

Review Article

Mechanisms Regulating Dynamics of Dissolved Organic Matter in Soils: A Review

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Abstract

Dissolved organic matter (DOM) is defined as the organic matter fraction in solution that passes through a 0.45 µm filter. Although DOM is ubiquitous in terrestrial and aquatic ecosystems, it represents only a small proportion of the total organic matter in soil. However, DOM, being the most mobile and actively cycling organic matter fraction, influences a spectrum of biogeochemical processes in the aquatic and terrestrial environments. Biological fixation of atmospheric CO₂ during photosynthesis by higher plants is the primary driver of global carbon cycle. A major portion of the carbon in organic matter in the aquatic environment is derived from the transport of carbon produced in the terrestrial environment. It plays a significant role in influencing the dynamics and interactions of nutrients and contaminants in soils and microbial functions, thereby serving as a sensitive indicator of shifts in ecological processes.

This review synthesized information in the literature to identify and discuss the main sources, elemental composition and mechanism which regulate dynamics of DOM in soils. Gaps and opportunities were identified to guide future studies on DOM.

Keywords: Dissolved organic carbon, main sources, composition, sorption, leaching, photodegradation and leaching

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Introduction

Dissolved organic matter is considered as the most mobile and reactive component of the soil organic matter pool despite its occurrence in only small quantities in soils. As such, it regulates major physical and biogeochemical processes not only in soils, but also in aquatic ecosystems. It helps in transformation and transport of essential nutrients (e.g., N, P, and S), organic pesticides (e.g., non-ionic organic herbicides and insecticides), complexation of environmentally important heavy metal(loid)s (e.g., Cu, Pb, Hg, and Cd), adsorption of metal(loid)s and organic compounds on clays and metal oxides, and transport of environmental contaminants. DOM is largely a by-product of microbial decomposition, it also serves as an energy substrate for the microbial processing of organic compounds, including indigenous organic matter. During the decomposition of organic material, most carbon is lost as CO₂ to the atmosphere by microbial oxidation. Soil type and landscape slope, leaching, and runoff are also important processes associated with DOM losses in the soil [1]. In well drained soils, leached DOC can reach the water table and release nutrients and pollutants that can contaminate groundwater [2-3], whereas runoff transports DOM and xenobiotics to other areas, rivers, and lakes.

DOM can be viewed to serve a dual function in the environment- as a link and as a bottleneck for various ecological processes. For example, as a link, DOM plays a vital role in mobilizing nutrients and heavy metal(loid)s to groundwater and surface water; as a bottleneck, it minimizes the bioavailability of certain inorganic (e.g., heavy metal(loid)s) and organic pesticides to terrestrial and aquatic biota.

Therefore, this literature review investigates discussions in previous studies on DOM and determined the current interest in this research topic. For that purpose, we analyzed information in the literature to describe importance, source and production, properties and chemical composition and mechanisms regulating dynamics of dissolved organic matter in soil ecosystem. Finally, gaps and opportunities were delineated to guide further research for a better understanding of the importance and implications of DOM changes in soils.

Definition and main sources of DOM

Dissolved organic matter is considered as the most mobile and reactive component of the soil organic matter pool despite its occurrence in very small quantities and has major role in global C cycling [4]. Dissolved organic matter is defined as the fraction of organic matter in solution that passes through a 0.45 µm filter [5]. But depending on the study intent, size of the DOM may range from 0.2 to 0.7 µm [6]. Dissolved organic matter consists of soluble organic materials derived from the partial decomposition of organic materials and soluble particles released by living

organisms like bacteria, algae and plants [7]. It regulates major physical and biogeochemical processes in soil. It is the reason for the dark tea colour formation on the surface of rivers and oceans.

Dissolved organic matter plays vital role in nutrient sequestration and supply, as an available carbon source for microorganisms and in carbon cycling. Soil DOM can be emanated from different sources (inputs), such as atmospheric carbon dissolved in rainfall, litter and crop residues, manure, root exudates, and decomposition of soil organic matter (SOM) [8]. All the DOM in soils derives from photosynthesis. The majority of DOM in soils and aquifers originates from the solubilization of SOM pile up through vegetation and addition of biological waste materials. The addition of biological waste materials, such as poultry and animal manures and sewage sludges, increases the amount of DOM in soils either by acting as a source of DOM or by enhancing the solubilization of the SOM [9].

All soils have organic matter dissolved in soil solution or in flood water, but its concentration is generally excessive in wetlands and aquatic ecosystems than agricultural soils. Leaf litters and freshly applied organic residues form the major source of DOM [10]. Total biomass of the thorn forest was positively influenced by the soil properties like pH, organic carbon and water-soluble carbon and the total biomass of the thorn forest was negatively influenced by soil EC, Bulk density [11]. The molecular weight, aromatic character and polycondensation degree of DOM decreased downward the soil profile. This result suggested that the aromatic portion of partially degraded lignin-derived compounds might be gradually adsorbed by mineral soil components, and protected from microbial degradation. These effects would limit the degradation process mostly in the upper soil layers [12].

Properties and Chemical Composition of Dissolved Organic Matter in Soils

DOM constituents can be grouped into labile DOM and recalcitrant DOM [13]. Labile DOM consists mainly of simple carbohydrate compounds (i.e., glucose and fructose), low molecular weight (LMW) organic acids, amino sugars, and LMW proteins. Recalcitrant DOM consists of polysaccharides (i.e., breakdown products of cellulose and hemicellulose) and other plant compounds, and/or microbially derived degradation products [9, 14-15]. Fulvic acid (FA) is typically the most abundant fractions of DOM [16]. The FAs consist of a physically and chemically heterogeneous mixture of relatively low molecular weight (500–2000 Da), yellow-to-light-brown/reddish organic molecules of mixed aliphatic and aromatic nature, and bearing acidic functional groups (mainly carboxylic and phenolic OH). The major oxygen-containing functional groups in FA are COOH and phenolic OH groups which are formed by secondary synthesis reactions of recalcitrant compounds with products of microbial and chemical decay and transformation of biomolecules originated from organisms during life and after death [17]. Chemical composition of DOM is given on **Table 1**.

Table 1 Chemical composition of dissolved organic matter

| Fraction | Compound |
|---------------------------------------|---|
| Hydrophobic neutrals | Hydrocarbons |
| | Chlorophyll |
| | Carotenoids |
| | Phospholipids |
| Weak (phenolic) hydrophobic acids | Tannins |
| | Flavonoids |
| | Other polyphenols |
| | Vanillin |
| Strong (carboxylic) hydrophobic acids | Fulvic acid and humic acid |
| | Humic-bound aminoacids and peptides |
| | Humic –bound carbohydrates |
| | Aromatic acids (including long-chain fatty acids) |

The elemental composition of DOM depends on its origin. The major elements accompanying carbon include oxygen, hydrogen, nitrogen, phosphorus, sulfur, and trace amounts of various cations including calcium, potassium, magnesium, and metal(loid)s including aluminum, iron, zinc, and copper. The dissolved organic nutrients were largely concentrated in the hydrophilic DOM fraction, which were more mobile in mineral soil pore water than the hydrophobic one. For example, [14] found that the organic forest floor layers were large sources for DOC, DON, DOP, and DOS. Consequently, the concentrations and fluxes of dissolved organic nutrients (DON, DOP, and DOS) decreased less with depth than those of DOC. DOM found in soil samples are much more aromatic, have more double bonds and a much lower H/C ratio but higher oxygen content, which indicates the availability of fresh plant material and less microbial processed material compared to stream samples [18].

Mechanisms Regulating Dynamics of Dissolved Organic Matter in Soils

Sorption/complexation

Like any other solute in soils, DOM undergoes both sorption and complexation reactions. While the sorption results in the retention of DOM with soil components and subsequent retardation of its mobility and degradation. Complexation can result in the formation of both soluble and insoluble DOM–metal(loid) complexes, thereby affecting both movement and degradation. While soluble DOM–metal(loid) complexes enhance the movement of DOM in soils, insoluble complexes result in the retardation of DOM movement [19-21]. When DOM percolates in the soil profile, it may interact with metal oxide surfaces, thereby forming a “shield” against microbial attack. In acid forest soils, Al and Fe can form relatively stable complexes with DOM, which can enhance solubility and transport, as might be the case during podsolization [20, 22]. The main process by which dissolved organic matter (DOM) is retained in forest soils is likely to be sorption in the mineral horizons that adds to stabilized organic matter (OM) pools. More over DOM sorption stabilizes about 24 Mg C ha⁻¹ highlighting the importance of sorption for accumulation and preservation of OM in soil. Stabilization of OM by sorption depends on the intrinsic stability of organic compounds sorbed [23].

Interactions of dissolved organic matter (DOM) with soil minerals, such as metal oxides and clays, involve various sorption mechanisms and may lead to sorptive fractionation of certain organic moieties. Sorptive fractionation resulted mainly from the preferential uptake of aromatic, carboxylic, and phenolic moieties of DOM. Soil metal-oxide content positively affected DOM sorption and binding of some specific carboxylate and phenolate functional groups. Desorptive fractionation of DOM was expressed by the irreversible-binding nature of some carboxylic moieties, whereas other bound carboxylic moieties were readily desorbed. Inner-sphere, as opposed to outer-sphere, ligand-exchange complexation mechanisms may be responsible for these irreversible, as opposed to reversible, interactions, respectively. The interaction of aliphatic DOM constituents with soil, presumably through weak van der Waals forces, was minor and increased with increasing proportion of clay minerals in the soil [24]. Complexation of potentially toxic metal(loid)s may not result in diminished biodegradability of DOM, but may even enhance microbial activity by sequestering the toxic effects from free metal(loid) ion activity. Similarly, formation of stable complexes between DOM and certain heavy metal(loid)s ions such as Cu, Hg, and Pb can alter the metal(loid) toxicity to fish and other aquatic organisms [21]. Two-stage washing of soil using 0.2 M Na₂S₂O₄ coupled with 1,500 mg L⁻¹ DOC solution at pH 2.0 removes around 15 %, 86 %, 32 %, and 52 % of Cr, Cu, Zn, and Ni, respectively [25].

The nature and extent of soil mineral-organic carbon-microbe interactions will ultimately decide the fate of DOM in the soil profile [26]. The bonding mechanisms of DOM onto the soil solid phase have already been elucidated by [27]. This includes bonding of negatively charged organics by ligand exchange especially in oxide-rich and allophanic soils, positively charged organics into negative surfaces by cation exchange, anion exchange onto subsoils and variably charged soils, and the less important mechanisms such as cation bridging, water bridging, hydrogen bonding, and van der Waals forces. From microcalorimetric, FTIR, and 13C NMR analyses, it can be concluded that ligand exchange between carboxyl/hydroxyl formational groups of the SOM and iron oxide surfaces were the dominant sorption mechanisms, mainly under acidic or slightly acidic pH conditions [28]. While the sorption of DOM in soils increases with increasing levels of Fe and Al oxides in soils, it decreases with increasing concentrations of organic matter. Sorption by soils is the dominant mechanism operating in soils of the Amazon basin that results in control of riverine DOC concentrations by riparian zones. Sorption is the dominant mechanism in removing DOC from soil solution during transport through soils to rivers [29]. DOM interact with atrazine adsorption in black soil. Adsorption capacity of Soil + DOM, Soil and DOM are 41.80, 31.45 and 9.35 mg kg⁻¹, separately, which indicate that DOM remarkably enhance the adsorption efficiency of atrazine by soil [30].

Biodegradation

10-44 % of DOM in soil solution is microbiologically degradable. The more labile fraction of DOM is more readily mineralized or assimilated into microbial biomass. Most DOM appeared to be resistant to decomposition, with the exception of that in litter leachate and some throughfall samples. Fulvic acid decayed very slowly. Biodegradability of DOM in the ecosystem profile declined vertically from throughfall to the A horizon. Adsorption in the A horizon was probably responsible for removing most of the DOC draining from the forest floor. The extent and rate of DOM biodegradation from less humified organic material (straw, litter and fermentation layers of forest floors) were high resulting in 61–93% of DOC being mineralized. In the total DOM pool, the labile fraction comprised 59–88%. Biodegradability of DOM extracted from agricultural soils was of an intermediate nature with a CO₂ evolution comprising 17–32% of total DOC. Labile DOC represented 14–25% of total DOC [31].

DOM biodegradation seems to result in organic matter properties being a precondition for the formation of stable carbon. These structural changes induced by DOM biodegradation should also result in stronger DOM sorption to the soil matrix additionally affecting DOM stabilization [31]. DOM from matured compost contained primarily lignins/carboxylic-rich alicyclic molecules (73.6%), the higher double bond equivalent (5.97) and aromaticity index (0.18), indicating that the molecular composition of DOM had changed substantially [32]. Severe changes in microbial community structure were also observed along with the DOM transformation process of composting. Network analysis further indicated that *Caldicoprobacter*, *Bacillus*, and *Dechloromonas* were associated with the most DOM subcategories. *Caldicoprobacter* could degrade carbohydrates, *Bacillus* accelerated the humification by transforming N-containing compounds, and *Dechloromonas* could degrade polycyclic aromatic hydrocarbons distributed in low O/C [32]. Crop residue derived organic matter accelerate the decomposition of native soil organic carbon in a temperate agricultural ecosystem [33].

Photodegradation

Photodegradation is an important process in regulating the dynamics of DOM in aquatic environment. Although photodegradation has minimal significance on the DOM dynamics in forest, grassland, and arable ecosystems, it may endeavour more effect in wetland soils or in soils prone to flooding. Photo-oxidation can enhance the turnover of DOM in aquatic systems, transforming labile into more recalcitrant (less bioavailable) components and vice versa. For example, photo-cleavage and photo-oxidation of high molecular weight (HMW) DOM resulted in the release of bioavailable low molecular weight (LMW) that stimulated bacterioplankton activity.

Photo-irradiation of DOM decreased the abundance of HMW components and formed new LMW components, including LMW carboxylic acids, that is, acetic, formic, and malonic acids [34]. Photo-irradiation decreases the UV- and visible light-absorbing properties of DOM, a process that may lead to decreased attenuation of photo-irradiation in lakes [35]. Naturally occurring DOM is more photoreactive than wastewater-derived DOM in ice. The photodegradation rates of DOM in ice were negatively correlated to DOC level. The photodegradation of DOM in ice, regardless of the origin, was facilitated by nitrate ion (NO_3^-), nitrite ion (NO_2^-), ferric ion (Fe^{3+}) and ferrous ion (Fe^{2+}), and on the other hand, was inhibited by chloride ion (Cl^-) and copper ion (Cu^{2+}) [36]. Photo-irradiation may also decrease the metal-binding affinity of DOM for metal(loid)s through the oxidation of carboxylic acid group [37]. [38] suggested that photochemical reactions are responsible for depletion of DOM and formation of ferrous iron (Fe(II)) in acidic soft-water lakes. There is an increase in photo-degradation of dissolved natural organic matter when there is an increase in pH of the water bodies. This has significant implications for the photo-degradation of dissolved natural organic matter during estuarine mixing, when high increase of pH is common [39]. Fulvic acid-like substances in algae and macrophyte-derived dissolved organic matter were susceptible to photodegradation, while protein-like substances were susceptible to both photodegradation and biodegradation [40].

Leaching

The leaching of DOM from the forest canopy (i.e., throughfall) and forest floor (i.e., litterfall) could also be an important source of N, and to a lesser extent of P, to the A horizon. [41] examined the leaching of DOC and DON, with focus on the period after cultivating grass-clover swards. During spring, grass-clovers were ploughed prior to sowing cereals followed by either catch crops or bare soil. The total percolation was 218 and 596–645 mm in the sandy loam soil and coarse sandy soil, respectively, which resulted in an annual leaching of 22–40 kg DOC ha⁻¹ and 3–4 kg DON ha⁻¹ and 174–310 kg DOC ha⁻¹ and 10–31 kg DON ha⁻¹ in the respective soil. It was found that leaching loss of DOC were higher under the catch crops than from bare soil. Introduction of maize cropping in the dry season of a continuous paddy-rice cropping system causes an initial increase of drainage and leaching losses of N and DOC [42].

Conclusion

DOM is considered the most mobile and reactive component of the SOM pool despite its occurrence in only small quantities in soils. DOM is regulated by lots of mechanisms, which includes sorption, biodegradation, photodegradation and leaching. As such, it regulates major physical and biogeochemical processes not only in soils but also in aquatic ecosystems. This includes processes such as transformation and transport of organic pesticides (e.g., non-ionic organic herbicides and insecticides), essential nutrients (e.g., N, P, and S), sorption of metal(loid)s and organic compounds on clays and metal oxides, complexation of environmentally important heavy metal(loid)s (e.g., Cu, Pb, Hg, and Cd), and mobility and transport of environmental contaminants. While land use and management practices affect directly the C fractions in the soil, there is little experimental data involving mechanisms regulating

dynamics of DOM. Future studies are essential to critically determine other factors influencing carbon sequestration of DOM and extend of DOM leaching in different land use systems.

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