

Review



Cite this article: Sarkar B, Mukhopadhyay R, Ramanayaka S, Bolan N, Ok YS. 2021 The role of soils in the disposition, sequestration and decontamination of environmental contaminants. *Phil. Trans. R. Soc. B* **376**: 20200177.
<https://doi.org/10.1098/rstb.2020.0177>

Accepted: 24 April 2021

One contribution of 17 to a theme issue 'The role of soils in delivering Nature's Contributions to People'.

Subject Areas:

environmental science

Keywords:

soil and the sustainable development goals, soil pollution and remediation, contaminant bioavailability and toxicity, microbial transformation

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The role of soils in the disposition, sequestration and decontamination of environmental contaminants

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Soil serves as both a 'source' and 'sink' for contaminants. As a source, contaminants are derived from both 'geogenic' and 'anthropogenic' origins. Typically, while some of the inorganic contaminants including potentially toxic elements are derived from geogenic origin (e.g. arsenic and selenium) through weathering of parent materials, the majority of organic (e.g. pesticides and microplastics) as well as inorganic (e.g. lead, cadmium) contaminants are derived from anthropogenic origin. As a sink, soil plays a critical role in the transformation of these contaminants and their subsequent transfer to environmental compartments, including groundwater (e.g. pesticides), surface water (phosphate and nitrate), ocean (e.g. microplastics) and atmosphere (e.g. nitrous oxide emission). A complex transformation process of contaminants in soil involving adsorption, precipitation, redox reactions and biodegradation control the mobility, bioavailability and environmental toxicity of these contaminants. Soil also plays a major role in the decontamination of contaminants, and the 'cleaning' action of soil is controlled primarily by the physico-chemical interactions of contaminants with various soil components, and the biochemical transformations facilitated by soil microorganisms. In this article, we examine the geogenic and anthropogenic sources of contaminants reaching the soil, and discuss the role of soil in the sequestration and decontamination of contaminants in relation to various physico-chemical and microbial transformation reactions of contaminants with various soil components. Finally, we propose future actions that would help to maintain the role of soils in protecting the environment from contaminants and delivering sustainable development goals.

This article is part of the theme issue 'The role of soils in delivering Nature's Contributions to People'.

1. Introduction

Being the most important component of the Earth's critical zone, soil provides numerous services to ecosystems and humans. Starting from agricultural production, plant growth to animal and human habitation, soil is at the core of supporting biodiversity on planet Earth, sequestering carbon (C) and nitrogen (N) to mitigate climate change, and protecting the environmental quality by controlling the disposition, fate and decontamination of toxic substances. Soil is not only considered as a source of nutrients and C for plant growth and

microbial functions, but also as a sink for the removal of contaminants from agricultural, industrial and mining activities.

The disposition of contaminants in soil can be of geogenic and anthropogenic sources. Some of the soil contaminants such as potentially toxic elements (PTEs) are derived directly from the weathering of parent materials. Anthropogenically, soil is seen as a site for waste disposal with the aim of achieving the 'cleaning' of these contaminants [1]. In addition, numerous industrial contaminants inclusion and agricultural practices themselves add a number of contaminants into the soil primarily via fertilizer, pesticide and sludge applications. Soil is the main source of contaminants reaching other environmental compartments, including groundwater, surface water, ocean and atmosphere. For example, soil serves as the source and/or sink for pesticide contamination of groundwater [2,3], nitrate and phosphate contamination of surface water [4], microplastics contamination of the ocean [5] and greenhouse gas emission to the atmosphere [6].

Soil constituents such as soil minerals and organic matter play vital roles for contaminant mobilization, retention and remediation as well. Soil physico-chemical properties such as pH, surface area (contributed by soil minerals), particle charges (conferred by soil minerals and organic matter), soil moisture and oxidation–reduction potential (under aerobic/anaerobic conditions) influence the fate of contaminants within soil, and their further movement into the groundwater [7,8]. Soil minerals and organic matter retain contaminants (organic and inorganic) on their surfaces due to the surface charge, often as a function of soil pH. Contaminants are retained by soil particles through various mechanisms such as electrostatic attraction, complexation, ligand exchange, ion exchange and precipitation reactions. In this way, soil minerals and organic matter can remove contaminants from soil water, bringing contaminants from the solution to the solid phase. Soil with high clay content thus can act as a physical barrier for contaminant movement, and prevent diffuse contamination at adjacent sites [9]. Additionally, soil aerobic and anaerobic conditions determine the transport, transformation and bioavailability of contaminants as a function of the redox potential. The change in soil redox potential alters contaminants' speciation including that of arsenic (As), chromium (Cr), selenium (Se) and vanadium (V), and transforms their toxicity levels to biological receptors [10,11].

Soil microorganisms (e.g. fungi, bacteria and actinomycetes) also play an important role in affecting the fate, transport and removal of soil contaminants. While some soil inhabiting microorganisms can be pathogenic, there are beneficial microorganisms that can decontaminate soil by biosorption, transformation and degradation of contaminants [8]. Selected microorganisms can use organic contaminant compounds as their primary energy (C) source, and result in the degradation of those compounds to CO₂ and water. Additionally, microorganisms secrete various organic acids and enzymes that can convert toxic contaminants into less toxic forms through biotransformation processes (e.g. methylation of mercury (Hg), lindane degradation by *Streptomyces* sp.) [12–14]. However, microbial degradation of persistent organic pollutants (POPs) such as dichlorodiphenyltrichloroethane (DDT) and per- and polyfluorinated alkyl substances (PFAS) is either impossible or extremely slow, raising the issue of widespread biomagnification [15,16].

In this article, we describe the geogenic and anthropogenic sources of contaminants reaching the soil, and shed light on the important role of soil constituents in contaminant sequestration and removal processes. We also highlight various soil factors and mechanisms that are responsible for governing the disposition, sequestration and decontamination of soil contaminants. As a novel approach, we illustrate the above topics in the context of contributions of soils to Nature's Contributions to People (NCP) and United Nations Sustainable Development Goals (SDGs).

2. Role of soils in the disposition of contaminants

The disposition of contaminants in the soil can occur through natural biogeochemical and/or anthropogenic processes. Contaminants undergo cycling across the pedosphere, hydrosphere, biosphere and atmosphere via biogeochemical cycles. Fluxes of contaminants between the four spheres depend on the quantity of the contaminants present and the surrounding physical, chemical and biological environments, and give an approximate quantitative estimate of the disposition of contaminants in the soil. Owing to the highly dynamic nature of the disposition and rapid changes in the species and fractions of the contaminants, often the quantification of the disposition degree (or transfer rate) becomes challenging [17]. During the biogeochemical cycling, contaminants can reach the soil from the atmosphere through wet deposition with rainfall and dry deposition of particles and gases contributing to the total contamination load. The processes occurring at the solid–solution interface either within the pedosphere (i.e. soil) or between the pedosphere and hydrosphere govern the concentration of dissolved contaminants and their transport in the soil. The solid–solution processes may involve chemical dissolution, precipitation, adsorption–desorption, redox transformation and biological activities leading to breakdown or biotransformation of contaminant species. In the case of organic contaminants, the water affinity of soil particles plays a major role where hydrophobic soils tend to retain a greater quantity of persistent organic contaminants than hydrophilic soils. In addition to the natural sources, numerous anthropogenic activities (e.g. dumping of wastes, addition of organic matter and fertilizers, irrigation with contaminated water, mining activities) add contaminants in the soil [8]. Contaminants can be introduced to the soil as a point source (microscale distribution) but can diffuse to large areas extending from national, regional and global scales with the passage of time. The spatial distribution of soil contaminants depends on where the contaminant is originated (i.e. source location), how the contaminant is transported (e.g. dispersal processes) and where the contaminant is finally deposited (i.e. sink processes) [18]. The following sub-sections will explain examples of three key disposition routes of contaminants in the soil environment via natural and agricultural practices.

(a) Geological source of contaminants

The chemical weathering of parent materials (i.e. primary minerals) is known to add a number of PTEs, and radionuclides into the soil environment. When silicate and carbonate minerals weather with the action of water-

dissolved CO₂ (i.e. carbonic acid) and other organic acids released by soil microorganisms and higher plants, various ions are released into the soil, constituting the chemical composition of the soil solution. Most of the PTEs are present in the soil parent materials and weathering of soil parent materials results in the release of these PTEs to soil [19]. For example, PTEs such as cadmium (Cd), zinc (Zn), lead (Pb) and copper (Cu) are often released from sulfidic minerals in parent materials [20]. Co-contamination of soils with Cr from parent rocks along with other PTEs, including nickel (Ni), Cd and As was also reported in various regions [8]. Although the anthropogenic As source resulting from waste disposal and mining activities is increasingly becoming important, the recent catastrophic episode of large-scale groundwater As-contamination in many countries, including Bangladesh, India, China and Mexico is a result of geological origin, mobilized from sedimentary rocks in the Himalayas over a long period [21,22], and the situation is likely to be aggravated by climate change [23]. Similarly, weathering of Se-rich rocks, such as black shales, carbonaceous limestones, carbonaceous cherts, mudstones and seleniferous coal is a major source of Se input in seleniferous soil [24]. Most of the PTEs found in the soil are known to show high affinity with soil clay and organic matter [25]. Naturally occurring parent rocks such as fluorspar, rock phosphate, cryolite, apatite and mica are the major source of fluorine (F) contamination in global soils including in Afghanistan, China, India, Japan, Iraq, Iran and Turkey [26]. Chemotoxic and radiotoxic uranium (U) species are accumulated in soil from U-containing rocks such as slate and granite, while abandoned U mines could also heavily contribute to soil U contamination [27]. The large-scale contamination of groundwater with U in India was primarily geogenic via the formation of soluble complexes of uranyl carbonate following the weathering of parent rocks [28,29].

(b) Contaminants from biowaste disposal to soil

Biowaste (waste of biological origin) such as sludge from sewage/wastewater treatment plants, compost and animal manures are widely used organic amendments in agricultural soils for improving soil fertility and crop productivity. Though biowaste is an excellent source of plant nutrients, it may contain contaminants such as pharmaceuticals and personal care products, PFAS, hormones, excess nitrate and phosphate, pathogens and toxins. Wastewater application into soil is practised in many countries, which too can transfer toxins into the soil. Biowaste thus can act as a vector for transporting emerging contaminants, toxic chemicals and pathogens into the soil. Biosolids, for example, are known as a major source of PTEs such as Pb and Cd inputs to soil. Emerging organic contaminants such as antibiotics and PFAS can also reach soil via biosolids from wastewater treatment plants [16]. Similarly, animal manures and manure by-products raise concern for off-site transport of N and phosphorus (P) causing contamination of aquatic bodies. Another important issue with manures is their high contents of PTEs such as Cu, Zn and As. These metal(loid)s are added in the animal feed as nutritional supplements, ultimately finding their way into the soil via manure application [30]. Similarly, pathogenic microorganisms and their toxins can enter into the soil system via compost application [31]. Furthermore, microplastics, which have emerged as a

contaminant of great concern in recent days, can be incorporated to soil via composts and biosolids [32]. Additives in plastics such as colourants containing toxic metals (e.g. Pd, Cr, As) and POPs such as PFAS and phthalates may apparently end up in soil as contaminants [33].

(c) Contaminants from agrochemicals

Chemical fertilizers are added to supply nutrients required for plant growth and crop production. However, when nutrients are applied in excess of food and fodder crops' requirements, they can escape from fields to surrounding soils, air and waterways, thereby leading to environmental degradation and economic loss [34,35]. Fertilizer input is the major source of nutrient contaminants such as nitrate and phosphate reaching groundwater sources, and nitrous oxide greenhouse gas emission to the atmosphere. Moreover, the portion of the nutrients harvested in food and fodder crops, and subsequently consumed by human and farm animals, is generally concentrated in the locations where humans and animals reside, with the majority of the nutrients excreted along with wastes, reaching the soil during the disposal of these wastes [35,36]. Similarly, P fertilizers are regarded as the primary source of PTE input to agricultural soil, especially Cd, in many countries, including Australia and New Zealand [37]. Phosphate rock which is used for the manufacture of various phosphate fertilizers contain a range of metal(loid)s including Cd. Cd contamination of agricultural soils is an important human health issue because it reaches the food chain through regular use of Cd-containing P fertilizers and biosolids. The application of P fertilizer was identified as the key source of U contamination in soils in countries like Switzerland [38]. Similarly, F contamination in soils could be traced back to long-term application of superphosphate fertilizers giving rise to increased plant available F concentrations in the soil [37,39]. In addition to fertilizer-associated contaminants, various pesticide residues, often in a cocktail with other contaminants, are encountered in intensively cultivated soils [40]. For example, pesticides such as glyphosate, DDT, boscalid, epoxiconazole, tebuconazole and some of their metabolites were frequently detected in some European soils at alarming concentrations [41].

3. Role of soils in the sequestration of contaminants

Soil is a porous and heterogeneous material containing minerals (inorganic silicate, metal oxides and non-crystalline minerals), organic matter, water and gases. Soil solid phase consisting of minerals and the organic matter mainly governs the retention of organic and inorganic contaminants and nutrients in soil [42]. The retention of contaminants on the soil solid surface depends primarily upon soil particle size, surface charge and their specific surface area which ultimately drive the cation and anion exchange reaction in soil [43]. The following subsections deal with how soils contribute to contaminant retention, mobilization and transformation.

(a) Sorption and immobilization

Geogenic PTEs, such as Pb, Cd, As, Cu, Zn, are closely linked to soil properties for their persistence in soil. The clay content

(inorganic silicates and oxides), soil organic C, and carbonates are the driving forces for sorption of contaminants in soil [8]. Heavy metals like Cd remain as sulfide within natural minerals along with other metals like Zn, Cu and Pb [20]. For example, sorption of Pb on soil solid is high owing to its high adsorption affinity towards soil minerals like manganese oxides [44]. On the contrary, Cd showed relatively low sorption capacity within soil owing to its lesser affinity towards soil minerals [45]. The soil pH is one of the most important factors that influence the metal sorption capacity on the soil surface. The low range acidic soil pH favours the bioavailability of metals to the plants, while the high range alkaline pH governs the retention of the metal contaminants in soil as insoluble forms [45], and make them less available to the plants. The soil organic matter (SOM) contains humic and fulvic acids having functional groups like phenolic, carboxylic and hydroxyl that also adsorb the contaminants (Cu, Hg) by making an insoluble complex in soil [46]. By contrast, humic and fulvic acids sometimes form soluble metal-organic matter complexes with Cd and Hg, respectively, enhancing the release of PTEs from the soil solid [47,48]. Further, the root exudates comprising of different organic acids form chelate to make the metals immobile in soil. Experimental data revealed that variable sorption capacity, hysteresis and slow rates of sorption and desorption are prime characteristics for hydrophobic organic contaminant interactions with soils and sediments [49]. The organic matter is typically negatively charged and enhances the release of anionic hydrophobic organic contaminants such as PFAS and polycyclic aromatic hydrocarbons (PAHs) owing to electrostatic repulsion. However, electrostatic attraction of PFAS occurs at low pH of soil medium with small organic carbon content [50]. Furthermore, the PFAS adsorption onto organic matter occurs due to hydrophobic interactions for larger retention of PFAS in soil [51]. By contrast, low natural organic matter content reduces the sorption of organic contaminants. The modification of organic matter by long chain surfactant or natural surfactant (derived from soil microbes) can improve the sorption capacity of soil (10–30 times) to retain the organic contaminants like benzene [52] or total petroleum hydrocarbon [53]. Therefore, organic matter content and inorganic minerals are considered as static parts that regulate the sorption and release of contaminants in soils and sediments.

Soil also acts as a barrier for contaminants. The mobility and transport of various contaminants could be minimized by soil, therefore, limiting the exposure of the contaminants to humans through drinking water and crops. The filtration capacity of soils also minimizes the leaching of contaminants into the groundwater. However, the filtration capacity of soil, mobility and transport of contaminants depend highly on soil composition especially clay and organic matter content, pH, ionic composition of soil solution and soil microorganisms. For example, the cationic dye adsorption capacity in a soil (sand, clay, silty soil) was studied in batch and fixed bed column. Results revealed that the column outlet did not exceed 4.5% of the initial concentration even after 214 days. Because of the presence of a smectite clay layer and capillary barriers, the transport of dye was minimized by high sorption capacity of clay and silty soil [54]. However, the soil may not retain all the contaminants, while it creates equilibrium (between solid–solution) with the existing contaminant solutes in solution phase. The buffering capacity of soil

mainly forms the chemical barrier in soil against the chemical transport and mobility of contaminants as a result of changes in pH and clay content. In addition, some physical parameters like pore blockage, pore constrictions of soil also act as barriers against contaminant transport [9,55]. Some artificial biogeochemical barriers (permeable reactive barriers) can be applied in soil contaminated zones for improving the efficiency of soil to minimize the transport and mobility of chemical contaminants [56]. Similarly, establishment of a plant cover on the surface of the contaminated sites (i.e. phytostabilization) can be aimed at reducing the mobility of contaminants within the vadose zone through accumulation by roots or immobilization within the rhizosphere, thereby reducing off-site contamination [57]. The concentration and movement of redox-sensitive pollutants was minimized by application of electron donors or acceptors through organic matter and waste to the soil for activation of anaerobic microorganisms to reduce the activity and concentration of radioactive elements, PTEs and organic contaminants [58]. In this way, soil provides the foundation for a biogeochemical barrier for a wide range of contaminants.

(b) Chemical mobilization, speciation and transformation

The mobilization, speciation and transformation of organic and inorganic contaminants are primarily driven by chemical factors like pH and oxidation–reduction (redox) potential (Eh). The redox potential of the soil regulates the mobility and speciation of toxic organic and inorganic contaminants in soil. For example, Fiedler *et al.* [10] studied V mobility in the oil production fields of the Agua Dulce District near Tabasco, Mexico. They reported that strongly reduced conditions in organic-enriched soils (Eh = 90 to –240 mV) aggravated the migration of V within soil which suggested its entry into the human food chain. The As speciation and solubility can change with prolonged oxidation and reduction conditions under the rice field coupled with coexistence of sulfate. Study revealed that an excess of sulfate reduced extractable, dissolved and soluble As(III) in soil under redox condition. About 50% of As(III) to the total As persisted over 32 days of soil aerobic condition (Eh > 400 mV), suggesting soil microsite sequestration against oxidation of As(III) into a less toxic As(V) form (compared to As(III)) [11]. The release of PTEs like thallium (Tl), antimony (Sb), and silver (Ag) from the soil is also influenced by redox potential, hence their retention in soil colloids in different phases (solid, colloidal, dissolve) are dominated by soil redox potential. Results indicated that a wide range Eh (–12 to +333 mV) of biochar-treated soil released more PTEs like Tl and Sb than untreated soil (Eh = –30 to +218 mV). Methylation of Hg occurs under aerobic and anaerobic conditions by microorganisms and their secreted enzymes, which is considered as a detoxification process for Hg [7,59]. The methylated Hg could be removed subsequently by volatilization. This reflects the impact of redox potential on retention, detoxification and mobilization of contaminants in soil [60]. Besides, mobilization of iron (Fe) and formation of oxides are highly influenced by fluctuations of Eh in soil. Under anaerobic conditions, Fe(III) accepts electrons from microbial oxidation of SOM and releases Fe(II) in soil, which forms Fe-oxides under aerobic conditions [61]. Similarly, P availability and mobilization in soil depends upon water content and redox

potential of the soil that minimize the leaching of P in the deeper soil profile [62].

The transformation of organic compounds occurs within a diverse redox regime [63]. High oxygen transfer rates often lead to the formation of a redox interface between the sub surface vadose zone and soil saturated zone with the occurrence of organic contaminants. Crawford *et al.* [64] studied the biodegradation of atrazine under diverse redox conditions in the absence or presence of electron acceptors (O_2 , NO_3^-) and glucose as electron donors. Results revealed that faster degradation occurred under anaerobic conditions with glucose and NO_3^- . However, further research should focus on deep sub surface redox processes that facilitate chemical contaminant cycling [61].

A chemical process that forms sorption complexes of metals on soil particles as a gradually increasing three-dimensional solid form is known as surface precipitation. In general, two mechanisms are observed in the formation of surface metal precipitation: (i) change in metal properties induced by soil solid surface, and (ii) change in soil solution composition near the metal and solid surface interface. However, increased ionic activity of contaminants at the solid–solution surface, oversaturation of contaminants owing to adsorption on a solid surface, and co-precipitation of ions at the solid–solution interface are the primary phenomena that form soil precipitates in alkaline soils [65]. The co-precipitation of metals in the presence of metal hydroxides and oxyhydroxide has been reported to make changes in the surface chemical properties of the substrate. Precipitation of aluminum (Al), Fe-phosphates in alkaline soils is considered as phosphate-induced immobilization of metals, when metal concentration becomes high [66]. Soil pH also governs the precipitation of the contaminants like PTEs within soil, which make them insoluble. The precipitation of contaminants on soil surface is, sometimes, required to recover the metals and metalloids for further use in the industry. However, the microorganism induced metal precipitation in soil is more beneficial than chemical reduction or oxidation in terms of purity and cost for recovery of contaminants [67]. A combined process of solubilization through sulfuric acid produced by sulfur-oxidizing bacteria with precipitation through metal sulfide produced by sulfate-reducing bacteria was conducted to recover purified metals in their sulfide forms. Results revealed that 99% of Cu(II), 96% of Cd(II) and 93% of Zn(II) were precipitated at pH 1.9, 3.0 and 4.0, respectively, in the soil leachate. Finally, 75% of Cu(II) and 86% of Zn(II) were recovered from the soil as CuS and ZnS which remain protected in soil and minimized to a large extent from its leaching to groundwater [68]. Similarly, microbial-induced carbonate (MIC) precipitation of Pb in the form of $PbCO_3$ and $CaCO_3$ also proved successful for contaminant sequestration in soil as an insoluble form. The MIC used for Pb precipitation was formed by soil bacteria, urease and carbonic anhydrase enzymes [69]. The various soil biochemical compositional factors, including pH, surface charge, soil bacteria and enzymes are closely responsible in the formation of contaminant precipitates, therefore, minimizing the mobility and leaching of contaminants to the groundwater. However, future research is required for a better understanding of the detailed mechanistic insights on soil surface precipitation of contaminants in order to achieve the conclusive evidence on the role of soils in protecting contaminants through precipitation.

4. Role of soil in the decontamination of contaminants

The soil constituents (clays and clay minerals, and organic matter) are useful to decontaminate various environmental contaminants besides their multiple beneficial functions like supporting plant growth, providing plant nutrients and protecting the contaminants within the soil medium. The soil medium acts as a filtration unit for removal of contaminants from the system. The soil solid constituents play a major role in removing contaminants from soil through adsorption, degradation and transformation of contaminants into less toxic forms (figure 1). Besides, soil is the habitat for diverse groups of microorganisms which also participate in the degradation of toxic organic contaminants. Here, we highlight the role of soil minerals, organic matter and microorganisms in removing contaminants from soil.

(a) Soil minerals

Soil minerals are considered mainly as clay minerals which are phyllosilicates constituted of silica and alumina frameworks. The clay minerals are secondary inorganic compounds of clay (less than $2\ \mu\text{m}$) size particles in soil regardless of their crystallinity [70]. The crystalline clay minerals include 2:1 (smectite, vermiculite, mica), 1:1 (kaolinite, halloysite) and 2:1:1 (chlorite) aluminosilicates and fibrous clay minerals such as palygorskite and sepiolite. Besides, oxides, hydroxides and oxyhydroxides of Fe, Al and manganese (Mn) and other metals are also considered as crystalline clays, while allophane and imogolite are non-crystalline clays [71]. These natural clays and clay minerals can be used as adsorbents for contaminant removal from soil and water owing to their low-cost, wide natural availability, and high specific surface area [72,73]. The natural clay minerals such as montmorillonite, kaolinite and palygorskite are used to remove various inorganic (PTEs) and organic (dyes and pesticides) contaminants from water or adsorb them in soil. For example, natural kaolinite and bentonite removed 6.80 and $11.20\ \text{mg g}^{-1}$ Cd [74], while montmorillonite and palygorskite removed 17.88 and $2.35\ \text{mg g}^{-1}$ Cu from water [75,76]. Similarly, kaolinite, bentonite and smectite removed $47.27\ \text{mg g}^{-1}$ and 91% crystal violet and malachite green [77], and $3300\ \mu\text{g g}^{-1}$ metalaxyl [78] from water. Likewise, natural palygorskite adsorbed 37.2 , 17.4 and $7.11\ \text{mg g}^{-1}$ Pb, Cu and Zn, respectively, in soil [79], while natural smectite and kaolinite showed 53.80 and 58.36% As immobilization efficiency via adsorption in soil [80]. However, the natural clays and clay minerals suffer from low adsorption capacity, especially for organic contaminants [81]. Therefore, the natural clay minerals are modified with surfactants, inorganic salts, and mineral acids in order to improve their functionality for adsorbing high quantities of contaminants [82,83]. For example, Fe-exchanged smectite had higher As adsorption capacity (72%) than natural smectite (53.8%) in soil [80]. Similarly, $AlCl_3$ modified bentonite adsorbed 61.4 and $32.3\ \text{mg g}^{-1}$ Cu and Zn in soil [84]. Besides, goethite (Fe-oxyhydroxides ($FeOOH$)) adsorbed around $75\ \text{mg g}^{-1}$ As in soil [85]. $FeOOH$ was also able to remove organic contaminants such as PFAS from water ($3.5\ \mu\text{g m}^{-2}$) [86]. Additionally, Fe-oxide (Fe_3O_4) removed $49.90\ \text{mg g}^{-1}$ NO_3^- from wastewater [87], while the starch modified- Fe_3O_4 [88]

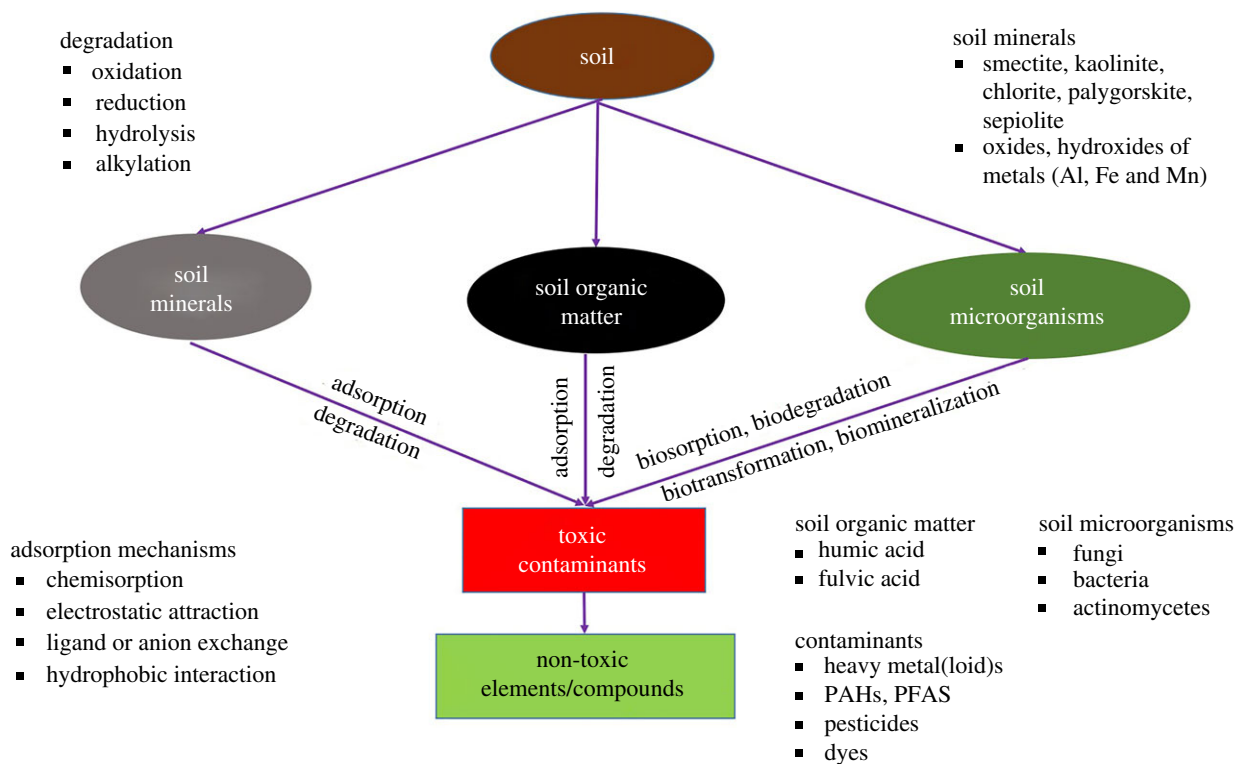


Figure 1. Processes and mechanisms of sequestration, transformation and decontamination of soil contaminants. Abiotic processes are mediated by soil minerals, whereas biotic processes involve soil microorganisms. SOM plays critical role at the juncture of biotic-abiotic processes governing the degradation (oxidation, reduction, hydrolysis, alkylation) and adsorption (chemisorption, electrostatic attraction, ligand exchange, hydrophobic interaction) mechanisms of contaminants. (Online version in colour.)

and humic acid modified boehmite (Al oxides) [89] removed 62.05 mg g^{-1} and $0.17 \text{ } \mu\text{g m}^{-2}$ PFAS, respectively.

The adsorption of contaminants onto clay minerals occurs through different mechanisms: (i) chemisorption occurs through formation of chemical bonds between solute and adsorbents, (ii) electrostatic attraction happens between two oppositely charged particles (ions and adsorbent) as a function of pH of the medium, and (iii) ligand and anion exchange occurs with exchange of a solid-phase ligand or anion with the solution phase ligand or anion with change in pH. Hence, the pH of the medium and surface charge of the clay adsorbents (intrinsic charge and charge generated as a function of pH) play a vital role in electrostatic attraction, the chemisorption and anion or ligand exchange mechanism between the clay surface and the contaminant [83]. At low pH, the surface charge of the clay adsorbents become positive favouring the adsorption of anionic contaminants, while under high pH, the clay adsorbents become negatively charged and favour the adsorption of cationic heavy metals. However, clay adsorbents suffer from dose optimization and high desorption potential when application is made in the soil medium. Therefore, future research should focus on contaminants remediation capacity of clays and clay minerals in soil.

(b) Soil organic matter

Like clays and clay minerals, SOM also helps in adsorbing contaminants in soil and water. The natural particulate organic matter and natural dissolved organic matter participate in contaminant adsorption [90]. Addition of different crop residues, municipal solid wastes and composts increases the capacity of SOM to retain contaminants through

adsorption, redox reactions and complexation. The increase in soil cation exchange capacity occurs owing to addition of SOM by dissociation of H^+ ions from functional groups of SOM, which in turn contributes to contaminant retention [7]. Metal contaminants of organic and inorganic origins make complexes in soil with organic matter. The Cd(II) adsorption onto kaolinite was increased owing to the presence of SOM and formed a layer of organic matter on the clay surface, which indicated that metal cations have high affinity towards SOM to form chelates owing to the presence of ligands or functional groups of SOM [91]. In addition, SOM can affect the degradation of hydrophobic organic contaminants such as PAHs and PFAS. Experimental results revealed that 2% SOM content of soil had higher degradation of PAHs than 20% SOM content of soil, which suggested a negative correlation between PAH bioavailability and SOM content [92]. Similarly, peat soil (rich in SOM) heated at $200\text{--}250^\circ\text{C}$ improved the decontamination efficiency of Cr(VI). About 99% of Cr(VI) was decontaminated initially, however, the increased heating temperature from 300 to 600°C reduced the Cr(VI) decontamination rate. The released lignin substances and carboxylic groups of SOM enhanced Cr(VI) reduction to Cr(III) at the initial stage upon heating the peat soil, while raising heating temperature (greater than or equal to 300°C) reduced the oxygen (O)-containing functional groups that led to decreased reduction of Cr(VI) [93]. The humic and fulvic acids are inseparable parts of SOM, and contribute to contaminant removal individually or in combination with other mineral adsorbents [89]. The humic acid fraction of SOM when used as coating to the clay minerals enhanced the removal of PFAS ($0.17 \text{ } \mu\text{g m}^{-2}$) through hydrophobic interaction [89]. Loading of biochar with water-soluble organic matter increased the O-containing

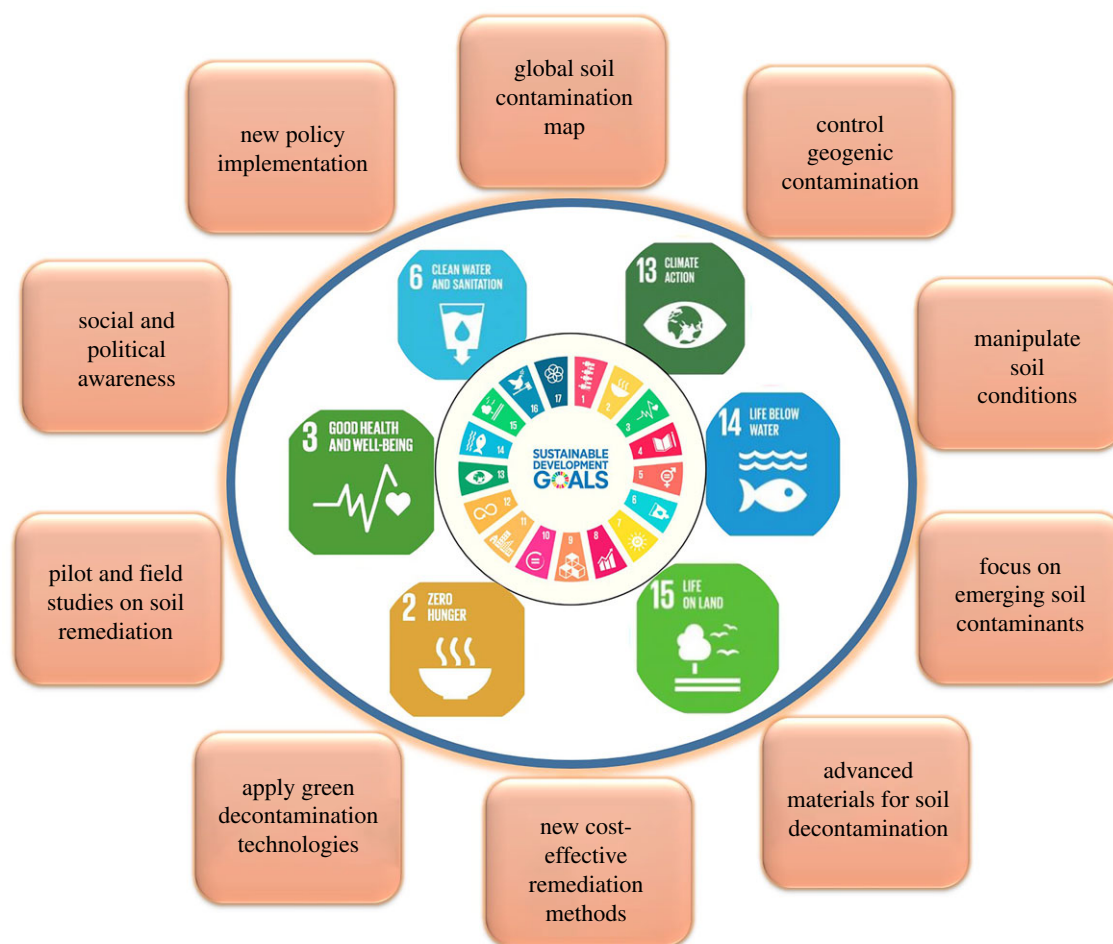


Figure 2. Proposed actions to maintain the role of soils in protecting the environment from contaminants and delivering SDGs. (Online version in colour.)

functional groups on the biochar surface owing to the complexation between biochar and water-soluble organic matter, which subsequently reduced the Cd(II) concentration in soil [94]. The reactive mineral matter mixed with SOM in soil interferes in the mobility of organic contaminants too. Acid treatment of such SOM removes the reactive mineral and enhances the sorption of hydrophobic contaminants, making them immobile [95]. However, SOM might be fractionated in the soil system, and the details of how properties change in SOM when coupled with contaminant behaviour are still not fully understood.

(c) Soil microorganisms

Soil is the habitat for diverse groups of microorganisms. Soil microorganisms including fungi, bacteria and actinomycetes play a significant role in decontaminating organic and inorganic contaminants by degradation or transformation into less toxic forms. Involvement of soil microorganisms in contaminant remediation is considered as inexpensive and eco-friendly although microbial remediation is mostly confined to a small area and at low contaminant concentration. Certain soil microorganisms have the ability to decontaminate soil pollutants naturally, but owing to the immutable bioavailability of contaminants, natural attenuation might not always be effective in remediating the soil. The attenuation of contaminants could be accelerated by human interventions such as application of certain types of amendments to the contaminated soil, resulting in some changes in the

biogeochemical processes in the soil, thereby increasing the rate of decontamination [7].

There are four probable ways by which soil microorganisms decontaminate contaminants in soils: biosorption, biodegradation, biotransformation and biomineralization [96]. For example, *Bacillus subtilis* adsorbed 95% of Cd(II) in the cell wall and cell membrane, and kept the remaining Cd(II) in the soluble fraction of the cell [97]. Polti *et al.* [12] evaluated *Streptomyces* sp. M7, isolated from co-contaminated environment with PTEs and pesticides for lindane and Cr(VI) decontamination, and found that the bio-accessibility of lindane and Cr(VI) were decreased by 42 and 52%. Likewise, fungal species *Aspergillus sydowii* showed potential to remediate soil contaminated with trichlorfon and Cd(II) [98]. Among soil fungi, mushrooms (Basidiomycota phylum) are highly efficient in the decontamination of organic and inorganic contaminants by secreting laccase and manganese dependent peroxidase (MnP) enzymes. Jia *et al.* [99] evaluated *Lentinus edodes* substrate in remediating dichlorophen and Cd(II) co-contaminated soil. The degradation rates of dichlorophen were 85–97%, and the substrate also reduced the bioavailability of Cd(II) in soil. In the case of co-contamination, the degradation is more favoured by the presence of low concentration of PTEs. The mechanisms involved in the microbial degradation of pesticides are oxidation, hydrolysis, and alkylation. Firstly, pesticides are converted into water-soluble and less toxic forms through oxidation, reduction, or hydrolysis. In the later stage, pesticides are combined with amino acids, which further promotes the formation of water-soluble and non-toxic compounds. Finally, the

metabolites are transformed into non-toxic secondary conjugates [100]. Besides biosorption and biodegradation, biomineralization and transformation of contaminants by soil microorganisms are highly appreciable. *Pseudomonas putida* has been shown to be capable of degrading organophosphorus pesticides and promoting biomineralization of Cd(II) [101]. Many fungi and bacteria also produce biosurfactants and extracellular enzymes that transform PTEs from toxic to non-toxic forms (e.g. Hg(II) to volatile Hg⁰ by mercuric reductase) [102]. Similarly, Se-reducing bacterium *Thauera selenatis* reduced selenate into selenite by the selenate reductase enzyme, and then periplasmic nitrite reductase reduced selenite into Se⁰ [103]. In addition, biotransformation of contaminants depends on the quantity of transforming metabolites produced by soil microorganisms, soil physico-chemical characteristics, and nature and concentration of concerned contaminants in soil.

5. Implications in Nature's Contributions to People and United Nations Sustainable Development Goals

With the aim to contextualize the 'Regulating NCP – Formation, protection and decontamination of soils and sediments' [104,105], this paper discusses how soils act both as a source and sink of contaminants contributing to potential positive (contaminant cleaning), negative (contaminant addition) and context-specific (contaminant bioavailability and leaching control) contributions to NCP. The contaminants governing functions of soils seem closely related to the NCP such as 'Food and feed', 'Medicinal, biochemical and genetic resources', 'Regulation of freshwater and coastal water quality', 'Habitat creation and maintenance', 'Regulation of air quality', and 'Regulation of organisms detrimental to humans' [106]. The role of soil is also important in the continuous efforts of achieving the SDGs by global communities. In addition to serving for SDG 'Zero hunger', soil contributes to achieve SDGs, such as 'Life on land', 'Climate action', 'Clean water and sanitation', 'Life below water' and 'Good health and wellbeing' via playing key roles in the disposition, sequestration and decontamination of contaminants [107] and the above-mentioned NCP [106,108]. In order to achieve the SDGs successfully and to protect the invaluable soil resource, we suggest the following actions to be undertaken (figure 2).

- (i) Accumulate soil contamination (contaminant types and concentrations) data and combine them with

the currently existing global soil map, and continuously improve the database [109].

- (ii) Reduce dumping of anthropogenic contaminants into soil while also undertaking measures to control geogenic contamination by avoiding land use and practices that can aggravate release of contaminants from soil parent materials (e.g. reduce extraction of groundwater for irrigation).
- (iii) Manipulate soil conditions to avoid the geogenic contaminants exposure to groundwater (e.g. As and Cr are sensitive to change to soil redox conditions).
- (iv) Concentrate research to understand the fate, transformation and transport of emerging contaminants in soil such as microplastics, PFAS and contaminant mixture.
- (v) Develop new cost-effective remediation methods that leave less C footprint to the environment.
- (vi) Use advanced materials such as biochar and modified minerals for the decontamination of soil, possibly by applying biomimetic approaches to emulate a system/model of nature to solve complex problems (e.g. renal dialysis-like system for water purification [110] and microbial co-metabolism of contaminants-like system for soil bioremediation) [8].
- (vii) Conduct case studies involving the application of various remediation technologies under field conditions.
- (viii) Apply green decontamination technologies such as phytoremediation and bioremediation using plants and microorganisms.
- (ix) Grow social and political awareness, establish monitoring programmes and inform policy makers for taking regulatory measures (e.g. banning certain types of fertilizers and pesticides for soil application).

Data accessibility. This article has no additional data.

Authors' contributions. B.S. wrote the first draft of the article, with input from R.M. All authors supplied information used in this paper, helped to revise drafts and approved the final version to be published.

Competing interests. We have no competing interests.

Funding. B.S. and S.R. were supported by the Lancaster Environment Centre Project. Y.S.O. received support from the Cooperative Research Program for Agriculture Science and Technology Development (project no. PJ01475801), Rural Development Administration, Republic of Korea. This work was also supported by the National Research Foundation of Korea (NRF) (grant no. NRF-2015R1A2A2A11001432), and the NRF Germany-Korea Partnership Program (GEnKO Program) (2018–2020).

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