



Soil Science

REVIEW ARTICLE

Controls on dissolved organic matter stabilization: sorption as a potential process

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ABSTRACT

Dissolved organic matter (DOM) can be regarded as a good indicator of a healthy soil ecosystem as it is comparatively much more responsive than total organic carbon to the environmental changes. It controls most important physical and biochemical processes both in terrestrial and aquatic ecosystems. The movement of DOM in soils could be restricted by its adsorption to surfaces of minerals available in the soils. The aim of this review is to gather and synthesize the literature on the quantity and quality as well as stabilization process of DOM in soil. Various processes have been proposed, including anion exchange, ligand exchange, cation bridging, hydrogen bonding, van der Waals forces for describing DOM-mineral associations. But still there is a challenge to describe and evaluate these mechanisms clearly and quantitatively in different soil types and ecosystems. The extent and rate of sorption of DOM depends on the mineralogy, quality of OM and soil solution. There is limited literature on the quantitative connection between mineralogy and chemical properties of adsorbed DOM, especially for the assessment of diverse DOM-mineral interactions. The reversibility of sorbed OM is also needed to be studied more considering the effect of DOM properties and changing environmental conditions. Most of the research on DOM-mineral interactions focused on the limited natural ecosystem (mainly temperate forest, grassland or stream etc.). Thus, there is still great scope to investigate the controls of DOM dynamics and stabilization in soils of different use and management, and also in different climate zones other than temperate area.

Keywords: Dissolved organic carbon, carbon flux, organic carbon stabilization, organo-mineral interaction

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1 Dissolved organic matter (DOM)

Dissolved organic matter (DOM) is one of the imperative constituents of total organic matter (TOM). It is operationally defined as the organic matter (OM) fraction in solution which passes through 0.45 μm filter (Herbert and Bertsch, 1995; Thurman, 1985; Zsolnay, 2003). However, DOM is spread out among diverse pore sizes and structures in soils with distinct attributes. It has been divided into three different classes by Zsolnay (2003): DOM I- found in microaggregates ($<0.2 \mu\text{m}$) which is physically inaccessible

from microorganism and could be bioavailable if exposed by disturbance; DOM III- concur to DOM in macroaggregates ($>6 \mu\text{m}$), is metabolized by microheterotrophs i.e., mobile and available fractions; and DOM II- lie in between these former two ($0.2\sim 6 \mu\text{m}$) which is available in situ but not mobile. Although DOM fractions represent only a small proportion of terrestrial and aquatic TOM, it is now well recognized that DOM dynamics have great influence on soil microbial activity (Flessa et al., 2000), metal and organic pollutants transport (Kalbitz and Knappe, 1997; Michalzik et al., 2001; Römken and Dolfing,

1998), soil forming process (Dawson et al., 1978), mineral weathering (Raulund-Rasmussen et al., 1998), podzolization (van Hees and Lundström, 2000), and nutrient budgets (Michalzik and Matzner, 1999). In very recent times, it has been used as a labile OM fraction and soil quality indicator in agricultural soils (Baldock and Nelson, 2000; Haynes, 2005). Therefore, Now-a-days, attention in DOM research considerably increased on terrestrial as well as aquatic ecosystem carbon (C) dynamics. There have been a large number of extensive review on the behavior and dynamics of DOM, such as: overall control on dissolved organic C (DOC), dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) dynamics (Kalbitz et al., 2000); microbial degradation of DOM (Marschner and Kalbitz, 2003); effect of land use and management practice (Chantigny, 2003); sorptive stabilization by forest soils (Guggenberger and Kaiser, 2003; Kaiser et al., 1996), linking dynamics to its environmental significance (Bolan et al., 2011); transport process (Deb and Shukla, 2011). Most of these studies mainly focused on the forest ecosystems; and there has been very little complete review linking the DOM chemistry and mineralogy to organo-mineral associations as a main process which control the dynamics of DOM in both forest and agricultural systems. Therefore, the objectives of this review to summarize the recent literature concerning controls of DOM (particularly DOC) composition and concentration of different ecosystems along with special emphasis on the DOM stabilization process through DOM-mineral interactions.

2 Sources of DOM

Ultimate source of DOM in soil is photosynthesis. This comprises fresh photosynthates such as leaf litter, root exudates, decaying fine roots, throughfall and stemflow (in case of forest ecosystems), as well as microbial by-products and leachates and decayed older soil organic matter (SOM) (Guggenberger and Zech, 1994; McDowell et al., 1998). In forest soils, DOM represents a significant share of the total C budget (Bolan et al., 2011), and litter and throughfall contribute as the main source of DOM (Laik et al., 2009). In agricultural soils, plant residues provide the major source of DOM and also different kind of amendments play a significant role (Fig. 1). Although several studies have been done on the origin of DOM, still there is notable discussion and ambiguity in the literature about significance of fresh litter vs. older SOM as source of DOC especially in forest ground soil solution (Kalbitz et al., 2000). (Qualls and Haines, 1991) reported that within a deciduous forest ecosystem, most increase in the DOM happened in the litter layer of the forest floor. Further, recent litterfall contributions were again justified by Qualls and Haines (1991) when they found strangely higher amount of hydrophilic neutral

DOM fractions in samples collected just after maximum litterfall. In agreement with this, Huang and Schoenau (1998) and Michalzik and Matzner (1999) also accounted litter layer as the greatest source for DOC and DON. In contrast with recent supply, some studies suggested native SOM stock (humified) as a dominant source of DOM as they found moderately high share of humus relating to litter in soils (Hagedorn et al., 2002; Zsolnay, 1996). Sanderman et al. (2008) suggested that DOC at the sub-surface depths is originated from within the mineral soil itself, and these DOCs are mainly similar to highly altered SOM rather than recent plant leachates. Karlton et al. (2005) also reported large portion of sub-surface (at 20 cm) DOC which is originated from older, pre-bomb C instead of from freshly fixed residual C. Similar kind of result was reported by Fröberg et al. (2006) for DOC coming out from B horizon of a podzol soil. In addition, Gregorich et al. (2000) revealed water extractable OM in agricultural soils which was resemble to the average SOM in place of fresh crop remains or the microbial biomass growing on the crop residues.

Generally, fluxes of DOM in surface soils range from 10-85 g C m⁻² yr⁻¹ while in subsoils it decreases to 2-40 g C m⁻² yr⁻¹ (Neff and Asner, 2001). The rhizosphere is usually associated with a heavy C flux as a result of root turnover and exudation (Müller et al., 2009). Microbial activity in the rhizosphere is augmented by the energy input of readily available organic substances (Phillips et al., 2008). Because of their turnover, soil microbial biomass is also believed as a possible source of DOM (Steenwerth and Belina, 2008). Recent studies of structural investigation of DOM in soil solutions have revealed that microbial metabolites represent a substantial proportion of DOM (Guggenberger and Zech, 1994; Kalbitz et al., 2000). As stated in these studies, the carbohydrate portion of DOM is chemically distinct from plant remains or bulk humus as it contains greater quantity of hexose and deoxy sugars than pentose sugars. As pentose sugars are barely observed in microbial cells (Huang and Schoenau, 1998), this carbohydrate fraction might be mainly of microbial derivation.

In short, current litter and humus are considered as the two major sources of DOM in forest soils. Likewise, crop residues, organic amendments (biosolids and manures) are also significant sources of DOM in arable soils (Fig. 1). In both forest and arable ecosystems, root and microbial contributions are also notable. Specially, root litter and rhizodeposition contribute more to the below ground input. But, the contribution of individual source to the DOM generation in soil is not completely understood. Identifying and quantifying the exact fraction of plant and microbial origin DOC in soil solution and justifying their turnover time is still a big challenge (Kalbitz et al., 2000; McDowell, 2003). These fundamental inquiries about sources and pathways are crucial to

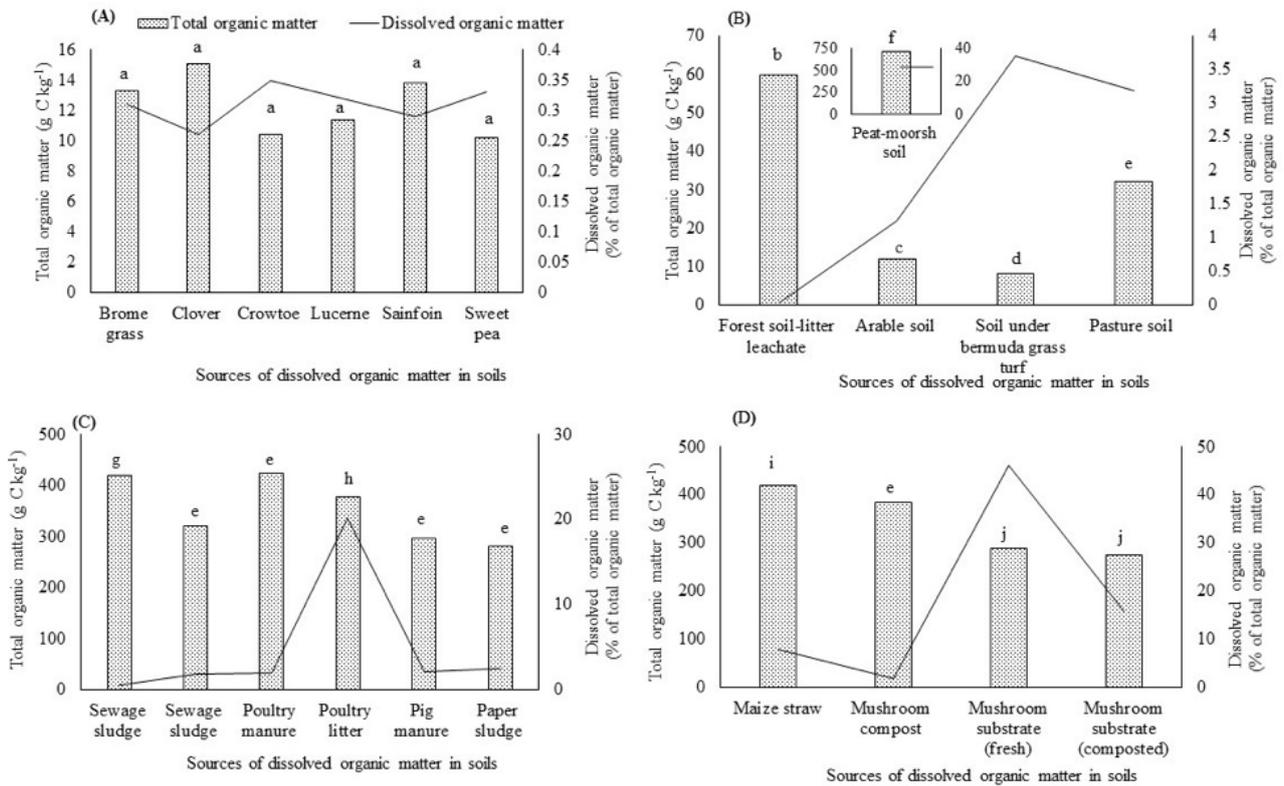


Figure 1. Sources of dissolved organic matter input in soils (adapted from Bolan et al. (2011)). Here, A = pasture grassland, B = soil, C = organic amendment (sources: animal + sludges) and D = organic amendment (source: plant). The lowercase letters on the top of the bars represent the reference of the data (both total and dissolved organic matters): a = Unkovich (2008), b = Jaffrain et al. (2007), c = Gonet et al. (2008), d = Provin et al. (2008), e = Bolan et al. (1996), f = Szajdak et al. (2007), g = Hanc et al. (2009), h = Guo et al. (2009), i = Kalbitz et al. (2003), j = Marin-Benito et al. (2009)

comprehend the long-term controls on DOC production which eventually important to formulate pragmatic evaluations of the impacts of different environmental fluctuations in soil C dynamics (Hagedorn et al., 2002).

3 Composition of DOM in soils

DOM is a complex blend of a wide range of organic compounds and humic ingredients in diverse ratios of various molecular weights ranging from 2000 to 100000 daltons. It consists of aliphatic organic acids, pheolic acids, phenols, free amino acids, carbohydrates, sugar and a large portion is humic substances. Approximately half of the soil organic C (SOC) can be classified as the chemically resistant element identified as humic substances (Lal, 2004). Traditionally, it has been considered that extractable humic substances contain novel types of cross-linked macromolecular structures. But recent investigation of the main constituents (carbohydrates, proteins, lignin and aliphatic biopolymers) of humic substances through advanced nuclear magnetic resonance methods advised that humic material in

soils is not a distinct chemical class, but is a complex combination of microbial and plant biopolymers and their decomposed derivatives (Kelleher and Simpson, 2006).

Considering elemental composition, along with C, there are other elements e.g., oxygen, hydrogen, nitrogen, phosphorus, sulfur; calcium, potassium, magnesium, aluminium, iron, zinc and copper (Bolan et al., 2011). The elemental composition of DOM is important in relation to mobilization and transportation of nutrients. DOM consists of bases, acids and neutral compounds with variable decomposability rates. Its characterization is not easy due to its high variability of compounds. However, DOM is isolated into fractions based upon molecular weight, solubility and sorption chromatography (Bolan et al., 2011). Conventionally, DOC can be fractionated into six categories (Table 1) based on their behaviour on non-ionic and ion-exchange resins: (i) hydrophobic neutrals, (ii) weak hydrophobic acids, (iii) strong hydrophobic acids, (iv) hydrophilic acids, (v) hydrophilic neutrals, and (vi) bases (Leenheer, 1981; Qualls and Haines, 1991). In most cases, approximately 40-60% of DOC is exhibit as hydrophobic acids (Qualls and Haines, 1991; Smolander et al., 2001) which thought to con-

tain mostly humic substances (Hyun and Lee, 2004). Weak hydrophobic acids are mainly phenols and account for 10-20% of DOC, whereas hydrophilic acids are about 20-30% which correspond to low molecular weight (LMW) humic and non-humic materials (Smolander et al., 2001). Hydrophilic neutrals (3-20%) contain carbohydrates and alcohols (Qualls et al., 1991). Hydrophobic and hydrophilic acids are the prevailing parts of DOC (Qualls and Haines, 1991).

4 Factors controlling DOM concentration and composition

The concentration and composition of DOM in soils depend on different factors including environmental aspects (e.g., landscape, hydrology and climate), edaphic factors (soil type, clay mineralogy and metal oxides), soil management (e.g., tillage, fertilization, crop and plant species selection), and land use (grassland, forest, cropped) (Chantigny, 2003; Kalbitz et al., 2000).

4.1 Environmental factors

Even though the amount of SOM is negatively linked with temperature in both the national and international scale (Post et al., 1982; Kirschbaum, 1995), the connection between temperature and DOM release is still ambiguous. DOC generation in watershed can be increased in warmer climates (Kramer et al., 1990). About 16% rise in DOC concentrations in forest soil solutions was reported by Liechty et al. (1995) with a difference of 2.1 °C soil temperature at the warmer compared to colder sites. Conversely, Cronan (1990) found an opposite relation between soil temperature and DOC concentration in well drained surface soil leachates. On the other hand, higher level of DOC concentrations in surface horizons is also observed despite of climatic condition in a poorly drained condition. These conflicting findings point towards less or no general climatic effect on DOC (Kalbitz et al., 2000). Numerous field researches about season-based DOC concentration also showed irregular results. Generally, DOC concentrations in soil solution found to be greater in summer than the winter season (Guggenberger et al., 1998; McDowell et al., 1998; Scott et al., 1998). Temperature effects on DOC concentrations between surface and sub-surface horizons reported as partial controlling factor where higher topsoil DOC was explained by higher molecular activity than sub-soil (Guggenberger et al., 1998). This fact is also sustained by the remark that carbohydrates (Guggenberger and Zech, 1994) and hydrophilic compounds (derivative of microbial sources) (Scott et al., 1998) are released preferably into the soil solution during the growing season instead of the inactive season. In contrast, no seasonality effects on DOC concentra-

tion in soil solution was also reported (Dosskey and Bertsch, 1997), which was explained by the comparatively brief, mild winters in the studied area (South Carolina) with neither concentrated growth seasons (summer), nor litterfall periods (autumn).

In addition to temperature, precipitation and water fluxes are also very much accountable for variations in DOC concentration in soils. High precipitation events in surface horizons could be the cause of substantial leaching and dilution of DOC, which ultimately end up with a converse affiliation between DOC concentration and water flows in organic soil (Easthouse et al., 1992). Storm actions can also influence DOC concentrations and its fluxes over the year by altering main flow paths to the direction of preferable flow via macropores, lateral flow and runoff (Kalbitz et al., 2000). Soil column studies in the laboratory by Kalbitz et al. (1997) also confirmed increased DOC release after larger rainfall events. In contrast, no rainfall effects on DOC concentration in sandy soils (Dosskey and Bertsch, 1997), and forest floors of a coniferous stand (Michalzik and Matzner, 1999) were also reported. In both field and laboratory studies, it has been found that DOC concentrations rise as a result of rewetting after dry periods (Chittleborough et al., 1992; Kalbitz et al., 1997; McDowell and Wood, 1984; Tipping et al., 1999; Zsolnay et al., 1999). This is probably because of the accumulation of microbial products, resulting from lower decomposition rate in dry soils. Along with this, cell death and lysis also can assist in increasing DOC concentrations in soil leachate after dry spells (Kalbitz et al., 2000). In contrast, no impact of soil moisture on DOC quantity and quality was reported by (Guggenberger et al., 1994). Overall, the Studies on relation of soil moisture with DOC concentration have revealed unstable outcomes.

4.2 Edaphic factors

Soil types (Table 2); clay mineralogy and metal oxides control DOC amount and composition in the soil solution. Within soil profile, concentration and fluxes of DOC in soil solution generally decrease with increasing soil depth (Table 2). Clay mineralogy is also influence DOC dynamics by binding, and making them unavailable to the microbial decomposition (details in section-dissolved organic matter stabilization). Soil characteristics which influence the physical and chemical ambience of microbial population are anticipated to have an effect on their activity, and consequently DOC dynamics in situ. However, inherent DOC properties are controlled by soil and soil solution qualities (Marschner and Kalbitz, 2003). As for example, pH can affect the release of DOC (Tipping and Woof, 1990), since solubility of DOC depends on the charge density, which is controlled by the pKa and pH of soil solution. Tipping and Woof (1990)

Table 1. Components identified in specific fractions of dissolved organic matter [from Bolan et al. (2011)]

Fractions	Compounds	Reference
Hydrophobic neutrals	Hydrocarbons Chlorophyll Carotenoids Phospholipids	Polubesova et al. (2008) Albrechtova et al. (2008) Leavitt et al. (1999) Yoshimura et al. (2009)
Weak (phenolic) HA [§]	Tannins Flavonoids Other polyphenols Vanillin	Suominen et al. (2003) Hernes et al. (2007) Suominen et al. (2003)
Strong (carboxylic) HA	Fulvic and humic acids Humic-bound amino acids and peptides Humic-bound carbohydrates Aromatic acids (including phenolic carboxylic acids) Oxidized polyphenols Long-chain fatty acids	Christensen et al. (1998) Lytle and Perdue (1981) Volk et al. (1997) Gigliotti et al. (2002) Serrano (1994) Jandl et al. (2002)
Hydrophilic acids	Humic-like substances with lower molecular size and higher COOH/C ratios Oxidized carbohydrates with COOH groups Small carboxylic acids Inositol and sugar phosphates	 Obernosterer et al. (1999) Monbet et al. (2009)
Hydrophilic neutrals	Simple neutral sugars Non-humic-bound polysaccharides Alcohols Proteins	Borch and Kirchman (1997) Rosenstock et al. (2005) Chefetz et al. (1998) Schulze (2004)
Bases	Free amino acids and peptides Aromatic amines Amino-sugar polymers	Yamashita and Tanoue (2004) Jones et al. (2005)

[§] HA = hydrophobic acids

Table 2. Dissolved organic matter concentrations in various soils [modified from Herbert and Bertsch (1995)]

Soil order	DOM concentration (mg L ⁻¹)		Reference
	Surface horizon	Subsurface horizon	
Andisol	22 (O) 23 (A)	–	Dawson et al. (1981)
Ultisols	36 (O) – 13.7 (O)	22 (BA) 10 (B) 2-13 (B) 2.1 (Bt) 0.78 (C)	Mayer (1994) Cronan (1990)
Spodosol	28.1 (A) 14 (O)	15-69 (<50 cm) 5.91 (Bs) 2.96 (B) 7.4 (B) 2.8 (BC)	Wallis et al. (1981) McDowell and Wood (1984) Cronan (1990)
Inceptisol	32.5 (O1)	–	Hertkorn et al. (2006)

Table 3. Dissolved organic carbon fluxes in various ecosystems [adopted from [Neff and Asner \(2001\)](#)]

Forest type	Site	DOM flux [§]		References
		Surface	Sub-surface	
Deciduous	Coweeta Forest, NC	42	–	Qualls and Haines (1991)
Coniferous	Harvard Forest, MA	23	17	Currie et al. (1996)
	Jutland, Denmark, Spruce	46	14	Nielsen et al. (1999)
Hardwood	Hubbard Brook, NH	21	2	McDowell and Likens (1988)
	Jutland, Denmark, Oak	26	2	Nielsen et al. (1999)
Temperate evergreen	Westlake, New Zealand	84	18	Moore (1989)
	Waldstein, Bavaria, Germany	11–17	2	Michalzik and Matzner (1999)
Temperate coniferous	Medicine Bows, WY	11	–	Yavitt and Fahey (1986)
Tropical evergreen	Central Amazon Basin, Brazil	–	2	McClain et al. (1997)
Tropical flooded	Central Amazon Basin, Brazil	–	40	
Eucalyptus & grasses	Adelaide, South Australia	22	2-3	Chittleborough et al. (1999)
	Adelaide, South Australia	2-5	3-5	
Heath	Jutland, Denmark, Heath	19	2	Nielsen et al. (1999)
Mixed Pine-Oak	Atlantic Plain, SC	13	6	Dosskey and Bertsch (1997)
Moss/Fern/Scrub	Westlake, New Zealand	69	69	Moore and Jackson (1989)

§ = DOM flux in $\text{g C m}^{-2} \text{y}^{-1}$

Table 4. Interaction with surfaces and metal ion (adopted from [v. Lutzow et al. \(2006\)](#); [Yuan and Theng \(2011\)](#))

Specific mechanism		Compounds/ mineral surfaces	
Primary interactions			
Ligand exchange	Anion exchange		OH groups on Fe- Al, Mn oxides OH groups at edge sites of phyllosilicates Allophane, imogolite OM with aliphatic or phenolic OH- groups Aliphatic acids (citric acid, malic acid)
	Anion exchange		Amines, ring-NH, heterocyclic-N
Polyvalent cation bridges	Electrostatic bridges	cation	Negatively charged functional groups: OH-, COO-
	(Fe ³⁺ < Al ³⁺ < Pb ²⁺ < Ca ²⁺ < Mn ²⁺ < Mg ²⁺)		Expandable layer silicates, e.g., smectite, vermiculite, illite OM functional groups: carboxyl, carbonyl, alcoholic OH-, microbial polysaccharides with glucuronic, galacturonic, mannuronic, pyruvic, succinic acid groups
Secondary interactions			
Weak interactions	Hydrophobic interactions		Non-polar, uncharged surfaces
	Van der Waals forces		Non-expandable layer silicates (kaolinite), neutral microsites on smectites Quartz sand OM: uncharged, non-polar groups (aromatic, alkyl-C)
	H-bonding		Any mineral with oxygen surfaces, e.g., kaolinite OM functional groups: carboxyl, carbonyl, phenolic OH-, amines, heterocyclic-N
Indirect interactions			
Entropy effects	Entropy effects		Arising from entropy gain caused by displacement of many water molecules from the clay surface by a single humic molecules

calculated that about 50% amount of mobilized OM in soil is increased with an increase of soil pH of 0.5 units. The metal ions in soil solutions can affect the release of DOC. Polyvalent cations generally reduce DOC leaching from organic soil horizons (Kalbitz et al., 2000).

4.3 Soil managements

4.3.1 Plant species

The composition of DOC is varied with sources. Kögel-Knabner (2002) examined plant material composition by solid-state ¹³C NMR and reported that beech (*Fagus sylvatica* L.) litter DOC was predominated by cellulose and hemicelluloses (polysaccharides), lignin and alkyl C (lipids and cutins). In other study, Rowell et al. (2001) also found higher aromatic (lignin) and alkyl (lipids, cutins, peptides) C in forest litter, while their concentration was lower in cereals - wheat (*Triticum aestivum* L.), barley (*Hordeum vulgare* L.), oat (*Avena sativa* L.) and rye (*Secale cereale* L.). The DOC of latter crop plants had mainly polysaccharide compounds. In most cases, forest litters are higher in lignin as a result of woody tissues whilst crop residues are higher in cellulose and hemicelluloses. It is also observed that different plant parts can have different type and quantity of chemical compounds. Example, Poirier et al. (2003) reported polysaccharides, lignin, lipids and alkyl-aromatics as the primary components of corn (*Zea mays* L.) leaves whereas Gregorich et al. (1996) found a wide range of fatty acids beside carbohydrates, lignin, lipids and alkyl-aromatics in corn roots. Investigating the dynamics and composition of DOC of some temperate and tropical tree species, Cleveland et al. (2004) has reported about 49% lignin of Naniton wood (*Hieronyma alchorneoides*) foliage and 57% of non-humic compounds (determined by XAD-8 fractionation scheme) in the leachates. In an average, they stated that 30-80% humic (hydrophobic) substances present in the DOC of the five tree species. Surprisingly, contradictory results have been reported by Smolander and Kitunen (2002). They reported no effect of plant species on DOC chemical composition.

Since the quantity and quality of DOM input to the soil are dependent on plant species, crop rotations in arable soils may also impact DOC concentration and composition (Chantigny, 2003). However, best of my knowledge, there is almost no study where the effect of crop rotations and plant species were directly compared with the in situ DOC concentrations during growing season.

4.3.2 Inorganic and organic amendment

Application of lime, inorganic fertilizers and organic amendments can affect DOC in soils. Generally, lime and organic amendments have been found to increase

DOM in soils (Fig. 1), while the outcome of inorganic fertilizers on DOM can differ with the type and amount of fertilizer added (Bolan et al., 2003). An increase in DOC concentration is confirmed following liming forest (Hildebrand and Schack-Kirchner, 2000) and arable soils (Karlik, 1995). Augmented microbial activity, OM solubility (Guggenberger and Zech, 1994) and dislocation of the previously adsorbed DOM by other anions (Kalbitz et al., 2000) might be the justification of this observable fact. Liming can also influence DOC composition by escalating the fraction of carboxylic groups (Karlik, 1995), hydrophobic acids (Andersson et al., 2000) and humic acids (Cronan et al., 1992) in DOC. Application of nitrogenous fertilizer has been shown to increase DOM concentration, mainly because of an initial rise in soil pH resulting from ammonification reactions, whereas phosphatic fertilizers normally decrease DOM due to soil acidification (Ruark et al., 2009).

Numerous studies have reported instant and considerable increase of DOC content in agricultural soil after applying organic amendments like, animal manure, crop residues and industrial wastes (Chantigny et al., 2000, 2002; Franchini et al., 2001; Björklund and Li, 2016). In general, this instant increment suggested the presence of soluble materials in the amendments (Chantigny et al., 2002). The chemical composition of soil DOC is also affected by the amendment type used. As for example, DOM in plant residues generally has LMW (710-850 dalton), whereas it is higher (2000-2800 dalton) for animal manure (Ohno and Cranell, 1996). Examining the composition of a sewage sludge and municipal waste compost, García-Gil et al. (2008) found aliphatic compounds with higher levels of C, hydrogen (H), N and Sulphur (S), but lower levels of oxygen (O), carboxyl and phenolic -hydroxyls, total acidity, and C:N and C:H ratios. Plaza et al. (2005) have elucidated properties of pig slurry and reported large amount of polysaccharide compounds and S- and N- containing functional groups; lesser carboxylic and phenolic hydroxyls, greater attraction for proton binding by phenolic and carboxylic groups; a dominant aliphatic nature and small extent of aromatic polycondensation, polymerization and humification. Both field and laboratory researches on arable soils constantly showed that existing DOM in organic amendments is highly decomposable and quickly used up by the microbes. However, long-term field experiments have showed higher net increment in DOM in organic farming than the conventional farming system (Herencia et al., 2008).

4.3.3 Land use

Among all those factors, land use can be considered as one of the most significant factors with the greatest long lasting influence (Ward et al., 2007) on DOC (Table 3), as it regulates the kind of vegetation grown

on the soil, and as the plant litter is the main origin of SOM (Chantigny, 2003). It is well known that in general, land use affects the distribution of labile OC fractions through manipulating soil physical and chemical properties which thereby possibly influence the quality and quantity of DOM throughout the soil profile. From different studies of SOC analysis, it is acknowledged that when natural vegetation is converted to arable and pasture land, pronounced decline of SOC as well as DOC has been noticed. Li et al. (2007) reported 11-40% loss of DOC in shifting native alpine pasture to introduced perennial pasture and annual oats which has been attributed mainly to net loss of C resulting from decomposition (Celik, 2005) and the shifting from agricultural to native will be vice-versa. This could be one of the reasons for low DOM in cultivated land (0.05-0.40% of SOC) when compared to native forest (0.25-2.0% of SOC) (Campbell et al., 1999b,a; Khomutova et al., 2000; Smolander et al., 2001; Ward et al., 2007; Jinbo et al., 2007). In most cases, DOC concentrations differ as: forest soils > grassland soils > arable soils, mainly because of diverse vegetation types (Delprat et al., 1997; Haynes, 2005). But there are also some studies which reported significant inconsistency in DOC following alteration in land use or management practices (Chantigny, 2003). As for example, contradictory unexpected results have been found from a field study by Akagi and Zsolnay (2008). They reported small/no qualitative (adsorptivity, biodegradability) changes of DOC along with 70% quantitative decrease as the effect of five decades of de-vegetation over rotational agricultural lands. This indicates that vegetational input into the DOM pool happens only to a negligible level and also indicate that there is a persistent 'buffering' in soils of newly added OM. Furthermore, Embacher et al. (2007) accounted pronounced variation of quantity of DOC than that of quality under different experimental sites and/or soils (type, texture); and quantity influenced mostly by seasons (vegetation periods). Divergent pattern of DOC dynamics is also showed in their field study when the similar field crop was cultivated on different experimental sites, which interlineate the outcomes reviewed by Chantigny (2003) that other factors (e.g., soil properties, climate and land management practices) can place over the actual influence of field crops.

There are suggestions that in the long run, vegetation type and the quantity of OM returned to the soil are the main aspects in determining the quantity and quality of DOC in soils (Campbell et al., 1999a,b; Delprat et al., 1997; Qualls et al., 2000). Most of the factors interact in the same or in different directions and that's why discrimination between factor and effect is often not possible especially in field condition (Embacher et al., 2007). The process liable for the variation between forest and arable soils have not been clearly determined (Chantigny, 2003). Till now, the

larger part of studies has focused on forest ecosystems (Table 3), and results on arable soils especially of tropical/arid region are very limited. So, there are still noticeable gaps in knowledge about DOC specially in relation to the control on DOC dynamics, properties and bioavailability particularly in subsoil, and role of DOC on the nature and extent of C sequestration in soils of different land use (agricultural farms, forest lands and also in wetlands) and in climatic zone other than the temperate area.

4.4 DOM stabilization

The world's soil stores approximately three times of the atmospheric C in the form of OM (Lal, 2004) which represents soils as one of the largest natural OC reservoirs on the earth surface. The amount of this SOC i.e. broadly the global C cycle is highly reliant on the turnover of SOM (Lal, 2001). Some part of the SOC is degraded easily (labile pool), while another C pool has a longer turnover time, with slower decomposition from annual to centennial or millennial. Since DOM contains high proportion of labile compounds and reactive soil C (Scaglia and Adani, 2009; Haynes, 2005), and also has control on soil physical properties e.g., soil structure, aggregation etc. (Six et al., 2001) this consecutively can have an impact on sequestration of atmospheric CO₂ (Kalbitz et al., 2000; Ruser et al., 2001; Six et al., 2000).

Several studies have focused on the capability of soils to retain DOC (Jardine et al., 1989; Kaiser et al., 1996; Kaiser and Zech, 2000; Kaiser and Guggenberger, 2000; Kothawala et al., 2009; Vandenberg et al., 2007). In general, three main mechanisms are proposed by several researchers (Baldock et al., 2004; Mayer, 2004; Sollins et al., 1996; v. Lutzow et al., 2006) to elucidate the formation of passive or resistant SOC pools. Physical protection of OM attributes to the compartmentalization of substrate through inclusion of OM into aggregates or micropores, and microbes by macro and microaggregates (low accessibility). Biochemical stabilization (recalcitrance) takes place because of the inherent complex chemical composition of the OM (Six et al., 2002); which is presumed to be the selective preservation of certain recalcitrant organic molecules (attributable to their molecular-level characteristics like molecular size, elemental composition, functional group and molecular conformation) that limit their decomposition rate (Marschner et al., 2008). Chemical stabilization refers to the decrease in availability of OM through chemical or physiochemical bindings between SOM and soil minerals (interaction with mineral particles), i.e., sorption of OM on soil minerals and precipitation. In recent times, increasing evidence from different SOC analysis studies (Marschner et al., 2008; Sollins et al., 2006; Thevenot et al., 2010) pointing towards chemical process as the most consistent explanation for longer

periods of SOM stabilization over physical and selective preservation. Humified C and even comparatively labile C compounds can be protected by strong organo-mineral interactions (Jastrow et al., 2006). Evidence comes from the fact that sorption of soluble OM on to the mineral surface reduced SOM mineralization up to 20-30% in comparison to the mineralization rate in soil solution (Kalbitz et al., 2005). The SOM in fine clay and silt fractions is older than OM in another SOM fraction (Eusterhues et al., 2003; Quideau et al., 2001). It is expected that DOC in sub-soil horizons stabilized more by mineral interactions (Rumpel and Kögel-Knabner, 2010). Furthermore, Hu et al. (2001) reported significant effect of adsorption on the concentrations of organic acids in soil solution. Generally, organic compounds are subjected to degrade gradually and to a lower degree when they are adsorbed to mineral surfaces, particularly when charged molecules like oxalate or citrate associate with charged surface of minerals like clay minerals or oxides (Jones and Edwards, 1998; Yeasmin et al., 2014). They found 85% adsorption of root derived citric acid onto $\text{Fe}(\text{OH})_3$ and thus almost absolute protection from bio-degradation. About 50-95% adsorption of added LMW carboxylic acids and about 10% of amino acids to solid phase were also reported by Jones and Brassington (1998) and Vanhees et al. (2003). On the contrary predominant control of microbial uptake and utilization over sorption on the fate of LMW organic substance was observed by Fischer et al. (2010).

Sorption is a phase distribution process that includes adsorption or accumulation of sorbate at the interface of an aqueous phase and sorbent as well as absorption or partitioning from the aqueous phase into the sorbent matrix. In other way, sorption describes the transition of molecules from the solution phase to the phase where they are fixed to any of the solid components of soil. The mechanisms involved in DOM immobilization with mineral surfaces are not well understood and are also complicated by the artefacts in the experiment (v. Lutzow et al., 2006). Various kind of binding mechanisms can take place between DOC and solid mineral surfaces such as, anion sorption, ligand exchange, protonation, hydrogen bonding, cation bridging, and physical adsorption (Table 4).

Ligand exchange is a vital mechanism for the formation of strong organo-mineral associations by exchanging anion between simple coordinated hydroxyl groups on mineral surfaces; carboxyls (COOH) and phenolic hydroxyl groups of the SOM. The bond formed via ligand exchange is very stable and can exist over hundred years (v. Lutzow et al., 2006). Organo-mineral interaction via this binding mechanism is reinforced with acidity, and maximal sorption was found in the range of pH 4.3 to 4.7, which corresponds to pKa values of the most abundant car-

boxylic and few amino acids in soils (Gu et al., 1994; Yeasmin et al., 2014). In a study of identifying the binding mechanism of forest floor OM on to goethite, pyrophyllite and vermiculite surface (pH 4), Mikutta et al. (2007) reported ligand exchange as the major process (>92%) when OM interacted with goethite, whereas for pyrophyllite and vermiculite surface it was only 13 and 7%, respectively. This could be explained by positively charged goethite and negatively charged pyrophyllite and vermiculite at pH 4. Generally, organic anions are repelled from negatively charged clay surfaces. Thus, humic and fulvic acids can be linked with clay minerals if polyvalent cations are present on the exchange complex. Polyvalent cations neutralize the solid surface via performing as a bridge and adjusting the negative charge of both acidic functional group of the OM (e.g., COO^-) and clay surface. The most important polyvalent cations accountable for the binding of fulvic and humic acids to clay surfaces are Ca^{2+} , Fe^{3+} and Al^{3+} . Divalent Ca^{2+} ion normally forms weak coordination complexes with organic molecules in comparison to the Fe^{3+} and Al^{3+} (v. Lutzow et al., 2006). The stability of organo-mineral association via cation bridges (onto phyllosilicates) is found relatively weaker than the ligand exchange (on Al and Fe hydroxides) (Kaiser and Zech, 2000).

Van der Waals forces results from temporary fluctuation in the electric charge density of specific atom or molecule. As for example, an electrically positive fluctuation in one atom is inclined to generate an electrically negative fluctuation in a neighboring atom. This attractive force is nonspecific which can form between any kinds of molecules. This process is important in the adsorption of neutral polar and nonpolar molecules, particularly, one with high molecular weight (HMW). Hydrogen bonding is another vital mechanism of organo-mineral interaction. This bonding can happen in two ways: one, polar organic molecules forms a hydrogen bond straightforwardly with water as it is not able to dislodge a water molecule solving a metal exchange cation. In another way, this H-bonding occurs between an organic cation on an exchange site and other organic molecule (Deb and Shukla, 2011). Non-polar compounds are bound by hydrophobic associations. This bonding mechanism usually occurs more at low pH while carboxyl and hydroxyl groups of OM become protonated as well as ionization of carboxyl group is restrained (v. Lutzow et al., 2006). Generally hydrophobic interaction is stronger than Van der Waals and hydrogen bond. Another primary mechanism has been identified for facilitating clay-OM interaction is the entropy-driven bonding that occurs primarily between hydrophobic compounds. These types of reactions are less important for highly soluble LMW organic acids.

4.5 Binding of non-humic compounds

Due to the complexity and heterogeneity of DOM, the OM-mineral interaction process is different for different types of chemical groups in DOM.

4.5.1 Carbohydrate groups

Although no clear mechanisms for sugar sorption have yet been suggested (Kuz'yakov and Jones, 2006), weak adsorption of glucose onto soil minerals is in line with the findings of Jones and Brassington (1998) and Jagadamma et al. (2012). Some studies proposed that weak association of glucose with minerals could be mainly via H-bonding and partially via hydrophobic interactions (Olsson et al., 2011; Wie and Fuerstenaу, 1974). This low sorption is also attributed to its lack of charge Jones and Edwards (1998). Importance of charge characteristics of both the sorbent and sorbate for sorption reaction is confirmed by Hyun and Lee (2004) and Strahm and Harrison (2008). Both found greatest sorption of LMW organic acids where the charge difference between solid matrix and compound solution was largest. In case of polysaccharides (HMW sugar polymer) adsorption, several hypotheses were proposed in early studies: mainly H-bonding and hydrophobic interactions (Afenya, 1982; Miller et al., 1983, 1984) and chemical complexation (starch with calcite and hematite) (Khosla et al., 1984). Microbial polysaccharides with negative charge (because of the occurrence of uronic acids) can also be sorbed strongly onto negatively charged mineral surfaces via polyvalent cation bridging (Chenu et al., 2017). Recent studies reported the role of metal-hydroxylated species present on mineral surfaces for polysaccharides, like, dextrin, starch or guar gum adsorption (Nyamekye and Laskowski, 1993; Raju et al., 1997; Rath and Subramanian, 1999). However, there were different beliefs concerning the idea how polysaccharide hydroxyls associated on the surface of minerals like metal-hydroxylated type. Starch (wheat) can be adsorbed on hematite by forming an eight-membered ring where the two hydroxyl groups attached to one Fe site on the mineral surface and the hydroxyl groups on the C-2 in one starch monomer and C-3' in the neighbouring monomer (Weissenborn et al., 1995). The associations of dextrin with calcium hydroxide or lead hydroxide was studied by Raju et al. (1998) and suggested that the interaction can happen via engaging all three hydroxyl groups in the 2 monomers (the OH groups on C-2, C-3, and C-6 positions).

4.5.2 Carboxylic groups

Generally, it is believed that the sorption of carboxylic acids on soil mineral surfaces is a very fast process, >70% of the sorption can take place within one minute (Jones and Brassington, 1998; Karlton,

1997). For example, di (e.g., oxalic) and tri (e.g., citric)-carboxylic acids are usually adsorbed immediately onto the Fe and Al oxyhydroxides surface (Vanhees et al., 2003). The level of sorption generally follows the series of oxalate \geq citrate \geq acetate. Carboxylates can be adsorbed on solids either forming inner-sphere or outer-sphere surface complexes (Duckworth and Martin, 2001; Hind et al., 2001). Inner sphere complexes formed when the carboxylate ion directly binds to the surface metal ion, whereas outer-sphere complexes involves electrostatic coulombic interactions, and driving force of formation is the attraction between the positively charged surface and the negatively charged carboxylate (Persson and Axe, 2005). Bidentate oxalate group sorption on gibbsite edge faces was explained by two modes, either chelating to a single Al³⁺ cation, or bridging between two cations in adjacent layers, since in both cases the O-O separation within the OH-H₂O pair replaced (Parfitt et al., 1977).

4.5.3 Phenolic groups

Phenolic acids can be sorbed on solids via different mechanisms, for instance, van der Waals or H-bonding (Cecchi et al., 2004) or can also be irreversibly sorbed through ligand exchange or oxidation reactions of the organic compound with minerals (Lehmann et al., 1987; McBride, 1987). Strong irreversible interaction is also explained by Dalton et al. (1989) as a result of adsorption on organometallic compounds or covalent bonding to organic particle or mineral surfaces. Polymerization is thought to be another process responsible for irreversible sorption which is exasperated by charge transfer from clay minerals (Wang et al., 1978) or by enzymes (Bollag et al., 1982). Non-crystalline hydroxyl-Al and Fe-compounds are far more responsive than clay minerals in adsorbing phenolic acids (Celis et al., 2005; Makino et al., 1996), which is ascribed to the high chemical reactivity of sorbent's positively charged functional groups to the oppositely charged organic groups-carboxyl and phenolic hydroxyl (Dubus et al., 2001). Polyvalent cations can also act as bridges in the binding of negatively charged phenolic acids onto site of clays and OM with negative charge (Greenland, 1971). Evidence showed that cinnamic acid derivatives sorption in soil is greater compared to the benzoic acid derivatives (Lehmann et al., 1987), and their sorption thought to be enhanced by methoxyl groups and lateral chains on acrylic acid on the benzene ring (Dalton et al., 1989). Polyphenol (tannin) binds rapidly and tightly to soils, and the polarity and molecular size are important determinants of the amount sorbed (Schmidt et al., 2012). Kaal et al. (2005) found higher retention of tannin on the quartz-ferrihydrite complexes than quartz-goethite complexes, which likely explained by easily formed

bidentate or tridentate of tannin with ferrihydrite than with goethite. However, the exact mechanism for phenolic acid and soil solid interaction has not been resolved clearly (Cecchi et al., 2004; Wang et al., 2011).

4.5.4 Amino groups

Three different mechanisms have been characterized for amino acids adsorption on soil solids: non-specific electrostatic adsorption and specific adsorption by covalent bond formation and hydrogen bonding (Lambert, 2008). The plausibility for different interactions certainly depends on the attributes of acid-base of the amino acid. Amino acids can occur as uncharged molecules ($\text{H}_2\text{N}-\text{CHR}-\text{COOH}$) or as zwitterions ($+\text{H}_3\text{N}-\text{CHR}-\text{COO}^-$) when they are sorbed in their globally neutral form. Generally, neutral form prevails for sorption from the gaseous phase onto dried solid surface, and the zwitterion for sorption from aqueous solutions (Lambert, 2008). In case of electrostatic bonding, charged amino acids may be retained near to a mineral surface carrying opposite charge and this state can be envisaged for major oxide and silicate minerals (Yeasmin et al., 2014). This type of bonding has been a vital feature of the protometabolism model of Wächtershäuser (1988). Conversely, Bebié and Schoonen (2000) reported adsorption of negatively charged amino acids on same charged pyrite surface and this adsorption behavior was not conceivably explained by the simple electrostatic adsorption model. In one of the former literatures, Collins et al. (1988) has been stated about the special reactivity of amino groups on the solid surfaces as a result of the formation of an anhydrite with surface hydroxyl groups. This was supported by the infrared work of Basyuk (1990), where presence of covalently linked amino acids on silica was reported. Besides that, it is also recognized that amino group can bind to clay minerals via forming H-bonds with the surface O atoms of the minerals (Naidja and Huang, 1994). Although H-bonds are weak, in association they might form forces that are both stably bound and highly specific (Lambert, 2008). H-bonding in amino acids sorption is also reported by Costa et al. (2007) and Lomenech et al. (2005). In another study of lysine sorption on quartz, Gambino et al. (2006) stated the combine existence of electrostatic interaction and H-bond which responsible for amino acid interaction with solid surface groups. Cation exchange and mutual molecular attraction of the amino acid were also suggested for lysine adsorption (Parbhakar et al., 2007).

4.6 Binding of humic compounds

Humic acids (HA) consist of a group of natural OM particularly stable against bio and geochemical mod-

ification. HA are water-soluble biopolymers with nanometer range sizes and an inherent chemical poly-functionality (Hayes et al., 1989). These chemical and dimension features are accountable for the capacity of HA to associate and transport trace metal ions in natural aquifers (Plaschke et al., 2005). Humic substances can bind to both external surfaces and internal layers of mineral colloids. Complexation reactions of humic and fulvic acids with structural cations of edges and hydroxyl Al or Fe coating on mineral colloids are significant binding mechanisms (Huang, 2004). Humic compounds can also be adsorbed via H-bonding (Schnitzer and Khan, 1972) and apparently by displacing bound and/or zeolitic water in the structural channels with undissociated fulvic acid (Kodama and Schnitzer, 1974). In case of interlayer adsorption, humic compounds (e.g., fulvic acid) enter the coordination shell of the leading cation in the clay and dislocate water coordinated to the cation in the clay interlayer. This water displacement relies on the attraction for water of the prevailing interlayer cation and on the rate of dissociation of the fulvic acid. As the latter instance is very little at low pH, undissociated acid may penetrate the clay interlayer. Thus, interlayer adsorption of fulvic acid is highest at low pH (Huang, 2004). The extent of (external surfaces and interlayer) adsorption of humic substances is controlled by the physical and chemical properties of the solid surface, the pH of the system, and its water contents.

5 Factors affecting DOM-mineral interactions

Adsorption of DOC relies upon the properties and nature of sites existing to associate with the molecules and ions occur in soil solution (Cornejo and Hermosin, 1996; Wu et al., 2015).

5.1 Mineral properties

Clays, including layer ($2\ \mu\text{m}$) and amorphous aluminosilicates ($<3\ \text{nm}$), short-range order Fe-oxides ($3\text{--}10\ \text{nm}$) and sesquioxides ($5\text{--}100\ \text{nm}$), provide the greater part of surface area in soils for the adsorption of DOC (Eusterhues et al., 2005; Kaiser et al., 1996; Kaiser and Guggenberger, 2007; v. Lutzow et al., 2006; Kleber et al., 2005). The chemical attributes of a mineral, primarily the surface chemistry, which comprises the surface structure of the mineral; physical attributes, e.g., the specific surface area (SSA) and the porosity control OM-mineral interactions. The DOC sorption capacity of layer silicates and Al and Fe (hydr)oxides is different due to the variations of the surface structures (Chorover and Amistadi, 2001). Layer silicates, and Al and Fe (hydr)oxides have hydroxylated surfaces with variable charge, conditional to the soil

solution pH and become gradually more negative with increasing pH. Clay minerals with a permanent negative surface charge (e.g., smectite and illite) are unaltered by pH (Sollins et al., 1996). There are different types of surface groups present on mineral; such as, silanol, aluminol and surface hydroxyl (Fe-OH) groups. Silanol group is an important phyllosilicates surface group which included some binding mechanisms like, proton exchange. Additionally, aluminol group also interact with OM via proton exchange as well as ligand exchange (Essington, 2004). Layer silicates have pH dependent charge that takes place generally at the edge sites of the layer structures. It is been agreed that edges and corners of layer silicates are the high energy sites where SOMs are preferably adsorbed (Cornell and Schwertmann, 2003). Usually, non-expanding layer silicates are poor OC sorbents in comparison to the Al and Fe oxides/hydroxides (Kaiser and Zech, 2000) possibly due to their limited ability to form chemisorptive bonds with organic acids (Kubicki et al., 1999). Minerals with dissimilar surface characters have specific affinities for functional moieties of OC. Kaolinite and montmorillonite surfaces favorably adsorb greater quantities of HMW hydrophobic fractions, whereas Fe and Al oxides adsorb great amounts of carboxylic functional groups (Gonet et al., 2008) with relatively LMW fractions over those with carbohydrate and aliphatic fractions. On the contrary, only weak sorption of LMW organic acids on montmorillonite, kaolinite and illite was found (Kubicki et al., 1999); while thermodynamically favourable sorption of relatively HMW fraction of OC on ferric hydroxides was observed (Genz et al., 2008). Moreover, Kaiser and Zech (2000) reported preferential sorption of hydrophilic OC onto clay minerals without any plausible explanation.

The extent of DOC retention in different soils is also controlled by the SSA (surface area that is possibly accessible for OM adsorption) offered by the clay minerals (Kaiser and Guggenberger, 2003; Sagar et al., 1996). Generally, ferrihydrite or amorphous Al hydr(oxides) have higher SSA ($>200 \text{ m}^2 \text{ g}^{-1}$) and goethite, montmorillonite or illite have intermediate whereas kaolinite and gibbsite provide smaller SSA (Kaiser and Guggenberger, 2003). DOC sorption appears to be increased with increasing SSA of soil minerals (Kaiser and Guggenberger, 2003). On the other way, they also found that DOC sorption on minerals can reduce the mineral SSA and this reduction is varied with amount sorbed and type of minerals. Author's one of the explanations for this decrease in SSA upon sorption was filling or clogging of small pores (Theng et al., 1999) or decrease in the surface roughness (Bock and Mayer, 2000). In case of small surface loading, sorption occurs mainly at sites for instance pores where multiple attachments to the sorbing surface are possible at minimum stretching or unfolding of the molecule (Kaiser and Guggenberger,

2003). Importance of micropores is also supported by their findings where goethite lost 27% of its total SSA but 90% of its micropore surface area upon DOC sorption, whereas ferrihydrite lost 15% SSA and 88% of its micropore surface area at the greatest loading.

5.2 DOM chemistry

Chemical structures of DOC can have an impact on the resistance against microbial decomposition in the soil. But still this effect on binding mechanisms and the potentiality of the bonding on mineral surface is not clear. The chemistry of OC also has a strong effect in controlling the degree and stability of OC adsorption. Furthermore, it has been stated that the sorptive stabilization of OM depends on the intrinsic stability of sorbed organic compounds (Kaiser and Guggenberger, 2003). Certain organic compounds demonstrate a strong affinity for certain mineral surfaces. Compounds with abundant aromatic structures and hydrophobic and/or HMW are adsorbed more strongly (with higher adsorption capacity and affinity) than the hydrophilic LMW aliphatic compounds (Kaiser et al., 1996). Preferential sorption of hydrophobic compounds over hydrophilic is evidenced (Jardine et al., 1989; Kaiser and Zech, 1998). This phenomenon sometimes explained by the physical sorption attributable to hydrophobic interactions or favorable entropy changes, along with the binding via ligand exchange (Ćosović and Vojvodić, 1989; Jardine et al., 1989). HMW and greater content of o-hydroxybenzoic acid structures also thought to be the cause for strong sorption of hydrophobic compounds (Jekel, 1986). Sorption of hydrophobic DOC having an inadequate binding sites is even occurred by the dislodgment of indigenous hydrophilic substances (Kaiser et al., 1996). Another key factor affecting sorption is the acidity of the adsorbing compounds. It appears that DOC adsorption is augmented with the number of carboxyl groups per molecule along with the increasing acidity of the carboxyl groups (Wang et al., 1997).

As DOC quantity and quality is greatly influenced by the source (i.e., vegetation), land use, climate and soil factors, it might logical that those factors also indirectly affect sorption stabilization of DOC. More about the control of those factors on DOC has discussed in the previous sections (factors controlling dissolved organic matter and dissolved organic matter stabilization). Thus, the mineral composition and organic compounds can influence the degree of sorption. Little information is existing on the connection between mineral properties and the chemistry of sorbed OC. Therefore, knowing the mineral-specific sorption patterns of definite organic compound group is must to understand the stabilization of OM at mineral surface.

5.3 Soil solution

In addition to the soil solids and DOC properties, soil solution chemistry, including pH, solution composition and ionic strength, is a vital factor for soil mineral and OM interactions (Sollins et al., 1996). The maximum adsorption capacity of different soil minerals varied with pH values (Kalbitz et al., 2000). Gu et al. (1994) reported the highly pH dependent OM sorption onto Fe oxides such as ferrihydrite, goethite and hematite. Several studies on acidic subsoil stated the significance of amorphous Fe and Al oxides for DOC stabilization but fewer data is existing for calcareous subsoils (Rumpel and Kögel-Knabner, 2010). Kaiser et al. (1996) have found very similar sorption of DOM to both carbonate-free and carbonate-containing soils, demonstrating that sorption in both types of soils may depend on the similar process and mechanisms. By exploring sorptive and desorptive behaviours of DOM on alkaline soils, Oren and Chefetz (2012) also mentioned that alkalinity of the studied soils did not lessen their DOM adsorption capacity compared to less alkaline soils. Anions in soil solution (sulfate and phosphate) compete with DOC for sorption sites and it has been shown that DOC adsorbed more than sulfate (Kaiser and Zech, 1998). OM previously present in soil and already adsorbed to mineral surfaces decreases sorption capacity of the minerals (Vance and Davis, 1992). When DOC sorption reaches an utmost level, it recommends a limited availability of sorption sites and a monolayer DOC adsorption on mineral surfaces (Mayer, 1994). Nevertheless, sorption of DOC to mineral phases and mineral soils is not unlimited, but approaches for soil sorption maxima estimation is limited (Kaiser and Zech, 1998; Kalbitz et al., 2000). Furthermore, sorption process is influenced by soil properties such as soil OC content, metal oxide and clay content, and by adsorbed SO_4^{2-} (Zech et al., 1994). Generally, soil C has shown negative effect on DOC sorption as a result of potentially blocking possible binding sites of the soil solids (Kaiser et al., 1996; Kaiser and Guggenberger, 2000). But contrasting finding is also reported by Lofts et al. (2001), and Oren and Chefetz (2012). Clay contents is also found to have influence on DOC sorption (Jardine et al., 1989; Shen, 1999); whilst other studies have reported relatively weak influence on DOC adsorption compared to metal oxides and oxyhydroxides (Kaiser and Zech, 2000; Kothawala et al., 2009). It has been also uncovered that top soils have weaker sorption capacity than the sub soils (Kaiser et al., 1996), which can be described by the low OC and high mineral content of the sub soils.

6 Stability of sorbed DOM

Association of DOC with mineral surfaces reduces its biodegradability (Kaiser and Guggenberger, 2000)

and it is still not clear why adsorbed OC is less degradable (Marschner and Kalbitz, 2003). As the stability of OM sorption is correlated to binding mechanisms; strong associations of DOM with minerals protect against biological mineralization (Watanabe et al., 2005) and can store for century to millennia (Dungait et al., 2012). Guggenberger and Kaiser (2003) reported quite opposite findings and confronted the common sorptive DOM stabilization. They found about 4-30 years of mean residence time of sorbed OC and assumed that generally natural soil surfaces may covered with biofilms which have very high attraction for DOM. So, sorptions on to this biofilmed soil surface possibly augment the biodegradation. They also mentioned that only sorption on to pure mineral surfaces would consequence in a successful stabilization of DOM.

Furthermore, in case of juvenile mineral surfaces, sorbed OM is unreachable for microorganisms (Kaiser and Guggenberger, 2003) that means expeditiously stabilized. When more OM is sorbed to the mineral surfaces with time, sorption ability becomes saturated and the bindings between OM and mineral surfaces are not strong enough (Kaiser and Zech, 1997) to protect them from heterotrophic microorganisms (Guggenberger and Kaiser, 2003). Thus, sometimes sorption is reversible, 'hysteresis' also can be observed. Microorganisms can use OM as energy source even after sorption to minerals (Singh et al., 2003; Kalbitz et al., 2005). Besides microbial decomposition and consumption after direct desorption of OM, displacement by microbial excretes desorption depends on the nature of sorbate and sorbent and as well as the bathing solution (Marschner and Kalbitz, 2003). Hysteretic sorption of OM can also connect to the molecular weight and chemical composition of the OM fractions (Mikutta et al., 2007). Components having higher affinity for sorptions are more resistant against desorption (Henrichs, 1995). It has been revealed that the hydrophilic DOM fraction is much more straightforwardly desorbed compared to the hydrophobic DOM fraction (Kaiser and Guggenberger, 2000). Organic macromolecule found to be more protected as it forms a strong multiple-site bonds which need concurrent detachment (Gu et al., 1995; Kaiser and Guggenberger, 2007). So, the types of organo-mineral interactions directly influence the biodegradability. Reversible sorption of phenolic acids such as benzoic acid onto soil solids by van der Waals or H bonding was reported by (Dalton et al., 1989) which can be desorbed and went back to solution phase in consequence of reducing strength of soil solution or by the existence of competing ions. On the contrary, characterizing the sorption-desorption of phenolic acids (both cinnamic and benzoic acids) on different soil types, irreversibility has been evidenced without any explicable cause or mechanism (Cecchi et al., 2004). Mikutta et al. (2007) revealed that aromatic

fractions, sorbed via ligand exchange were less influenced by dilution desorption while OM sorbed via weak Ca^{2+} bridges and van der Waals were more susceptible to be desorbed. On the other hand, they also found unexpectedly low desorption from pyrophyllite where OM was retained by these two weak mechanisms. Thus, it has been concluded that both the strong binding and inherent stability of sorbed OM are imperative aspects controlling sorptive stabilization of DOM in soils (Kalbitz et al., 2005; Mikutta et al., 2007).

7 Ecological implications of DOM sorption

The fate of DOM dynamics in soil is important not just from the viewpoint of soil C stabilization but also for the assessment of contaminants reactivity in the soil environment (Oren and Chefetz, 2012). Mobility of DOC in soils is restricted through its adsorption to mineral surfaces (McDowell and Likens, 1988); these binding possibilities could also retain pollutants, anthropogenic toxic compounds arriving at soil systems. Since, generally DOM is chemically fractionated during interaction with minerals, there could have a great opportunity to control contaminants' chemical associations by considering the extent of sorptive association of DOM in soil system and the degree of sorption-desorption hysteresis (Oren and Chefetz, 2012). Interactions of soil minerals with DOM also has been evidenced to have vast controls on the transformation and dynamics of SOM (Huang et al., 1995), nutrient cycling for plants (Barber, 1995; Duxbury et al., 1993), toxicity of pesticides (Huang and McDuffie, 1994) and soil formation and physical properties (Theng and Orchard, 1995). Therefore, organo-mineral association should have enormous influences on plant nutrition as well as biological productivity of soils.

8 Summary

Although DOM, coequally DOC represents only a very tiny section of SOM, it is considered as a key contributor of numerous processes in soil and water including nutrient availability and cycling, soil and water pollution, and consecutive CO_2 flux between the soil and atmosphere. Adsorption of DOC on soil minerals is the main potential mechanism for OC preservation in soils. This process is controlled by the reactivity of soil minerals and nature of OC as well as the soil solution chemistry. The chemical characteristics of a mineral, particularly the surface chemistry, which comprises the surface structure of the mineral; physical properties e.g., the specific surface area and the porosity control OM-mineral interactions. The chemistry of OC also has a strong impact in regulating the degree and stability of DOC adsorption. In

addition to the soil solids and DOC properties, soil solution chemistry, including pH, solution composition and ionic strength is a vital factor for soil mineral-OM interactions. A majority of the studies have dealt with an inadequate number of DOC and/or minerals as well as soils sampled from a narrow range of sites, which have a limited capability to compare among DOC natures and soil properties. A detailed mechanistic understanding of the adsorption process in different soil types is still lacking and is complicated due to the inherent complexities of DOC, involvement of several mechanism, highly variable soil conditions and also the artifacts in the experiments. Thus, future research efforts must focus on the connection between mineralogy and chemistry of sorbed DOC from a wide range of sites to understand the controls and mechanisms of DOM stabilization which is important to quantify the varying rates of C cycling and storage in response to global climate change.

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Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

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