano et al., 2002).

Interactions with specific anions/ligands in soil solution

The pH sensitive interactions of HMs with specific inorganic (for example, Cl^-, S^{2-}, OH^-, HPO_4^{2-}, NO_3^-, CO_3^{2-} and SO_4^{2-}) and organic (for example, citrate, oxalate, fulvate and dissolved organic carbon) ligand ions through precipitation-dissolution reactions can also affect HMs sorption processes (Bolan et al., 2003a). HM cations form sparingly soluble precipitates with phosphate (HPO_4^{2-}), sulphides (S^{2-}), carbonate (CO_3^{2-}), hydroxide (OH^-) and other anions (Lindsay, 2001). The precipitation of HMs is highly pH-dependent and increases with pH for most metal cations.

Arsenate and other HM oxyanions can form insoluble precipitates with multivalent cations including Fe, Al and Ca. The HM mineral (precipitate) formed may control the amount of HM in solution hence their mobility and availability (Basta et al., 2005). Precipitation occurs when the ionic product of the dissolved metal exceeds the solu-

bility product of that phase. In normal soils, precipita-tion of metals is unlikely, but in highly contaminated soils, this process can play a major role in the immobilisation of metals, especially under alkaline conditions (Bolan et al., 2010).

Interactions with soil microorganisms

Soil microorganisms including bacteria and fungi can bioaccumulate HMs through either biosorption onto microbial biomass or absorption and uptake (Bolan et al., 2010). Bacteria and fungi are capable of biosorbing HMs via ion-exchange processes involving surface functional groups such as -COO^-, -NH_2, OH^-, PO_4^{3-} and -SH (Srinath et al., 2002).

The affinity of HMs for the surfaces of microorganisms has been reported as: Ni >> Hg > As > Cu > Cd > Co > Cr > Pb (Lopez et al., 2000). Soil microorganisms can also take up the HM ions and metabolically convert them into harmless forms by either precipitation or comple-xation. For example, *Desulphovibrio* (the sulphate reducing bacteria) releases hydrogen sulphide, precipi-tating the metal sulphides in the process; some bacteria produce iron-sequestering organic molecules (sidero-phores) in the form of phenols, catechols or hydroxa-mates; while some produce metal-binding proteins (metallothioneins) that serve as detoxicants (Suarez and Reyes, 2002; Cabrera et al., 2006; Bolan et al., 2010). Soil microorganisms may, however, suffer toxic effects from HMs during uptake (Wyszkowska et al., 2007).

The HMs can also partake in microbially mediated oxidation-reduction reactions in soil to which, As, Cr, Hg and Se are most amenable (Bolan et al., 2010). Arsenic in soils can be oxidised to AsO_4^{3-} [As(V)] by bacteria (He and Hering, 2009). Since AsO_4^{3-} is more strongly retained than AsO_2^- [As(III)] by inorganic soil components, microbial oxidation results in the immobilisation of As. Under reducing conditions, As(III) is the dominant form of As in soils, but elemental arsenic (As°) and arsine (H_2As) may also be present. As(III) is much more toxic and mobile than As(V).

In the case of Cr, the Cr(III) is strongly adsorbed onto soil particles, while Cr(VI) is only weakly adsorbed and is readily available for plant uptake and leaching into groundwater (James and Bartlett, 1983). Reduction of Cr(VI) to Cr(III) is enhanced in acidic rather than alkaline soils and can enhance the immobilisation of Cr, thereby, rendering it less bioavailable (Bolan et al., 2003b). The HMs can also be volatilised through microbial conversion to their respective metallic, hydride or methylated form. Methylation is considered to be the major process of volatilisation of As, Hg and Se in soils (and sediments), resulting in the release of the methylated forms of these elements as toxic gas (Cernansky et al., 2009). Although methylation of HMs occurs through both chemical and biological processes, biological methylation (biomethyla-
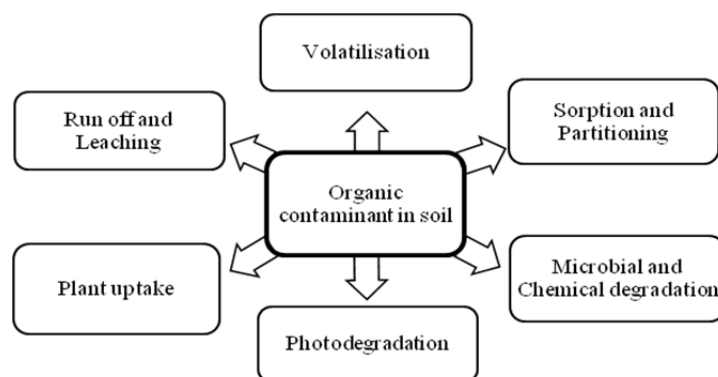
Figure 2. A simplified scheme of processes controlling behaviour (fate and transport) of organic contaminants in soil.

tion) is considered to be the dominant process in soils and aquatic environments (Bolan et al., 2010).

ORGANIC CONTAMINANT INTERACTIONS IN SOIL

The fate and behaviour of OCs in soil is influenced by soil characteristics, compound properties and environmental factors such as temperature and precipitation (Reid et al., 2000). Once introduced to the soil environment, OCs may undergo volatilisation, photodegradation, or be transported by soil run-off and/or erosion to surface waters. Later on, the OCs may be leached into ground-water, and/or undergo adsorption/desorption onto/from soil inorganic/organic solid and colloidal components, partial or total chemical decomposition and/or biodegra-dation, and uptake by plant roots (Loffredo and Senesi, 2006; Pignatllo et al., 2010). The methodological approaches used to characterise the forms, fate and transport OCs in soil have been extensively covered elsewhere (Northcott and Jones, 2000). The various processes influencing the forms, fate and transport of OCs in soil, are however, highlighted herein and summarised in Figure 2.

Volatilisation/leaching

The loss of OCs from soils is often biphasic, whereby a short period of rapid dissipation is followed by a longer period of contaminant release. Volatilisation and leaching are two dissipation processes of OCs in soil that exhibit similar behaviour. Volatilisation and leaching of OCs are responsible for their transfer from soil into the atmos-phere and subsurface environments, respectively (Beck et al., 2009). As with the solubility, it is important to know the contribution of OC volatilisation in predicting its residual amount and thus, its persistence in the environ-ment. The solubility of a gas dissolved in an aqueous solution is well defined by the Henry constant, K_H. For high K_H values, the molecule prefers to leave the liquid phase in order to pass into the atmosphere. This constant is useful to describe the OC fugacity from soil solid com-ponents which are always surrounded by water in adsorbed form (Pierzynsky et al., 2000; Braschi et al., 2011). The primary rate-limiting factors governing volatili-sation and leaching are postulated to be fundamental sorption/desorption mechanisms, including intra-particle diffusion, intra-sorbent diffusion and chemisorption, which control the distribution of contaminant between the solid and aqueous or gaseous phases of soils and, hence, the supply of contaminant available to the various dissipation processes (Beck et al., 2009). These are, in turn, determined by the chemical and physiochemical proper-ties of the contaminant (vapour pressure, solubility, the structure and nature of the functional groups), concen-tration, soil properties (soil moisture content, porosity, density, and organic matter and clay contents, depth) and environmental factors like temperature, humidity and wind speed (Pierzynsky et al., 2000; Braschi et al., 2011).

Photodegradation

The photodegradation of OCs is induced by sunlight either through direct or indirect process. Direct photolysis is initiated through excitation of the OC molecule by absorption of sunlight, followed by its conversion to photoproducts. In indirect photolysis, sunlight is first absorbed by organic or inorganic chromophoric com-pounds present in soil, other than the OC molecule itself. These compounds (for example, clay minerals, metal oxides and hydroxides, transition-metal ions, and various fractions of HSs) may then either transfer the energy to the OC molecule (photosensitisation) or produce specific, greatly reactive, short-lived photoreactants such as the solvated electron, singlet oxygen, superoxide radical anion, peroxy and hydroxyl radicals, hydrogen peroxide and various oxireductive species, which may then react with the target OC (photoinduction) (Senesi and Loffredo, 1997; Pierzynsky et al., 2000; Braschi et al., 2011).

Microbial degradation

Microbial degradation is one of the principal mechanisms for the attenuation of persistent OCs (for example, PAHs) in soils and is affected predominantly by contaminant bioavailability and catabolic ability of indigenous microbial populations (Reid et al., 2000). Microbial degradation is characterised by processes such as hydrolysis, oxidative coupling, hydroxylation, *β*-oxidation, epoxidation, N-dealkylation, decarboxylation, ether cleavage, aromatic ring cleavage, heterocyclic ring cleavage, sulphoxidation and several synthetic reactions (Alexander, 1999; Dec et al., 2002). Various intracellular and extracellular enzymes involved in these processes, include hydrolases, esterases, amidases, phosphatases, proteases, lyases, various phenoloxidases, oxidoreductases, mono-oxygenases and various mixed function oxidases (Dec et al., 2002). The OCs with chemical structures similar to that of HSs are usually more susceptible to microbial degradation than those having little structural resemblance to HSs. Microbial degradation of OCs in the soil may be a function of (i) the specific OC the soil has been pre-exposed to, (ii) exposure concentration, (iii) the duration and form of prior exposure and (iv) antagonistic or synergistic effects of co-contaminants. The antagonistic or synergistic effects of co-contaminants can have implications for microbial degradation in terms of biodegradation and bioremediation (Couling et al., 2010).

Soil sorption/partitioning

Sorption is probably the most important process influencing the fate and bioavailability of OCs entering soil environments (Sun et al., 2010; Yang et al., 2013). Sorption processes are driven by forces or combinations of forces related to the bonding of the sorbing species to surfaces (enthalpy-related forces) and/or the lack of solvation of the solute in the solvent (entropy-related forces). Typical sorption-related interactions between OCs and soil include: van der Waals forces, electrostatic forces, π-bonding, hydrogen bonding, ligand exchange reactions, dipole-dipole interactions and chemisorptions (Gevao et al., 2000; Northcott and Jones, 2000). For apolar, nonionic, hydrophobic OCs, sorbate-sorbent interactions are relatively simple, in that sorption to soil is essentially driven by the hydrophobic effect. However, for highly polar organic compounds, sorbate-sorbent interactions are often more complex and both soil organic matter fraction and the clay mineral fraction of the soil can make significant contributions to sorption (Schwarzenbach et al., 2003; Zhang et al., 2014).

Most soil minerals, including Fe, Mn, Al (hydr)oxides, aluminosilicates (for example, allophane), clay-size layer silicates, and even primary minerals common in soil, possess catalytic properties and are able to mediate several OC transformations. For example, the surfaces of mineral colloids behave as Brönsted acids and have the ability to protonate many uncharged OCs, and thus favour their degradation reactions by surface acid catalysis. Mineral phases also contribute markedly to the complexity of biodegradation processes by surface adsorption of microorganisms, thus altering, and drastically reducing, their biological activity and mobility (Loffredo and Senesi, 2006).

The soil organic matter content (especially the HSs fraction) influences the adsorption of OCs in soil to a large extent (Xing, 2001; Gu et al., 2000; Sun et al., 2010). HSs possess favourable attributes (aromatic/heterocyclic polydispersed skeletons with chemically reactive functional groups; very reactive organic free radical moieties with high hydrophilicity/hydrophobicity and surface activity) which permit various interactions between them and OCs with important implications for contaminant biovailability and biotoxicity. For instance, HSs are shown to be able to: (i) modify the solubility of relatively water-insoluble, non-ionic OCs (for example, PAHs, PAEs, PCBs and *n*-alkanes), possibly by partitioning into or adsorption on HSs, or by an overall increase in solvency; (ii) exert catalytic activity in some OCs transformations and (iii) act as photosensitisers in promoting the photodegradation of some OCs (Loffredo and Senesi, 2006; Pignatello et al., 2010).

Adsorption and partitioning are probably the most important modes of interaction of OCs with HSs. The OCs can be adsorbed onto HSs through specific physical and chemical binding mechanisms and forces at varying degrees and strengths. These include ionic, hydrogen, and covalent bonding, charge-transfer or electron donor-acceptor mechanisms, dipole-dipole and van der Waals forces, ligand exchange and cation and water bridging (Gevao et al., 2000; Northcott and Jones, 2000). HSs can either "attenuate" or "facilitate" the migration of OCs in soil depending on whether the adsorption occurs on insoluble, immobile HSs such as humic acids, or on dissolved or suspended, mobile fractions such as fulvic acids. Important properties that influence adsorption/-desorption include: the molecular structure; the number and type of functional groups; the size, shape, and configuration; the polarity, polarisability, and charge distribution; solubility of both HSs and OCs; and the acidic or basic or neutral, ionic or nonionic nature of the OCs. The conditions of the medium, such as pH, ionic strength, redox potential and amount of water, will also greatly influence adsorption of OCs onto HSs in soil (Loffredo and Senesi, 2006; Zhang et al., 2014). Adsorption of non-polar (hydrophobic) OCs can be better described in terms of non-specific, hydrophobic, or partitioning processes between soil, water, and the HSs organic phase. The degree of chemical partitioning of hydrophobic OCs between water and HSs as well as their toxicity can be predicted by the compound-specific orga-
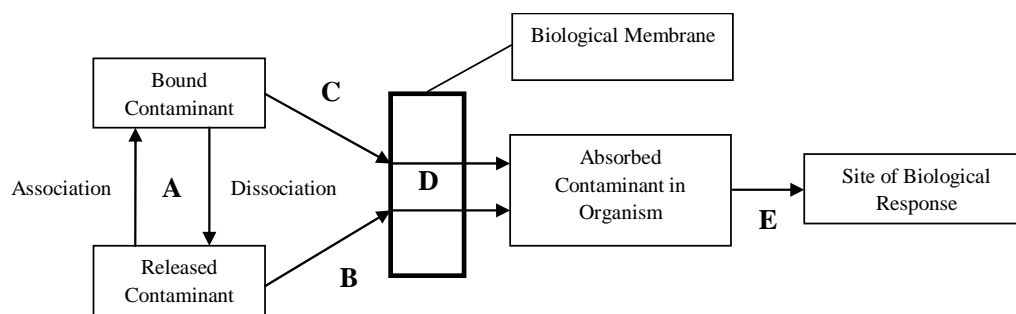
Figure 3. Bioavailability processes in soil (Ehlers and Luthy, 2003; NRC, 2003).

nic carbon normalised partition coefficient, K_{oc} (Schwarzenbach et al., 2003). The K_{oc} values for soils are largely consistent worldwide, such that K_{oc} values can serve as a sensor to assess the sorption of nonpolar OCs to the organic matter of different soils in order to save time and cost for contamination studies (Chiou and Kile, 2000). Several mechanisms of adsorption may operate simultaneously and/or in sequence for any given OC. Initially, the OC molecule may be adsorbed by HS sites providing the strongest binding (hard or glassy domain), followed by progressively weaker sites (soft or amorphous domain) as the stronger sites become filled. Once adsorbed, the OC may be subject to other processes (Loffredo and Senesi, 2006). From a toxicological perspective, binding of OCs to HS leads to: (i) a decrease of material available to interact with biota; (ii) a reduction in the toxicity of the compound; and (iii) immobilising the compound, thereby reducing its leaching and transport properties (Gevao et al., 2000). Hydrophobic partitioning is less important for polar/ionisable OCs because their retention is influenced by a complex set of physico-chemical processes, and so, it is difficult to generalise trends in their behaviour, however, their retention is more dependent on solution chemistry (especially pH and dissolved organic carbon) than is the case for nonpolar OCs (Peijnenburg and Vijver, 2007).

IMPLICATIONS OF MIXED CONTAMINANT INTERACTIONS FOR BIOAVAILABILITY, RISK ASSESSMENT AND SOIL REMEDIATION

Mixed contaminants in the form of HMs and OCs in soil may originate from diverse natural processes (soil parent material, windblown dusts, volcanic eruptions, marine aerosols, forest fires, microbial activity) and anthropogenic activities such as agriculture (fertilisers, biosolids and animal wastes used as amendments, pesticides and irrigation water); mining and smelting (metal tailings, smelting, refining and transportation); secondary metal production and recycling operations (melting of scrap, refining, plating alloying); urban-industrial complexes (incineration of wastes and waste disposal) and auto-

mobile emissions (combustion of petroleum fuels) and emissions from power stations (Reichman, 2002; Basta et al., 2005; Wuana and Okieimen, 2011; de Souza et al., 2013).

The mixed contaminants may eventually become bioavailable to both humans and ecological receptors when exposed to them (Naidu et al., 2010). Even though ill-defined, the bioavailable contaminant may be considered as the fraction of the contaminant's total amount that is freely available to cross an organism's cellular membrane from the medium (for example, soil) the organism inhabits at a given time (Semple et al., 2004; 2007). Bioavailability of HMs and OCs in soils can be examined using a wide variety of physical, chemical and biological techniques. A comprehensive review and evauation of these methods is provided in NRC (2003). It has been argued that the routine physico-chemical and biological techniques designed to measure the bioavailable fraction actually measure the bioaccessible fraction; defined as that which is available to cross an organism's cellular membrane from the environment, if the organism has access to the contaminant; however, it may be either physically removed from the organism or only bioavailable after a period of time (Semple et al., 2004, 2007). This methodological pitfall poses a big challenge for keying of bioavailability concept to the terrestrial regulatory framework (Naidu et al., 2010). However, it has been reasoned that measurement of the bioavailable fraction may be adopted for risk assessment purposes; while the bioaccessible fraction may be preferable when predicting remediation endpoints (Semple et al., 2007). The scheme of processes culminating in the bioavailability of contaminants in soil is illustrated in Figure 3. Figure 3A represents the release of a bound or recalcitrant contaminant to a more accessible form, B and C describe the transport of contaminant to a cellular membrane, and D represents the uptake of a contaminant across a cellular membrane (Ehlers and Luthy, 2003; NRC, 2003). Strictly speaking, process D addresses bioavailability, whereas processes A–D encompass bioaccessibility (Semple et al., 2004, 2007).

To have a physiological or toxic (hazardous) effect, the

bioavailable fraction of a contaminant has to enter the organism's cell. A risk may then be expressed as the product of contaminant toxicity (hazard) and an organism's exposure under certain doses (NEPI, 2000; Clothier et al., 2010). Knowledge of bioavailability is required for both human and ecological risk assessment to improve the accuracy of the overall risk assessment process and prioritise remedial options (Latawiec et al., 2010). In toxicity assessment, it is imperative to understand differences in contaminant bioavailability in actual populations versus a laboratory toxicity studies. Knowledge of variations in bioavailability of the contaminant in particular populations of plants and animals may also be needed to identify sensitive receptors in the population/-sub-populations (NEPI, 2000); since not all species are equally susceptible to toxicants due to differences in uptake-elimination kinetics, internal sequestering mechanisms, biotransformation rates, nature or presence of biochemical receptors, rate of receptor regeneration and efficiency of repair mechanisms (Semenzin et al., 2007). Even though the level of toxicity has been quan-tified for many contaminants, the challenge is to quantify better the exposure pathways (Clothier et al., 2010). In exposure assessment, knowledge of bioavailability is necessary if toxicity data from one route of exposure to a contaminant is extrapolated to another route of exposure. Even within the same exposure route, differences in bioavailability will occur when mixed contaminants are present in different soils (NEPI, 2000).

Due to the great differences between the environmental behaviour of HMs and OCs (for example, OCs are subject to various abiotic and biotic degradation processes; while HMs are essentially re-distributed among various pools in soil with varying bioavailability and toxicity), it is generally becoming accepted that risk assessments for HMs should be designed differently from those for OCs. Most risk-assessment approaches have been developed for synthetic OCs (Smith, 2007), so that, for the hydrophobic OCs, a general mechanism of their toxicity is the non-polar narcotic mode of action, and it is partitioning to organic phases (measured by the compound-specific K_{oc} values) that is predominantly modulating effects (Schwarzenbach et al., 2003; Peijnenburg and Vijver, 2007). Since K_{oc} values for soils are largely consistent worldwide, K_{oc} can serve as a cost-effective sensor to assess soil contamination by OCs (Chiou and Kile, 2000). In the case of HMs, Di Toro et al. (2001) proposed a generalised framework that linked metal speciation in solution, competition of cations for binding to and accumulation on physiologically active sites (biotic ligand, BL) and ensuing toxicity responses (US EPA, 1999; Santore et al., 2001) which culminated in the biotic ligand model (BLM).

The BLM is a mechanistic-based framework in which (i) metal speciation calculations are performed, (ii) metal-organic matter interactions are accounted for by WHAM-Model V and (iii) metal-BL interactions and resulting toxicity are established by relating critical levels of metal accumulation on the BL to dissolved metal median lethal concentration, LC50 or median lethal dose, LD50 (or other effect criteria) (Janssen et al., 2003). For mixtures of HMs and OCs in soils, any risk assessment approach must take into cognisance (i) contaminant heterogeneity across sites and interactions among co-contaminants/-toxicants/stressors, (ii) complexity of soil chemistry phenomena (sorption, partitioning, speciation) with attendant effects on bioavailability/toxicity, (iii) essentiality of some HMs (for example, Cr, Cu, Ni and Zn) for plants, and (iv) differences in physicochemical characteristics of soils (van Straalen, 2002; Hund-Rinke and Kordel, 2003; Lander and Reuther, 2004; McBride, 2007). Unfortunately, contemporary literature and environmental regulatory frameworks are based on single contaminant rather than mixture effects capable of reducing or enhancing contaminant toxicity due to antagonistic or synergistic processes (Naidu et al., 2010). It is possible that contaminant mixtures do influence local ecosystems, in a site-specific way defined by all aspects along the source (local mixture)-pathway (local availability)-receptor (local species types) line, with strong possible influences of other stressors (Posthuma et al., 2008). The presence of toxicant mixtures in the field has been implicated in the differences between laboratory and field based toxicity data (laboratory-to-field dilemma) (Naidu et al., 2010).

One of the main points to consider for mixed contaminants is whether contaminants interact and produce an increased or decreased overall response as compared to the expected sum of the effects if each contaminant acts independently of each other. The interactions between different contaminants in a mixture may result in either a weaker (antagonistic) or a stronger (synergistic, potentiated) combined effect than the additive effect that would be expected from knowledge on the toxicity and mode of action of each individual compound. Interactions may take place in the toxicokinetic phase (processes of uptake, distribution, metabolism and excretion) or in the toxicodynamic phase (effects of contaminants on the receptor, cellular target or organ) (VKM, 2008; IGHRC, 2009). An additive effect occurs when the combined effect of two contaminants corresponds to the sum of the effects of each contaminant given alone.

An antagonistic effect occurs when the combined effect of two contaminants is less than the sum of the effects of each contaminant given alone (this phenomenon is well known for substances competing for the same hormonal or enzymatic receptor sites). A synergistic effect occurs when the combined effect of two contaminants is greater than the sum of the effects of each contaminant given alone (for example, the result of increased induction of metabolising enzymes when the effect is due to a metabolite).

Potentiation occurs when the toxicity of a contaminant

on a certain tissue or organ system is enhanced when given together with another contaminant that alone does not have toxic effects on the same tissue or organ system (for example, carbon tetrachloride toxicity to the liver is enhanced with isopropanol) (VKM, 2008; IGHRC, 2009). For the purpose of evaluating mixtures effects, risk assessors commonly use two simplifying toxicological models: (i) concentration addition and (ii) independent action, based on the concentration response curve of individual contaminants (VKM, 2008; Liu et al., 2013a). These models are used to classify the combined effects of contaminant mixtures as being antagonistic, additive and synergistic (also referred to as "less than additive", "strictly additive", and "more than additive", respectively). Both models use contaminant concentrations in media (soil/organism) to generate concentration-response curves for individual contaminants, and these data are then used to generate specific critical concentrations for mixture models.

In the concentration addition model, all contaminants in a mixture are added together to predict toxicity; differing potencies are taken into account by converting chemical concentrations to an equitoxic dose, such as toxic units (TUs) or toxicity equivalence factors (TEFs), which convert all contaminants to one concentration. Concentration addition is often used when the constituents are known or assumed to act through the same or similar mode of toxic action. In the effects addition model, differing potencies are ignored, and the effect of each contaminant's concentration in a mixture is combined to predict mixture toxicity.

The effects addition model is used when constituents act or are assumed to act independently (different modes of action) (NEPC-EPHC, 2003; Peijnenburg and Vijver, 2007). A unifying hypothesis of mixture toxicity- the funnel hypothesis states that as the number of components in mixtures increases there is an increased tendency for the toxicity to be additive. Conversely, as the number of components decreases the tendency is for the toxicity of mixtures to increasingly deviate from additivity (NEPC-EPHC, 2003).

Consequently, a second-order polynomial model describing the effect of the different independent contaminant concentrations on toxicity can be expressed as:

$$Y = \beta_o + \sum_{i=1}^{m} \beta_i X_i + \sum_{i<j} \beta_{ij} X_i X_j + \varepsilon$$

(1)

Where, Y is the predicted response parameter, X is the independent variable corresponding to the concentration of the different contaminants in the mixture, and β is the regression coefficients estimated by the stepwise regression method (Shen et al., 2006).

Metal-metal interactions

Mixtures of HMs metals are commonly encountered in soil environments due to the wide range of soil characteristics and various forms by which HMs can be added to soil. In typical soil solution, there may be 10 - 20 different metal cations that can react with as many different inorganic and organic ligands to form 300 to 400 soluble complexes and up to 80 solid phases (Thavamani et al., 2011a). Naturally, HMs occurs in specific mineralogical associations in soil due to chemical and physical similarities of various elements. For instance, Zn ores contain significant amounts of Pb and Cd, while As is often associated with Au or Cu ores, such that one element by itself is rarely the source of contamination (Naidu et al., 2010; Zovko and Romić, 2012). Additionally, many divalent metal cations (for example, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) are structurally very similar and the tetrahedral structures of oxyanions such as CrO_4^{2-} and AsO_4^{3-} resemble those of SO_4^{2-} and PO_4^{3-}, respectively (de Souza et al., 2013; Olaniran et al., 2013). Due to their structural similarities, competitive interactions occur between HMs which can strongly affect their sorption onto soil solid surfaces.

Fontes et al. (2000) and Fontes and Gomes (2003) found that competition strongly influences the adsorptive capacity and mobility of metals, modifying the fitting of adsorption models. In general, the Langmuir model gives the best fit to adsorption data. Gomes et al. (2001) reported a Cr > Pb > Cu > Cd > Zn > Ni selectivity sequences. Fontes and Gomes (2003) found that in competitive adsorption some metals such as Cr, Cu, and Pb maintain their strong affinity with the surface, while others such as Ni, Zn and Cd were displaced from the surface. Competitive sorption isotherms of Cd, Cu, Ni, Pb and Zn as a function of pH for two soils, revealed that competition was enhanced as the initial metal concentration increased with approximate sequence of metal affinity for both soils being: Pb > Cu > Ni ≥ Cd ≈ Zn (Basta and Tabatabai, 1992). The competitive sorption of Cd, Cu, Ni, Pb and Zn on three soils studied through fractional factorial design confirmed that the presence of the competing cations reduced the amount of the five metals retained, but the presence of Cu and Pb in the system depressed Ni, Cd and Zn sorption more than the inverse (Echeverría et al., 1998). Markiewicz-Patkowska et al. (2005) also observed that the adsorption of Cd, Cu, Cr, Pb and Zn on a sandy loam was more effective in the single-element than under multi-element conditions due to competitive effects. Multi-element adsorption processes in soils can be described most conveniently using the Freundlich and Langmuir multi-component models (Goldberg, 2005).

It has been demonstrated that competitive interactions between HMs may either increase or decrease significantly the level of each other depending on whether the

interactions are synergistic or antagonistic. Syner-gism implies that increasing the level of one of the interacting element increases the level of the other (more than additive), while antagonism implies the converse (less than additive). Synergism particularly may have serious implications in the context of HMs contami-nation since it may increase the level and bioavailability of toxic elements, thereby affecting risk assessment and reme-diation endpoints (Kalavrouziotis et al., 2009).

Investigations of forty binary interactions of Cd, Pb, Ni, Cu, Zn and Co in soil revealed either 'one-way' or 'two-way' synergistic metal-metal interactions. A 'one-way' synergistic interaction implies that only the increase or decrease of one of the interacting elements increases or decreases the level of the other one; whereas a 'two-way' synergistic interactions means that an increase in the level of one of the interacting elements results in the increase of the other, and vice versa (Kalavrouziotis et al., 2008; Kalavrouziotis et al., 2009). The presence of co-contaminants (Cr, Cd, Ni) in kaolin and glacial till retarded the electrokinetic migration and removal of Ni and Cr in both soils due to synergistic increase in the concentration of ions in the system (Reddy et al., 2001). In soils receiving various single or mixed (binary, ternary, quartenary, quinternary and sexternary) treatments of Ni, Zn, Cu, Pb, Cd, Cr, NiZn, NiCu, NiPb, NiCd, NiCr, NiZnCu, NiZnPb, NiZnCd, NiZnCr, NiZnCuPb, NiZnCuCd, NiZnCuCr, NiZnCuPbCd, NiZnCuPbCr, NiZnCuPbCdCr; Wyszkowska et al. (2007) noted significant decreases in oat yield and growth inhibition of *Azotobacter* spp. upon concurrent metal application. The greatest changes in oat yield occurred when Cr was applied alone, and with Ni applied in combination with two other metals (ternary mixtures), especially when oat was grown on lighter soil. An inverse relationship has also been reported between the level of mixed metal (Pb, Zn, Cd, Ni, Mn, Cu, Cr, Co and V) contamination in community soils and school children performance in standardised tests, implying the synergistic nature of the metal-metal interactions (Zahran et al., 2012).

At the soil solution-(biological) membrane interface, the reduction in the bioavailability of undesirable HMs through competition with high concentrations of compe-ting ions may be beneficial to crop quality but has negative implications for phytoremediation. For instance, at the root interface, inhibition of uptake of one HM another in the presence of competing cations (e.g., Ni, Cu, and Zn) has been reported (Clarkson and Luttge, 1989). There also exists, evidence of an antagonistic interaction between Zn and Cd, with Zn additions to Zn-deficient soil leading to a reduction in the Cd content of wheat and young lettuce and spinach leaves (Oliver et al., 1999), young lettuce and spinach leaves (McKenna et al., 1993) and tomato plants (Mohammad et al., 2009). Cadmium and Zn appear to compete for certain organic ligands *in vivo*, Cd competes with Zn in forming protein

complexes through antagonistic association between the two metals (Thavamani et al., 2011a).

Metal-organic contaminant interactions

In co-contaminated soils, the transport of HMs may be enhanced in the presence of OCs due to: (i) facilitated transport caused by metal association with mobile colloidal size particles, (ii) formation of metal organic and inorganic complexes that do not adsorb to soil solid surfaces, (iii) competition with other constituents of waste, both organic and inorganic, for sorption sites, and (iv) decreased availability of surface sites caused by the presence of a complex waste matrix (Puls et al., 1991). For the OCs, microorganisms use them either as carbon source or transform them into nontoxic products with the assistance of various enzymes and extracellular products; however, the presence of HMs interferes with the microbial processes both physically and metabolically and may inhibit the biodegradation of OCs (Thavamani et al., 2011a). Metal toxicity depends on the bioavailable concentration and not necessarily the total metal content. It has been suggested that, typically, strongly complexed metals are less toxic to organisms than weakly complexed forms, which in turn, are less toxic to organisms than the free ions (Adriano, 2003). However, information on the concentrations of available as well as free metal species capable of inhibiting biodegradation is not available (Thavamani et al., 2011a). The development of techniques capable of reliably predicting the bioavailability of OCs to catabolically active soil microorganisms is required for predicting bioremediation rates and endpoints (Semple et al., 2007).

The presence of high concentrations of some metals can impact on the mobility and accessibility of PAHs in soil, with negative implications for the risk assessment and remediation of PAH contaminated soil. For instance, Obuekwe and Semple (2013) considered the effects of Zn, Cu, Al and Fe (50 and 500 mg kg^{-1}) on the loss, sequential extractability (using various extractants), and biodegradation of ^{14}C-phenanthrene in soil over 63 day contact time and noted that the presence of Cu and Al (500 mg kg^{-1}) resulted in larger amounts of ^{14}C-phenanthrene being extracted. The amounts extracted directly predicted the biodegradation of the PAH in the presence of the metals, with the exception of 500 mg kg^{-1} Cu and Zn. Shen et al. (2006) also studied the combined effect of different levels of concentrations of HMs (Cd, Zn, Pb) and PAHs (phenanthrene, fluoranthene and benzo(*a*)pyrene) toward soil urease activity at different days of exposure (7-28 days) under controlled conditions and noted that the toxicity of HMs on urease activity decreased in the order Cd > Zn > Pb during the whole incubation time. Zinc interacted more easily with PAHs than Pb or Cd such that at 14 days, the interaction between Zn and phenanthrene was antagonistic, while at

21 days it was synergistic. At 28 days, the interaction between phenanthrene and fluoranthene was synergistic.

The magnitude and type of combined effects depend not only on the components but also on the concentrations of mixtures and incubation time. Zn is a major competitor for Cd and Pb sorption sites. Therefore, Cd and Pb can trigger the release of Zn to soil solution and enhance the bioavailability of zinc. The interaction between Zn and other pollutants may occur more easily than Pb and Cd (Shen et al. 2006).The complexation ability of an OC and divalent metal cations is necessary when evaluating their mobility in soils. The cosorption behaviour of tetracycline and HM ions onto three selected Chinese soils evaluated using batch adsorption experiments indicated that the presence of HM cations promoted tetracycline adsorption through an ion bridging effect in the order Cu (II) > Pb (II) > Cd (II), which is in accordance with their complexation ability with tetracycline. The addition of tetracycline affected metal adsorption differently depending on the solution pH and metal type (Zhao et al., 2013).Lin et al. (2006) reported that in soils co-contaminated with increasing doses (0 – 300 $mgkg^{-1}$), of Cu and pentachlorophenol (PCP), both plant growth and microbial activity were inhibited at higher Cu and PCP concentrations. In soil with the initial PCP concentration of 50 $mgkg^{-1}$, plants grew better with the increment of soil Cu level (0, 150 and 300 $mgkg^{-1}$), implying that combinations of inorganic and organic pollutants sometimes exerted antagonistic toxic effects on plant growth. The observed higher PCP dissipation in soil spiked with 50 $mgkg^{-1}$ PCP in the presence of Cu and the less difference of PCP residual between strongly and loosely adhering soils further suggests the occurrence of Cu-PCP interaction the enhanced degradation and mass flow are two possible explanations. In copper co-contaminated soil with the initial PCP concentration of 100 $mgkg^{-1}$, however, both plant growth and the microbial activity were inhibited with the increment of soil Cu level. The lowered degrading activity of microorganisms and the reduced mass flow were probably responsible for the significantly lower levels of PCP dissipation in copper co-contaminated soil (Lin et al., 2006).A negative effect of Cu-pyrene co-contamination on shoot and root dry matter and an inhibition of copper phytoextraction by *Brassica juncea* has also been reported (Chigbo et al., 2013) in which the level of pyrene was significantly decreased in planted and non-planted soils accounting for 90-94% of initial extractable concentration in soil planted with *B. juncea* and 79-84% in non-planted soil which shows that the dissipation of pyrene was enhanced with planting. Lin et al. (2008) also noted that increments of Cu level increased the residual pyrene in the planted soil, suggesting that the change of the microbial composition and microbial activity or the modified root physiology under Cu stress was unbeneficial to the dissipation of pyrene. The inhibition of Cu phytoextraction and degra-

dation of pyrene under co-contamination may reduce the viability of phytoremediation in sites containing multiple pollutants (Chigbo et al., 2013).

Organic-organic contaminant interactions

In soils containing mixtures of OCs, competitive displacement processes between OCs may reverse their sequestration in soil during which a competing OC displaces the adsorbed OC into solution, taking its place in the soil matrix with attendant release of the formerly unavailable OC to the environment (Xing et al., 1996). The presence of mixed OCs may affect the sorption/-desorption rates and the equilibrium concentration of the primary contaminant (White and Pignatello, 1999) and this may negatively impact OC transport predictions and soil remediation efforts in soils manifesting nonlinear sorption behaviour (McGinley et al., 1993). The effectiveness of a competitor in displacing a primary contaminant might be related to the physicochemical properties of the competitor. Just as for HMs, structurally similar OC molecules have been shown to display a stronger competitive effect because their interchangeability within the pore structure exhibits the greatest overlap (Ju and Young, 2004; Faria and Young, 2010). Xing and Pignatello (1998) reported the existence of competitive sorption between OCs and aromatic acids; implying that naturally occurring compounds may be capable of increasing the mobility and bioavailability of anthropogenic OCs. Faria and Young (2010) assessed the competitive effect for binary systems of 1,2-dichlorobenzene and other chlorobenzenes, by comparing the ability of each competitor to reduce sorption of the primary solute by measuring K_{OC}; while a measure of competitor uptake was given by the volume of competitor in the solid phase (cm^3/kg organic carbon) at equilibrium. Results indicated that competitors with structural properties closer to those of the primary contaminant had a competitive behaviour similar to that of primary contaminant itself (Ju and Young, 2004; Faria and Young, 2010).

The competitive effects of 1,2,4-trichlorobenzene (1,2,4-TCB) and tetrachloroethene (TCE) on the sorption of 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB) by three soils/sediments from South China with different fractions of natural organic matter showed that cosolutes 1,2,4-TCB and TCE exhibited apparent competition against 1,2,4,5-TeCB in all the three soils. 1,2,4-TCB was a more effective competitor than TCE because the structure of 1,2,4-TCB is very close to that of 1,2,4,5-TeCB. Furthermore, the extent of competition depended on the rigidity of soil natural organic matter matrices (Shu et al., 2013; Baderna et al., 2013).

Couling et al. (2010) compared single- and multiple mixture systems of three ^{14}C-PAHs (naphthalene, phenanthrene and pyrene) and found that the presence of all three PAHs caused statistically significant

differences in the various biodegradation parameters (lag phases, maximum rates and cumulative extents of mineralisation). Any differences observed between the two systems often increased as the soil-contaminant contact time increased.

CONCLUSION

A majority of contaminated sites in the world contain complex mixtures of HMs and OCs from diverse natural processes and anthropogenic activities. In the soil, OCs are subject to various biotic and abiotic degradation processes, while HMs are essentially re-distributed in various pools with varying mobility, bioavailability and toxicity. Contemporary approaches aimed at the effective characterisation of co-contaminated sites for risk assessment, remedial and regulatory purposes are frequently challenged by knowledge gaps in contaminant bioavailability coupled with mixed contaminant effects. Mixed contaminant effects arise from the synergistic or antagonistic interactions of the contaminants and are site-soil-waste specific. Since, evaluation of contaminant bioavailability is a necessary component of the overall assessment of a site for establishing either bioavailability based or risk-based, site-specific remedial options, understanding mixed contaminant interactions at the elemental and molecular levels is imperative, not only to explain the underlying mechanisms controlling the fate and transport of these contaminants in soils, but also predict their bioavailability, ecotoxicological effects on natural communities under realistic exposure conditions and remediation endpoints. This would help push back the frontiers of this aspect of environmental science which is currently dominated by investigations of single contaminant effects and exposure.

Conflict of Interests

Authors have declared that there are no competing interests, neither are they foreseen.

REFERENCES

Abd-Elfattah A, Wada K (1981). Adsorption of lead, copper, zinc, cobalt, and cadmium by soils that differ in cation-exchange materials. J. Soil Sci. 32(2):273-283.

Adriano DC, Bolan NS, Koo B-J, Naidu R, Lelie D, Vangronsveld J, Wenzel WW (2002). Natural remediation processes: Bioavailability interactions in contaminated soils, Proceedings of 17th WCSS 14 – 21 August, 2002, Thailand, pp. 501-1 – 501-12

Adriano DC (2003). Trace Elements in the Terrestrial Environments: Biogeochemistry, Bioavailability, and Risks of Heavy Metals. (2nd ed.) Springer-Verlag, New York.

Alexander M (1999). Biodegradation and Bioremediation (2nd ed.), Academic Press, San Diego.

Amor L, Kennes C, Veiga MC (2001). Kinetics of inhibition in the biodegradation of monoaromatic hydrocarbons in presence of heavy metals. Bioresour. Technol. 78(2): 181-185.

Atagana HI (2011). Bioremediation of co-contamination of crude oil and heavy metals in soil by phytoremediation using *Chromolaena odorata* (L) King & H.E. Robinson. Water Air Soil Pollut. 215(1-4):261-271.

Baderna D, Colombo A, Amodei G, Cantù S, Teoldi F, Cambria F, Rotella G, Natolino F, Lodi M, Benfenati E (2013). Chemical-based risk assessment and in vitro models of human health effects induced by organic pollutants in soils from the Olona valley. Sci. Total. Environ. 463-464:790-801.

Basta NT, Ryan JA, Chaney RL (2005). Trace element chemistry in residual-treated soil: Key concepts and metal bioavailability. J. Environ. Qual. 34(1):49-63.

Basta NT, Tabatabai MA (1992). Effect of cropping systems on adsorption of metals by soils: III. Competitive adsorption. Soil Science 153:331-337.

Beck AJ, Wilson SC, Alcock RE, Jones KC (2009). Kinetic constraints on the loss of organic chemicals from contaminated soils: Implications for soil-quality limits. Crit. Rev. Environ. Sci. Technol. 25(1):1-43.

Bertsch PM, Seaman JC (1999). Characterization of complex mineral assemblages: Implications for contaminant transport and environmental remediation. Proc. Natl. Acad. Sci. USA 96:3350-3357.

Bolan NS, Adriano DC, Mani P, Duraisamy A, Arulmozhiselvan S (2003a). Immobilization and phytoavailability of cadmium in variable charge soils: I. Effect of phosphate addition. Plant and Soil 250(1):83-94.

Bolan NS, Adriano DC, Natesan R, Koo BJ (2003b). Effects of organic amendments on the phytoavailability of chromate in mineral soil. J. Environ. Qual. 32(1):120-128.

Bolan N, Naidu R, Choppala G, Park J, Mora ML, Budianta D, Panneerselvam P (2010). Solute interactions in soils in relation to the bioavailability and environmental remediation of heavy metals and metalloids. Pedologist. pp. 1-18.

Braschi I, Gessa CE, Blasioli S (2011). The Fate of Herbicides in Soil, Herbicides and Environment. In: Kortekamp, A. (Ed.) Herbicides and Environment, InTech, China, pp. 175-194.

Buekers J (2007). Fixation of cadmium, copper, nickel and zinc in soil: kinetics, mechanisms and its effect on metal bioavailability. Ph.D. Thesis, Katholieke Universiteit Lueven, Dissertationes De Agricultura, Doctoraatsprooefschrift nr.

Cabrera G, Pérez R, Gómez JM, Ábalos A, Cantero D (2006). Toxic effects of dissolved heavy metals on *Desulfovibrio vulgaris* and *Desulfovibrio* sp. Strain. J. Hazard. Mater. 135:40-46.

Cazanga M, Gutierrez M, Escudey M, Galindo G, Reyes A, Chang AC (2008). Adsorption isotherms of copper, lead, nickel, and zinc in two Chilean soils in single- and multi-component systems: sewage sludge impact on the adsorption isotherms of Diguillin soil. Aust. J. Soil Res. 46:53-61.

Cernansky S, Kolencik M, Sevc J, Urik M, Hiller E (2009). Fungal volatilization of trivalent and pentavalent arsenic under laboratory conditions. Bioresour. Technol. 100(3):1037-1040.

Chapman PM (2002). Integrating toxicology and benthic ecology: Putting the "eco" back into ecotoxicology. Marine Pollut. Bull. 44:7-15.

Chekol T, Vough LR, Chaney RL (2002). Plant-soil-contaminant specificity affects phytoremediation of organic contaminants. Intern. J. Phytoremediation 4(1):17-26.

Chigbo C, Batty L, Bartlett R (2013). Interactions of copper and pyrene on phytoremediation potential of *Brassica juncea* in copper-pyrene co-contaminated soil. Chemosphere 90(10):2542-2548.

Chiou CT, Kile DE (2000). Contaminant sorption by soil and bed sediment, Is There a Difference. US Geological Survey (Science for a Changing World), Fact Sheet-087-00.

Clarke BO, Smith SR (2011). Review of 'emerging' organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids. Environ. Int. 37(1):226-247.

Clarkson DT, Luttge U (1989). Mineral nutrition: divalent cations, transport and compartmentation. Progress in Botany 51:93-112.

Clothier B, Green S, Deurer M, Smith E, Robinson B (2010). Transport and fate of contaminants in soils: challenges and developments. Proceedings of the 2010 19th World Congress of Soil Science, Soil Solutions for a Changing World, 1 - 6 August 2010, Brisbane, Australia. pp.73-76.

Couling NR, Towell MG, Semple KT (2010). Biodegradation of PAHs in soil: Influence of chemical structure, concentration and multiple amendment. Environ. Pollut. 158(11): 3411-3420.

D'amore JJ, Al-abed SR, Scheckel KG, Ryan JA (2005). Methods of speciation of metals in soils. J. Environ. Qual. 34(5):1707-1745.

de Souza RB, Maziviero TG, Christofoletti CA, Pinheiro TG, Fontanetti CS (2013). Soil Contamination with Heavy Metals and Petroleum Derivates: Impact on Edaphic Fauna and Remediation Strategies. In: Soil Processes and Current Trends in Quality Assessment. InTech, China. pp. 175-203.

Dec J, Bollag J-M, Huang PM, Senesi N (2002). Interactions Between Soil Particles and Microorganisms. John Wiley, New York.

Di Toro DM, Allen HE, Bergman HL, Meyer JS, Paquin PR, Santore RC (2001). Biotic ligand model of the acute toxicity of metals: I. Technical basis. Environ. Toxicol. Chem. 20: 2383-2396.

Dube A, Zbytniewski R, Kowalkowski T, Cukrowska E, Buszewski B (2001). Adsorption and migration of heavy metals in soil. Polish J. Environ. Stud. 10(1):1-10.

Echeverría JC, Morera MT, Mazkiarin C, Garrido JJ (1998). Competitive sorption of heavy metal by soils. Isotherms and fractional factorial experiments. Environ. Pollut. 101(2):275-284.

Ehlers LJ, Luthy RG (2003). Contaminant bioavailability in soil and sediment. Improving risk assessment and remediation rests on better understanding of bioavailability. Environ. Sci. Technol. 302 A.

Erdogan S, Baysal A, Akba O, Hamamci C (2007). Interaction of metals with humic acid isolated from oxidized coal. Polish J. Environ. Stud. 16(5):671-675.

Essington ME (2004). Soil and Water Chemistry: An Integrative Approach. CRC Press, Boca Raton, FL.

Faria IR, Young TM (2010). Modeling and predicting competitive sorption of organic compounds in soil. Environ. Toxicol. Chem. 29(12):2676-2684.

Filgueiras AV, Lavilla I, Bendicho C (2002). Chemical sequential extraction for metal partitioning in environmental solid samples. J. Environ. Monitor. 4:823-857.

Fontes MPF, Matos AT, Costa LM, Neves JCL (2000). Competitive adsorption of zinc, cadmium, copper and lead in the three highly weathered Brazilian soils. Commun. Soil Sci. Plant Anal. 31(17-18)2939-2958.

Fontes MPF, Gomes PC (2003). Simultaneous competitive adsorption of heavy metals by the mineral matrix of tropical soils. Appl. Geochem. 18(6):795-804.

Gevao B, Semple KT, Jones KC (2000). Bound pesticide residues in soils: a review. Environ. Pollut. 108(1):3-14.

Gismera MJ, Lacal J, da Silver P, Garcia R, Sevilla MT, Procopio JR (2004). Study of metal fractionation in river sediments. A comparison between kinetic and sequential extraction procedures. Environ. Pollut. 127(2):175-182.

Goldberg S (2005). Equations and Models Describing Adsorption Processes in Soils. In: Chemical Processes in Soils, Soil Science Society of America, SSSA Book Series, No 8, pp. 489-517.

Gomes PC, Fontes MPF, Silva AG, Mendon¸ca ES, Netto AR (2001). Selectivity sequence and competitive adsorption of heavy metals by Brazilian soils. Soil Sci. Soc. America J. 65(4):1115-1121.

Gu B, Chen J, Vairavamurthy MA, Choi S, Tratnyek PG (2000). Chemical and biological reduction of contaminant metals by natural organic matter. Symposium on "Chemical-Biological Interactions in Contaminant Fate", the 220th American Chemical Society National Meeting, 20-25 August 2000, Washington, DC.

Hajdu R, Slaveykova VI (2012). Cd and Pb removal from contaminated environment by metal resistant bacterium Cupriavidus metallidurans CH34: importance of the complexation and competition effects. Environ. Chem. 9:389-398.

He YT, Hering JG (2009). Enhancement of arsenic (III) sequestration by manganese oxides in the presence of iron(II). Water Air Soil Pollut.

203:359-368.

Hettiarachchi GM, Ryan JA, Chaney RL, LaFleur CM (2003). Sorption and desorption of cadmium by different fractions of biosolids-amended soils. J. Environ. Qual. 32(5):1684-1693.

Hlavay J, Prohaska T, Weisz M, Wenzel WW, Stingeder GJ (2004). Determination of trace elements bound to soils and sediment fractions. Pure Appl. Chem. 76(2):415-442.

Hoffman DR, Okan JL, Sandrin TR (2005). Medium composition affects the degree and pattern of cadmium inhibition of naphthalene biodegradation. Chemosphere 59(7):919-927.

Hund-Rinke K, Kordel W (2003). Underlying issues in bioaccessibility and bioavailability: experimental methods. Ecotox. Environ. Safety 56:52-62.

Hwang H-M, McArthur N, Ochs C, Libman B (2005). Assessing interactions of multiple agrichemicals by using bacterial assemblages in a wetland mesocosm system. Int. J. Environ. Res. Public Health 2(2):328-334.

IGHRC, Interdepartmental Group on Health Risks from Chemicals (2009) Chemical Mixtures: A Framework for Assessing Risk to Human Health (CR14). Institute of Environment and Health, Cranfield University, UK.

James BR, Bartlett RJ (1983). Behavior of chromium in soils: VII. Adsorption and reduction of hexavalent forms. J. Environ. Qual. 12(2):177-181.

Janssen CR, Heijerick DG, De Schamphelaere KAC, Allen HE (2003). Environmental risk assessment of metals: tools for incorporating bioavailability. Environ. Int. 28:793-800.

Ju DY, Young TM (2004). Effects of competitor and natural organic matter characteristics on the equilibrium sorption of 1,2-dichlorobenzene in soil and shale. Environ. Sci. Technol. 38:5863-5870.

Kabala C, Singh BR (2001). Fractionation and mobility of copper, lead and zinc in soil profiles in the vicinity of a copper smelter. J. Environ. Qual. 30:485-492.

Kalavrouziotis IK, Koukoulakis PH, Robolas PK, Papadopoulos AH, Pantazis V (2008). Essential plant nutrients interactions in a soil cropped with Brassica oleracea var. Italica, irrigated with treated municipal wastewater, and their environmental implications. Fresenius Environ. Bull. 17(9a):1272-1280.

Kalavrouziotis IK, Koukoulakis PH, Papadopoulos AH (2009). Heavy metal interrelationships in soil in the presence of treated waste water. Global NEST Journal 11(4):497-509.

Khan FI, Husain T, Hejazi R (2004). An overview and analysis of site remediation technologies. J. Environ. Mgt. 71:95-122.

Laha S, Tansel B, Ussawarujikulchai A (2009). Surfactant-soil interactions during surfactant-amended remediation of contaminated soils by hydrophobic organic compounds: A review. J. Environ. Mgt. 90:95-100.

Lai H, Chen, Z (2005). The EDTA effect on phytoextraction of single and combined metals-contaminated soil, using rainbow pink (Dianthus chinensis), Chemosphere 60:1062-1071

Lake DL, Kirk PW, Lester JN (1984). Fractionation, characterization, and speciation of heavy metals in sewage sludge and sludge-amended soils: A review. J. Environ. Qual. 13:175-183.

Lander L, Reuther R (2004). Environmental Pollution. Metals in Society and in the Environment: A critical review of current knowledge on fluxes, speciation, bioavailability and risk for adverse effects of copper, chromium, nickel and zinc. Kluwer Academic Publishers.

Latawiec AE, Simmons P, Reid BJ (2010). Decision-makers' perspectives on the use of bioaccessibility for risk-based regulation of contaminated land. Environ. Int. 36:383-389.

Leal RMP, Alleoni LRF, Tornisielo VL, Regitano JB (2013). Sorption of fluoroquinolones and sulfonamides in 13 Brazilian soils. Chemosphere 92(8):979-985.

Lin Q, Wang ZW, Ma M, Chen YX (2006). Evaluation of dissipation mechanisms by Lolium perenne L, and Raphanus sativus for pentachlorophenol (PCP) in copper co-contaminated soil. Sci. Total Environ. 368:814-822.

Lin QI, Shen K, Zhao H, Li W (2008). Growth response of Zea mays L. in pyrene-copper co-contaminated soil and the fate of the pollutants.

J. Hazard. Mater. 150:515-521.

Lindsay WI (2001). Chemical Equilibria in Soils, The Blackburn Press. Caldwell, New Jersey.

Liu S, Wang C, Zhang J, Zhu X, Li W (2013a). Combined toxicity of pesticide mixtures on green algae and photobacteria. Ecotoxicol. Environ. Saf. 95:98-103.

Liu H, Zhang D, Li M, Tong L, Feng L (2013b). Competitive adsorption and transport of phthalate esters in the clay layer of JiangHan plain, China. Chemosphere 92(11):1542-1549.

Loffredo E, Senesi N (2006). Fate of anthropogenic organic pollutants in soils with emphasis on adsorption/desorption processes of endocrine disruptor compounds. Pure Appl. Chem. 78(5):947-961.

López A, Lázaro N, Priego JM, Marqués AM (2000). Effect of pH on the adsorption of nickel and other heavy metals by *Pseudomonas fluorescens* 4F39. J. Ind. Microbiol. Biotechnol. 24(2):146-151.

Ma LQ, Rao GN (1997). Chemical fractionation of cadmium, copper, nickel and zinc in contaminated soils. J. Environ. Qual. 26(1):259-264.

Mackay D, Fraser A (2000). Bioaccumulation of persistent organic chemicals: mechanisms and models. Environ. Pollut. 110(3):375-391.

Maiz I, Arambarri I, Garcia R, Millán E (2000). Evaluation of heavy metal availability in polluted soils by two sequential extraction procedures using factor analysis. Environ. Pollut. 110(1):3-9.

Markiewicz-Patkowska J, Hursthouse A, Przybyla-Kij H (2005). The interaction of heavy metals with urban soils: sorption behaviour of Cd, Cu, Cr, Pb and Zn with a typical mixed brownfield deposit. Environ. Int. 31(4):513-521.

Mattina MI, Lannucci-Berger W, Musante C, White JC (2003). Concurrent uptake of heavy metals and persistent organic pollutants from soil. Environ. Pollut. 124(3):375-378.

Mattsson A, Lundstedt S, Stenius U (2009). Exposure of HepG2 cells to low levels of PAH-containing extracts from contaminated soils results in unpredictable genotoxic stress responses. Environ. Mol. Mutagen 50(4):337-348.

McBride TJ (2007). Influence of Metal Mixtures on Co-occurring Toxic Metal Bioavailability and Effects in Adult and Developing Deer Mice. PhD Dissertation, Texas Tech University.

McGeer J, Henningsen G, Lanno R, Fisher N, Sappington K, Drexler J, Beringer M (2004). Issue Paper on the Bioavailability and Bioaccumulation of Metals. U.S. Environmental Protection Agency Risk Assessment Forum 1200 Pennsylvania Avenue, NW, Washington, DC 20460.

McGinley PM, Katz LE, Weber WJ (1993). A distributed reactivity model for sorption by soils and sediments. 2. Multicomponent systems and competitive effects. Environ. Sci. Technol. 27:1524-1531.

McGrath SP, Semple KT (2010). Bioavailability of metals and organic contaminants in soils. Proceedings of the 19th World Congress of Soil Science, Soil Solutions for a Changing World, 1 – 6 August 2010, Brisbane, Australia.

McKenna IM, Chaney RL, Williams FM (1993). The effects of cadmium and zinc interactions on the accumulation and tissue distribution of zinc and cadmium in lettuce and spinach. Environ. Pollut. 79(2):113-120.

Megharaj M, Ramakrishnan B, Venkateswarlu K, Sethunathan N, Naidu R (2012). Bioremediation approaches for organic pollutants: A critical perspective. Environ. Int. 37(8):1362-1375.

Mohammad A, Moheman A, Seema (2009). The influence of single and multiple soil contamination of cadmium with lead and zinc on growth, chlorophyll contents, uptake and translocation of cadmium in tomato plants. Archives Agron. Soil Sci. 55(4):407-413.

Morelis S, van den Heuvel H, van Noort PCM (2007). Competition between phenanthrene, chrysene, and 2,5-dichlorobiphenyl for high-energy adsorption sites in a sediment. Chemosphere 68(11):2028-2032.

Morera MT, Echeverría JC, Mazkiarán C, Garrido JJ (2001). Isotherms and sequential extraction procedures for evaluating sorption and distribution of heavy metals in soils. Environ. Pollut. 113(2):135-144.

Naidu R, Wong MH (2013). Contaminants of emerging concern. Sci. Total Environ. 463-464:1077-1078.

Naidu R, Bolan N, Megharaj M, Juhasz A, Lombi E, Smith E (2010).

Human and ecological risk assessment of contaminated sites – Key knowledge gaps. 2010 19th World Congress of Soil Science, Soil Solutions for a Changing World, 1 – 6 August 2010, Brisbane, Australia.

NEPC-EPHC, National Environment Protection Council Service Corporation and Environment Protection and Heritage Council (2008). A Review of the Ecotoxicity of Mixtures, Approaches to, and Recommendations for, their Management, Proceedings of the Fifth National Workshop on the Assessment of Site Contamination, Adelaide, SA.

NEPI, National Environmental Policy Institute (2000). Assessing the Bioavailability of Metals in Soil for Use in Human Health Risk Assessments Bioavailability Policy Project Phase II. Metals Task Force Report, Summer 2000, Washington D.C.

Nikolaidis NP, Shen H (2000). Conceptual site model for evaluating contaminant mobility and pump-and-treat remediation. Global Nest: The Int. J. 2(1):67-76.

Northcott GL, Jones KC (2000). Experimental approaches and analytical techniques for determining organic compound bound residues in soil and sediment. Environ. Pollut. 108(1):19-43.

NRC, National Research Council (2003). Bioavailability of contaminants in soils and sediments: Processes, Tools and Applications. National Academies Press, Washington, DC.

Obuekwe IS, Semple KT (2013) Impact of Zn, Cu, Al and Fe on the partitioning and bioaccessibility of ^{14}C-phenanthrene in soil. Environ. Pollut. 180:180-189.

Okoro HK, Fatoki OS, Adekola FA, Ximba BJ, Snyman RG (2012). A review of sequential extraction procedures for heavy metals speciation in soil and sediments. Scientific Reports 1(3):181.

Olaniran AO, Balgobind A, Pillay B (2013). Bioavailability of heavy metals in soil: Impact on microbial biodegradation of organic compounds and possible improvement strategies. Int. J. Mol. Sci. 14:10197-10228.

Oliver DP, Tiller KG, Alston AM, Naidu R, Cozens GD (1999). A comparison of three soil tests for assessing Cd accumulation in wheat grain. Aust. J. Soil Res. 37:1123-1138.

Pearson RG (1968). Hard and soft acids and bases, HSAB I. Fundamental principles. J. Chem. Educ. 45:581-587.

Peijnenburg WJGM, Vijver MG (2007). Metal-specific interactions at the interface of chemistry and biology. Pure Appl. Chem. 79(12):2351-2366.

Pierzynski GM, Sims JT, Vance GF (2000). Soils and Environmental Quality (2nd ed.). CRC Press, London.

Pignatello JJ, Katz BG, Li H (2010). Sources, interactions, and ecological impacts of organic contaminants in water, soil, and sediment: an introduction to the special series. J. Environ. Qual. 39(4):1133-1138.

Posthuma L, Eijsackersb HJP, Koelmans AA, Vijver MG (2008). Ecological effects of diffuse mixed pollution are site-specific and require higher-tier risk assessment to improve site management decisions: A discussion paper. Sci. Total Environ. 406(3):503-517.

Puls RW, Powell RM, Clark DA, Paul CJ (1991). Facilitated transport of inorganic contaminants in ground water: Part II. colloidal transport. EPA/600/M-91/040. U.S. EPA Robert S. Kerr Environ. Res. Lab., Ada, OK.

Rao CRM, Sahuquillo A, Lopez Sanchez JF (2008). A review of the different methods applied in environmental geochemistry for single and sequential extraction of trace elements in soils and related materials. Water Air Soil Pollut. 189:291-333.

Reddy KR, Chinthamreddy S, Al-hamdan A (2001). Synergistic effects of multiple metal contaminants on electrokinetic remediation of soils remediation. Summer 2001: 85-109.

Reichman SM (2002). The responses of plants to metal toxicity: A review focusing on copper, manganese and zinc. Aust. Min., Energy Environ. Found. 14:1-14.

Reid BJ, Jones KC, Semple KT (2000). Bioavailability of persistent organic pollutants in soils and sediments- a perspective on mechanisms, consequences and assessment. Environ. Pollut. 108(1):103-112.

Romić M (2012). Bioavailability of trace metals in terrestrial environment:

Methodological issues. Eur. Chem. Bull. 1(11):489-493.

Salbu B, Krekling T, Oughton H (1998). Characterizationof radioactive particles in the environment. Analyst 123:843-849.

Santore RC, Di Toro DM, Paquin PR, Allen HE, Meyer JS (2001). Biotic ligand model of the acute toxicity of metals: 2. Application to acute copper toxicity in freshwater fish and *Daphnia*. Environ. Toxicol. Chem. 20:2397-2402.

Schwarzenbach RP, Gschwend PM, Imboden DM (2003). Environmental Organic Chemistry (2nd ed.). Wiley Interscience, New York.

Semenzin E, Temminghoff EJM, Marcomini A (2007). Improving ecological risk assessment by including bioavailability into species sensitivity distributions: An example for plants exposed to nickel in soil. Environ. Pollut. 148(2):642-647.

Semple KT, Doick KJ, Jones KC, Burauel P, Craven A, Harms H (2004). Defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated. Environ. Sci. Technol. A:229-231.

Semple KT, Doick KJ, Wick LY, Harms H (2007). Microbial interactions with organic contaminants in soil: Definitions, processes and measurement. Environ. Pollut. 150(1):166-176.

Sharma P, Mayes MA, Tang G (2013). Role of soil organic carbon and colloids in sorption and transport of TNT, RDX and HMX in training range soils. Chemosphere 92(8):993-1000.

Shen G, Lu Y, Hong J (2006). Combined effect of heavy metals and polycyclic aromatic hydrocarbons on urease activity in soil. Ecotox. Environ. Saf. 63:474-480.

Shiowatana J, McLaren RG, Chanmekha N, Samphao A (2001). Fractionation of arsenic in soil by a continuous flow sequential extraction method. J. Environ. Qual. 30(6):1940-1949.

Shu Y, Liu P, Zhang Q, Wei D (2013). Competitive sorption between 1,2,4-trichlorobenzene/tetrachloroethene and 1,2,4,5 tetrachlorobenzene by soils/sediments from South China. Sci. Total Environ. 463-464:258-263.

Smith KS (2007). Strategies to predict metal mobility in surficial mining environments. In DeGraff, J.V. (ed.) Understanding and Responding to Hazardous Substancesat Mine Sites in the Western United States, Geological Society of America Reviews in Engineering Geology, v. XVII, p. 25-45, doi: 10.1130/2007.4017(03).

Sposito G (1994). Chemical Equilibria and Kinetics in Soils. Oxford University Press, New York.

Srinath T, Verma T, Ramteke PW, Garg SK (2002). Chromium(VI) biosorption and bioaccumulation by chromate resistant bacteria. Chemosphere 48(4):427-435.

Srinivasan P, Sarmah AK, Manley-Harris M (2013). Co-contaminants and factors affecting the sorption behaviour of two sulfonamides in pasture soils. Environ. Pollut. 180:165-172.

Suarez P, Reyes R (2002). Heavy metal incorporation in bacteria and its environmental significance. Interciencia 27:160-172.

Sun K, Gao B, Zhang Z, Zhang G, Zhao Y, Xing B (2010). Sorption of atrazine and phenanthrene by organic matter fractions in soil and sediment. Environ. Pollut. 158(12):3520-3526.

Templeton DM, Ariese F, Cornelis R, Danielsson L, Muntau H, Van Leeuwen HP, Lobiński R (2000). Guidelines for terms related to chemical speciation and fractionation of elements. Definitions, structural aspects and methodological approaches. Pure Appl. Chem. 72(8):1453-1470.

Tessier A, Campell PGC, Bisson M (1979). Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51(7):844-851.

Thavamani P, Megharaj M, Krishnamurti GSR, McFarland R, Naidu R (2011a). Finger printing of mixed contaminants from former manufactured gas plant (MGP) site soils: Implications to bioremediation. Environ. Int. 37(1):184-189.

Thavamani P, Megharaj M, Naidu R (2011b). Multivariate analysis of mixed contaminants (PAHs and heavy metals) at manufactured gas plant site soils. Environ. Monitor. Assess. 184(6):3875-3885.

US EPA, United States Environmental Protection Agency (1999). Integrated approach to assessing the bioavailability and toxicity of metals in surface waters and sediments. A report to the EPA Science Advisory Board, Office of Research and Development, Washington, DC, USEPA 822-R-00-005.

Ure AM, Quevauviller PH, Muntau H, Griepink B (1993). Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of Commission of the European Communities. Int. J. Environ. Anal. Chem. 51(1-4):135-151.

van Straalen NM (2002). Assessment of soil contamination - a functional perspective. Biodegradation 13:41-52.

Van Zwieten L, Ayres MR, Morris SG (2003). Influence of arsenic co-contamination on DDT breakdown and microbial activity. Environ. Pollut. 124(2):331-339.

Violante A, Cozzolino V, Perelomov L, Caporale AG, Pigna M (2010). Mobility and bioavailability of heavy metals and metalloids in soil environments. J. Soil. Sci. Plant Nutr. 10(3):268-292.

VKM, Vitenskapskomiteen for mattrygghet/Norwegian Scientific Committee for Food Safety (2008). Combined toxic effects of multiple chemical exposures, Opinion of the Scientific Steering Committee of the Norwegian Scientific Committee for Food Safety.

Voegelin A, Barmettler K, Kretzschmar R (2003). Heavy metal release from contaminated soils:Comparison of column leaching and batch extraction results. J. Environ. Qual. 32(3):865-875.

White JC, Pignatello JJ (1999). Influence of bisolute competition on the desorption kinetics of polycyclic aromatic hydrocarbons in soil. Environ. Sci. Technol. 33:4292-4298.

Wuana RA, Okieimen FE (2011a). Evaluation of heavy metal speciation in single and multi-metal contaminated soils using BCR sequential extraction. Niger. J. Appl. Sci. 29:87-102.

Wuana RA, Okieimen FE (2011b). Heavy metals in contaminated soils: A review of sources, chemistry, risks and best available strategies for remediation. ISRN Ecology. pp.1-20.

Wuana RA, Yiase SG, Iorungwa PD, Iorungwa MS (2013). Evaluation of copper and lead immobilisation in contaminated soil by single, sequential and kinetic leaching tests. Afr. J. Environ. Sci. Technol. 7(5):249-258.

Wyszkowska J, Boros E, Kucharski J (2007). Effect of interactions between nickel and other heavy metals on the soil microbiological properties. Plant Soil Environ. 53(12): 544-552.

Xing B (2001). Sorption of naphthalene and phenanthrene by soil humic acids. Environ. Pollut. 111:303-309.

Xiao B, Huang W (2011). The equilibria of bisolute sorption on soil. Chemosphere 83(7): 1005-1013.

Xing BS, Pignatello JJ (1998). Competitive sorption between 1,3-dichlorobenzene or 2,4-dichlorophenol and natural aromatic acids in soil organic matter. Environ. Sci. Technol. 32:614-619.

Xing BS, Pignatello JJ, Gigliotti B (1996). Competitive sorption between atrazine and other organic compounds in soils and model sorbents. Environ. Sci. Technol. 30:2432-2440.

Yang F, Wang M, Wang Z (2013). Sorption behavior of 17 phthalic acid esters on three soils: Effects of pH and dissolved organic matter, sorption coefficient measurement and QSPR study. Chemosphere 93(1):82-89.

Zahran S, Mielke HW, Weiler S, Hempel L, Berry KJ, Gonzales CR (2012). Associations between standardized school performance tests and mixtures of Pb, Zn, Cd, Ni, Mn, Cu, Cr, Co, and V in community soils of New Orleans. Environ. Pollut. 169:128-135.

Zhang D, Hou L, Zhu D, Chen W (2014). Synergistic role of different soil components in slow sorption kinetics of polar organic contaminants. Environ. Pollut. 184:123-130.

Zhang H, Young SD (2006). Characterizing the availability of metals in contaminated soils. II. The soil solution. Soil Use Mgt. 21:459-467.

Zhao Y, Tan Y, Guo Y, Gu X, Wang X, Zhang Y (2013). Interactions of tetracycline with Cd (II), Cu (II) and Pb (II) and their cosorption behavior in soils. Environ. Pollut. 180:206-213.

Zhou P, Yan H, Gu B (2005). Competitive complexation of metal ions with humic substances. Chemosphere 58(10):1327-1337.

Zovko M, Romić M (2011). Soil contamination by Trace Metals: Geochemical Behaviour as an Element of Risk Assessment. In: I.A. Dar and M.A. Dar eds. Earth and Environmental Sciences, Intech, China, pp. 437-456