

Dynamics and environmental significance of dissolved organic matter in soil

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Abstract

“Dissolved organic matter (DOM) comprises only a small part of soil organic matter; nevertheless, it affects many processes in soil and water including the most serious environmental problems like soil and water pollution and global warming” (Kalbitz and Kaiser 2003). DOM is considered to represent the most mobile and reactive organic matter fractions, thereby controlling a number of physical, chemical and biological processes in both terrestrial and aquatic environments. Much of the terrestrially-borne DOM is microbially consumed, photo-degraded, or adsorbed in soils and sediments. DOM can be envisioned both as a link and bottleneck among various ecological compartments. For example, as a link DOM plays a vital role in mobilizing and transporting nutrients from terrestrial ecosystem to aquatic ecosystem. On the other hand, as a bottleneck DOM inhibits the bioavailability of these nutrients to aquatic biota through the formation of organic complexes. Combined with its dynamic nature, this enables DOM to serve as a sensitive indicator of the extent and shifts in ecological processes. The present review aims to quantify the production of DOM in soils under different management regimes, identify its sources and sinks, and integrate its dynamics with environmental significance in relation to the mobilization of nutrients, complexation of heavy metals and partitioning of organic pesticides.

Key Words

C sequestration, sorption, biodegradation, metal complexation, pesticide partitioning

Introduction

The total organic matter in terrestrial and aquatic environments consists of two operationally defined phases, particulate organic matter (POM) and dissolved organic matter (DOM). For all practical purposes DOM is defined as the organic matter fraction in solution that passes a 0.45 µm filter. Some workers have used finer filter paper (i.e., 0.2 µm) to separate ‘true’ DOM from colloidal materials which are not retained in 0.45 µm filters (Dafner and Wangersky 2002). In the case of studies involving soils, the term, water soluble organic matter (WSOM) or water extractable organic matter (WEOM) is also used which represents the fraction of the soil organic matter extracted with water or dilute salt solution that passes a 0.45 µm filter (Zsolnay 2003).

DOM represents one of the most mobile and reactive organic matter fractions, thereby controlling a number of physical, chemical and biological processes in both terrestrial and aquatic environments. In aquatic environment, the easily oxidisable compounds in the DOM can act as chemical- and biological- oxygen-demand compounds, thereby capable of depleting the oxygen concentration in the aquifers and influencing aquatic biota. It has often been shown that organic pesticides added to soil and aquifers are partitioned preferentially onto DOM, which can act as a facilitator for the movement of pesticides residues to groundwater. Similarly, the organic acids present in the DOM can act as a chelating agent, thereby enhancing the mobilisation of toxic heavy metals (Kalbitz and Kaiser 2003).

DOM can be viewed both as a link and bottleneck among various ecological constituents. This combined with its dynamic nature enables DOM to serve as a sensitive indicator of the nature, extent and shifts in ecological processes, especially in aquatic systems. Hence a large number of studies have devoted to examining the dynamics of DOM and monitoring its concentration in aquatic system (Dafner and Wangersky 2002). Only recently the significance of DOM in terrestrial environment has been appreciated and attempts have been made to transpose the dynamics of DOM in aquatic environment to terrestrial environment (McDowell 2003). The present review aims to delineate the production of DOM in soils under different management regimes, identify its sources and sinks, and integrate its dynamics with environmental significance.

Sources of dissolved organic matter in soils

The sources and the sinks of DOM in soils are presented in Figure 1. DOM originates mainly from the decomposition of soil organic matter that had accumulated through vegetation and the addition of biological

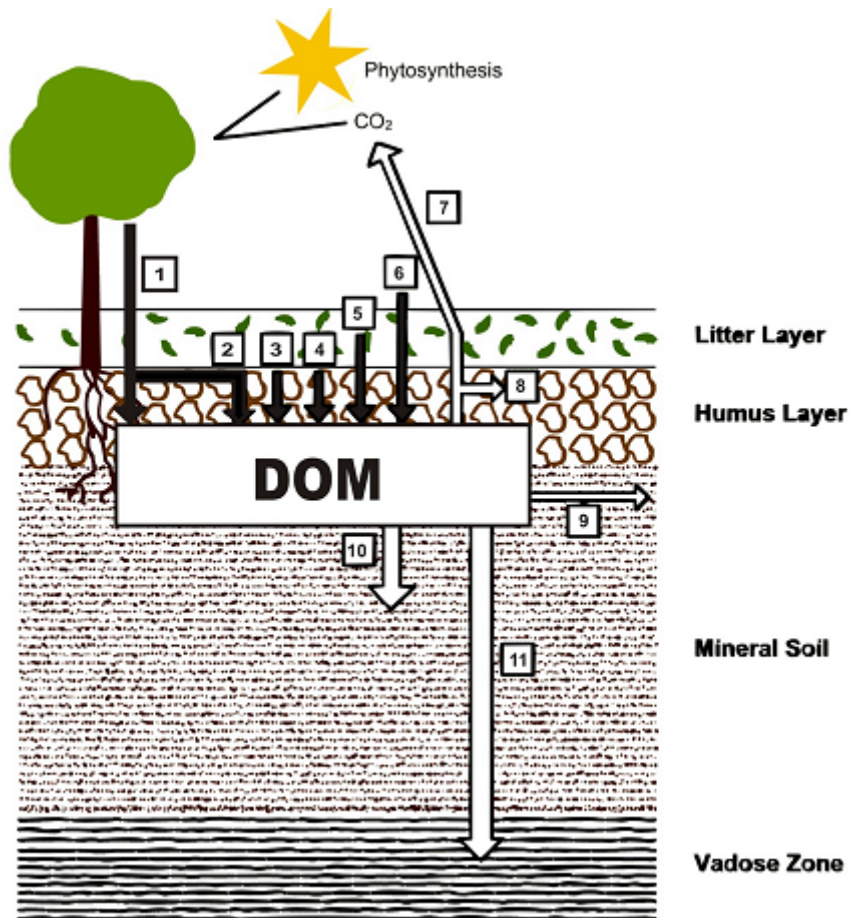


Figure 1. Sources and sinks of dissolved organic matter (DOM) in soils (Sources: 1. Throughfall; 2. Root exudates; 3. Microbial lysis; 4. Humification; 5. Litter and root decomposition; 6. Organic amendments. Sinks: 7. Microbial degradation; 8. Microbial assimilation; 9. Lateral flow; 10. Sorption; 11. Leaching)

waste materials, the release of root exudates, and the lysis of microorganisms. Addition of biological waste materials, such as livestock manure and sewage sludge increases the concentration of DOM in soils either by acting as a direct source of DOM especially upon their decomposition or by enhancing the solubilization of the soil organic matter.

In cultivated and pastoral soils, plant residues provide the major source of DOM while in forest soils, litter and throughfall serve as the major source. In forest soils, DOM represents a significant proportion of the total carbon budget. For example, Liu *et al.* (2002) calculated the total C budgets of Ontario's forest ecosystems (excluding peat lands) to be 12.65 Pg (10^{15} g), including 1.70 Pg in living biomass and 10.95 Pg in DOM and soil. Koprivnjak and Moore (1992) determined DOM concentrations and fluxes in a small subarctic catchment, composed of an upland component with forest over mineral soils and a peat land in the lower section. DOM concentrations were low (1-2 mg/L) in precipitation and increased in tree throughfall and stem flow (50 and 150 mg/L), shrub throughfall (17 mg/L), the leachate of the surface lichens and mosses (30 mg/L), and the soil A horizon (40 mg/L). Concentrations decreased in the B horizon (17 mg/L) and there was evidence of strong DOM adsorption by the subsoils.

Most of the DOM in soil is the end product of microbial metabolism of organic residues. Fresh litter also contributes significantly to the production of DOM indicating the presence of DOM in the original litter. Ludwig *et al.* (2000) studied the production of DOM in soils from two sites with different microbial activities using C¹³-depleted plants of differing decomposability (*Epilobium angustifolium* and

Calamagrostis epigeios). Cumulative DOM production was markedly higher in the readily decomposing *Epilobium* experiment (2% of the added C) than in the slow decomposing *Calamagrostis* experiments (0.1% of the added C).

Khomutova *et al.* (2000) examined the mobilization of organic matter in undisturbed soil monoliths of a deciduous forest, a pine plantation, and a pasture under constant temperature (20° C) and moisture. After 20 weeks of leaching with synthetic rain water at pH 5 the cumulative values of DOM production followed: coniferous forest > deciduous forest > pasture, which was related to the nature of carbon compounds in the original residues. The residues from the coniferous forest were found to contain high levels of easily oxidisable organic components.

Measurement and characterization of dissolved organic matter

Various methods have been used to measure the concentration of DOM in soils and aquifers. These methods are grouped into three categories – spectrophotometry, wet oxidation and dry combustion (Dafner and Wangersky 2002).

The most frequently used method involves the measurement of absorption of light by DOM using spectrophotometer at a wavelength of 250 nm. The relationship between the absorbance and the concentration of DOM is often found to vary amongst DOM sources, which have been related to the difference in the nature of organic matter and the presence of coloured inorganic compounds, such as soluble iron oxides. It is to be noted that groups of organic compounds are known to have different extinction coefficients so that the difference in the relative amount of these groups may produce differences in absorbance, independent of DOM concentration (Moore 1987).

The second method involves wet oxidation of samples containing DOM and the subsequent measurement of either the CO₂ released or the amount of oxidant consumed. Dichromate or permanganate are the most common oxidising agent used in this method and the amount of oxidant consumed in the oxidation of DOM is measured either by titration with a reducing agent or by colorimetric method. The proportion of DOM oxidised by wet oxidation is often found to vary amongst DOM sources which may be attributed to the differences in the nature of soluble carbon. DOM with low molecular weight fractions are considered to be highly mobile and are liable for both chemical and microbial oxidation. Meili (1992) observed that most estimates of organic carbon from wet oxidation using chromate were within 80 and 90% of DOM.

The third method involves dry oxidation of DOM to CO₂ at high temperature in the presence of a stream of oxygen. The amount of CO₂ produced is measured either by infra red detector or by titration after absorbance in an alkali or by weight gain after absorbance in ascarite. The most commonly used dry combustion techniques include LECO combustion and total organic carbon (TOC) analyzer. Since LECO combustion measures the total dissolved carbon the values are generally higher than those obtained by the TOC analyser in which the DOM concentration is often corrected for the concentration of inorganic carbon. Chen and Wangersky (1993) described a modified high-temperature catalytic oxidation method for DOM measurement. The method has high oxidation efficiency and a precision of 1-2%.

DOM is characterized by separating into fractions based on molecular weight and sorption chromatography. DOM is often fractionated into three nominal molecular weight (Da) fractions (<5000, 5000 - 100000 and >100,000) using Sephadex chromatography gels with different exclusion limits. The most common technique for the fractionation of DOM is based on the sorption of DOM to non-ionic and ion-exchange resins (Leenheer 1981). Based on this, DOM is fractionated to hydrophobic acid, hydrophobic base, hydrophobic neutral, hydrophilic acid, hydrophilic base and hydrophilic neutral fractions. Some of the organic compounds present in DOM of root exudates are given in Table 1.

Table 1. Nature of organic compounds identified in DOM originating from root exudates (Koo *et al.* 2005)

Major group	Compounds identified
Organic acid	Acetic, butyric, citric, glutaric, lactic, maleic, malic, malonic, oxalic, propionic, pyruvic, succinic, tartaric, valeric
Amino acid and amide	α -Alanine, β -alanine, arginine, asparagine, aspartic acid, cystine/cysteine, glutamine, glycine, histidine, lysine, methionine, phenylalanine, proline, serine/homoserine
Enzyme	Amylase, invertase, phosphatase, protease, polygalacturonase
Growth factor	ρ -Amino benzoic acid, auxins, biotin, choline, inositol, η -methyl nicotinic acid, niacin, pantothenate, pyridoxine, thiamine
Phenolic acid and coumarin	Caffeic acid, cinnamic acid, coumarin, ferulic acid, salicylic acid, syringic acid, vanillic acid
Sugar	Arabinose, fructose, fucose, galactose, glucose, maltose, oligosaccharide, raffinose, rhamnose, ribose, sucrose, xylose
Others	Nucleotide, flavonone, fatty acids, proteins, sterols, lipids, aliphatics, aromatics, carbohydrates

Dynamics of dissolved organic matter in soil

DOM undergoes sorption onto soil particles, and photochemical and microbial degradation in soil.

Sorption of DOM onto soil particles is an important process which controls its transport and persistence in soil.

Donald *et al.* (1993) measured the sorption of DOM and its fractions by soil horizons from a catenary sequence. Variation in DOM sorption among the soil horizons was related to differences in the clay content and citrate-dithionate-extractable Fe, Al, and Mn. The hydrophobic acid and the hydrophilic acid fractions were the most abundant in the soil solution (72% of the total DOM) and accounted for most of the sorption of DOM in the Bt and C horizons.

Moore *et al.* (1992) obtained DOM sorption isotherms for 48 soil samples derived from Humaquepts, Inceptisols, and Spodosols in southern Quebec using a DOM solution derived from a swamp peat. Forty-six of the samples had DOM sorption adequately represented by the linear initial mass isotherm. Null-point DOM concentrations (DOM_{np}), where there is zero net DOM sorption, ranged from 6.7 to 85.4 mg/L. Distribution coefficients (K_d) averaged $1.00 \times 10^{-2} \text{ m}^3/\text{kg}$, suggesting that DOM sorption by soils is of moderate strength compared with inorganic anions. DOM_{np} values were strongly related positively to organic C content and negatively to oxalate-extractable Al and dithionite-extractable Fe, which explained 70% of the variation in DOM_{np} .

Kaiser and Zech (1997) obtained DOM sorption isotherms for 135 soil horizons from 36 profiles of the major forest soils of the temperate zones (leptosols, vertisols, cambisols, luvisols, podzols, stagnosols, and gleysols). When solutions containing no DOM were added, the release of DOM was highest for horizons rich in organic C. In subsoil horizons DOM release was much lower. Most of the top soil horizons showed a weak DOM sorption. This was caused by low contents of sorbents (clay and sesquioxides) and/or high contents of organic C. Organic C seems to reduce the DOM sorption by occupying the binding sites. Subsoils rich in clay and sesquioxides showed a strong retention of DOM. The majority of the soils preferentially sorbed hydrophobic DOM. This was caused by the higher affinity of hydrophobic DOM to oxide/hydroxide soil constituents.

Although DOM undergoes photochemical and microbial degradation, the former process dominates in aquatic system and the later in the terrestrial system. Friese *et al.* (2002) suggested that photochemical reactions are responsible for depletion of DOM and formation of ferrous iron (Fe(II)) in acidic soft-water lakes. They noticed the coupling of DOM degradation with Fe(II) release when water samples from an acidic mining lake were irradiated with natural sunlight. Up to 50% of the DOM was transformed to CO_2 after 300 min of irradiation, and the light-induced production of Fe(II) was increased by 450%.

It has often been found that the rate of biodegradation of DOM varies amongst the sources, which has been attributed to the differences in its composition. Some of the hydrophobic compounds extracted in the DOM are less accessible to microbial degradation than hydrophilic compounds (Kalbitz *et al.* 2003). Based on biodegradation kinetics, DOM in soils is grouped into various categories such as labile and non-labile fractions.

Environmental significance of dissolved organic matter in soil

DOM plays a major role in the mobilization and export of nutrients, complexation and immobilization of metals, and the partitioning movement of organic pesticides.

Mobilization of nutrients

Organically bound nutrients can contribute largely to the export of N, P, and S from soil into aquatic systems. Kaiser *et al.* (2001) suggested that one possible determinant for the losses of dissolved organic nutrients could be their distribution between DOM fractions of different mobility in soil. They determined the concentrations and fluxes of DOM and dissolved organic N, P and S in soil water under a Scots pine (*Pinus sylvestris* L.) and a European beech (*Fagus sylvatica* L.) forest. The dissolved organic nutrients were mainly concentrated in the hydrophilic DOM fraction which proved to be more mobile in mineral soil pore water than the hydrophobic one.

Donald *et al.* (1993) noticed that phosphorus in the hydrophobic neutral fraction of DOM from boreal forest soils constituted 64% of the total P measured in various fractions. The high P content and low sorption of the hydrophobic neutral fraction suggests that the leaching of these fractions may be a possible mechanism for the redistribution and loss of P in these soils. Similarly, Vance and David (1992) suggested that DOM can influence the mobility and sorption of inorganic solutes in soils. They noticed that in the presence of DOM (5.6 mmol C/L), SO_4^{2-} sorption by three Spodosols decreased. Although DOM reduced the amount of SO_4^{2-} adsorbed by each soil, the great affinity that mineral horizons have for DOM can rapidly reduce DOM concentration in soil leachates. This would decrease the competitive DOM effect on SO_4^{2-} sorption, resulting in their retention in lower mineral horizons. Furthermore, the overall SO_4^{2-} budget may also be influenced by the release of SO_4^{2-} through organic decomposition.

Complexation of heavy metals

The transport of heavy metals in water and soil can be strongly influenced by their complexation with DOM.

Businelli *et al.* (1999) compared the Cu binding ability (maximum complexing capacity - MCC) of the DOM from pig slurry with that of humic (HA) and fulvic (FA) acids extracted from a clay-loam soil. Gel filtration chromatography showed that the DOM from pig slurry was mainly composed of a fraction with an apparent molecular weight higher than 5000 Da and the Cu naturally present in the slurry was completely complexed by this fraction. The MCC of pig slurry DOM and soil HA, which contained a similar concentration of carboxylic groups, were analogous, while MCC of soil FA, which contained double the concentration of carboxylic groups, was higher.

Strobel *et al.* (2001) investigated the kinetics of Cd and Cu release from an unpolluted arable soil applied with forest floor soil solution isolated from Norway spruce (*Picea abies* (L.) Karst.). Cadmium release rates were very low at $\text{pH} > 5$ and increased exponentially as pH decreased to < 5 and was not affected by DOM. In experiments without DOM the release rate of Cu was slightly lower at high pH than at low pH . In experiments above $\text{pH} 5$, the presence of 5 mM DOM in the solution increased the release rate of Cu. However, the Cu release was retarded by DOM in the pH range 3.8 to 5.0, which coincided with a maximum retention of DOM in the soil.

Many studies have implicated DOM as an important contributor to the elevated mobility of trace metals in soils amended with biosolids. Ashworth and Alloway (2004) examined the extent of mobility of DOM and co-mobility of Cu, Ni and Zn released from a surface-application of anaerobically-digested sewage sludge in a sandy loam. Leaching of DOM through the soil column was found to be almost un-retarded. Similar behaviour was exhibited by Ni suggesting that it migrated as organic complexes. Whilst Cu was also found to be leached, significant retardation was evident. The presence of DOM did not prevent Zn from becoming completely adsorbed by the soil solid phase.

Al-Wabel *et al.* (2002) noticed that biosolid application increased both DOM and Cu in the leachates, resulting in a positive correlation between Cu and DOM across application rates. Both Cu and Pb were mobilized under conditions of low EC. This may be the result of the release of a strong metal-binding component of DOM under these conditions. Conversely, Zn mobility was positively correlated with EC, suggesting that either cation exchange or the formation of inorganic complexes influences Zn mobility.

Anodic stripping voltammetry measurements indicated that only a small percentage of the total dissolved metals existed as free ions or inorganic complexes; the remainder appears to be complexed with DOM.

Han and Thompson (1999) examined the combined effect of molecular weight and hydrophobicity on the Cu-binding ability of DOM in biosolid. The Cu-binding ability of DOM decreased significantly with increasing molecular weight, indicating that low-molecular-weight DOM had more metal-binding sites than high-molecular-weight DOM. Within each MW fraction, the hydrophilic and the hydrophobic components also exhibited differences in Cu-binding ability. For the DOM with molecular weight 500-3500 Da, the hydrophilic fraction showed a greater Cu-binding capacity than did the hydrophobic fraction, whereas the hydrophobic acid components were most important in binding Cu for DOM with molecular weight > 3500 Da. The maximum Cu-binding capacities of different biosolid-derived DOM fractions ranged from 1.85 to 14.3 mmol Cu/mol C.

Land application is a cost-effective way of disposing of wood ash. However, high volume wood ash application tends to increase soil pH, solubilizing soil organic matter, and enhancing metal mobility. Chirenje *et al.* (2002) monitored the leaching of Cu and Ni in an ash-amended soil. In the ash-only columns, Cu leaching was in the form of soluble complexes with Cl. When wood ash was mixed with soil, Cu leached as soluble complexes with DOM at high pH. Although the solubility of many heavy metals increases under acid pH conditions, an increase in pH is likely to increase the mobility of heavy metals associated with DOM.

Partition of organic pesticides

DOM has high affinity for organic non-ionic hydrocarbons and pesticides, thereby affecting their retention and transport in soils.

Raber and Kogel Knabner (1997) investigated DOM from soil, sewage sludges, waste disposal sites, and composts as sorbent and potential carrier for hydrophobic polycyclic aromatic hydrocarbons (PAHs) in soil. Partition coefficients ($\log K_{\text{doc}}$) for PAH compounds were 4.8-4.9 for DOM from soil, 4.5-4.7 from composts, and 4.3-4.4 from sewage sludges. Leachates from waste disposal sites did not sorb PAHs. The DOM from composts contained a large percentage of organic molecules >14 000 Da (32-46%), whereas DOM from waste disposal leachates contained only 7-10%, thereby binding less PAHs.

Herbert *et al.* (1993) quantified the interactions between pyrene and fractions of DOM, HA, and FA using fluorescence-quenching spectroscopy. Pyrene partition coefficients to the smaller DOM fractions varied between 4.1×10^3 and 6.8×10^3 L/kg, while partition coefficients (K_{doc}) for the largest fraction of DOM, HA, and FA were 1.5×10^4 , 1.7×10^5 , and 1.1×10^4 L/kg, respectively. Pyrene partitioning data to the largest DOM fraction suggest that the presence of colloidal organic matter suspended in the soil solution may have a large influence on non-ionic organic compounds transport.

Pennington *et al.* (1991) examined the interactions of DOM with the herbicides bromacil, metribuzin, alachlor, diquat, and paraquat to determine if these interactions can improve predictions of herbicide leaching potential. DOM fractions were predominantly anionic in nature with some hydrophobic character. The amount of paraquat bound by DOM ranged from 1.1 to 2.1 mmol/g DOM with K_d values from 0.050 to 0.187 L/kg. Diquat was bound at 0.9 to 1.5 mmol/g DOM with K_d values from 0.044 to 0.143 L/kg. Bromacil, metribuzin, and alachlor did not bind to the extracts tested. DOM did not increase paraquat solubility in the presence of soil. Binding of these herbicides to DOM in the soils used in this study would not be a significant mechanism for increased mobility and groundwater contamination potential.

Seol and Lee (2000) examined the effect of atrazine and prometryne association with DOM extracted from municipal wastewater, swine-derived lagoon wastewater, and HA on sorption by two soils. Pesticide association to DOM normalized to organic matter ranged from 30 to 1000 L/kg DOM. DOM sorption by soil ranged from 1.5 to 10 L/kg, with a silt loam having a higher affinity for the DOM than the sandy loam. DOM up to 150 mg DOM/L did not significantly suppress sorption by soils of either atrazine or prometryne.

Conclusions

DOM originates mainly from the decomposition and solubilization of soil organic matter that accumulate from plant residue and the addition of biosolid amendments. DOM controls a number of physical, chemical and biological processes in both terrestrial and aquatic environments. In a number of countries including New Zealand and Australia, large amount of DOM is introduced to soil through the addition of organic amendments such as poultry and animal manures, and effluent irrigation. This review suggests that there is an urgent need to undertake research on following aspects:

- characterisation and quantification of DOM
- dynamics of DOM in relation to its adsorption/desorption behaviour and kinetics of degradation
- mobilization and transport of nutrients such as N, P and S
- complexation and immobilization of heavy metals such as Cu and Cd
- partition and movement of organic compounds such as hydrocarbons and pesticides.

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