



Engineered nanomaterials as a potential metapedogenetic factor: A perspective



Bruno Yaron, Ishai Dror *, Brian Berkowitz

Department of Earth and Planetary Sciences, Weizmann Institute of Science, Rehovot 7610001, Israel

ARTICLE INFO

Article history:

Received 4 September 2015

Received in revised form 9 December 2015

Accepted 4 February 2016

Available online 16 February 2016

Keywords:

Engineered nanomaterials (ENMs)

Anthropogenic soils

Intercalation

Sorption

Irreversible change

ABSTRACT

Chemical action as an anthropogenic factor in soil formation was suggested 50 years ago as a part of the metapedogenetic process. Initially, agricultural practices such as irrigation with saline water and soil liming by natural carbonated earth materials (marling) were considered as examples of chemical contamination that alter soil properties. Over the years, however, new anthropogenic substances have emerged, and their disposal on the land surface, whether intentionally or by accident, is acting as another metapedogenetic factor, leading to formation of contemporary soils with altered properties. In this context, potential transformation of natural soils may occur as a result of exposure to engineered nanomaterials (ENMs). Due to the relatively small amounts used to date, and their size and associated chemical properties, the impact of ENMs on soil may be questioned. We argue here, however, that ENMs disposed on the land surface are irreversibly retained in the soil matrix, accumulating over time and becoming a metapedogenetic factor. In support of this hypothesis, we present examples from the literature which demonstrate that deposition of carbon-based and metal-based ENMs may cause, under specific conditions, changes to the matrix and properties of soil constituents and formation of contemporary anthropogenic soils. These examples reconfirm the hypothesis that chemicals are a factor in anthropogenically-induced metapedogenesis.

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1. Metapedogenesis revisited

Over the years, the structure and properties of a soil have been considered to be the result of natural processes occurring over geological time scales. Despite the fact that soil has in many cases been affected by human impact, anthropogenic factors that define soil structure and properties have been largely neglected. Only 50 years ago, human impacts on soil properties were suggested as an integral, independent factor in addition to the five recognized natural-forming factors, namely geological/parent material, climate, topography, biota, and time. In contrast to these natural factors, the rate of change of anthropogenically-induced processes is relatively rapid, with fundamental soil properties being altered within decades. Yaalon and Yaron (1966) argued that these changes occur within a new reference system, in which the natural soil (S_1) serves as a parent material at an initial state relative to the new anthropogenically-formed soil. They suggested the function

$$S_2 = f(S_1, m_1, m_2, m_3, \dots)$$

where S_2 is the new soil produced by action of metapedogenetical factors (m_1, m_2, m_3, \dots) acting singly or in combination, and grouped as topographical, hydrological, chemical, and cultivation-cropping factors.

The differences between the rates of impact on soil characteristics of anthropogenic and natural-environmental factors support the view that anthropogenically-induced changes to soil matrix and properties represent an additional, independent soil-forming factor which acts at a different rate. As one of the metapedogenetic factors, Yaalon and Yaron (1966) included the “chemical” impact resulting from agricultural practices, such as irrigation with saline water and soil liming by natural earth materials (e.g., marling).

Over the last decades, the anthropogenic role in soil formation has received further recognition, with human factors being added to the classical, natural factors. As a result of human effects, the time scale and rate of irreversible soil modification has shortened (Yaalon, 1971; Amundson and Jenny, 1991; Chadwick and Chorover, 2001; Brantley et al., 2007; Richter, 2007; Richter and Yaalon, 2012; Richter et al., 2015). The importance of an independent “sixth” factor of soil formation – the anthropogenic impact that occurs across all natural soils and should not be considered as deviation but as part of the genetic soil – was considered by Dudal et al. (2002). Until now, most of the recognized human impact on soil modification has focused on physical and mechanical changes. Chemical impacts have received much less attention despite the fact that toxic chemical compounds – which are

* Corresponding author.

E-mail address: ishai.dror@weizmann.ac.il (I. Dror).

produced and used by modern society in enormous quantities – reach the land surface and soil environment directly or indirectly.

In the many publications on contaminant interactions with the soil geosystem, most research has focused on effects of the soil on the fate of contaminants, rather than on the impact of chemical contaminants in the soil region. Some studies have noted contaminant-induced changes in the soil matrix and properties, but these changes were generally considered as deviations from the “normal” situation which will disappear by natural attenuation or by restoration procedures. However, chemical contaminants often induce significant alteration of the soil matrix and properties, which may lead over a “human lifetime” scale to irreversible changes. 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 and to natural attenuation. Some of these changes occur following addition of chemical contaminants by adsorption–desorption processes, with irreversibility implied by both hysteresis and soil-conditioning phenomena. As the soil domain is an open thermodynamic system, it will not generally return to its initial state following exposure to chemical contamination, and new soils with different matrix structure and properties will be formed by changing the existing system (Yaron et al., 2008, 2010, 2012; Berkowitz et al., 2014; Dror et al., 2015). The extent of irreversible changes to the soil structure and properties following exposure to chemical contaminants is controlled by the amount and chemistry of the contaminant and by the environmental conditions. As a consequence, chemical contamination may be considered a metapedogenetic factor causing formation of anthropogenic soils with structure and properties different than those of the original soil.

2. ENMs as soil contaminants

Aggregation and deposition are the primary processes governing ENM redistribution from the land surface to groundwater. ENMs can be transported into the soil water phase or deposited on the soil solid phase. The fate of ENM deposition through a soil layer occurs mainly by two distinct pathways: (1) free flow through soil channels, and (2) diffuse movement into the soil pore space. The deposition of ENMs in soil can occur as a result of interaction with the surface of natural minerals (e.g., clays) and organic matter (e.g., humic acids), or after induced ENM aggregation (e.g., due to soil solution chemistry) that leads to retention within the soil porous medium. ENM interactions with the soil solid phase may then occur within or on the surface of soil. The extent of ENM deposition, dissolution and retention on the soil solid phase is affected by the soil matrix and the chemistry of the soil (Zhou et al., 2012).

Comprehensive information on ENM fate, transport, persistence and toxicological impact as affected by soil solution chemistry and solid phase surface properties appears in many review publications (e.g., Nowack and Bucheli, 2007; Petosa et al., 2010; Pan and Xing, 2012; Bertsch et al., 2012; Yang et al. 2014; Wang 2014; Garner and Keller, 2014; Dror et al., 2015). However, only a few studies have appeared to date that focus on the impact of ENMs on natural soil constituents and physicochemical properties. Due to their size and associated physicochemical properties, it has been suggested that ENMs have a similar impact on the soil solid phase as other chemical contaminants. Westerhoff and Nowack (2013) addressed this question via a conceptual model based on the tendency of ENMs to behave like molecules dissolved in aqueous solution or colloids in suspension, as a function of their relative size. In some cases, very small ENMs display attributes of large molecules. Based on size-dependent thresholds, Westerhoff and Nowack (2013) concluded that ENMs in heterogeneous environments may behave similarly to other chemical pollutants. Extrapolating these considerations to the case of soil, ENM constituents can be visualized as manufactured particles that interact with natural soil material, with two interrelated processes at play: (1) ENMs may

be affected by natural soil constituents, and (2) the soil matrix may show persistent modification by exposure to ENMs.

3. ENM-induced changes to the soil matrix

Clay minerals and humic and fulvic acids should be considered in defining the impact of ENMs on the soil matrix and properties. Here we discuss interactions of soils and soil components with two major ENM groups: (1) carbon-based materials, and (2) metal and metal oxide substances. In support of the argument that, under specific conditions, ENMs act as a metapedogenetic factor in formation of anthropogenic soils, we selected from the literature several examples that demonstrate different changes to soil matrix or properties.

3.1. Carbon-based ENMs

This class of ENMs contains pure carbon structures and includes fullerenes, nanotubes and graphene. Fullerenes generally have 60 atoms of carbon (C_{60}) but may exhibit a higher mass with various geometric structures from C_{70} to C_{80} . Carbon nanotubes may have single-walled or multi-walled structures. The environmental applications of manufactured carbon-based nanomaterials are extensive and include roles as sorbents, high-flux membranes, depth filters, antimicrobial agents, environmental sensors and materials used in renewable energy technology. Waste materials may reach the soil directly or indirectly. As an example of ENMs acting as a soil metapedogenetic factor, we examine interactions between fullerenes (C_{60}) with two key soil constituents, clays and humic substances.

3.1.1. Carbon-based ENM–clay interactions

One of the first reports on interactions between clay minerals and fullerenes (C_{60}) was given by Mehrotra et al. (1992). They used X-ray diffraction (XRD) to show that amino-functionalized fullerenes could be intercalated into mica-type fluorohectorite, with an interlayer spacing (gallery height) of 16.9 Å (d spacing of 26.5 Å). In comparison, addition of (molecular) ethylenediamine resulted in interlayer spacing of only 3.6 Å.

Intercalation of a fullerene derivate (fulleropyrrolidine) in Wyoming sodium montmorillonite was observed by Gournis et al. (2004). Clay modification was verified by Raman spectroscopy. Comparison of Raman spectra of the fullerene (C_{60}) and fullerene derivate to the spectra of the clay–fullerene composite revealed the formation of a new broad band in the composite material. The Raman characteristic peaks of the fullerene derivate (1469, 1421 and 1570 cm^{-1}) were found also in the spectra of the reacted clay, showing that the clay layer was intercalated by the fullerene. In an additional study, Gournis et al. (2006) examined incorporation of a fullerene derivative (fulleropyrrolidine) into three typical smectites (Wyoming montmorillonite – SWY, Kunipia sodium montmorillonite – KUN, and a trioctahedral hectorite – Lap) with different particle size and cation exchange capacity. The protonated fullerene derivative in aqueous solution was readily adsorbed by exchange into the clays. The changes in each host clay were determined by XRD and IR measurements. The XRD data (Fig. 1a–c) show an increase in the interlayer spacing (d_{001}) of the three clays after intercalation of C_{60} -fulleropyrrolidine. Gournis et al. (2006) underline the fact that the clay layers were not organized (stacked in perfect registry), but had slipped laterally, being disordered turbostratically. In this type of crystalline structure, the basal plane slipped laterally, causing the spacing between planes to be greater than ideal (minimal). An additional change, observed through XRD measurements, is the absence of reflection peaks of the crystalline phase of the fullerene-treated clays, indicating that no C_{60} -fulleropyrrolidine aggregates were found on the external clay surfaces even after washing.

Other studies reported by Fortner et al. (2012), examining interaction of fullerenes with clays (montmorillonite and kaolinite), indicated a change in clay structure due to an association process; see, for example,

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