soil systems

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Review

The Fate of Chemical Pollutants with Soil Properties and Processes in the Climate Change Paradigm—A Review

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Abstract: Heavy metal(loid)s and organic contaminants are two major groups of pollutants in soils. The fate and exposure of such pollutants in soil depends on their chemical properties, speciation, and soil properties. Soil properties and processes that control the toxicological aspects of pollutants include temperature, moisture, organic matter, mineral fractions, and microbial activities. These processes are vulnerable to climate change associated with global warming, including increased incidences of extreme rainfall, extended dry periods, soil erosion, and a rise in sea level. Here we explain evidence that relates to the effects of climate change-driven soil processes on the mobility, transport, and storage of pollutants in soil. The review found that changes in climate could increase human exposure to soil contaminants mainly due to processes involving soil organic carbon (SOC), surface runoff, redox state, and microbial community. However, uncertainties remain in relation to the extent of contaminant toxicity to human health, which is linked to global change drivers.

Keywords: soil contaminants; soil process; climate changes; ecotoxicity of pollutants

1. Introduction

Manipulation of naturally available chemicals and the synthesis of new compounds has played a vital role in human development. However, conflict between the ever-increasing development of human civilization and the need to reduce chemical pollutants has become apparent since the development of the discipline of environmental toxicology in the middle of the 20th century [1]. Economic growth and the demand for goods has brought up approximately 80,000 synthetic chemicals over the last 50 years' time [2]. Synthetic chemicals produce goods and services for us but also emit contaminants to the environment. Every year 2000–3000 new chemicals are reviewed by the United States Environmental Protection Agency (US-EPA) and many are identified as hazardous [3,4]. The Earth's critical zone is defined as the "heterogeneous, near-surface environment in which complex interactions involving rock, soil, water, air, and living organisms regulate the natural habitat and determine the availability of life-sustaining resources" [5]. Soil dominates the flow and transformation of mass, energy, and genetic information [6], and therefore significantly dominates the above- and below- ground systems of this zone. In the Anthropocene, the age defined as that with significant

human impacts on the environment, this critical zone is a front-line natural resource vulnerable to climate change [7]. The empirical and research data across various geochemical spaces suggest that climate change is one of the ten planetary boundaries [8] potentially impacting environmental sustainability [9–14]. Excessive production of greenhouse gases (GHG) (e.g., CO_2, N_2O, NO_x, CH_4, etc.), which lead to global warming, changes the frequency and intensity of rainfall, drought, and the intensity of storms and soil erosion; all of which affect soil properties and functions [15,16].

Climate change and its effects on public health are related to the exposure of environmental contaminants and pathogens that are discussed in a previous communication [17]. Also, in the marine food webs such relations revealed that the bioaccumulation and transfer of several contaminants (e.g., persistent organic pollutants) were altered due to climate change [18]. On the other hand, soil systems control several processes in performing ecological functions. In a recent review, Lipczynska-Kochany [19] stressed the effect of climate changes on humic substances, which had a potential link to the fate of contaminants in soil, surface, and groundwater. The author concluded that climate changes might enhance the biodegradation of humic substances and thus soil contaminants could be desorbed and re-immobilized [19]. Indeed, the exposure of soils to pollutants is critically important to aspects of the ecotoxicity of pollutants in soils [20]. However, from a toxicological perspective, the occurrence, fate, and transport of chemical pollutants in soils are largely driven by the properties of the pollutants; however, the properties of soils are also important. Therefore, in this review, we develop an understanding of the dynamics of pollutants in soils with various properties, subject to a range of processes under the climate change influences.

2. Understanding Soil Properties and Processes and the Dynamics of Chemical Pollutants

Toxic substances including heavy metal(loid)s, such as arsenic (As), mercury (Hg), lead (Pb), cadmium (Cd), and chromium(VI) (Cr(VI)) and organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs) (e.g., benzo[a]pyrene), persistent organic pollutants (POPs) (e.g., polychlorinated biphenyl) or emerging pollutants (e.g., per- and poly-fluoroalkyl substances, polybrominated biphenyls, etc. that present unique issues and challenges to environmental quality) have been detected in soils [21]. The available fractions of such pollutants in soil are often toxic to soil organisms and humans [22–24].

Adsorption and desorption of chemical pollutants in soils largely depend on pH, redox conditions, and the available chemical species. Inorganic ions, such as HPO_4^{2-}, NO_3^-, Cl^-, and SO_4^{2-} and organic ligands, such as citrate, oxalate, fulvic, and dissolved organic carbon (DOC) can affect pollutant behavior in soils [25–27]. Inorganic ions can influence adsorption through their interactions with metal(loid)s. For example, metal(loid)s complexed with such ions exhibit less sorption affinity to soils [28] than free ions, but free states of some ions (e.g., PO_4^{3-}) in soil increase net negative surface charge and therefore increase the sorption of cationic metal(loid)s [29]. Soil organic constituents, such as soil organic matter (SOM), which is often estimated and expressed as soil organic carbon (SOC) [30], play an important role in the sorption of soil pollutants [31]. Some SOM, such as humic substances have a high affinity for metal cations [32]. The heavy metal ion-binding ability of humic substances is attributed to the negative surface charge, particle size, and diffusion coefficient of humic acid as well as the content of oxygen-containing functional groups, including -OH, -COOH, -SH, and -C=O [33,34].

Another important process in soil is the microbial activity relative to the fate and transformation of pollutants. For example, the microbial degradation of petroleum hydrocarbons [35] is experienced as the natural clean-up process of organic pollutants. Also, heavy metal(loid)s can be remediated using the soil-grown plants (commonly accepted as "phytoremediation"), particularly with the microbial-assisted rhizosphere [36].

3. Changing Environments–Climate Change and the Soil Properties and Processes

The principal climate change factors and results that affect soil properties and processes are (i) presence of GHG, (ii) air and soil warming or extreme surface temperature, (iii) extreme rainfall and saline water intrusion, and (iv) land and surface soil erosion [7,37–39]. The processes that can induce changes in soil properties and processes include temperature, hydrologic cycle, soil moisture, salinity, redox condition, and the organic carbon fractions of soil systems [20,40–45].

The IPCC [46] reported a significant increase in GHG, mainly during the last 60 years. For instance, during the past six decades, the anthropogenic CO_2 emitted to the atmosphere was 2040 ± 310 Gt, and the amount of CH_4 and N_2O followed with the similar trend [46] (Figure 1). However, a large portion of GHG is deposited in the terrestrial systems, such as soil and plants, which contribute soil organic carbon (SOC) pool in soil or increase N uptake in plant systems [47,48]. Soils are impacted by climate changes and the total environmental process involves air and water systems as well (Scheme 1). Climate change has induced an increase of global mean surface temperature by about 0.3–0.6 °C in the past century and is expected to remain elevated [46]. The warming of the atmosphere in the Anthropocene, which was particularly evident from 1983 to 2012 [46], is likely to have increased temperature in soils [16].

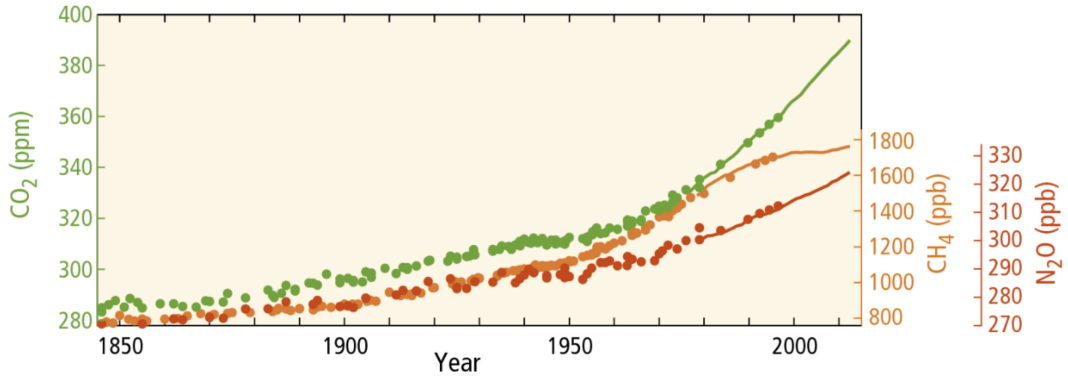


Figure 1. A global average greenhouse gas concentration trend. The figure was retrieved from the Intergovernmental panel on climate change with permission (IPCC [46]).

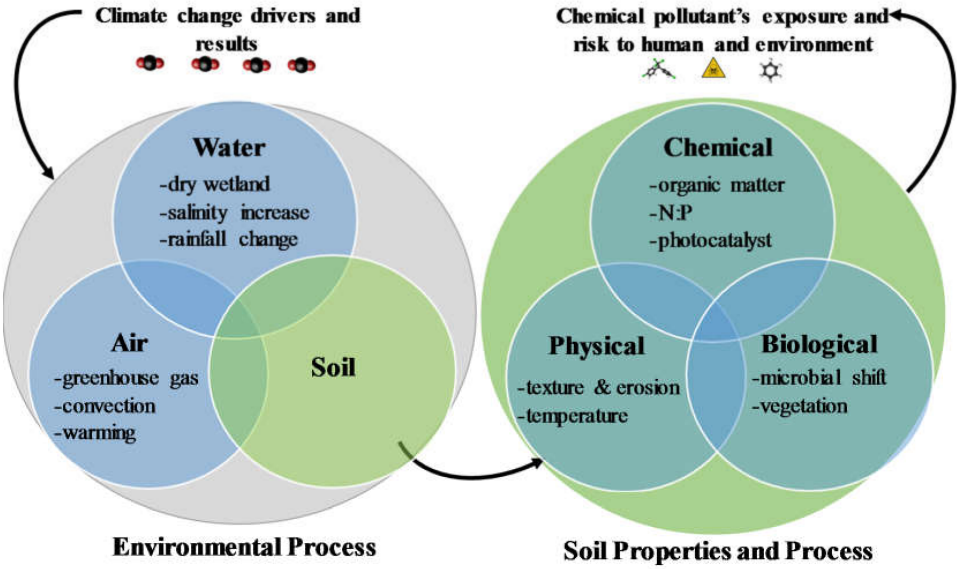
Temperature significantly influences the organic carbon dynamics of soils, imposing substantial loss to "no detectable" loss of soil organic carbon [49]. A considerable uncertainty exists on the soil carbon loss due to global warming as reported in the literature. The focus of our review avoids an explicit explanation of this aspect. However, Crowther et al. [50] reported that up to 1 °C of soil surface warming would lead to the loss of carbon (30 ± 30 petagrams to 203 ± 161 petagrams) from the upper soil horizons (0–15 cm). Furthermore, modeling predicted that the effects of elevated temperatures would slightly increase soil organic carbon (SOC) but decrease dissolved organic carbon (DOC) in the soils of forest systems, but both would decrease in agricultural soils [38]. Using a carbon-nitrogen model, Peng et al. [51] reported an overall decrease of SOC in the forest soils of north-eastern China in response to increased CO_2 emissions and air temperature. However, in that case, the net primary productivity and carbon biomass were increased in the forest soil. In addition to temperature, other climate change-affected factors, such as hydrological process and the relative abundances of organic-C substances, influence the sensitivity of SOC decomposition in soils [52].

In the case of precipitation, the dissolved organic carbon (DOC) is affected higher than SOC [38]. The leaching rate of DOC is an important factor for assessing the effect of precipitation. Water-logging in an extreme precipitation event affects the carbon flux in soil and the plant's uptake of ambient CO_2. Also, topsoil erosion, in this case, could accelerate this loss of particulate organic carbon and DOC [53].

The dynamics of pH in soil is slow in comparison to freshwater and ocean. The acidification of waterbodies is due to the anthropogenic addition of sulfuric and nitric acids (mainly through the

oxidation of sulfur and nitrogen gas) and increased amount of atmospheric CO_2 [54]. On the other hand, ion exchange by the available soil minerals buffers the soil pH and therefore the pH of soil does not change rapidly. From the climate change perspective, increased rainfall could accelerate the leaching of basic cations and thus increase soil acidity [55]. The deposition of atmospheric N coupling with acidic species (SO_3^{2-}, NO_3^-, etc.) has a positive effect on soil acidification. In a field simulation experiment, Zheng et al. [56] reported that these acid dispositions decreased soil respiration by 0.23%, which were further exacerbated up to 1.54%, while both acid and N deposition occurred in soil.

As discussed in Sections 2 and 3, the contamination of soils by pollutants and their transport, diffusion, and persistence in soils are affected by physical, chemical and biological properties and processes [57] (Scheme 1). In the following sections, we will expound linkages among climate change drivers, soil processes, and the exposure of chemical pollutants from empirical and predictive research perspective.



Scheme 1. The impact of climate change drivers on the soil dynamics, resulting in further risk to the exposure of chemical pollutants. The left circle indicates that climate changes and any factors responsible for climate changes influence soil properties and processes directly and via the atmosphere and hydrosphere. On the other hand, the right circle represents the physical, chemical, and biological processes involved in that soil system and the effects of these on the contaminants' fate and exposure.

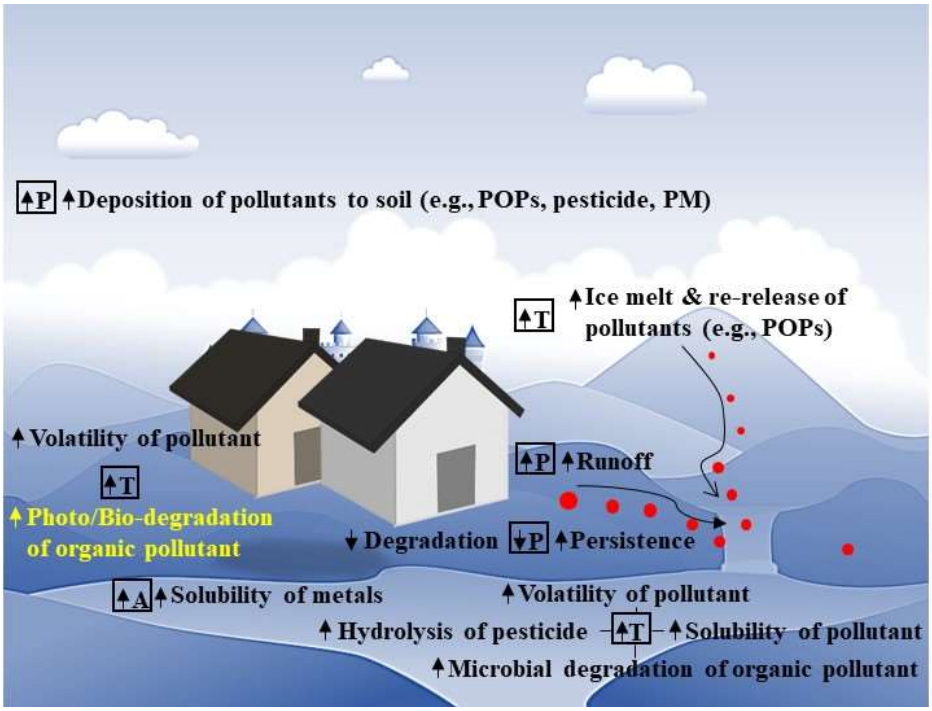
4. Effects of Climate Change on Soil Properties and Processes and the Exposure of Pollutants

Under climate change scenarios, direct impacts on the fate of contaminants have been reported, especially on their transportation between the environmental compartments of the atmosphere, water, soil, sediment, and biota [18]. This occurs through physical, chemical, and biological processes, including possible dilution, concentration, and bifurcation of contaminants [20,45,58]. In addition, under climate change-induced alternations of soil conditions, climate can change surface runoff, air-surface exchange, wet and dry deposition, dissolution by rain, and the transformation of contaminants (e.g., photolysis, biodegradation, oxidation in air, and dilution) [20,43,59].

4.1. Soil Temperature, Water, and Erosion

In relation to the warming world, the changed and changing transport pathways of contaminants, including volatilization, precipitation, surface runoff, degradation and transformation have been well documented during the past decade [20,45,58] (Scheme 2). Briefly, the major events are as follows: (i) In the atmosphere: persistent organic pollutants and particulate matters can be deposited into the soil and water by increased rainfall; (ii) Polar, ice and glacier region: increased temperature

could increase the release and mobility of persistent organic pollutants towards the downstream; (iii) On soil surface: volatilization and degradation of organic contaminants are positively correlated to temperature; on the other hand, increased precipitation might increase runoff of contaminants from soil to water system; and (iv) In waterbodies: warming conditions could enhance the volatilization, hydrolysis, and microbial degradation of contaminants, while both temperature and acidic condition of water favor solubility of heavy metals in water (Scheme 2).



Scheme 2. Generalized view of the impact of extreme warming and precipitation on the dynamics of the chemical pollutants. The upside arrow (↑) indicates "increased" while downside arrow (↓) is for "decreased". T = temperature, P = precipitation, A = acidification, POPs = persistent organic pollutants, and PM = particulate matter. The content in the scheme is presented in detail and further instructed in the text. The scheme was modified after Noyes, et al. [20] with copyright permission of Elsevier Ltd.

Soil warming due to climate change has resulted in an increased transportation of contaminants in soils [60]. For example, simulating geomembrane assisted contaminant remediation in Arctic landfill resulted in elevated temperature (+2 °C) in the soil surface and geomembranes increased the mobility of benzene, toluene, ethylbenzene, and xylene (BTEX) [61]. Also, higher soil surface and air temperatures, and faster wind speed enhanced the volatilization and dispersion of volatile organic and inorganic contaminants such as methane, ammonia, nitrous oxide, sulfides, and mercury from soils to air [43]. For example, the elevated temperature can increase the methylation rate of inorganic mercury in soil [62] and water and sediment [18,63]. In an anoxic environment, Yang et al. [62] reported that arctic soil temperature increased from −2 °C to +8 °C and favored the methylation of freshly added inorganic mercury by 10-fold, mainly as a result of methanogenesis. In the case of elemental mercury (Hg^0), a 1 °C–3.7 °C increase of surface soil warming in a climate change vulnerable region (Qinghai-Tibet Plateau permafrost) could increase the concentration of Hg^0 by 9.4–40% in the surface soil (0–5 cm). The conversion from a less bioavailable form to a more bioavailable form of mercury is reported for mainly aquatic systems due to the increase of temperature [43,63]. However, due to the very limited evidence that exists of the bioavailable species of mercury in various soils, it is not known how the more bioavailable and toxic species of mercury (e.g., methylmercury) will affect humans. Using environmental biological receptors, the toxic effects of some other metal(loid)s have

been reported [61]. For example, comparing two air temperatures (20 and 25 °C) and using a drought simulation (50% and 30% moisture of water holding capacity of soil), González-Alcaraz and van Gestel [64] reported that in an extreme scenario (30% moisture but 25 °C temperature) invertebrates in watercourse soil could accumulate more Cd, Pb, and Zn in their body and become severely damaged. In the Arctic, except for the above-mentioned changes of contaminant pathways, the temperature warming may shift ice/snow into water or trigger the thawing of previously permanently frozen soil layers and hence have immense consequences for physical and biological systems [58,65,66]. Such thawing/melting might trigger the exposure of previously frozen compounds in the arctic soils, alter hydrological flow paths, accelerate soil erosion and an increase in the surface runoff of contaminants [65]. In mining sites, downstream could also face an inflow of pollutants and increased temperature could accelerate this mobility. For example, temperature-induced snowmelt and its runoff carried a burden of Zn, SO_4, and Mn to the riven basis from the adjacent mining sites in the Colorado's rocky mountain areas [67]. In the case of organic contaminants, the volatilization could increase biotransformation, photodegradation, and biodegradation so that their removal or degradation occurs more favorably than transportation by surface runoff [20,43,58–60,68,69]. Some pesticides could also cause a higher level of oxidative stress to the soil organisms (e.g., earthworms) while they are exposed to the elevated ambient temperature (25 °C compared to 20 °C) [70].

Precipitation also strongly affects the transfer of contaminants in soils [45]. In areas affected by climate change, the annual precipitation may decrease [42], increase [43,59] or extremely fluctuate depending on the latitude and regional atmospheric circulation pattern [71]. For example, with a climatic condition of increased precipitation, the concentration of perfluorooctanesulfonic compound (PFOS) was projected to be lower in urban soil and freshwater due to the surface runoff flow towards the rural soil and coastal habitat [45]. In some cases, increased flooding caused by climate change (e.g., rain surge) may lead to the mobilization of toxic chemicals (e.g., pesticide) stored in the soil or the remobilization of chemicals adsorbed on the soils [17]. For example, Pb and Cd appeared in soils of floodplains after the flooding of the river Meuse during the winter of 1993–1994 [17]. Increased soil moisture can increase the exposure, accumulation and ecotoxicity of inorganic mercury (e.g., Hg(II)) [72] in soils when they have been impacted by mercury deposition from the air. Submergence by flooding or rising sea level leads to oxygen deprivation and reducing conditions in soils (low redox potential, *Eh*) [37,41,43]. This affects the speciation, degradation, mobility, transport and cycling of various contaminants [37,43]. Arsenic methylation can occur in flood-affected anaerobic soils [73]. Another compelling example is that the reducing condition in coastal soils caused by sea or river water inundations induces a reductive dissolution of geogenic As-bearing mineral oxides and thereby releases As [37].

On the other hand, surface runoff and erosion, caused by the increased intensity and frequency of rainfall, storms or flooding, can increase the transportation of contaminants outside the parental soils. Dioxins, heavy metal(loid)s, cyanide, hydrophobic organics, ammonium, and hydrocarbons, from contaminated soils can be transported in a runoff to uncontaminated water and soil [40–43]. Intense rainfall events enhance the transfer of agrochemicals particularly from arable land to aquatic ecosystems with surface runoff and erosion [42]. On the other hand, soil tilling and crop harvesting can cause the release of soil particle-bound contaminants like steroids, pesticides, and polycyclic aromatic hydrocarbons from soils to air [74]. The hotter and drier summers as a result of climate change can worsen the contaminant release during these processes. At mining sites, more contaminant runoff or interruption of mining activities can occur following a possible disruption of the hydraulic structures like dams, ditches, spillways and holding ponds during heavy rainfall and flooding events under climate change scenarios [69].

4.2. Soil Organic Carbon

Climate change can alter organic carbon cycling and SOC dynamics in soils, leading to changes in the bioavailability of contaminants that are bound to SOC [66]. Increased soil temperature can

accelerate the biological degradation of SOC, leaching, and surface runoff of DOC from soils, resulting in decreases in both SOC and DOC concentration in agricultural systems [38,43,60,75]. The released SOC-bound contaminants after erosion and contaminants bound to DOC in suspended particles in runoff increase accession of soil contaminants to water bodies [43,75]. Organic matter degradation showed little temperature sensitivity in a highly weathered clay-rich mature tropical forest soil due to the chemical protection of C by mineral surfaces, whereas a higher temperature sensitivity would be expected for the SOM in a freshly tilled temperate prairie soil [52]. Studies by Giardina and Ryan [76] also demonstrated that SOC decomposition rates in mineral forest soils were not dependent on temperature alone. Similarly, Melillo et al. [77] showed that the acceleration of organic matter decomposition by soil warming is limited and short-lived for mid-latitude forests, which was attributed to the small labile SOC pool. Hence, global warming may increase SOC-bound contaminant release from some soils, but this is not necessarily the case for all soils, especially mineral soils.

4.2.1. SOC for the Exposure of Organic Contaminants

Increasing concentrations of organic matter in soil reduce the toxicity of some contaminants as they interact and diffuse into the organic matter [78,79]. Semple et al. [78] proposed that the bioavailability and extractability of hydrophobic organic contaminants can be represented by four fractions: (i) readily available, (ii) degradable and removal fraction, (iii) recalcitrant, and (iv) non-extractable fraction (Figure 2). Certain factors manipulate those fractions. For instance, organic matter and soil texture influence how much of a contaminant would be readily available or lost from the soil system over time. Similarly, microbial composition and abundance in soils and the oxidative and catalytic status (e.g., light intensity and soil enzyme) could determine the extent of removal and degradation of the readily available fraction of contaminants. As proposed in Figure 2, some consequences of climate change such as the alteration of SOC and microbial composition have governing roles in the model proposed by Semple et al. [78]. For example, in the global warming scenario, a sequestered portion of contaminants may become labile or the labile portion becomes more readily bioavailable [80]. A rise in temperature, generally, increases the toxicity of organic contaminants and is likely to enhance the rates of chemical and photodegradation [20] by increased light intensity. The oxidized but partially degraded final product could be more toxic than the original substrate [81].

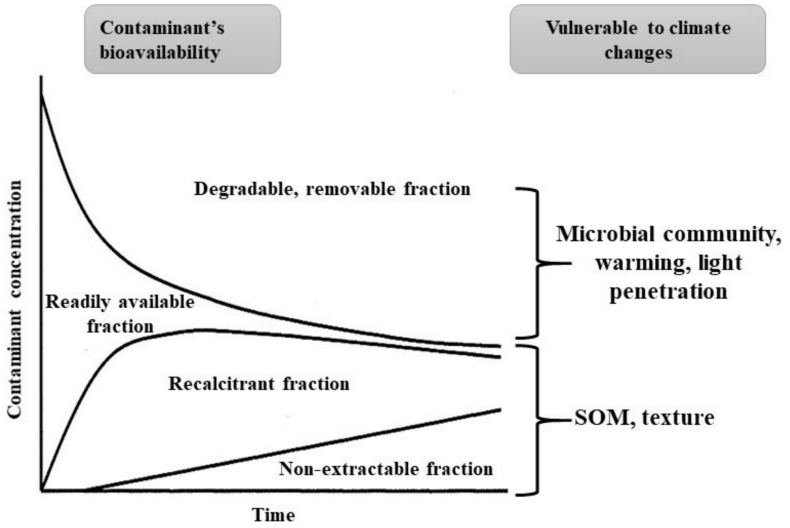


Figure 2. Various states of hydrophobic organic contaminant's bioavailability and extractability and the responsible soil properties that are vulnerable to climate changes. The figure is modified after Semple, et al. [78]. For the explanation of each line graph, see the text in Section 4.2.1.

4.2.2. SOC and Release of Metal(loid)s

The availability and mobility of heavy metals depend on their adsorption and desorption in soils [82], which are strongly related to SOM (see Section 2). SOM affects the bioavailability and retention of heavy metals (e.g., Cd, Pb, Cu, Ni and Zn) in an exchangeable or complex form [83]. SOM acts either as a source of organic chemicals to the pore water or as a sink, strongly binding with heavy metals [84–87].

Warming and CO_2: As discussed in Section 3, increased temperature [88] and CO_2 enrichment [89] both exert almost equipotential influence on organic carbon contents in soil, but in opposite directions. Thus globally, in warmer areas where increased atmospheric CO_2 concentration is dominating, SOC content is expected to increase, whereas decreased SOC content may be observed in cooler regions where the effect from an increased temperature dominates [90]. Therefore, changes in soil temperature may affect the behavior of metal(loid), such as the adsorption-desorption process in soil, indirectly through their impacts on SOM [91,92]. Such changes in SOM have been reported to be responsible for a higher load of heavy metal (e.g., total Hg) in soil subjected to CO_2 enrichment [93]. It is generally agreed that the decomposition of SOM due to the increased temperature could reduce cation exchange capacity and therefore the soil lost capacity to retain heavy metal (research reviewed by Rajkumar et al. [94]). In other words, biological receptors, such as plant, could uptake more heavy metals of these available fractions in soil solution [94]; the insights are discussed in Section 4.5. Other variable soil properties such as pH and ionic strength relative to climate changes [55] could influence the extent of reaction between organic matter (e.g., humic acids) and metal ions and also the stability constant of metal-humic complexes [95].

Soil erosion: Climate change-induced soil erosion would increase the loss of surface soil that contains significantly greater amounts of SOM than deeper layers. Some scenarios predict a greater frequency and intensity of storms, which will have significant impacts on soil erosion [96]. This could lead to a significant loss of surface soil in any single year, 70–300 t ha^{-1} in comparison with typical losses of 60–80 t ha^{-1} (bare fallow), 8 t ha^{-1} (under a crop) and 0.24 t ha^{-1} (under pasture) [97]. This could lead the transport and migration of pollutants bound to SOC at transboundary scale and thus has become a great concern for human health [98–100]. In addition to its effect on SOM, soil erosion results in losses of the finer mineral fractions from the surface soil so that the suspended sediment has a greater sorption capacity for metals than the original soil (see Section 4.4.1 below).

4.3. Soil Nitrogen and Phosphorus

There is compelling evidence on the effect of chemical pollutants (e.g., heavy metals) on the N and P cycle due mainly to the interruption of microbial functions in these processes by those pollutants [101–103]. However, the coinciding phenomena has rarely been addressed. Considering key climate change effects, such as increased temperature, precipitation, and soil erosion, the soil runoff that contains N and P nutrients can cause eutrophication in lakes and coastal waters [104].

In a long-term study (May 2004 to April 2005) in the Mediterranean shrubland, Sardans et al. [13] reported a decrease of soil enzyme activities, such as urease, protease and β-glucosidase, which might further manipulate N cycle in soil. For example, applying artificial soil warming, these researchers argued that a ~5 °C to 1 °C increase of soil temperature might result in an excess amount of NO_3^-, but a low amount of NH_4^+ species. Drought imposed a similar interference in the soil enzymes but the net loss/gain of N in the soil was not concluded [13]. On the other hand, the soil deposition of the atmospheric NO_x and N_2O can change soil processes such as leaching, acidification, mineralization of organic matter, and nitrification rates [105]. It is not known whether the nitrogen stock and the speciation of nitrogen in soil have a direct effect on the mobility contaminants. However, the process related to N has a direct effect on the N accumulation on plants [13]. Nitrogen addition caused increased growth and dominance of some grass types and has been linked to increased rates of soil acidification and a loss of species diversity [106–108]. These two changes with soil pH and loss of biodiversity impact the mobility of heavy metals and the biologically mediated degradation or

transformation of chemical pollutants. For example, in a study of a Dutch forest, van Breemen and van Dijk [109] reported that excess deposition of atmospheric N might cause soil acidification and therefore some pollutants (e.g., Al^{3+}) could become more available to the biological receptors living in soil. Further on, the fate of soil biological processes and contaminants is discussed in Section 4.5.

Extreme climatic conditions could increase P runoff from land erosion in soil. For example, the higher precipitation and lower temperature in winter in northern temperate coastal regions led to a 3.3–16.5% higher amount of P runoff [110]. Apart from the nutrient pollution of such runoff [104], the fate of pollutants present at the point of soil erosion can also be influenced. For example, in soils contaminated with a high concentration of heavy metal(loid) ions, the presence of HPO_4^{2-} along with other anions such as SO_4^{2-}, CO_3^{2-} and OH^- cause the immobilization of metal(loid)s [111–113]. McGowen et al. [114] observed a decrease in the leaching of Cd, Pb, and Zn due to the formation of metal(loid)-P precipitates. However, in the P-limiting condition in agricultural soil (e.g., paddy soil), iron plaque is formed, which immobilizes heavy metals (e.g., Cd) [115]. In the case of temperature-induced soil acidification, this metal-binding complex is affected and thus a greater amount of metals becomes available to the plant-root system [116]; it further influences the plant accumulation of metals, such as the translocation of metals from root to shoot and disperses them into the shoot systems.

4.4. Soil Minerals and the Exposure of Chemical Pollutants

4.4.1. Clay Minerals

Clay minerals are naturally occurring phyllosilicate found in soil, sediments, and rocks. The history of clay mineralogy in soil is several decades old and still prospective in earth science [117]. The clay minerals in soil are complex and dependent on the weathering process in specific types of geological status; however, commonly occurring or exploring clay minerals in soils are mica, illite, smectite, kaolinite, etc. Descriptions of the structure and properties of clay minerals and their modified products can be found elsewhere [118,119].

There is no conclusive evidence that climate change directly impacts soil clay minerals. However, their fine particle size and associated organic matter strongly influence the bioavailability, and transport of pollutants [35,120]. In particular, organo-clay complexes in soil respond to soil warming and the release of bound heavy metals that may become available in soil [121,122].

Increased soil erosion caused by climate changes [123] causes the loss of clay from the surface of agricultural soils [124] and affects the transport of chemical contaminants bound to clay fractions [125]. Extreme rainfall and other means of erosion can also leach out dissolved salts from the soil surfaces that further destabilize the soil due to the lack of conductivity, leading to a loss of clays from the soil structure through the dispersion of clay particles. The mobility of contaminants is subjected to such destabilization of soil [41]. Clay minerals suspended in runoff could increase the adsorption of pollutants from solution to the solid phase. On the other hand, emerging research has shown the potential synergistic interaction between bacteria and clay minerals [126] for the enhanced bacteria-modulated biodegradation of organic pollutants such as PAHs [35,127–130], and pesticides [35,131].

Another aspect of the effects of climate change is the photodegradation of organic pollutants due to the direct effects of soil warming and light intensity [81,132]. The authors argued that partial degradation creates toxic intermediate metabolites in soils. In this instance, the photodegradation changes were affected by the texture of soil—the more clay minerals in soils the more degradation of PAH and atrazine [81,132]. However on balance, the benefits of clay minerals in the rhizosphere [133], for the stabilization of enzymes [134] and carbon in soils [135], might outweigh any detrimental effects in the challenge of increased radiation at the soil surface resulting from climate change.

4.4.2. Non-Clay Minerals

In addition to clay minerals, other minerals such as feldspar, carbonates, micas, iron oxides, sulfides and chlorites [136] influence the behavior of contaminants. Under increased CO_2 and temperature conditions, weathering and dissolution of these minerals might be the key process to consider [137,138] and hence the sorption and mobility of contaminants in soil. However, direct evidence is rare in the available literature whether these climate change factors are governing the fate of such contaminants; rather, pH-mediated contaminant mobility can occur. As discussed in Section 3, the soil minerals help buffer pH in soil. However, under elevated soil temperature, the availability of some minerals drops or raises soil pH. For example, dissolution of pyrite, arsenopyrite and marcasite could generate acidity in soil and thus release mineral-bound heavy metal(loid)s into the soil solution [40,69]. On the other hand, the presence of other minerals such as calcite, dolomite, and limestone, dissolution of native and rock dust gypsum or weathering of aluminosilicate minerals can lead to higher pH that favors the precipitation of oxides and hydroxy sulfates and binds metals from solution [69].

Another important impact of climate change on soil non-clay minerals relates to flood immersion or rising sea levels that alter soil hydrological regimes featured by oxygen deprivation and also lower redox potential (*Eh*) [37]. Under submerged conditions, the reductive dissolution of As-bearing Fe- and Mn(hydro)- oxides may occur due to oxygen deprivation [37]. This dissolution caused elevated levels of arsenic from geogenic and anthropogenic sources along many coasts around the world, including south and southeast Asia and the United States [37]. However, when high SO_4^{2-} is present under such anoxic conditions, metals can be immobilized as insoluble sulfides through their surface complexation. This reduction reaction of sulfate inhibited the dissolution of metal-bearing Fe oxides [37]. Flooding and the drying cycle of soils leads to fluctuating soil redox conditions, exerting direct or indirect influence on trace metal dynamics through changing soil pH, DOC, and the chemistry of Fe, Mn, and S minerals [139]. The redox cycling of trace metals and/or their host minerals determine the immobilization of these inorganic contaminants [140]. When the flooded soils are dried, the oxidation of reduced solute and solid-phase species occurs. A particular case is extreme soil acidification caused by pyrite oxidization when flooding recedes or sea level drops. Such soil acidification may release a range of contaminants including soil adsorbed NH_4^+, Al from clays, and other metal(loid)s such as As, Co, Fe, Mn, Ni, and Zn from pyrite [141].

4.5. Soil (Micro)organisms, Enzymes, and Plant Receptors

Soil microorganisms and enzymes play pivotal roles in the decomposition of organic matter, nutrient cycling, energy flow, improvements in soil physicochemical qualities as well as pollutants' transformation [47]. The ecosystem services provided by the microbial community in soils are greatly influenced by climate drivers due to the fact that the growth and functions of microorganisms are largely driven by soil temperature and moisture [142,143]. In fact, a projected soil warming by +4 °C in temperate forest could significantly increase (34–37%) soil respiration in whole-soil (0–100 cm depth) due to the decomposition of decadal-aged carbon [144]. With such insights of the decomposition of mineral-associated SOC in the subsoil, it will be an interesting future study to understand the fate (e.g., degradation and re-immobilization) of adsorbed pollutants using the *in situ* depth-gradient approach. Under climate change, CO_2 enrichment is also thought to have positive effects on plant productivity and growth, and in reducing heavy metal(loid) accumulation and increasing phytoremediation [145,146]. The increased photosynthesis and photosynthate allocation to the root system might increase root exudation and so enhance the bioavailability of contaminants to plants [147]. Root exudates act as ecological drivers for the microorganisms by supplying them with carbon and energy, and enhancing hydrocarbon degradation in the rhizosphere [148]. As a result, a distinct contaminant distribution gradient develops opposite to the gradient of root exudates, with the least contaminant concentration and the highest exudate concentration close to the roots [149]. The main role of root exudates in petroleum hydrocarbon degradation is a provision of energy

and nutrients for microbial growth and activity [150]. A recent review by Hussain et al. [151] demonstrated that the remediation of total petroleum hydrocarbons (TPH) is effective with the synergies of phytoremediation and bioremediation (collectively called "rhizoremediation"). However, concern emerges with convincing evidence that soil warming and excess N input to soil impose stresses on the rhizobial microbial community [152]. In particular, changes in arbuscular mycorrhizal fungi (AMF) have been reported in several crop systems and the damage to AMF communities could reduce plants' capacity to resist chemical pollutants. In addition, increased atmospheric CO_2 concentration may increase soil acidity by an increased input of carbonic acid released from root and microbial respiration [153,154]. Decreased pH decreases the adsorption of trace metals onto organic matter and metal oxides [91], thereby increasing their bioavailability and uptake by plants [155,156]. This may result in higher bioavailability of pollutants to humans and other animals that consume affected plants [157].

In an in situ experiment using a thermal gradient of 4–40 °C in Antarctica, the Arctic, and the tropics [158] reported that the relative activity of fungal hydrolase enzyme increased with rising temperature in the soils in polar regions. This indicates the potential for warming climates to lead to more decomposition of organic molecules in the soil, which is related to the bioavailability of chemical pollutants in those regions. However, the reverse consequence can also occur if released heavy metals are toxic. In other words, the interactive effects of heavy metals and soil warming might have negative impacts on the microbial enzymatic functions [159]. In various contrasting soils, Tan, et al. [159] reported that higher temperatures, especially in alkaline soils, might cause damage to the alkaline phosphatase activity of soil microorganism. The mechanisms underpinning such damage could be the temperature-induced Cd availability that posed an inhibitory effect on microorganisms [159]. Sardans et al. [160] noticed an increased As solubility (67%) and decreased total As (21%) in soil while soil warming was recorded as a 0.95 °C increment at −5 cm soil depth. The higher phosphatase activity in such warming soil releases a greater amount of soluble phosphorous, and the anion exchange of arsenate by phosphate increases soil soluble As, hence an available element for the plant's uptake [160].

However, the overall effects of climate change on the bioavailability of contaminants depends on the interactions between contaminants, soil factors, and environmental receptors. For example, during an eight year warming and drought manipulation of a Mediterranean shrubland, drought increased total Hg concentrations by 350% in soils but had no significant effects on trace element accumulation in aboveground biomass [160]. Sardans et al. [160] showed increased bioavailability of heavy metals due to changing environments and soil properties. The authors found that warming increased aboveground accumulation of Al, As, Cr, Cu, and partially Pb by plant root uptake, and this increase varied with plant types. Drought increased As (40%) and Cd (55%) in *Elaeagnus multiflora* stems, whereas it decreased Cu (50%) in leaves, Ni (28%) in stems and Pb (32%) in leaf litter of *Globularia alypum* [160].

5. Conclusions, Challenges, and the Way Forward

In summary, major mechanisms by which climate change influences soil contaminant processes are the changes in contaminant exposure and alteration of transport pathways related to changes in precipitation, including surface runoff, precipitation, evaporation, and degradation. The other primary pathway was that climate change induces changes of soil conditions such as soil temperature, soil moisture, pH and redox potential, SOC, nitrogen and phosphorus, soil minerals and alter contaminant's binding/releasing, oxidation/reduction and species of contaminants. This review summarized several of such processes that are affected by climate changes (Table 1).

Table 1. Summary of climate change drivers on soil properties and processes and toxicological aspects of chemical pollutants.

Properties and Processes	Potential Impact of Climate Changes	Generalized Toxicological Results	Details in Section
pH	Warming: pH can drop due to formation of sulfate and rhizosphere acidification; pH can raise due to presence of calcite, dolomite or dissolution/weathering of gypsum and aluminosilicates Inundation: pH can raise (if pyrite is formed in the initially during inundation; pH can drop when flood recedes or water level drops due to dissolution of pyrite. Atmospheric deposition: N coupling with acid species increase soil acidity	Soil acidification could increase desorption of heavy metal(loid)s from their mineral-bound complex or favor re-mobilization	Sections 3, 4.1 and 4.4
Temperature	Global warming: Increase of soil temperature; Degradation of SOC increases/more labile fractions to microorganisms; microbial feedback to temperature might be positive	More bioavailability of chemical pollutants; Biodegradation of organic pollutants might increase; Dissolution of metals from its substrate	Section 3, Section 4.1
SOC	Warming: Degradation of SOC increases/both persistent and labile fractions are vulnerable Erosion: Loss of SOC from soil	More bioavailability of chemical pollutants Mobility of chemical pollutants	Section 3, Section 4.2
Moisture/rainfall	Water repellence: Growth of microorganism decreases; less vegetation Inundation: Anoxic environment in soil Extreme rainfall pattern: Soil inundation, surface runoff and salt imbalance in soil	Longer residence of pollutants Redox controls the mobility of chemical pollutants; mineral's dissolution can release toxic metals, such arsenic	Section 3, Section 4.1, Section 4.4.2
N and P	Deposition of atmospheric N and load of P from land-use practice: Increase of N and P in soils; acidification of soil	(Im)mobilization of metals (e.g., Cd) in P-supplemented soils; nutrient pollution and surface runoff	Section 4.3
Clay minerals	Erosion: Loss of surface soils Warming: Increase of soil temperature Intensity of light: Light penetration in soil is high	Clay-organic matter disintegration might release heavy metals; loss of clay could reduce microbial function in rhizosphere; partial photodegradation could result in a more toxic metabolite of organic pollutants and thus increased bioavailability of them	Section 4.4.1
Other minerals (e.g., oxides)	Extreme rainfall pattern: Inundation of soils affects redox of soils Temperature: Increase of soil temperature	Redox controls the mobility of chemical pollutants; mineral's dissolution can release toxic metals, such as arsenic	Section 4.4.2
Microorganisms, enzyme and plants	Warming: Microbial activity may increase but community structure changes GHG in soil: Community structure changes	Biodegradation of organic pollutants may be increased but the contaminant-specific microbial functions could be affected; plant uptake of metal(loid)s is affected due to climatic influence in rhizosphere	Section 4.4.2

Overall, humanity's exposure to contaminants could be increased due to climate change. The key mechanisms for this risk may be the desorption and remobilization of soil contaminants. However, reaching a conclusion on whether climate changes have any direct effects on the magnitude of chemical toxicity is difficult due to the limited availability of studies. The extent of identified pathway depends on both the state and properties of contaminants; these includes the solubility, hydrophobicity and volatility of the contaminants. From toxicological perspective of soil contaminants, one important factor is the speciation of contaminants. This review finds limited evidence that few species of contaminants, such as methylation of mercury and arsenic or metabolites of polycyclic aromatic hydrocarbons or pesticides, might increase the toxicity risk for humans. This aspect should be studied and priority contaminants identified. The microbial feedback to climate change could be another key aspect that should be counted in relation to the fate of chemical pollutants and the exposure of them and their metabolites to humans. Although our charge in this study is not to review the molecular details of

the potential change in the microbial community structure due to climate change, we observed that microbial feedback to the addition of greenhouse gases in soil is the alteration of their community. Hence, further research should be directed at how these changes at the molecular level influence the microbial-assisted transformation and degradation of pollutants at the short-and long-term scale. The knowledge summarized by this review and future insight can pave our way to addressing the connections between the two critical planetary boundaries that are 'climate change' and 'chemical pollutants'.

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