REVIEW

Microchemical contaminants as forming agents of anthropogenic soils

Ishai Dror, Bruno Yaron, Brian Berkowitz

Abstract Within historically accepted, major soil-forming major processes, the role of chemicals as a human-induced factor was neglected until the middle of the last century. Over the years, however, anthropogenic chemicals have emerged and are being released on the land surface in large amounts. Irreversible changes in the matrix of soil and soil constituents may occur as a result of both intentional and accidental release of anthropogenic chemicals, as well as a byproduct of human activity. After presenting an historical evolution of the discussion on soil-forming factors, we focus here on human impacts and examine the abiotic role of anthropogenic microchemical contaminant (AMCC) interactions with soils at the molecular level. Selected examples of microchemical contaminants, including heavy metals, pesticides, hydrocarbons, and engineered nanomaterials, are presented to demonstrate that AMCCs—even at low concentration—may irreversibly alter the matrix of the soil and soil constituents and lead to the formation of anthropogenic soils with different properties than those of the pristine soils.

Keywords Engineered nanomaterials · Heavy metals · Organic contaminants · Soil constituents and properties · Soil formation factors

INTRODUCTION: HUMAN IMPACT ON SOIL FORMATION

Soil formation has been considered for many years to be the result of natural processes occurring over geological time scales, under various climatic conditions. Until the nineteenth century, soil formation was related strictly to the degradation of geological material, due to weathering processes, at the land–water–air–atmosphere interface. It was only in the late nineteenth century that Darwin (1881), in England, Dokuchaev (1883, 1899), in Russia, and Hilgard (1906), in the USA, reached the conclusion (based on different approaches) that soil is a living body formed under various natural processes. While the Dokucheav approach was largely adopted, Darwinian understanding of soil formation was virtually ignored. However, both noticed the formation of a soil profile with a similar number of horizons, notwithstanding that different factors leading to horizon formation were considered (Johnson and Schaetzl 2015).

From Darwin (1881), Dokuchaev (1883), and Hilgard (1906) to Jenny (1941, 1961), soil-forming factors referred only to natural "virgin" soils formed, under natural environmental conditions, over geological time scales. However, human activity impacts pristine soils, changing them irreversibly, and forming new bodies with different constitutions and properties. Agricultural practices such as terrace construction, deep plowing, irrigation, application of natural or anthropogenic agrochemicals, and fire have led to irreversible changes in soils.

Soil formation processes affected by human intervention have generally been considered to be deviations, which can be reversed over time by natural attenuation or as a result of remediation processes. However, a classical example of human impact on soil changes, during 1000 years of rice paddy cultivation, is the study of a chronosequence consisting of five soil profiles derived from the same calcareous sediments located in Zhejiang Province, China (Zhang and Chen 2010). Comparison between chemistry of non-cultivated and cultivated soils revealed increased depletion of $CaCO_3$ with increasing paddy cultivation, which led to significant clay accumulation in the lower soil horizons after 700 and 1000 years; the distribution pattern of iron was similar to the clay content. In contrast, soil organic

carbon accumulation in the upper soil horizon remained constant over the entire chronological sequence.

Yaalon and Yaron (1966) argued, for the first time, that human-induced changes in soil-forming processes should be considered as an integral, independent factor to be added to the recognized forming factors. In contrast to natural factors, the rate of change of human-induced processes is relatively rapid, and the fundamental properties of natural soils are changed quantitatively within a short time. These anthropogenic changes represent an additional factor within a new reference system wherein the natural soil serves as parent material and an initial state for the newly formed soil. Amundson and Jenny (1991) accepted the human factor in soil formation, but stated that anthropogenic factors are contained implicitly in the previously identified organism factor. However, anthropogenic effects and their impact on the rate of soil modification were recognized subsequently as an independent factor (e.g., Dudal 2005; Brady and Weil 2007; Richter 2007; Richter and Yaalon 2012; Certini et al. 2013; Certini 2014).

Dudal (2005) introduced the notion of "anthropogenic soils" to describe human impacts on pristine soils, with changes to soil class, soil horizon, parent material, and landform, and with consequences for soil classification and nomenclature. In a comprehensive discussion of human transformation of the Earth's soil, Richter (2007) distinguished between contemporary and historic periods in soil formation. Positing soils as the most appropriate marker, Certini and Scalenghe (2011) suggested consideration of approximately 2000 year BP as the start of the Anthropocene, when the natural state of the terrestrial surface began to be altered. As a consequence, Anthropocene formation coincides with the beginning of anthropedogenesis process suggested by Richter and Yaalon (2012). This process is defined by three overlapping time scales: multimillenial pedogenesis of traditional natural bodies, the historic legacy of human forcing, and contemporary human impacts.

The effects of chemicals on the formation of contemporary soils have generally been considered in terms of agricultural activities such as irrigation with saline water, use of gypsum or lime for soil reclamation, and fertilizer application. However, over the years, a wide range of anthropogenic microchemicals has reached the land surface, applied to improve crop production, or disposed of as industrial and municipal wastes. Recently, irreversible changes in natural soils were found to occur as a result of soil contact with chemicals of anthropogenic origin. By "irreversible changes," we refer to long-term, stable, and persistent transformations of soil physical and chemical properties—on a human time scale—which are also resistant to remediation procedures. Some of these changes occur following deposition or adsorption–desorption of chemical contaminants, with irreversibility implied by hysteresis or soil conditioning.

In Fig. 1, we suggest a general time-scale scheme for soil change that emphasizes the fast alteration process of anthropogenic soils (time frame of less than 10^4 years), relative to geological time scales of up to millions of years for natural soil formation processes. These changes are especially pronounced for high volume, modern industrial and urbanization processes. It is further noted that release of anthropogenic microchemical contaminants (AMCCs) to the environment is one of the outcomes of recent scientific and technological advances that drive industrial and urbanization processes, and even from warfare (Certini et al. 2013).

Additional information available from other studies on interactions among anthropogenic chemicals and soil has been used to support the argument that anthropogenic chemicals are a factor in contemporary soil formation (Yaron et al. 2008, 2010, 2012, 2016; Berkowitz et al. 2014; Dror et al. 2015). Based on research results reported in ∼900 publications, Capra et al. (2015) offered a worldwide perspective on anthropogenic soil. Many facets of human factors leading to the formation of anthropogenic soil were noted. However, the input and influence of chemical contaminants were essentially neglected, despite the fact that their input represents addition of anthropogenic materials to soils (e.g., Tu et al. 2013; Kelepertzis 2014; Romić et al. 2014).

In the present paper, we argue that despite their relatively low concentrations on the land surface, AMCCs may act also as a factor in anthropogenic soil formation, by irreversibly changing soil properties and the natural matrix of reactive soil constituents. We first illustrate selected modes of interaction between the main reactive soil constituents (clays and humic substances) and AMCCs ("Anthropogenic microchemical contaminant (AMCC) impacts on soil constituents" section). These interactions are then shown to lead to irreversible changes in the structure and surface chemistry of clays and humic substances at the molecular level. In the last part ("AMCC-induced changes to soils: selected examples" section), we discuss how the cumulative effects of these changes over time and at large scales may result in alteration of natural soil properties such as wettability, retention capacity of associated solutes, and soil morphology.

ANTHROPOGENIC MICROCHEMICAL CONTAMINANT (AMCC) IMPACTS ON SOIL CONSTITUENTS

As a thermodynamically open system, soil will never return to its initial state after being modified by an external factor.
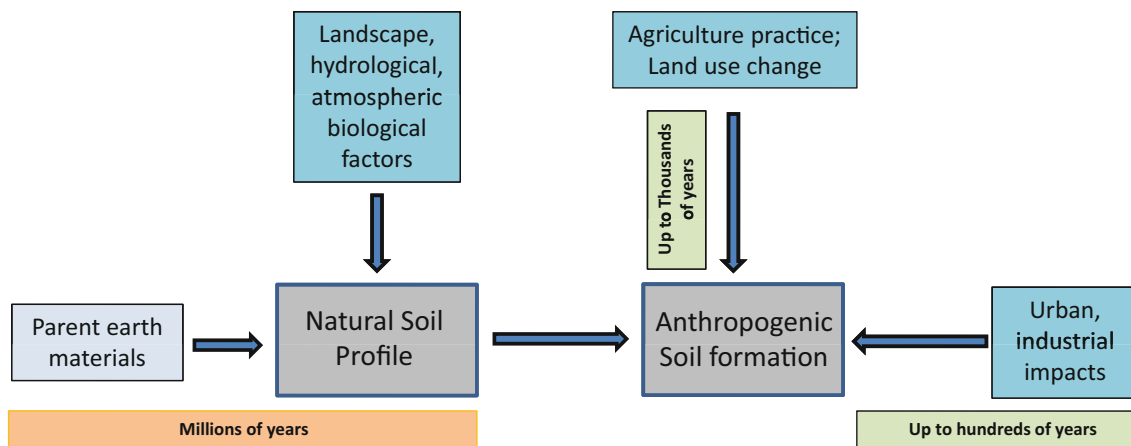
Fig. 1 Time scale for soil change history: from natural weathering of the parent material (potentially stretching back for several millions of years) to anthropogenic soil change by historic human activity (potentially stretching back for several thousands of years), and further to modern urbanization and industrial processes and products that lead to AMCC release, which in turn modify soil (potentially stretching back for several decades)

Because chemical contaminants may, under specific conditions, change soil constituents, it is logical to expect that irreversible retention of AMCCs and their transformation products may also change soil properties, thus leading to contemporary soil formation (Yaron et al. 2012). On the other hand, due to their low concentrations, the impact of AMCCs on soil, and consequently on the formation of new anthropogenic soils with different matrix and properties, may be questioned. However, molecular studies on AMCC interactions with soil reactive constituents (i.e., clays, humic substances) provide valuable information on potentially induced changes to host materials (e.g., Bertsch and Hunter 1998). Table 1 depicts a list of potential contaminant-induced changes to the soil matrix and properties (after Yaron et al. 2009). In "Anthropogenic microchemical contaminant (AMCC) impacts on soil constituents" and "AMCC-induced changes to soils: selected examples" sections of this article, we illustrate irreversible changes to soil constituents by providing new examples. We show also

that the amount of AMCCs retained in different soils is controlled by the ratios among various soil constituents.

Changes to soil clay minerals

As a function of their structural properties, clays may be affected in different ways by interactions with organic and inorganic AMCCs. The permanent negative charge of clay minerals must be balanced by a positive charge situated at or in vicinity of the mineral surface. When the surface is negatively charged, positively charged cations of AMCCs are attracted electrostatically to the clay surface. Processes leading to 2:1 clay modification include adsorption, ion exchange, binding with inorganic and organic cations, and interlamellar polymerization (e.g., Bergaya and Lagaly 2001; Yariv and Cross 2002; Sanchez-Martin et al. 2006). These changes, in turn, affect surface properties, and chemical and physical interactions, of clay with its surrounding.

Table 1 Selected potential contaminant-induced irreversible changes in the soil and subsurface: matrix configuration and properties. After Yaron et al. 2009 with permission from IUSS

Matrix configuration		Properties	
Aqueous phase	Solid phase	Aqueous phase	Solid phase
Salinity/alkalinity	Charge of clay surface	Acidity	Infiltration rate
Ionic composition	Cation exchange capacity	Redox potential	Hydraulic conductivity
Presence of organic ligands	Organic matter configuration	Solubility	Retention capacity
Heavy metals	Hydration status	Salinity	Porosity
Toxic organic substances	Clay redistribution with depth	Turbidity	Rheological properties
Radionuclides		Surface tension	Water repellency
Colloids			

Induced modification of soil clays via AMCC exchange

Heavy metal ion sorption on clay surfaces leads to change in the clay matrix, via two mechanisms (Schlegel et al. 1999): (1) adsorption of metal ions as surface complexes in the outer sphere, on exchange sites, or on inner sphere crystallite edges, and (2) co-precipitation of sorbate and sorbent species. Extensive information on heavy metal adsorption–desorption processes leading to heavy metal retention in various soils may be found in the reviews of Bradl (2004) and Selim (2013). We choose from the literature the case of irreversible retention of lead and zinc on clays.

The effects of ionic strength and pH on the adsorption of lead (Pb) on montmorillonite clay were shown by Strawn and Sparks (1999). Based on batch experiments, it was found that at low ionic strength, Pb adsorption is pH independent, consistent with an outer sphere complexation mechanism where the majority of Pb is accumulated on the planar sites. At high ionic strength, Pb adsorption is pH-dependent, suggesting inner sphere complexation where adsorption occurs on functional groups existing on the montmorillonite edges. TEM observations showed that Pb-exchanged on a natural bentonite surface displayed micro-aggregates or microstructure units, consisting largely of an association of small particles packed together without interparticle pore space (Jozja et al. 2006).

Another example of irreversible sorption, and in turn, change of clay structure is given by zinc incorporation into hydroxyl-Al interlayers. The interaction of Zn with hydroxyaluminum and hydroxyaluminum-smectite complex was studied by EXAFS analysis (Jacquat et al. 2009). The authors showed that Zn is octahedrally coordinated with oxygen at 2.06–2.08 Å, and surrounded by Al atoms at 3.03–3.06 Å in the second shell with increasing molar Zn/hydroxyaluminum ratio. The coordination number of the second shell Al decreases from 6.6 to 2.1. A progressive shift was observed with increasing Zn loading, from Zn trapping in vacancies of the mineral Al polymer, to Zn adsorption on incomplete Al polymers, and finally to uptake by cation exchange in the polymer free interlayer space. The irreversible adsorption of Zn on silicate complexes causes a significant reduction in permanent negative charge, a substantial increase in pH-dependent negative charge, a drastic reduction of internal surface, and a slight increase in external surface area (Barnhisel and Bertsch 1989).

Cationic pesticides are adsorbed to clay minerals by ion exchange processes. Diquat and paraquat, for example, are cationic herbicides used broadly for crop protection. The adsorption–desorption of these pesticides was thought to be directed by charge pattern interactions (Lagaly 1986). Their retention and release on bentonite and kaolinite,

investigated by Weber and Weed (1968), showed that the extent of adsorption is controlled by the cation exchange capacity of the minerals. Herbicide leaching with an aqueous electrolyte solution led to desorption of 80 % from kaolinite and only 5 % from montmorillonite, which was explained by interlamellar absorption. Similar induced interlamellar absorption of other organic substances was shown to modify the microstructure of clay layers. For example, Ogawa et al. (2003) illustrated (schematically) microstructure changes to montmorillonite as a function of exposure to different concentrations of azobenzene (Fig. 2).

Induced modification of soil clays via AMCC binding

Nonionic pesticides include chemical groups such as chlorinated hydrocarbons, organophosphates, carbamates, ureas, anilines, anilides, and benzonitriles. Only slightly soluble in water, nonionic pesticides may bond to clay surfaces through various mechanisms such as cation dipole, coordination, hydrogen, π and van der Waals interactions. Advanced instrumental techniques (e.g., DTA, XRD, FTIR, NMR, and EXAEFS) and molecular modeling provide the possibility to define the mechanism of nonionic pesticide–clay complex formation and stability within soil clays.

Parathion is an organophosphorus insecticide that was used mainly as a crop protection chemical. The adsorption isotherms of parathion from hexane solution, performed on
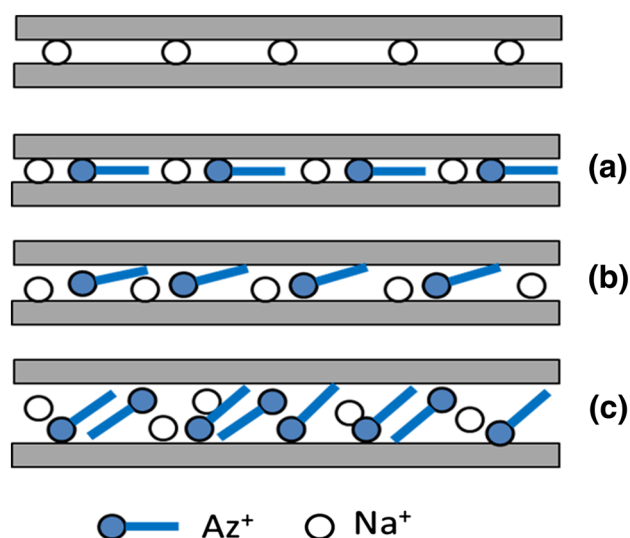

Fig. 2 Impact of amount of azobenzene (Az^+) intercalated in montmorillonite clay as expressed in the microstructure of newly formed clay-pesticide complexes *a* 13, *b* 37 and 66, and *c* 94 and 105 meq/100 g clay of adsorbed Az^+. Reprinted from Ogawa et al., Intercalation of a cationic azobenzene into montmorillonite Applied Clay Science, 22, 179–185, Copyright (2003), with permission from Elsevier

different types of clays, showed that montmorillonite (2:1 type) and attapulgite (fibrous) have a similar retention capacity, while adsorption on kaolinite (1:1 type) is much lower (Prost et al. 1977). The impact of parathion interactions, as reflected in structural changes to clay, is controlled by the type of mineral. For example, X-ray studies showed an increase in the basal spacing for Ca and Al clays (Saltzman and Yariv 1976). These authors also showed by infrared studies a competition between water and parathion, that leads to a change in the coordination between hydrated and nonhydrated clay-parathion complexes.

Alachlor, a chlorinated herbicide, interacts with montmorillonite clay (which is saturated with various cations), revealing a correlation between adsorption and the polarizing power of exchangeable cations (Bosetto et al. 1993). XRD measurements showed that alachlor penetrated the interlayer space of the clay, while FTIR analysis confirmed that alachlor (with the molecular structure of a tertiary aromatic amide) is adsorbed by coordination through the interlayer space of the montmorillonite, replacing interlayer water. Results based on SEM analysis (Nasser et al. 1997) showed a difference in clay morphology before and after alachlor contamination. While Na-montmorillonite exhibited a plate-like structure, the alachlor-Na-montmorillonite complex displayed flocks having significant edge-to-edge association of the blocks. These authors also observed that once the alachlor adsorbed and modified the clay surface, even after it was degraded with aging, its products continued to maintain the morphology changes when compared to the uncontaminated mineral.

Engineered nanomaterials (ENMs) were examined during early stages of nanotechnology research for the possibility of interactions with clay minerals. For example, Mehrotra et al. (1992) found intercalation of amino-functionalized fullerenes (C_{60}) in fluorohectorite, a mica type silicate by XRD and IR spectra. The XRD pattern of fluorohectorite in an amino-functionalized C_{60} aqueous suspension showed a relatively well-ordered multilayered structure corresponding to a primary repeating unit of 26.5 Å or a gallery height of 16.9 Å. In contrast, a gallery height of 3.6 Å was observed when only ethylenediamine was intercalated in fluorohectorite (Mehrotra et al. 1992). The same authors observed changes in the mica-type mineral matrix following intercalation of fullerenes (C_{60}) into fluorohectorite in FTIR studies. IR spectra of the fullerenes (C_{60}) intercalated silicate, compared to the pure fullerenes (C_{60}) spectra, show presence of fullerenes (C_{60}) clusters (Lieber and Chen 2009).

Intercalation of a C_{60} fullerene (fulleropyrrolidine) derivative into Wyoming Na-montmorillonite was studied by Gournis et al. (2004). Organophilic derivatives were intercalated into organic modified clays, while water-soluble fulleropyrrolidine was introduced into clay galleries by ion exchange. Derivatization of the fullerene (C_{60}) was manifested by shifts and formation of a new broad band in the Raman spectrum. When the clay fullerene derivate composite was examined, the same major peaks (found at 1460, 1421, and 1570 cm^{-1}) showed that the derivate was intercalated in the clay. Microscopic studies on interactions of clay minerals with water-stable fullerene (C_{60}) aggregates indicated a change in clay structure due to association between the fullerene and kaolinite or smectite clays (Fortner et al. 2012). Avanasi et al. (2014) confirmed the role of clay minerals for C_{60} fullerene accumulation in soil.

AMCC-induced changes to humic substances

In the soil system, humic substances are of major importance and have an enormous impact on the retention and persistence of anthropogenic chemicals reaching the land surface. Use of advance instrumental and analytical techniques in soil and water chemistry (electrospray ionization (ESI) coupled with Fourier transform ion cyclotron resonance mass spectroscopy (FTICR MS)) over the last decades has advanced knowledge on molecular characterization of both particulate and dissolved terrestrial organic matter. For example, irreversible sorption of chemical contaminants on humic substances is linked to their irreversible structural expansion. The irreversible structural change of a humic acid was reported by Sander et al. (2006). They demonstrated that irreversible sorption is caused by expansion of humic substances and creation of internal micropores by penetrating molecules.

Recent experimental evidence portrays humic substances as heterogeneous supramolecular mixtures, which associate dynamically through noncovalent interactions involving hydrogen bonding and hydrophobic forces (Orsi 2014). Dissolved organic matter is described as a complex mixture of low molecular weight substances and larger molecular weight biomolecules such as proteins and polysaccharides, together with exocellular macromolecules (Nebbioso and Piccolo 2013). However, it should be recognized that data on acid–base properties obtained from dissolved humic substances will be different from those obtained on the basis of humic acid in soils, due to soil buffering capacity.

Induced modification of humic substances due to inorganic AMCCs

Heavy metal bonding to humic substances can be viewed as an ion exchange process between H^+ and metal ions on acidic functional groups. X-ray absorption fine structure (XAFS) spectral data for metal-loaded humic substances

showed that acidic functional groups in humic acid are principal binding sites for metals. It was also shown that the static exchange capacity of humic acid toward heavy metal ions (e.g., Cu^{2+}, Ni^{2+}) is directly dependent on the carboxylic group content of humic acid; as a consequence, the maximal sorption capacity of humic acid toward heavy metals is governed by the carboxylic groups (Lishtvan et al. 2006). Heavy metal ion adsorption–desorption isotherms on and from humic substances originating from peat, for example, show a hysteretic process which points to irreversible retention. The high degree of selectivity shown by organic matter for certain metals suggests that some metals coordinate directly by forming inner space complexes with the functional groups (McBride 1989). These interactions change the basic structure of the humic substances. Following this approach, the hysteresis of heavy metals on humic substances is due not only to cationic exchange but also to an associated ligand exchange process.

Another example of changes to humic substance configuration, and in turn aggregate stability, was reported by Christl et al. (2001). They studied the binding of Cu^{2+} and Pb^{2+} to soil fulvic and humic acids and found that despite differences in chemical composition and protonation behavior, the two types of humic substances exhibited very similar binding behavior. No difference between Cu^{2+} adsorption on fulvic and humic acids was observed at $pH = 4$; however, at $pH = 6$ and 8, Cu^{2+} was bound more strongly to humic acids. Christl et al. (2001) attributed this binding behavior to the different chemical structures and types of linkage of the functional groups to the carbon backbone. They considered that adjacent carboxyl and phenolic groups on aromatic rings such as phthalic or salicylic acids, which are capable of forming strong complexes with Cu^{2+}, are higher in humic acids than in fulvic acids. The total number of binding sites was found to control Pb^{2+} binding on humic acid. The fact that proton metal ion exchange ratios of humic substances are lower for lead than for copper may explain the differential aggregation of humic substances with Cu^{2+} and Pb^{2}. It was observed that Pb-fulvate complexes precipitated at much lower mole ratios of metal ion to fulvic acid than Cu-fulvate, which showed again the dependence of aggregation behavior on the metal cation. As the stability of soil aggregates is governed by humic substances, heavy metal impact on humic substances will in turn affect soil aggregate formation and stability.

Induced modification of humic substances due to organic AMCCs

Molecular level transformation of humic substances can be observed by advanced techniques such as NMR spectroscopy $^1H(^{19}F)$RHSTD and cross-polarization magic angle spinning CPMAS^{13}CNMR spectroscopy (e.g., Chefetz et al. 2000). Polyaromatic hydrocarbons (PAHs) comprise a large group of AMCCs which may be irreversibly retained on humic substances, thus altering their pristine state. Studies on phenanthrene, for example, showed that like other hydrophobic organic contaminants, it has a strong affinity for aliphatic domains of humic substances, and in some cases this affinity is higher than that for aromatic domains (Chefetz and Xing 2009). Phenanthrene binding to modified humic substances is affected greatly by structural and chemical changes of humic acids and humins (Kang and Xing 2005). Irreversible changes occurring in humic substances following phenanthrene pollution were demonstrated by sorption hysteresis (Oren and Chefetz 2005). In general, sorption hysteresis of hydrophobic organic compounds by soil organic matter was confirmed by the formation of metastable states of adsorbate in fixed mesopores and irreversible deformation of the sorbent by the sorbate (Sander et al. 2005; Ge et al. 2006).

Pesticides may adsorb on humic substances by ion exchange. Because humic substances have flexible exchange sites, the charge density of humic substances is pH dependent thus affecting ionic pesticide retention. Acidic pesticide retention on humic substances may occur through a physical process. A comprehensive review by Senesi and Chen (1989) discussed adsorption mechanisms of toxic organic chemicals, including many examples of interactions with pesticides that may lead to irreversible modification of humic substances. The early infrared (IR) studies of Sullivan and Felbeck (1968) proved that ionic bonding can occur between a protonated secondary amino group of the s-triazine and a carboxylate anion of the humic acid. Senesi et al. (1987) confirmed these results and provided evidence of possible involvement of the acidic phenolic group of humic acid. The direct relationship among pH, dissociation constant, and adsorption is strong evidence that protonated alkali pesticides can be adsorbed on humic substances through an ion exchange process. Pesticides that may bind covalently with humic substances include phenylcarbamates, dinitroaniline herbicides, nitroaniline fungicides, and organophosphorus insecticides. Their binding involves carbonyl, quinone, and carboxyl groups of humic substances (Gevao et al. 2000 and references within).

Nonpolar and hydrophobic pesticides can undergo sequestration during prolonged residence or aging in soils. Pignatello and Xing (1996) considered this process to involve two concurrent mechanisms, partitioning and hole filling, in which the pesticide is sorbed in either rubber or glass-like regions of humic substances. The existence of pesticide hysteresis was observed due to some sorbed pesticides being irreversibly retained through different mechanisms on humic substances (e.g., Mamy and Barriuso 2007; Barriuso et al. 2008).
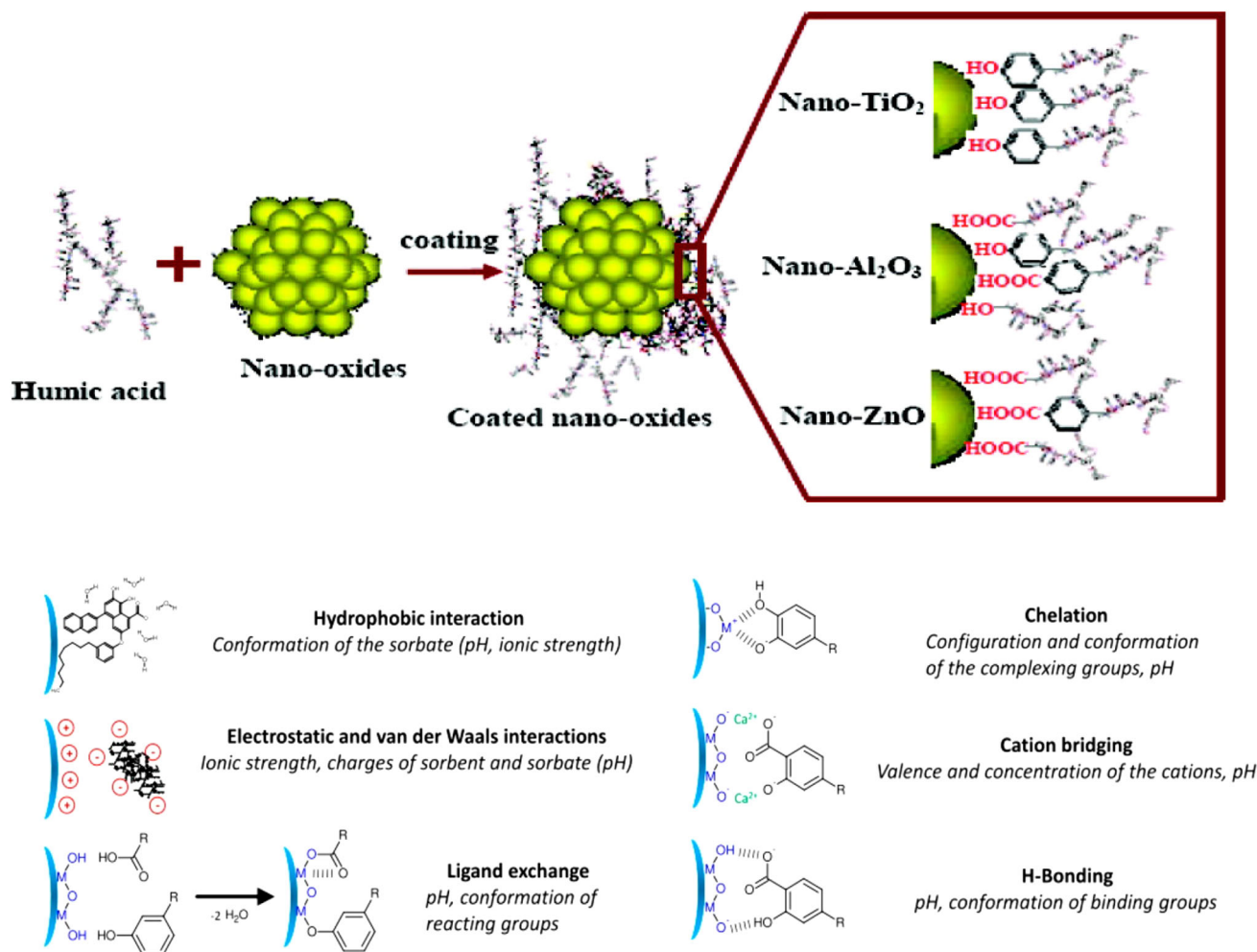
Fig. 3 Schematic diagram showing possible interactions of nanoparticles with humic substances. Adapted with permission from Yang et al., Interactions of humic acid with nanosized inorganic oxides. Langmuir 25, 3571–3576. Copyright (2009) American Chemical Society and from Philippe and Schaumann (2014) adapted with permission from Interactions of dissolved organic matter with natural and engineered inorganic colloids: A review. Environmental Science and Technology 48, 8946–8962 Copyright (2014) American Chemical Society

Engineered nanomaterial (ENM) retention on soils as a function of soil carbon content has been reported (e.g., Avanasi et al. 2014). The impact of ENMs on humic substances has been observed, for example, by an FTIR study of nanosized TiO$_2$, SiO$_2$, Al$_2$O$_3$ and ZnO. Yang et al. (2009) identified interactions between functional groups of soil organic matter and inorganic oxide nanomaterials. A schematic illustration of possible interactions of nanoparticles with humic substances, and their possible mechanisms, is given in Fig. 3. It is noted that strong interactions, as shown for example for metal oxide nanoparticles, modify the structure of the humic substance and its capacity to interact with other substances in the soil environment.

It was observed that COOH groups are responsible for humic acid ligand exchange with TiO$_2$, and that there are strong TiO$_2$ interactions with humic acid phenolic OHs.

This finding indicated TiO$_2$-induced modification of the natural humic acid structure (Gournis et al. 2004). Using fluorescence spectroscopic methods, Klavins and Ansone (2010) studied interactions of fullerene (C$_{60}$) with humic acids. They reported that signal quenching is proportional to fullerene (C$_{60}$) concentration, providing information on complex formation between fullerenes (C$_{60}$) and humic acids. Fluorescence spectroscopy was also used to confirm the chemical changes to soil organic matter when CuO ENMs and strong oxidation conditions were applied (Ben-Moshe et al. 2013). In addition, ENMs may interact and change the structure and behavior of dissolved organic matter (DOM) from the soil pore water through various mechanisms, such as ligand exchange with surface hydroxyl groups (Yang et al. 2009), or π–π interactions with aromatic groups of carbon-based ENMs (Sedlmair et al. 2012). DOM-ENM interactions may capture and block

many DOM functional groups (Cornelis et al. 2014), thus leading to reduction in DOM availability for other interactions, involving DOM net charge, steric limitation due to already existing DOM-ENM interactions, and hetero-aggregation.

AMCC-INDUCED CHANGES TO SOILS: SELECTED EXAMPLES

The literature contains a large spectrum of research results that show irreversible alteration of soil matrix and properties following anthropogenic chemical contamination.. General persistence trends that demonstrate the long-range impact of a few AMCCs, in comparison to soil fertilizer components in sandy soil, are depicted in Fig. 4. It may be seen that heavy metals such as Zn and Cu, and several persistent anthropogenic organic compounds such as DDT and PCBs, remain in soil for periods much longer than human lifetimes, and therefore can be considered to be retained irreversibly.

Inorganic AMCC impacts on soil

AMCC-induced changes to soil properties are highly dependent on association with processes such as adsorption, nucleation, precipitation, coagulation and coprecipitation. Under prevalent conditions in the soil environment, and due to coprecipitation processes, heavy metal solubility, for example, decreases and a solution can be formed with soil hydroxides, carbonates and phosphates. This behavior is demonstrated by the deposition of Cd, Cu, and Zn from solution onto carbonates and oxyhydroxides of the soil solid phase. In such cases, the soil retention capacity is
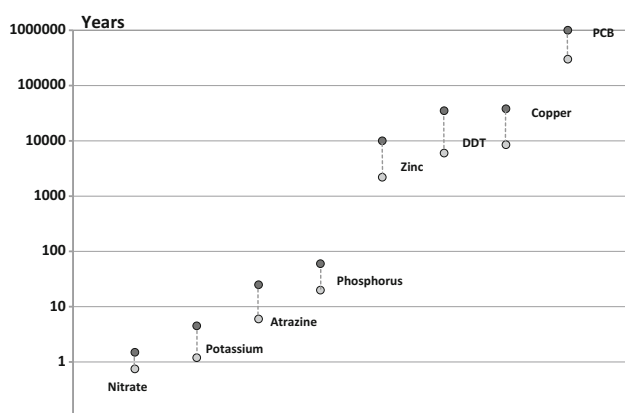
Fig. 4 Time needed to remove chemicals from 1 m of sandy soil by natural leaching. Reprinted from Salomons (1995). Long-term strategies for handling contaminated sites and large scale areas. In Salomons W. and Stigliani W.M. Biogeodynamics of Pollutants in Soils and Sediments. Springer pp 1–30, with permission of Springer

higher than the natural soil adsorption capacity (e.g., Hass et al. 2010). Copper and zinc disposed on land surface as agrochemicals bind on the clay fraction of soils by ion exchange, fixation, and hydrolysis reactions that are pH dependent. Cavallaro and McBride (1984) found that the oxide fraction of a soil acid phase strongly controls Cu^{2+} and carbon fixation. At pH in the range 4–7, 95 % of the sorbed metal was irreversibly retained. López-Periago et al. (2008) analyzed Cu^{2+} retention kinetics, demonstrating irreversibility and showing that release rate coefficients are not dependent on metal loading.

It is further noted that accumulation of Cu^{2+} salts in soils after long-term application has toxic effects on soil bacterial populations, by inhibiting the activity of dehydrogenase, urease, acid phosphoric and alkali phosphatases, as well as on earthworms which are crucial promoters of soil structure and porosity (Spurgeon et al. 1994; Wyszkowska et al. 2006). Because the microbial population contributes indirectly to the formation and stabilization of soil aggregates, Cu^{2+} accumulation leads to a change in soil physical properties by altering the process of aggregate formation and aggregate stability.

Organic AMCC impacts on soil

Once disposed on the land surface, effluents and wastewaters containing hydrophobic organic contaminants may affect the repellency of natural soils. Changes in soil water repellency are reflected in the rate of wetting, retention, and transport of water from the land surface to groundwater. Organic compounds such as aliphatic hydrocarbons and amphiphilic substances may induce soil–water repellency by hydrophobic coating. High molecular mass polar compounds as fatty acids, amides, aldehydes/ketones, alkanes and complex ring-containing structures were found in water-repellent sandy soils from Netherlands and UK (Mainwaring et al. 2004). In a field experiment (Coastal Plain, Israel) where a citrus orchard was irrigated with treated wastewater, an increase in soil water repellency was determined using the water drop penetration time method (Wallach and Graber 2007). The authors linked the results to soil humidity and wastewater composition, which in turn impact biological activity and soil water repellency. Soil water repellency caused by petroleum hydrocarbon contamination was reported by Roy et al. (2003), based on a study of 12 hydrocarbon contaminated soils from Alberta, Canada. The results indicated that petroleum hydrocarbon induced repellency is predominantly a surface phenomenon. Persistence of water repellency is much greater in sandy soils than in clayey soils. Adams et al. (2008) explain these differences by the reduced field capacity of the sandy soils, which after rapid drying favor the deposition of a hydrocarbon film with repellent properties. In

contrast, clay soils require a longer time for dehydration, delaying deposition of hydrocarbon repellent film on the soil surface. Such changes in soil water transmission properties can be considered irreversible although they may be partially mitigated by remediation treatments.

Adsorption and retention capacity of soils, from a water solution, may be affected by the presence of nonionic PAHs. The retention of PAHs in soils is dependent on the specific structure and physicochemical properties of the PAH compound, its concentration in the water solution, and the soil solid phase. The ^{14}C NMR spectra and the sorption coefficient of aromatic hydrocarbons of contaminated sediments suggest that sorption occurring on aromatic and aliphatic moieties of the sedimentary organic matter, and rigid crystalline paraffinic domains, may contribute to linearity of PAH sorption (Oren and Chefetz 2005). However, the extent of PAH adsorption and retention in soil may be affected by the presence in the water solution or an organic co-contaminant which may affect properties of the soil adsorbing phase (e.g., Bayard et al. 2000).

Engineered nanomaterial (ENM) impacts on soil

Irreversible impacts of ENMs on soil were recently reviewed by Dror et al. (2015). It was shown, for example, that ENM retention on soils and sediments may lead to changes in their natural surface properties. Wang et al. (2014) reported changes in clay rich Ultisol soil surfaces as a result of contamination by polyvinylpyrrolidone (PVP)-coated silver nanoparticles (AgNPs). TEM images confirmed that negatively charged PVP-AgNPs preferentially bind to the edges of the positively montmorillonite clay fraction, enriching the soil with clusters of large aggregates with a relative high charge density. Similarly, other materials are often utilized as synthetic binding agents to form clusters of large aggregates; for example, anionic polyacrylamide (PAM) is added to irrigated arable soils (e.g., Sojka et al. 2007), or to soils affected by wildfires to prevent post-fire erosion (e.g., Inbar et al. 2015). Deposition of copper oxide and iron oxide on a Mediterranean red sandy clay soil and on Rendzina soil from an arid region, studied by fluorescence spectroscopy, showed also that ENMs are retained on soil aggregates, changing their surface morphology (Ben-Moshe et al. 2013).

The combined effects of electric double layer repulsion, London–van der Waals attraction, Born repulsion, and hydrodynamic forces affect the fate of ENM deposition on soil, leading to modification of the soil solid phase surface (Arab and Pourafshary 2013). In a soil–water system, ENM-induced charge modification of the solid phase may lead to more positive surface potential, which in turn reduces the electric double layer repulsive forces between suspended nanoparticles and the surfaces.

Exposure to ENMs may lead to changes in the retention capacity of pristine soils for associated AMCCs. For example, Cheng et al. (2005) reported that the retention of naphthalene in soil was affected by C_{60} presence. In a column experiment, C_{60} was added to a Lula silty loam soil (Pennsylvania, USA) and its retention was determined following naphthalene application. An increase in the retardation factor from 8.5 to 13.1 was determined by comparing pristine soil to the soil amended with C_{60}. This increase was related to sorption of naphthalene on the C_{60} in the soil. In another study, retention of arsenic in sandy and red-clay soils following application of stabilized iron-based ENMs (zero valent iron, iron sulfide and magnetite (Fe_3O_4)) was studied by Zhang et al. (2010). The Fe_3O_4 nanoparticles appeared to be particularly effective for As retention: 58 % was retained in the sandy soil and 67 % was retained in the red clay soils. Increases in the natural retention capacity of soils for other inorganic contaminants, such as $Pb(NO_3)$ and $Zn(NO_3)_2$, as a result of prior addition of zero valent iron nanoparticles, was also observed by Gil-Díaz et al. (2014).

CONCLUDING REMARKS

After discussing the human impacts on soil-forming factors, we examined AMCCs as agents that may alter soil constituents and matrices that lead to the formation of anthropogenic soils with different properties than those of the pristine one. We provided examples of changes to soil clays and humic substances, induced by interactions at the molecular level with various AMCCs. We show that even low concentrations of AMCCs released on the land surface may irreversibly modify, at a molecular level, the matrix of soil constituents, which in turn leads to changes in soil properties. It is noted that although only a few publications have to date provided direct evidence of these phenomena, the literature contains findings from many other studies that can be used to support conclusions regarding such changes.

Because of the high volume of AMCCs used in increasing numbers of processes and applications worldwide, their impact is expected to become a significant factor affecting anthropogenic soil formation. This legacy should therefore be considered in designing adequate management of newly formed soils.

REFERENCES

Adams, R.H., F.J. Guzmán Osorio, and J. Zavala Cruz. 2008. Water repellency in oil contaminated sandy and clayey soils. *Environmental Science and Technology* 5: 445–454. doi:10.1007/BF03326040.

Amundson, R., and H. Jenny. 1991. The place of humans in the state factor theory of ecosystems and their soils. *Soil Science* 151: 99–109. doi:10.1097/00010694-199101000-00012.

Arab, D., and P. Pourafshary. 2013. Nanoparticles-assisted surface charge modification of the porous medium to treat colloidal particles migration induced by low salinity water flooding. *Colloids and Surfaces A* 436: 803–814. doi:10.1016/j.colsurfa.2013.08.022.

Avanasi, R., W.A. Jackson, B. Sherwin, J.F. Mudge, and T.D. Anderson. 2014. C60 fullerene soil sorption, biodegradation and plant uptake. *Environmental Science and Technology* 48: 2792–2797.

Barnhisel, R.I., and P.M. Bertsch. 1989. Chlorites and hydroxy interlayered vermiculite and smectite. In *Minerals in Soil Environments*, 2nd ed, ed. J.B. Dixon, and S.B. Weed, 729–788. Madison, WI: Soil Science Society of America.

Barriuso, E., P. Benoit, and I.G. Dubus. 2008. Formation of pesticide nonextractable (bound) residues in soil: magnitude, controlling factors and reversibility. *Environmental Science and Technology* 42: 1845–1854. doi:10.1021/es7021736.

Bayard, R., L. Barna, B. Mahjoub, and R. Gourdon. 2000. Influence of the presence of PAHs and coal tar on naphthalene sorption in soils. *Journal of Contaminant Hydrology* 46: 61–80.

Ben-Moshe, T., S. Frenk, I. Dror, D. Minz, and B. Berkowitz. 2013. Effects of metal oxide nanoparticles on soil properties. *Chemosphere* 90: 640–646. doi:10.1016/j.chemosphere.2012.09.018.

Bergaya, F., and G. Lagaly. 2001. Surface modification of clay minerals. *Applied Clay Science* 19: 1–3. doi:10.1016/S0169-1317(01)00063-1.

Berkowitz, B., I. Dror, and B. Yaron. 2014. *Contaminant geochemistry*. Berlin: Springer.

Bertsch, P.M., and D.B. Hunter. 1998. Elucidating fundamental mechanisms in soil and environmental chemistry: the role of advanced analytical, spectroscopic, and microscopic methods. *Future Prospects for Soil Chemistry* 55: 103–122. doi:10.2136/sssaspecpub55.c5.

Bosetto, M., P. Arfaioli, and P. Fusi. 1993. Interactions of alachlor with homoionic montmorillonites. *Soil Science* 155: 105–113. doi:10.1097/00010694-199302000-00004.

Brady, N.C., and R.R. Weil. 2007. *The nature and properties of soils*, 14th ed. New York: Pearson.

Bradl, H.B. 2004. Adsorption of heavy metals ions on soils and soil constituents. *Colloid and Interface Science* 277: 1–17.

Capra, G.F., A. Ganga, E. Grilli, S. Vacca, and A. Buondonno. 2015. A review on anthropogenic soils from a worldwide perspective. *Soils and Sediments* 15: 1602–1618. doi:10.1007/s11368-015-1110-x.

Cavallaro, N., and M.B. McBride. 1984. Zinc and Copper sorption and fixation by an acid soil clay: Effect of selective dissolutions. *Soil Science Society of America Journal* 48: 1050–1054. doi:10.2136/sssaj1984.03615995004800050020x.

Certini, G. 2014. Fire as soil forming factor. *Ambio* 43: 191–195.

Certini, G., and R. Scalenghe. 2011. Anthropogenic soils are the golden spike for the Anthropocene. *The Holocene* 8: 1269–1274. doi:10.1177/0959683611408454.

Certini, G., R. Scalenghe, and W. Woods. 2013. The impact of warfare on the soil environment. *Earth Science Reviews* 127: 1–15.

Chefetz, B., A.P. Deshmukh, P.G. Hatcher, and E.A. Guthrie. 2000. Pyrene sorption by natural organic matter. *Environmental Science and Technology* 34: 2925–2930. doi:10.1021/es9912877.

Chefetz, B., and B. Xing. 2009. Relative role of aliphatic and aromatic moieties as sorption domains for organic compounds: A review. *Environmental Science and Technology* 43: 1680–1688. doi:10.1021/es803149u.

Cheng, X., A.T. Kan, and M.B. Tomson. 2005. Study of C_{60} transport in porous media and the effect of sorbed C_{60} on naphthalene transport. *Materials Research* 20: 3244–3254. doi:10.1557/jmr.2005.0402.

Christl, I., C.J. Milne, D.G. Kinniburgh, and R. Kretzschmar. 2001. Relating ion binding by fulvic and humic acids to chemical composition and molecular size. 2. Metal binding. *Environmental Science and Technology* 35: 2512–2517. doi:10.1021/es0002520.

Cornelis, G., K. Hund-Rinke, T. Kuhlbusch, N. van den Brink, and C. Nickel. 2014. Fate and bioavailability of engineered nanoparticles in soils: a review. *Critical Reviews in Environmental Science and Technology* 44: 2720–2764. doi:10.1080/10643389.2013.829767.

Darwin, C. 1881. *The formation of vegetable mold through the actions of worms, with observations on their habits*. London: John Murray.

Dokuchaev, V.V. 1883. Russian chernozen. In *Selected works of VV Dokuchaev* 1 1948 (English trans: Jerusalem Dokuchaev VV (1883) Russian Chernozem). Jerusalem: Israel Program for Scientific Translation.

Dokuchaev, V.V. 1899. *A contribution to the theory of natural zones: Horizontal and vertical soil zones*. St. Petersburg: Mayor's Office Press (in Russian).

Dror, I., B. Yaron, and B. Berkowitz. 2015. Abiotic soil changes induced by engineered nanomaterials: A critical review. *Journal of Contaminant Hydrology* 181: 3–16. doi:10.1016/j.jconhyd.2015.04.004.

Dudal, R. 2005. The sixth factor of soil formation. *Eurasian Soil Science* 38: S60–S65.

Fortner, J.D., C. Solenthaler, J.B. Hughes, A.M. Puzrin, and M. Plötze. 2012. Interactions of clay minerals and a layered double hydroxide with water stable, nano scale fullerene aggregates (nC_{60}). *Applied Clay Science* 55: 36–43. doi:10.1016/j.clay.2011.09.014.

Gevao, B., K.T. Semple, and K.C. Jones. 2000. Bound pesticide residues in soils: A review. *Environmental Pollution* 108: 3–14. doi:10.1016/S0269-7491(99)00197-9.

Ge, X., Y. Zhou, C. Lü, and H. Tang. 2006. AFM study on the adsorption and aggregation behavior of dissolved humic substances on mica. *Science in China, Series B: Chemistry* 49: 256–266. doi:10.1007/s11426-006-0256-1.

Gil-Díaz, M., A. Pérez-Sanz, M. Ángeles Vicente, and M. Carmen Lobo. 2014. Immobilisation of Pb and Zn in soils using stabilised zero-valent iron nanoparticles: effects on soil properties: Metal soil immobilisation using zero-valent iron nanoparticles. *Clean: Soil, Air, Water* 42: 1776–1784. doi:10.1002/clen.201300730.

Gournis, D., V. Georgakilas, M.A. Karakassides, T. Bakas, K. Kordatos, M. Prato, M. Fanti, and F. Zerbetto. 2004. Incorporation of fullerene derivatives into smectite clays: A new family of organic–inorganic nanocomposites. *Journal of the American Chemical Society* 126: 8561–8568. doi:10.1021/ja049237b.

Hass, A., U. Mingelgrin, and P. Fine. 2010. Heavy metals in soils irrigated with wastewater. In *Treated wastewater in agriculture*, ed. G.J. Levy, P. Fine, and A. Bar-Tal, 247–285. Hoboken: Wiley-Blackwell.

Hilgard, E.W. 1906. *Soils: Their formation, properties, composition and relation to climate and plant growth in humid and arid regions*. New York: Macmillan.

Inbar, A., M. Ben-Hur, M. Sternberg, and M. Lado. 2015. Using polyacrylamide to mitigate post-fire soil erosion. *Geoderma* 239–240: 107–114.

Jacquat, O., A. Voegelin, and R. Kretzschmar. 2009. Local coordination of Zn in hydroxy-interlayered minerals and implications for Zn retention in soils. *Geochimica et Cosmochimica Acta* 73: 348–363. doi:10.1016/j.gca.2008.10.026.

Jenny, H. 1941. *Factors of soil formation*. New York: McGraw-Hill NY.

Jenny, H. 1961. Derivation of state factor equations of soils and ecosystems. *Soil Science Society of America Journal* 25: 385. doi:10.2136/sssaj1961.03615995002500050023x.

Johnson, D.L., and R.J. Schaetzl. 2015. Differing views of soil and pedogenesis by two masters: Darwin and Dokuchaev. *Geoderma* 237–238: 176–189. doi:10.1016/j.geoderma.2014.08.020.

Jozja, N., P. Baillif, J.C. Touray, F. Muller, and C. Clinard. 2006. Incidence of lead uptake on the microstructure of a (Mg, Ca)-bearing bentonite (Prrenjas, Albania). *European Journal of Mineralogy* 18: 361–368. doi:10.1127/0935-1221/2006/0018-0361.

Kang, S., and B. Xing. 2005. Phenanthrene sorption to sequentially extracted soil humic acids and humins. *Environmental Science and Technology* 39: 134–140.

Kelepertzis, E. 2014. Accumulation of heavy metals in agricultural soils of Mediterranean: Insights from Argolida basin, Peloponnese, Greece. *Geoderma* 221–222: 82–90.

Klavins, M., and L. Ansone. 2010. Study of interaction between humic acids and fullerene C_{60} using fluorescence quenching approach. *Ecological Chemistry and Engineering* 17: 351–362.

Lagaly, G. 1986. Interaction of alkylamines with different types of layered compounds. *Solid State Ionics* 22: 43–51. doi:10.1016/0167-2738(86)90057-3.

Lieber, C.M., and C.C. Chen. 2009. Preparation of fullerene and fullerene based metalics. *Advances in Solid State Physics* 48: 109–147.

Lishtvan, I.I., F.N. Kaputsky, Y.G. Yanuta, A.M. Abramets, V.P. Strigutsky, and E.V. Kachanova. 2006. Humic acids: Interaction with metal ions, features of structure and properties of metal humic complexes. *Chemistry for Sustainable Development* 14: 367–373.

López-Periago, J.E., M. Arias-Estévez, J.C. Nóvoa-Muñoz, D. Fernández-Calviño, B. Soto, C. Pèrez-Novo, and J. Simal-Gándara. 2008. Copper retention kinetics in acid soils. *Soil Science Society of America Journal* 72: 63–72. doi:10.2136/sssaj2006.0079.

Mainwaring, K.A., C.P. Morley, S.H. Doerr, P. Douglas, C.T. Llewellyn, G. Llewellyn, I. Matthews, and B.K. Stein. 2004. Role of heavy polar organic compounds for water repellency of sandy soils. *Environmental Chemistry Letters* 2: 35–39. doi:10.1007/s10311-004-0064-9.

Mamy, L., and E. Barriuso. 2007. Desorption and time-dependent sorption of herbicides in soils. *European Journal of Soil Science* 58: 174–187. doi:10.1111/j.1365-2389.2006.00822.x.

McBride, M.B. 1989. Reactions controlling heavy metal solubility in soils. In *Advances in soil science*, ed. B.A. Stewart, 1–56. New York: Springer.

Mehrotra, V., E.P. Giannelis, R.F. Ziolo, and P. Rogalskyj. 1992. Intercalation of ethylenediamine functionalized buckminsterfullerene in mica-type silicates. *Chemistry of Materials* 4: 20–22. doi:10.1021/cm00019a008.

Nasser, A., M. Gal, Z. Gerstl, U. Mingelgrin, and S. Yariv. 1997. Adsorption of alachlor by montmorillonites. *Journal of Thermal Analysis* 50: 257–268. doi:10.1007/BF01979566.

Nebbioso, A., and A. Piccolo. 2013. Molecular characterization of dissolved organic matter (DOM): A critical review. *Analytical and Bioanalytical Chemistry* 405: 109–124. doi:10.1007/s00216-012-6363-2.

Ogawa, M., T. Ishii, N. Miyamoto, and K. Kuroda. 2003. Intercalation of a cationic azobenzene into montmorillonite. *Applied Clay Science* 22: 179–185.

Oren, A., and B. Chefetz. 2005. Sorption–desorption behavior of polycyclic aromatic hydrocarbons in upstream and downstream river sediments. *Chemosphere* 61: 19–29. doi:10.1016/j.chemosphere.2005.03.021.

Orsi, M. 2014. Molecular dynamics simulation of humic substances. *Chemical and Biological Technologies in Agriculture* 1: 1–14. doi:10.1186/s40538-014-0010-4.

Philippe, A., and G.E. Schaumann. 2014. Interactions of dissolved organic matter with natural and engineered inorganic colloids: A review. *Environmental Science and Technology* 48: 8946–8962.

Pignatello, J.J., and B. Xing. 1996. Mechanisms of slow sorption of organic chemicals to natural particles. *Environmental Science and Technology* 30: 1–11. doi:10.1021/es940683g.

Prost, R., Z. Gerstl, B. Yaron, J. Chaussidon. 1977. Infrared studies of parathion attapulgite interactions. *Special Publication Agricultural Research Organization, Volcani Cent. Div. Sci. Publ.*, 27–32.

deB Richter, D. 2007. Humanity's transformation of earth's soil: Pedology's new frontier. *Soil Science* 172: 957–967. doi:10.1097/ss.0b013e3181586bb7.

deB Richter, D., and D.H. Yaalon. 2012. "The changing model of soil" revisited. *Soil Science Society of America Journal* 76: 766. doi:10.2136/sssaj2011.0407.

Romić, M., L. Matijević, H. Bakić, and D. Romić. 2014. Copper accumulation in vineyard soils: distribution, fractionation and bioavailability assessment. In *Environmental risk assessment of soil contamination*, ed. M.C. Hernandez Soriano. Rijeka: InTech.

Roy, J.L., W.B. McGill, H.A. Lowen, and R.L. Johnson. 2003. Relationship between water repellency and native and petroleum-derived organic carbon in soils. *Journal of Environmental Quality* 32: 583–590.

Salomons, W. 1995. Long term strategies for handling contaminated sites and large scale areas. In *Biogeodynamics of pollutants in soils and sediments*, ed. W. Salomons, and W.M. Stigliani, 1–30. Berlin: Springer.

Saltzman, S., and S. Yariv. 1976. Infrared and X-ray study of parathion-montmorillonite sorption complexes. *Soil Science Society of America Journal* 40: 34. doi:10.2136/sssaj1976.03615995004000010013x.

Sanchez-Martin, M.J., M.S. Rodriguez-Cruz, M.S. Andrades, and M. Sanchez-Camazano. 2006. Efficiency of different clay minerals modified with a cationic surfactant in the adsorption of pesticides: Influence of clay type and pesticides hydrophobicity. *Applied Clay Science* 31: 216–228.

Sander, M., Y. Lu, and J.J. Pignatello. 2005. A thermodynamically based method to quantify true sorption hysteresis. *Journal of Environmental Quality* 34: 1063. doi:10.2134/jeq2004.0301.

Sander, M., Y. Lu, and J.J. Pignatello. 2006. Conditioning-annealing studies of natural organic matter solids linking irreversible sorption to irreversible structural expansion. *Environmental Science and Technology* 40: 170–178. doi:10.1021/es0506253.

Schlegel, M.L.K., L. Charlet, and A. Manceau. 1999. Sorption of metal ions on clay minerals. *Journal of Colloid and Interface Science* 220: 392–405. doi:10.1006/jcis.1999.6538.

Sedlmair, J., S.C. Gleber, S. Wirick, P. Guttmann, and J. Thieme. 2012. Interaction between carbon nanotubes and soil colloids studied with X-ray spectromicroscopy. *Chem. Geol.* 329: 32–41. doi:10.1016/j.chemgeo.2011.08.009.

Selim, H.M. 2013. Transport and retention of heavy metal in soils: Competitive sorption. *Advances in Agronomy* 119: 275–308.

Senesi, N., and Y. Chen. 1989. Interactions of toxic organic chemicals with humic substances. In *Toxic organic chemicals in porous media, ecological studies*, ed. Z. Gerstl, Y. Chen, U. Mingelgrin, and B. Yaron, 37–90. Berlin: Springer.

Senesi, N., C. Testini, and T.M. Miano. 1987. Interaction mechanisms between humic acids of different origin and nature and electron donor herbicides: A comparative IR and ESR study. *Organic Geochem.* 11: 25–30. doi:10.1016/0146-6380(87)90048-9.

Sojka, R.E., D.L. Bjorneberg, J.A. Entry, R.D. Lentz, and W.J. Orts. 2007. Polyacrylamide in agriculture and environmental land management. In *Advances in agronomy*, ed. D.L. Sparks, 75–162. Cambridge: Academic Press.

Spurgeon, D.J., S.P. Hopkin, and D.T. Jones. 1994. Effects of cadmium, copper, lead and zinc on growth, reproduction and survival of the earthworm Eisenia fetida (savigny): Assessing the environmental impact of point-source metal contamination in terrestrial ecosystems. *Environmental Pollution* 84: 123–130.

Strawn, D.C., and D.L. Sparks. 1999. The use of XAFS to distinguish between inner- and outer-sphere lead adsorption complexes on montmorillonite. *Journal of Colloid and Interface Science* 216: 257–269. doi:10.1006/jcis.1999.6330.

Sullivan, J.D., and G.T. Felbeck. 1968. A study of the interaction of s-triazine herbicides with humic acids from three different soils. *Soil Science* 106: 42–52. doi:10.1097/00010694-196807000-00007.

Tu, H.L., T.B. He, X.H. Lu, Y.C. Lang, and L.B. Li. 2013. Accumulation of trace elements in paddy topsoil of the Wudang County, Southwest China: Parent materials and anthropogenic controls. *Environmental Earth Sciences* 70: 131–137.

Wallach, R., and E.R. Graber. 2007. Infiltration into effluent irrigation-induced repellent soils and the dependence of repellency on ambient relative humidity. *Hydrological Processes* 21: 2346–2355. doi:10.1002/hyp.6748.

Wang, D., L. Ge, J. He, W. Zhang, D.P. Jaisi, and D. Zhou. 2014. Hyperexponential and nonmonotonic retention of polyvinylpyrrolidone-coated silver nanoparticles in an Ultisol. *Journal of Contaminant Hydrology* 164: 35–48. doi:10.1016/j.jconhyd.2014.05.007.

Weber, J.B., and S.B. Weed. 1968. Adsorption and Desorption of diquat, paraquat, and prometone by montmorillonitic and kaolinitic clay minerals. *Soil Science Society of America Journal* 32: 485. doi:10.2136/sssaj1968.03615995003200040020x.

Wyszkowska, J., J. Kucharski, and W. Lajszner. 2006. The effects of copper on soil biochemical properties and its interaction with other heavy metals. *Polish Journal of Environmental Studies* 15: 927–934.

Yaalon, D.H., and B. Yaron. 1966. Framework for man-made soil changes-an outline of metapedogenesis. *Soil Science* 102: 272–277.

Yang, K., D. Lin, and B. Xing. 2009. Interactions of humic acid with nanosized inorganic oxides. *Langmuir* 25: 3571–3576. doi:10.1021/la803701b.

Yariv, S., and H. Cross. 2002. *Organo-clay complexes and interactions*. New York: Marcel Dekker.

Yaron, B., I. Dror, and B. Berkowitz. 2008. Contaminant-induced irreversible changes in properties of the soil-vadose-aquifer zone: an overview. *Chemosphere* 71: 1409–1421. doi:10.1016/j.chemosphere.2007.11.045.

Yaron, B., I. Dror, and B. Berkowitz. 2009. Chemical contaminants as factor of soil-subsurface metagenesis. *IUSS Bulletin* 115: 11–12.

Yaron, B., I. Dror, and B. Berkowitz. 2010. Contaminant geochemistry—A new perspective. *Naturwissenschaften* 97: 1–17. doi:10.1007/s00114-009-0592-z.

Yaron, B., I. Dror, and B. Berkowitz. 2012. *Soil-subsurface change*. Berlin: Springer.

Yaron, B., I. Dror, and B. Berkowitz. 2016. Engineered nanomaterials as a potential metapedogenetic factor: A perspective. *Catena*. doi:10.1016/j.catena.2016.02.003.

Zhang G.L., and L.M. Chen. 2010. Soil genesis along a paddy soil chronosequence in a millennium scale. Presented at the Proceedings of the 19th World Congress of Soil Science: Soil solutions for a changing world, Brisbane, Australia, 1-6 August 2010. Symposium 1.3.1 Pedogenesis: ratio and ranges of influence, International Union of Soil Sciences (IUSS), c/o Institut für Bodenforschung, Universität für Bodenkultur, 88–91.

Zhang, M., Y. Wang, D. Zhao, and G. Pan. 2010. Immobilization of arsenic in soils by stabilized nanoscale zero-valent iron, iron sulfide (FeS), and magnetite (Fe_3O_4) particles. *Chinese Science Bulletin* 55: 365–372. doi:10.1007/s11434-009-0703-4.

AUTHOR BIOGRAPHIES

Ishai Dror (✉) is an Associate Staff Scientist in the Department of Earth and Planetary Sciences, Weizmann Institute of Science, Rehovot, Israel. His research focuses on environmental chemistry in soil–water and aquifer environments.
Address: Department of Earth and Planetary Sciences, Weizmann Institute of Science, 7610001 Rehovot, Israel.
e-mail: ishai.dror@weizmann.ac.il

Bruno Yaron is a Professor Emeritus, active as a consultant in the Department of Earth and Planetary Sciences, Weizmann Institute of Science, Rehovot, Israel. His research interests include pedology, soil geochemistry, and soil chemical contamination.
Address: Department of Earth and Planetary Sciences, Weizmann Institute of Science, 7610001 Rehovot, Israel.

Brian Berkowitz is a Professor in the Department of Earth and Planetary Sciences, Weizmann Institute of Science, Rehovot, Israel. His research interests focus on modeling and experimental analysis of chemical transport in natural geological porous media.
Address: Department of Earth and Planetary Sciences, Weizmann Institute of Science, 7610001 Rehovot, Israel.