Chapter from the book *Soil Health and Land Use Management*

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1. Introduction

The knowledge achieved during the last decades on the dynamics of organic matter (OM) and inorganic elements in soils has been essential to predict long-term effects of land management and develop sustainable practices that contribute to mitigate the decline in soil quality and the potential threats for human health. Knowledge about soil organic matter (SOM) properties is essential to understand soil processes. The distribution and chemical speciation of organic carbon (OC) in soil have a major role on biogeochemical processes, e.g. its own chemical stability and the mobility and bioavailability of nutrient and contaminants (Eusterhues et al. 2005; von Lutzow et al. 2008). Therefore, SOM properties are directly related to essential environmental processes, e.g. plant production, carbon sequestration or water pollution. The decline in SOM quality results in land degradation, increasing flooding events or the rates of irrigation and fertilization necessary for agricultural activities.

Organo-mineral associations and complexation of SOM with metals ions largely determines the stability and degradability of OM (Kogel-Knabner et al. 2010). The relevance of inter-molecular interactions of OM with metal ions in solution on substrate degradation, e.g. complexation with aluminum (Al), has been already highlighted in the existing literature (Sollins et al. 1996) and prompted the research presented.

1.1 Stability of organic carbon in soils

Overall, this chapter addresses the relevance of understanding the mechanisms responsible for OC stabilization in soil. For instance, knowledge on SOM stability is essential to develop strategies for carbon sequestration in soil. Soil organic matter constitutes approximately 2/3 of the global terrestrial C pool (Batjes 1996), and OC dynamics in soils control a large part of the terrestrial carbon (C) cycle. In general, human activities cause a net release of CO₂ to the atmosphere of about 800 Gt C per year (Schlesinger 1984; Schlesinger and Andrews 2000) and more concretely, forest conversion to agriculture can release up to 75% of stored soil OC as CO₂ (Lal 2004). Besides, world soils have constituted a major source of enrichment of atmospheric concentration of carbon dioxide (CO₂) ever since the dawn of settled agriculture, about 10,000 years ago.

Nowadays carbon sequestration in soils is a main area of research because of the importance of soils for food production and its role in the global carbon cycle. Depending on
environmental conditions and land use, soils may act as sources or sinks for C. Therefore, understanding the mechanisms that control stabilization and release of C is essential for the prediction of the effects of global climate change and for the development of management strategies to increase carbon sequestration in soils, which constituted a major demand at the Kyoto Protocol on climate change in 1992.

In general, it can be assumed that the pool of stable SOM in the soil solid phase is in equilibrium with the soluble organic matter (dissolved organic carbon, DOC) in the soil solution (Fig. 1). The term SOM refers to all organic substances in the soil. Organic carbon in soil can originate from natural or anthropogenic inputs, i.e. plant and animal litter decomposition, substances synthesized through microbial and chemical reactions and biomass of soil micro-organisms, but also soil addition with organic amendments. The turnover of C in soils is controlled mainly by water regimes and temperature, but is modified by factors such as size and physicochemical properties of C additions in litter or root systems or distribution of C within the soil matrix and its interactions with clay surfaces (Oades 1988).

The stabilization of organic materials in soils by the soil matrix is a function of the chemical nature of the soil mineral fraction and the presence of multivalent cations in the soil solution (Fig. 1), the presence of mineral surfaces capable of adsorbing organic materials, and the architecture of the soil matrix. The degree and amount of protection offered by each mechanism depends on the chemical and physical properties of the mineral matrix and the morphology and chemical structure of the organic matter. Thus, each mineral matrix will have a unique and finite capacity to stabilize organic matter (Baldock and Skjemstad 2000).

Three types of pathways are commonly considered in the formation of stable OM in soils (Christensen 1996; Sollins et al. 1996): Selective enrichment of organic compounds, which refers to the inherent recalcitrance of specific organic molecules against degradation by microorganisms and enzymes (Fig. 1); Chemical stabilization, involving all intermolecular interactions between organic substances and inorganic substances leading to a decrease in availability of the organic substrate due to surface condensation and changes in conformation, i.e., sorption to soil minerals and precipitation; Physical stabilization, related to the decrease in the accessibility of the organic substrates to microorganisms caused by occlusion within aggregates. According to Kogel-Knabner et al. (2008), the protection against decomposition imparted to soil organic carbon (SOC) by these mechanisms decreases in the order: chemically protected > physically protected > biochemically protected > non-protected. Hence, the relationship between soil structure and the ability of soil to stabilize SOM is a key element in soil C dynamics.

The sorption of OM is assumed as a chemisorptive process that occurs concomitantly with changes in OM conformation. Organomineral interactions lead to aggregations of clay particles and organic materials, which stabilizes both soil structure and the C compounds within aggregates, but due to the heterogeneity of natural soil systems different adsorption mechanism(s) may operate. Besides, different studies have evidenced the different depth distribution of OC in soils (Kaiser and Guggenberger 2000; Gillabel et al. 2010) and the dissimilarity in controls on C dynamics and decomposition of soil OC with depth in topsoil and subsoil (Fontaine et al. 2007; Salomé et al. 2009). For instance, according to Guggenberger and Kaiser (2003) sorptive preservation by location of OM in small pores rarely occur in topsoil horizons but primarily in subsoil horizons. Furthermore, the authors indicated that Fe oxides may be the most important sorbents for the formation of organo-mineral associations in the subsoils, which was later corroborated by Kogel-Knabner (2008).
Chemical protection involves interactions of OM with minerals; physical protection makes OC inaccessible to microbes and enzymes; and biochemical protection results from differential degradability of organic structures. Chemical stabilization may result from association of OC compounds with mineral surfaces primarily in silt- and clay-sized particles (Sollins et al. 1996), but the mechanisms by which different OM fractions adsorb onto mineral surfaces and the relationship between mineralogy and the chemistry of OM bound in organo-mineral associations are not yet fully understood.

1.2 Chemical protection of organic matter

For the purposes of the research discussed, this chapter focuses on the mechanisms involved in chemical stabilization. The primary scope is to provide a comprehensive understanding of chemical stabilization of OC in subsoil, considering the following statements:

- Chemical protection of OM might be predictable from soil clay mineralogy and extractable forms of Fe and Al (Kögel-Knabner et al. 2008).
- Complexation of fresh organic matter with Fe or Al oxides might constitute a major mechanism for OM stabilization (Eusterhues et al. 2005), forming aggregates protected from microbial degradation. Moreover, organic matter has been described to be more protected in subsoils than in topsoils (Gillabel et al. 2010). The total amount of C in subsoils is in general larger than in topsoils, but concentrations are in general lower in subsoil. The specific surface area (SSA) available in the subsoil for adsorbing OM is determined by the subsoil mineralogy and therefore the amount of OM that can be stabilized before reaching saturation (Eusterhues et al. 2005).

1.3 Complexation of aluminum by organic compounds

Aluminium is the third most abundant element in the Earth’s crust, occurring at about 8%, and is a main or secondary component of numerous minerals, especially silicates. The only
stable ion, Al$^{3+}$, is known to coordinate with oxygen-bearing ligands (Kabata-Pendias 2011). Metal ions in aqueous solution exist as aqua ions, where water molecules act as ligands, and coordinate to the metal ion via the oxygen donor atoms. Solution properties of Al are complex (Fig. 2), it is present as Al$^{3+}$, Al(OH)$^{2+}$, Al(OH)$_2^+$ at pH<5 but above pH 7.5 the dominant specie might be Al(OH)$_3^-$ (McBride 1994). Aluminum is a strongly hydrolyzing metal and relatively insoluble in the neutral pH range (6.0 to 8.0) (May et al. 1979). Under acidic (pH <6.0) or alkaline (pH >8.0) conditions, and/or in the presence of complexing ligands, the solubility of Al is enhanced, making it more available for biogeochemical transformations.

![Species distribution diagram](image)

**Fig. 2.** Species distribution diagram (logarithmic) for Al(III) in aqueous solution.

The chemistry of Al in soils has been thoroughly evaluated (Sposito 1996) and highlighted as a major scientific problem, due to the worldwide concern about deforestation and acidic deposition and the resulting environmental impact. The bioavailability and potential toxicity of Al in soils and waters are highly dependent on chemical interactions with natural organic matter. Solution Al (M$^{3+}$, Fig. 1) is the most chemically and biologically available form, although this pool represents an extremely small fraction of total Al in the environment. Within the aqueous phase, Al may be associated with a variety of inorganic or organic ligands. The extent of complexation depends on the availability of soil/sediment Al, solution pH, concentrations of complexing ligands, ionic strength and temperature (Driscoll and Schecher 1990). Aqueous A1 may be redeposited to free soil/sediment pools, assimilated by living biomass or transported from the system (Figure 1).

Boudot et al. (1989) showed the direct protective effect of amorphous Al compounds against the mineralization of various associated organics. The results indicated that insoluble metallic hydroxides were responsible of capturing organic molecules, and therefore either preserving them from the access by soluble soil enzymes or preventing their movement to immobile enzymatic constituents associated with microbial cells, which would better account for a protective effect than chemical binding.
Organic matter has been described to floculate with Al salts. Maison et al. (2000) described the existence of specific binding sites for Al for given structures or ligands within the OM composition. Those results suggested that the organic ligands present in the OM are responsible for the distribution of metals.

1.4 Methodological approaches to characterize aluminum-organic interactions
The chemical complexity of SOM, the heterogeneity of its distribution and the variations in size and decomposition rate create significant analytical problems and partly explain the current deficiency in our understanding of SOM chemistry and dynamics (Lehmann et al. 2010).

Spectroscopic techniques are powerful tools in environmental research and a growing field of research (Schulp et al. 2008; Scheckel et al. 2010). The momentum of synchrotron research is leading to a continuous success of synchrotron studies addressing complex environmental issues and moreover, it can be expected that regulations and policy decisions will increasingly rely on such techniques.

Fluorescence spectroscopy has the required sensitivity to characterize metal ion binding properties of organic matter and determine its micromolar complexing capacities, i.e. to allow differentiating the binding sites or the ligand types involved in the formation of metal-organo complexes (Ryan and Weber 1982). Besides, the fact that fluorescence differentiates free from bound ligand provides an excellent complement to other complexing capacity techniques which measure free metal ion, like anodic stripping voltammetry or ion selective electrode potentiometry. Thus, fluorescence spectroscopy has been probed as valuable for the analysis of complexes between humic materials and several metal ions. For instance, fulvic acid exhibits fluorescence that is quenched upon binding to a paramagnetic metal ion.

2. Spectroscopic analysis to determine the formation of aluminum-organo complexes
Several methods are available for examining aluminium interactions with natural organic ligand solutions. Spectroscopic approaches allow an accurate characterization of metal-organic complexes. Thus, ultraviolet, infrared, fluorescence and $^{13}$C NMR spectroscopy are used to evaluate the functional groups involved in binding, i.e. the aluminium-organic complexes. Fluorescence spectroscopy is well-known as a powerful technique useful for chemical characterization of humic acids while Fourier transform infrared spectroscopy (FTIR) can provide an insight into structural characteristics of complex organic macromolecules and allow typing organic molecules at the micrometer resolution. For instance, FTIR mapping have shown the location of organic C forms in relation to mineral surfaces, and relevant information on microaggregate formation.

2.1 Ultraviolet spectrophotometric determination of aluminum-organic complexes
Spectrophotometric titrations with Al(III) were carried out for gallic acid (Figure 3a) and salicylic acid (Figure 3b) to demonstrate the formation of the metal-organo complexes. UV–visible spectra were recorded for increasing concentrations of Al(III). A proportional decrease was observed for the absorbance at 220 and 270 nm for gallic acid (GA) and at 240 and 300 nm for salicylic acid (SA). The two isosbestic points (IUPAC 2007) confirmed the formation of the metal-organo complexes and are indicative of a transition between two light absorbing species in all recorded spectra (Harrington et al. 2010).
Fig. 3. Spectrophotometric titration of a) gallic acid 50 µM and b) salicylic acid 50 µM with Al(III).

Titrations were carried out at a pH range 3.91–4.25, which corresponds with a fraction of GA dissociated of 86-92%, 90-94% for SA and 7–13% hydrolization of Al(III). Therefore the
decrease in absorbance can be mostly related with the formation of an inner-sphere complex. The shift of the absorbance maximum at the highest concentrations of Al(III) can be only partially explained by the pH variation and might be largely related to the formation of outer-sphere complexes.

2.2 Luminiscence spectrophotometric determination of aluminum-organic complexes

Fluorescence excitation-emission spectra were collected to characterize the formation of aluminium:gallic acid (Al:GA) complexes. Multidimensional fluorescence spectroscopy has been previously demonstrated to provide better characterization of metal binding to organic compounds than traditional quenching at a single excitation-emission wavelength.

![Excitation-Emission spectra for gallic acid 50 µM (a) and Al:GA 1:1 (b).](image)

Fig. 4. Excitation-Emission spectra for gallic acid 50 µM (a) and Al:GA 1:1 (b).
Aluminum complexation with GA varied the fluorescence fingerprinting and therefore provided information on the types of metal-organic complexes, which depended on Al(III) concentration in solution (Ohno et al. 2008). Spectral variations confirmed the formation of metal-organo complexes (Figure 4) but furthermore suggested the formation of at least two different types of complexes (Figure 4b).

Similarly, for the titration of glucose (Glu) with Al(III) a shift in the maximum of fluorescence was determined, as well as an increase in the intensity of the signal for Al:Glu ratios up to 1:1, as depicted for the excitation-emission at 240 nm (Figure 5).

![Figure 5. Excitation-Emission spectra for glucose 1mM (a) and Al:Glu 1:1 (b).](image)

The multidimensional spectra of Glu and Al:Glu 1:1 (Figure 6) provides a better portrayal of the complexation of Al with Glu. The tendency of Al(III) ions to displace aliphatic hydroxyl protons from various ligands in which they are in positions favourable for metal ion coordination, as might be the anomeric carbon, was already described by Motekaitis and Martell (1984).

Those results are particularly relevant to explain the stability of organic matter. Bartoli and Philippy (1990) described association of exchangeable Al with organic matter rich in polysaccharides as one of two major types of organo-mineral associations responsible for aggregate stability. Moreover, they described such aggregates to be easily disrupted by Al/Na exchange, a process that might partially explain the effect of sodicity in the increase of organic matter solubility in salt-affected soils.

The turnover of soil organic matter pools is a slow process, essential for soil structure and to promote soil biodiversity and support phytoremediation (Burke et al. 1995). Thus, soil addition with organic materials might decrease water run-off and erosion potential of topsoil.

Artificial soils were created according to the OECD guidelines (2010): 20% kaolinite, 70% sand, ≤1% CaCO3 and 10% Pahokee peat were mixed, moistened with deionised water at field capacity and autoclaved. Soils were equilibrated for 1 week in order to
equilibrate/stabilise the acidity. For the determination of pH a mixture of soil and 1 M KCl solution in a 1:5 ratio was used. The pH value was 6.0 ± 0.5. Subsamples of the artificial soil
were added with a solution of glucose 1 mM or an Al(III) complex Al:Glu 1:1. The soil solution was normalized to a UV-Absorbance 0.2 at 254 nm by adequate dilutions and analyzed by luminescence spectroscopy. Emission spectra were recorded over the range of 250 to 500 nm at a constant excitation wavelength of 240 nm. Relative fluorescence intensity was based on a unitless reciprocal to the gain used to normalize each emission spectrum and was expressed in arbitrary units (Plaza et al. 2006).

Despite the chemical diversity of dissolved organic matter (DOM), similar steady state fluorescence spectra has been observed for DOM excitation –emission matrices (EEM), indicating the presence of common pool of fluorophores (Cory and McKnight 2005). Thus, EEM spectroscopy provides the sensitivity to examine subtle changes in dissolved organic matter (DOM) fluorescence and provide insight into alteration of DOM pool composition (Coble et al. 1998). Thus, fingerprinting of soil organic pools allows a thorough characterization of the organic matter in a given soil and provides a relevant tool to evaluate the alterations due to a particular soil addition with organic materials.

Otherwise, metal ion mobility and bioavailability in soil is extensively controlled by soil organic matter (Sposito 1996), and especially humic substances, of which humic acids (HAs) and fulvic acids (FAs) represent two major fractions. These materials are the most important soil organic ligands in terms of metal binding capacity due to their large content of oxygenated functional groups, including various carbonyl, carboxyl, phenolic, alcoholic and enolic hydroxyl groups (Tipping et al. 2002).

Soil addition with Al:Glu 1:1 resulted in a significant increase of the visible humic-like organic matter pool (Ex/Em 320-360/400-460) (Figure 7) compared to soil added with Glu.

This substantial increase in the fraction of UV and visible humic-like organic matter suggest that glucose complexation with Al(III) hampers the degradation of such labile compound, increasing the pool of highly stable, low degradation rate organic matter. Moreover, the increase in fluorescence intensity confirms the presence of a metal-organo complex in the solution Al:Glu 1:1. These results are consistent with previous results describing the preferential binding of aluminium to polysaccharides (Masion et al. 2000). The authors attempted to describe a model structure where cellulose is partially responsible for the locally ordered arrangement of Al atoms. Because of the complex chemical nature of humic and fulvic materials, which represent up to 70% of DOC and are major components of natural organic matter, these results are of major relevance for better understanding organic matter structure at a molecular level. Currently, little is known about stabilization of organic matter by formation of insoluble Al–OM complexes, which has been already described as a major pathway for the formation of stable soil OM (Scheel et al. 2007).

3. Future perspectives: The role of aluminum-organo complexes on carbon speciation, a health benchmark in salt-affected soils

Soil health is the balance of inherent soil properties (physical, chemical and biological), environmental conditions and management practices. Soil health is measured in terms of individual ecosystem services provided relative to a specific benchmark: e.g. microbial activity, CO₂ release, or humus level.
Fig. 7. Excitation-Emission spectra for pore water extractions from artificial soils added with glucose 1mM (a) or Al(III) complexes Al:Glu 1:1 (b).
A healthy soil is productive, sustainable and profitable. In general, a healthy soil presents the following characteristics which promote the health of plants, animals and humans while also maintaining environmental quality:

1. Soil organic matter equilibrium maintained
2. Soil fertility is balanced
3. Water entry, storage & supply optimised
4. Enhanced soil biological function
5. Supports productive land uses
6. Enhances environmental & community health and well-being

Among these properties, knowledge about soil organic matter (SOM) properties is central to soil health. The optimal level of SOM for any given soil is one which supports the functional capacity of the soil to hold and supply plant available water, store plant nutrients, provide energy for soil fauna, improve crop/biomass yields, and moderate net greenhouse gas emissions. Decomposition of organic matter (OM) regulates the flow of energy and nutrients in soil. It plays a key role in C, N, S and P cycling and also acts to improve soil structure. Agricultural practices and plant inputs influence both the quantity and quality of SOM, which in turn directly impacts on soil productivity and the ability of soil to recover from stress (soil resilience). For instance, the increasing use of wastewater for irrigation purposes in areas of southern Europe introduces surfactants in the soil system. Surfactants present in wastewater can have side-effects such as the increase of soil sodicity. A study conducted for a collection of calcareous soils correlated surfactants effect with soil properties, and additionally the effect of some amendments commonly used in agriculture was evaluated. Increasing sodicity and calcium sequestration were the mechanism driving trace metal release from soil treated with anionic surfactants (Hernandez-Soriano et al. 2011).

The amount of OM in a soil is used as an indicator of the potential sustainability of a system. Salt-affected soils present low OM contents due to poor plant growth, dispersion, erosion and leaching. Altered physical, biological and chemical properties directly impact SOM dynamic, particularly the active pool (rapid turnover). Thus, disruption of soil aggregates, changes in OM distribution and increased solubility of OM in the presence of Na increase SOM mineralization (Nelson et al. 1996; Oster and Shainberg 2001), while salinity alters soil microbial biomass (Rietz and Haynes 2003; Wong et al. 2008). Moreover, the opposing saline and sodic processes and the effects of OM result on conflicting effects of OM addition to saline and sodic soils. Currently, our understanding about carbon stocks and fluxes in saline and sodic soils is still limited while data related to carbon dynamics in such soils is contradictory (Wong et al. 2010).

A better understanding of the mechanisms of chemical protection of organic matter will contribute to protect and ameliorate soils health. This knowledge can be achieved by the accomplishment of the following goals:

- To characterize the specific binding mechanisms in organomineral associations using high-resolution spectroscopic techniques;
- To characterize the composition of the organic matter associated with minerals and/or ions and determine molecular-level changes in soil Fe and Al species for relevant scenarios.

The organomineral associations provide an alteration of the molecular structure of organic matter (organic compounds) such that enzymes for decomposing specific functional groups
will be inactive. Thus, another major goal for future research is to relate soil respiration rates and biological transformation of organic matter to organomineral associations.

4. Conclusions

Aluminium complexation with organic compounds plays a fundamental role in the dynamics of organic matter. Spectrometric analysis can help demonstrating the formation of complexes of Al (III) with organic compounds, but also identifying the types of metal-organic complexes in aqueous solution, which largely depends on metal concentration. Spectra alteration for the complexation of Al with gallic acid, salicylic acid and glucose, confirmed the formation of metal-organo complexes. Structural changes to organic molecules due to metal complexation might alter their biological transformation and similar processes can be expected to control soil organic matter turnover.

A comprehensive characterization of soil organic matter properties is central to soil health. The increasing concern about salt-affected soils and the necessity of developing feasible preventive and remediation strategies demand a better knowledge on carbon dynamics, particularly for the management of agricultural soils. Therefore, characterization of metal-organo complexes in the soil system constitutes a major research goal for soils scientist. Moreover, a multidisciplinary approach is required for such knowledge to truly contribute to the preservation of organic matter equilibrium in soil.

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6. References


Soils play multiple roles in the quality of life throughout the world, not only as the resource for food production, but also as the support for our structures, the environment, the medium for waste disposal, water, and the storage of nutrients. A healthy soil can sustain biological productivity, maintain environmental quality, and promote plant and animal health. Understanding the impact of land management practices on soil properties and processes can provide useful indicators of economic and environmental sustainability. The sixteen chapters of this book orchestrate a multidisciplinary composition of current trends in soil health. Soil Health and Land Use Management provides a broad vision of the fundamental importance of soil health. In addition, the development of feasible management and remediation strategies to preserve and ameliorate the fitness of soils are discussed in this book. Strategies to improve land management and relevant case studies are covered, as well as the importance of characterizing soil properties to develop management and remediation strategies. Moreover, the current management of several environmental scenarios of high concern is presented, while the final chapters propose new methodologies for soil pollution assessment.

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