Review Article

Microaggregates in soils

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Abstract

All soils harbor microaggregates, *i.e.*, compound soil structures smaller than 250 μm. These microaggregates are composed of diverse mineral, organic and biotic materials that are bound together during pedogenesis by various physical, chemical and biological processes. Consequently, microaggregates can withstand strong mechanical and physicochemical stresses and survive slaking in water, allowing them to persist in soils for several decades. Together with the physiochemical heterogeneity of their surfaces, the three-dimensional structure of microaggregates provides a large variety of ecological niches that contribute to the vast biological diversity found in soils. As reported for larger aggregate units, microaggregates are composed of smaller building units that become more complex with increasing size. In this context, organo-mineral associations can be considered structural units of soil aggregates and as nanoparticulate fractions of the microaggregates themselves. The mineral phases considered to be the most important as microaggregate forming materials are the clay minerals and Fe- and Al-(hydr)oxides. Within microaggregates, minerals are bound together primarily by physicochemical and chemical interactions involving cementing and gluing agents. The former comprise, among others, carbonates and the short-range ordered phases of Fe, Mn, and Al. The latter comprise organic materials of diverse origin and probably involve macromolecules and macromolecular mixtures.

Work on microaggregate structure and development has largely focused on organic matter stability and turnover. However, little is known concerning the role microaggregates play in the fate of elements like Si, Fe, Al, P, and S. More recently, the role of microaggregates in the formation of microhabitats and the biogeography and diversity of microbial communities has been investigated. Little is known regarding how microaggregates and their properties change in time, which strongly limits our understanding of micro-scale soil structure dynamics. Similarly, only limited information is available on the mechanical stability of microaggregates, while essentially nothing is known about the flow and transport of fluids and solutes within the micro- and nanoporous microaggregate systems. Any quantitative approaches being developed for the modeling of formation, structure and properties of microaggregates are, therefore, in their infancy. We respond to the growing awareness of the importance of microaggregates for the structure, properties and functions of soils by reviewing what is currently known about the formation, composition and turnover of microaggregates. We aim to provide a better understanding of their role in soil function, and to present the major unknowns in current microaggregate research. We propose a harmonized concept for aggregates in soils that explicitly considers the structure and build-up of microaggregates and the role of organo-mineral associations. We call for experiments, studies and modeling endeavors that will link information on aggregate forming materials with their functional properties across a range of scales in order to better understand microaggregate formation and turnover.

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Finally, we hope to inspire a novel cohort of soil scientists that they might focus their research on improving our understanding of the role of microaggregates within the system of aggregates and so help to develop a unified and quantitative concept of aggregation processes in soils.

1 Introduction

Soil is a heterogeneous, dynamic and biologically active porous medium, with its functions intimately linked to its three-dimensional 'architecture'. While some soils may lack macroscopic structure (being coherent or 'structureless') or have a single-grain structure like Arenosols, *i.e.*, quartz-rich soils of sandy texture (*IUSS Working Group WRB*, 2015), most soils develop an aggregate structure as a consequence of pedogenesis (Fig. 1). As such, aggregation is one of the specific and distinct features of soils (*Churchman*, 2010a). Based on the stability of the soils against ultrasonic excitation, *Edwards* and *Bremner* (1964) concluded that soils are built of macroaggregates (> 250 μm) and microaggregates (< 250 μm), with macroaggregates being the consequence of weakly associated microaggregates. This concept was further developed into the aggregate hierarchy model by *Tisdall* and *Oades* (1982). They based their model on the different stability, when exposed to ultrasonic agitation, of composite aggregate structures of progressively smaller size found in surface soils. A hierarchically organized system of aggregates (*Tisdall* and *Oades*, 1982) has been described for a number of reference soil groups including Cambisols, Luvisols, Planosols, Gleysols, Vertisols, and Chernozems (*Tisdall* and *Oades*, 1982; *Field* and *Minasny*, 1999). Other soils like tropical, oxidic soils do not show such a hierarchical system across scales (*Oades* et al., 1989) but still feature microaggregates as their basic structural elements (*Six* et al., 2000b) and, interestingly, the hierarchic organization on the micron to submicron scale (*Vrdoljak* and *Sposito*, 2002; *Asano* and *Wagai*, 2014). Whereas there is consensus on an upper size limit of 250 μm for soil microaggregates, the lower size limit depends on the classification system for soil texture. *Tisdall* and *Oades* (1982) denoted particles in the 20–250 μm range as microaggregates, corresponding to the 20 μm limit for silt or silt-sized microaggregates. However, when silt is defined as particles < 50 μm or < 53 μm, as in the US or French system, respectively, the lower limit of microaggregates corresponds to this size limit (*e.g.*, *Jastrow* et al., 1996; *Six* et al., 2000a; *Six* et al., 2004; *Fernández-Ugalde* et al., 2013; *Hurisso* et al., 2013). Sometimes 63 μm is used as the upper limit of silt, which corresponds to the German system (*John* et al., 2005; *Hbirkou* et al., 2011). Some investigations differentiate between small microaggregates defined as between 20 μm and 50 μm in size, and large microaggregates in the 50–250 μm range (*Virto* et al., 2008; *Lobe* et al., 2011). However, particles even smaller than 20 μm or 50 μm are often organized into structural units that involve minerals, organic matter (OM), as well as microbial biomass and debris (*Tisdall* and *Oades*, 1982; *Chenu* and *Plante*, 2006; *Asano* and *Wagai*, 2014) and, thus, are technically defined as aggregated. In our review, we therefore consider all composite soil structures smaller than about 20 μm as *small microaggregates*, those between 20 μm and 250 μm as *large microaggregates*, and those > 250 μm as macroaggregates (see glossary). At the lower size range, the concept of aggregation also includes the colloidal and nanoparticulate mixed phases and the organo-mineral associations (*e.g.*, *Chenu* and *Stotzky*, 2002; *Kögel-Knabner* et al., 2008; *Lehmann* et al., 2007), sometimes also called 'mineral-organic associations' (*Kleber* et al., 2015). Such nanoparticulate and colloidal sized 'aggregates' are found in soils both as immobile constituents of the solid phase and as colloidally dispersed components of the mobile phase (*e.g.*, *Buettner* et al., 2014; *Totsche* et al., 2006; *Fritzsche* et al., 2015). Consequently, in our review we consider all organo-mineral associations as composite building units within the system of aggregates; as such, they comprise an important fraction of the microaggregates.

The three-dimensional structure of soil microaggregates defines a rather stable and complex system of interconnected and dead-end voids and pores of various size, shape and geometry, which provides an extremely large, heterogeneous and morphologically complex internal and external biogeochemical interface (*Totsche* et al., 2010). As a continuous network, the internal pore system allows for the flow of liquids and gases and the transport of dissolved compounds and colloidal particles. A fundamental feature of this structure, in combination with variable boundary conditions, is the dynamic and spatial variation in soil properties and states, *i.e.*, how such factors as redox potential, pH, osmotic pressure, moisture content, and biological activity fluctuate locally and temporally, which results in a continuous cycle of aggregate formation and destruction. Soil aggregates harbor a vast range of physico-chemical niches, which provide the space for the growth and the movement of soil microorganisms and communities. These respond to and act on the architecture of the soil, so allowing the development of a high level of biological diversity, which spreads and forms changing distribution patterns reflecting the interaction between microorganisms and the soil (*Young* and *Crawford*, 2004). In turn, changes in aggregate architecture have major implications for many soil functions, *e.g.*, water storage and transport, biological activity and habitat, and the storage and biogeochemical cycling of carbon, nitrogen and other elements.

Of particular significance to the formation of microaggregates are those associations built by the interaction of minerals with organic matter (OM) during pedogenesis—in accordance with *Lehmann* and *Kleber* (2015), OM denotes a vast variety of organic materials that ranges from plant materials to highly oxidized, low molecular weight, organic acids. This process is dependent on the supply of reactive mineral surfaces provided by weathering, as exemplified by chronosequence

studies (*e.g.*, *Mikutta* et al., 2009; *Dümig* et al., 2011). Under temperate climatic conditions the accretion of newly formed soil components, such as microbial residues or hydrous Fe oxides, seems to be a rapid process completed within approximately 200 years, as deduced from chronosequence studies (*Zehetner* et al., 2009; *Roth* et al., 2011; *Kalbitz* et al., 2013). From this, one may suppose that the formation of soil micro-aggregates follows a similar time-scale. In contrast, the build-up (and decay) of larger aggregate units occurs much faster and reaches a steady-state equilibrium within one or two decades (*e.g.*, *Lobe* et al., 2011; *Kösters* et al., 2013). Hence, macroaggregates are less stable than microaggregates, show faster turnover rates in soil, and are more susceptible to soil management practices. While in recent decades much progress has been made in understanding macroaggregates, mainly with respect to their biological formation, composition, and response to a changing soil environment (*Jastrow*, 1996; *Six* et al., 2004), much less is known about microaggregates.

This review summarizes our current knowledge on the formation, build-up and turnover of microaggregates, and their role in soil functions. We also report on the major unknowns and propose challenges for future microaggregate research. Starting with a discussion of the concepts for aggregation in soil, we present the diverse mineral and organic aggregate forming materials and the processes and mechanisms involved in the formation of the building units up to the full-scale of the microaggregates. We then consider the state of our current understanding concerning the stability of microaggregates and its intimate link to the turnover of their structural components with a particular focus on organic carbon (OC). We describe quantitative methods and modeling approaches that are used to study the formation and turnover of microaggregates. In the last section we discuss the characteristics and properties of microaggregates and their role in the functioning of soil with specific focus on the pore system, habitat, water retention, and biogeochemical cycles. As members of the scientific community define a number of technical terms slightly different, we provide a consistent and harmonized terminology in a glossary at the end of this review.

2 Concepts for the formation of soil microaggregates

Our current understanding of aggregation in soils has been presented in the form of a number of different concepts, viz: the structural entropy concept (*Dexter*, 1977), the aggregate hierarchy concept (*Tisdall* and *Oades*, 1982), and the concept of primary, secondary, and tertiary levels of structural organization as summarized by *Christensen* (2001). *Dexter* (1977) applied the concept of entropy, which is used in physics and
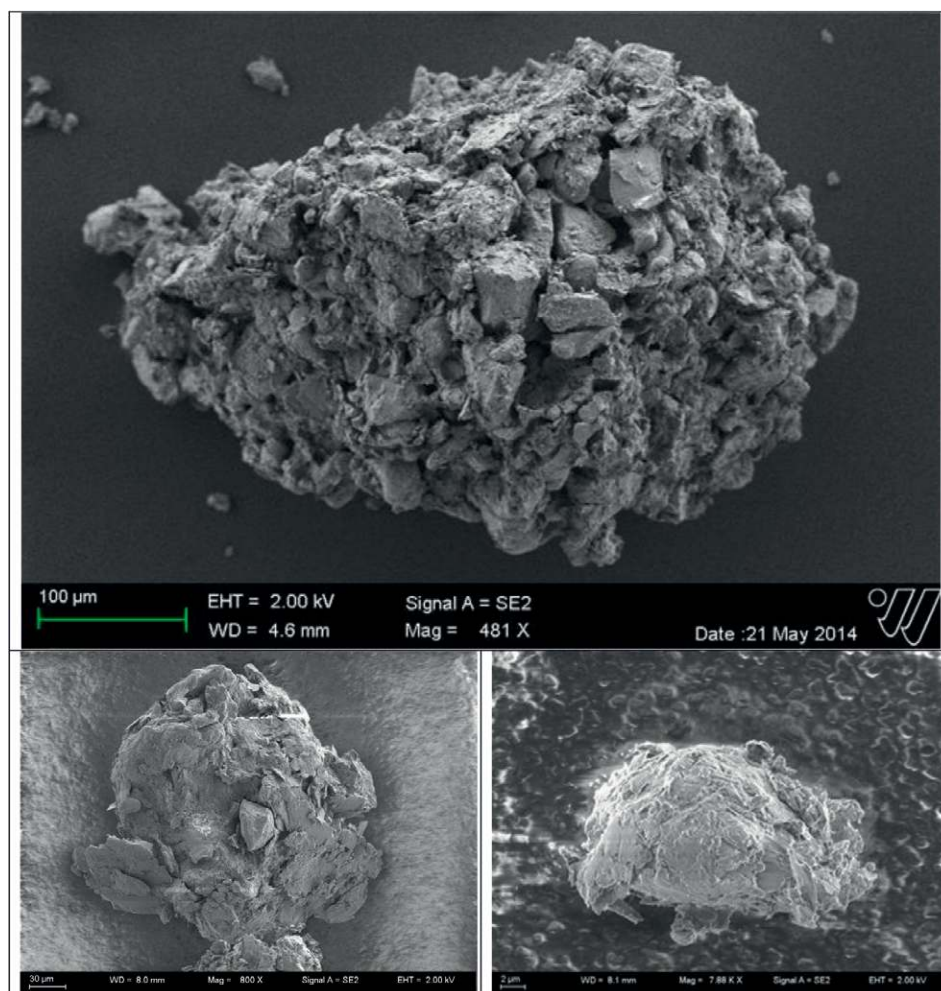

Figure 1: Scanning electron micrograph of a large (top, Image provided by D. Uteau and S. Peth) and small (bottom left and right) soil microaggregate separated from two Luvisols. The aggregate forming phyllosilicates and quartz grains can be detected (bottom left). Plant residue encrusted and embedded within a 'shell' built from phyllosilicates (bottom right). From these images it is intuitively possible to visualize the three dimensional, complex-shaped interior pore space defined by the three-dimensional arrangement of the building units.

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chemistry as a measure for the degree of disorganization of a system, to describe the soil structure in terms of the spatial organization of pores and solids and referred to it as 'structural entropy'. Based on this concept, *Dexter* (1977) found that re-aggregation after tillage resulted in a decrease of structural entropy with time, suggesting that the concept of entropy is a valuable and sensitive approach for the structural organization of soils. Approaches based on entropy have also been used in other, more recent studies as a morphological descriptor for porous media. *Andraud* et al. (1997) used local geometry entropy to describe random but correlated microstructures. When testing this approach on different image datasets, including sandstone, they found entropy to be a sensitive parameter to describe microstructural heterogeneity in porous media. *Chun* et al. (2008) used the normalized entropy function suggested by *Andraud* et al. (1997) to quantify pore arrangement from wooded and cultivated soils and found, similar to *Dexter* (1977), that cultivation (tillage) reduced the entropy of pore structure compared to non-cultivated soils. They further found that entropy increased with aggregate size, suggesting that pore morphology and the spatial distribution of intra-aggregate pores are scale dependent or hierarchical.

The two concepts by *Tisdall* and *Oades* (1982) and *Christensen* (2001), although they are both based on the separation and analysis of singular structural units, do not coincide with each other. This problem is further impaired by the difficulties that arise when isolating the conceptual functional entities as structural elements, *e.g.*, microaggregates, from soils (*von Lützow* et al., 2007).

Surface properties, such as charge, allow organic and mineral particles to adhere together to form micro-structured clay- and silt-sized compound particles (*Chorover* et al., 2004; *Ilg* et al., 2008). These compound particles then act as composite building units and include the so-called 'organo-mineral associations' (*Chenu* and *Stotzky*, 2002; *Lehmann* et al., 2007; *Kögel-Knabner* et al., 2008), nano-sized, organo-mineral composites as part of the 'presumed building blocks' (*Asano* and *Wagai*, 2014) or 'mineral-organic associations' (*Kleber* et al., 2015).

Christensen (1996, 2001) considered such primary organo-mineral associations from fully dispersed soil as the basic structural units in soil, with the surface reactions between OM, organisms, and minerals being the main regulatory mechanisms for their formation. Christensen's concept further includes secondary complexes that reflect the degree of aggregation of primary organo-mineral complexes, which is referred to as the second level of complexity (*Christensen*, 2001), while the structurally intact soil (the soil *in situ*) constitutes the third level of complexity.

As pointed out by *Chenu* and *Plante* (2006), "…true primary organo-mineral complexes (in the sense of *Christensen*, 1996) must be regarded as conceptual entities because the high energies required to fully disperse the clay-sized fraction are likely to render the results meaningless in natural systems and are also likely to result in the breakdown of intact organic or mineral particles." In line with this, results by *Gregorich* et al. (1988), *Kaiser* et al. (2012), and *Kaiser* and *Berhe* (2014) gave no evidence for the disintegration of sand and silt-sized mineral particles, even at rather high energy levels (up to 700 J cm^{-3}). Indeed, it is difficult to imagine that mineral particles or aggregates, formed from minerals and organic matter by covalent bonds, might be destroyed more easily than the compound particles formed by weaker, *e.g.*, electrostatic interactive forces. *Tisdall* and *Oades* (1982), and later *Oades* and *Waters* (1991), differentiate aggregation at different hierarchical scales, according to the organic binding agents involved, into transient (mainly polysaccharides), temporary (roots and hyphae), and persistent (strongly sorbed polymers and polyvalent cations). The microaggregates $< \approx 20\,\mu m$, including the composite building units, seem to be stabilized mostly by short range van-der-Waals forces and electrostatic binding involving also ions, predominantly cations (Tab. 1). Surprisingly, the role of water (capillary interaction) in the stabilization of small microaggregates is ignored. This is rather astonishing as these capillary forces are essentially electrostatic forces mediated by H-bonding and are thus in the same order of magnitude. This calls for future studies on the formation and stabilization of microaggregates in order to elucidate the role of water.

At the larger microaggregate scale, the stabilizing agents seem to be OM compounds that act as gluing agents and cementing agents, such as oxides, hydroxides, and oxy-hydroxides of iron (Fe), manganese (Mn), aluminum (Al), silicon (Si), aluminosilicates, and carbonates (*Oades* and *Waters*, 1991), with the OM possibly enriched at the microaggregate surfaces (*Amelung* et al., 2002). There is also evidence that polysaccharides are specifically relevant in binding microaggregates $< 50\,\mu m$ (*Puget* et al., 1998; *Six* et al., 2004). The microaggregates seem then to be bound together into macroaggregates ($> 250\,\mu m$) by temporary binding agents such as roots and hyphae, but also by transient extracellular polymeric substances (EPS) and EPS biomolecules, including polysaccharides and proteins (*Six* et al., 2000a; *Rodionov* et al., 2001; *Kleber* et al., 2007).

The concept of an aggregate hierarchy may be generally valid and also applicable at the micron and submicron scale. Evidence of a hierarchic built up of microaggregates smaller than approximately $20\,\mu m$ is, however, still scarce and so far limited to Vertisols (*Field* and *Minasny*, 1999), Oxisols (*Vrdoljak* and *Sposito*, 2002) or allophanic Andosols (*Asano* and *Wagai*, 2014). In these studies, the authors were able to disintegrate smaller microaggregates in a stepwise fashion by applying progressively higher levels of ultrasonic energy. This suggests that the stabilizing interactions, as well as the interaction processes that result in the formation of the submicron-sized microaggregates, seem to differ from those among the larger microaggregates. One may hypothesize that the higher energy levels required to disperse the submicron-sized aggregates relate to the increasing role of both the surface properties (*e.g.*, roughness, step edges, kinks, vacancies) and the role of organic coatings, in controlling the interaction forces. This, however, needs more detailed investigations—in particular in the build-up and stability of the submicron-sized aggregates—that take into account the morphology and mechanical properties of the interacting surfaces. In conclu-

Table 1: Microaggregate forming materials and their roles in formation and stabilization processes.

Microaggregate forming material		Examples	Role for formation	Stabilization and major interactions mechanisms
Class	**Type**			
Biota	Fine roots	Trees, shrubs, grasses	Precipitation template, exudation of organic matter	Enmeshment by mechanical interactions
	Fungal hyphae	*Schizophyllum commune*	Precipitation template, production of mucilage	Enmeshment by mechanical and physicochemical interactions, hydrophilic-hydrophobic crosslinking hydrophilic and hydrophobic domains
	Bacteria, archea, fungi	*Bacillus subtilis*	Surface alteration, biofilm formation, EPS production	Cohesion by physicochemical interactions
Organic matter	Particulate organic matter	Cell and tissues remnants, root debris	Formation nuclei	Cohesion by physicochemical interactions
	Humified organic matter	Humic acids	Gluing agent, surface alteration	Sorption and cohesion by physicochemical and chemical interactions
	Charred biomass and charred OM, 'black carbon'	Charcoal, soot	Precipitation nuclei	Sorption and cohesion by physicochemical and chemical interactions
Biotic Organic Macromolecules and macromolecular mixtures	Proteins	Glomalin, hydrophobin	Gluing agent, surface alteration	Sorption and cohesion by physicochemical and chemical interactions
	Polysaccharides	Lignin, cellulose, hemicellulose	Gluing agent, surface alteration	Sorption and cohesion by physicochemical and chemical interactions
	Lipids	Lauric acid, oleic acid	Wettability, gluing agent, surface alteration	Sorption and cohesion by physicochemical and chemical interactions
	Extracellular polymeric substances	Macromolecular mixture (proteins, polysaccharides, lipids, nucleic acids)	Gluing agent, surface coating, biofilms, wettability	Agglutination and cohesion by physicochemical and chemical interactions, embedding and entrapment
	Mucilage	Macromolecular mixture (glycoprotein, polysaccharide)	Gluing agent, surface coating	Agglutination and cohesion by physicochemical and chemical interactions, embedding and entrapment

Table 1. Continued.

Class	Type	Examples	Role for formation	Stabilization and major interactions mechanisms
Inorganics / minerals	Primary minerals (weathering remnants)	Quartz, feldspar	Sorbent, precipitation nuclei	Sorption by physicochemical and chemical interactions
	Phyllosilicates and neutral minerals	Muscovite, kaolinite	Sorbent, precipitation nuclei	Sorption by physicochemical and chemical interactions
	Well crystalline oxyhydroxides	Goethite, gibbsite	Sorbent, cementing agent, precipitation nuclei	Encrusting and cementing by physicochemical and chemical interactions
	Short-range ordered oxyhydroxides	Ferrihydrite, birnessite, boehmite	Surface coating, organo-mineral associations	Encrusting and cementing by physicochemical and chemical interactions
	Carbonates, sulfates, Si-oxides	Calcite, Dolomite, Gypsum,	Cementing agent	Embedding, encrusting, and cementing by physicochemical and chemical interactions
Organomineral associations	Oxyhydroxides-OM	FeH-OM	Precipitation nuclei, sorbent	Embedding and encrusting by physicochemical and chemical interactions
	Clay-OM	Illite-OM	Precipitation nuclei, sorbent	Embedding, and encrusting by physicochemical and chemical interactions

sion, these studies suggest that the hierarchic disintegration of microaggregates by sonication is a unique behavior of many soils rich in reactive oxide-type minerals and perhaps expandable clays.

3 Microaggregate forming materials

Microaggregates are built up from a wide variety of mineral, organic and biological soil components (which we describe below as microaggregate forming materials; see glossary), that may act as either the core or nucleus of a building unit, a gluing agent, or a cementing agent. The spatial dimensions of the individual microaggregate forming materials may span more than three (microorganism) or six orders of magnitude (minerals, see Fig. 2). The extremely broad size-range of the abiotic components is inherited from the parent rocks or results from the progress of pedogenesis. Consequently, any compound structure that is built by the spatial arrangement of a (large) number of these diverse individual aggregate forming materials will be characterized by a three-dimensional, (micro-)porous, chemically heterogeneous architecture (Fig. 1). In consequence, the interrogation of the inner architecture and composition of aggregates and the aggregate system in soils using solely size fractions will give limited information since a mixture of individual particles, mineral grains, organisms, and even complete microaggregates may be present within a particular size fraction. Future studies should therefore include procedures designed to explore the intact microaggregate. This may be possible through a combination of tomographic, spectroscopic and microscopic techniques (*Rennert* et al., 2012).

3.1 Minerals involved in microaggregate formation

Carbonates ($CaCO_3$), Fe- and Al-(hydr)oxides, and clay minerals are considered to be the most important minerals for microaggregate formation (*e.g.*, *Barral* et al., 1998; *Watts* et al., 2005; Tab. 1). Weathering of primary minerals leads to the formation of highly reactive secondary clay-sized minerals in soils that contain a variety of phyllosilicates associated with short-range ordered phases, including metal oxides and hydroxides as well as aluminosilicates (*Churchman*, 2010b; *Basile-Doelsch* et al., 2015). *Oades* and *Waters* (1991) called attention to the fact that it was not possible to distinguish in electron micrographs the steps of aggregation within aggregates < 20 μm. As clay minerals can be detected well with electron microscopy, they are often seen as the major and only relevant mineral phase. But this may be due to the fact that other relevant minerals are not observed with the analytical approach used, either because they are of nanometer size, not well crystallized, or both. *Pronk* et al. (2012) found in a long-term incubation experiment (18 months) of artificial soils composed of different mineral components, such as clay minerals, Fe oxides, and charcoal, that soil microaggregates were formed with either metal oxides or phyllosilicate clays serving as their nucleus. Yet so far, only a few studies have directly addressed the effect of the mineral composition on the formation, structure and turnover of microaggregates.
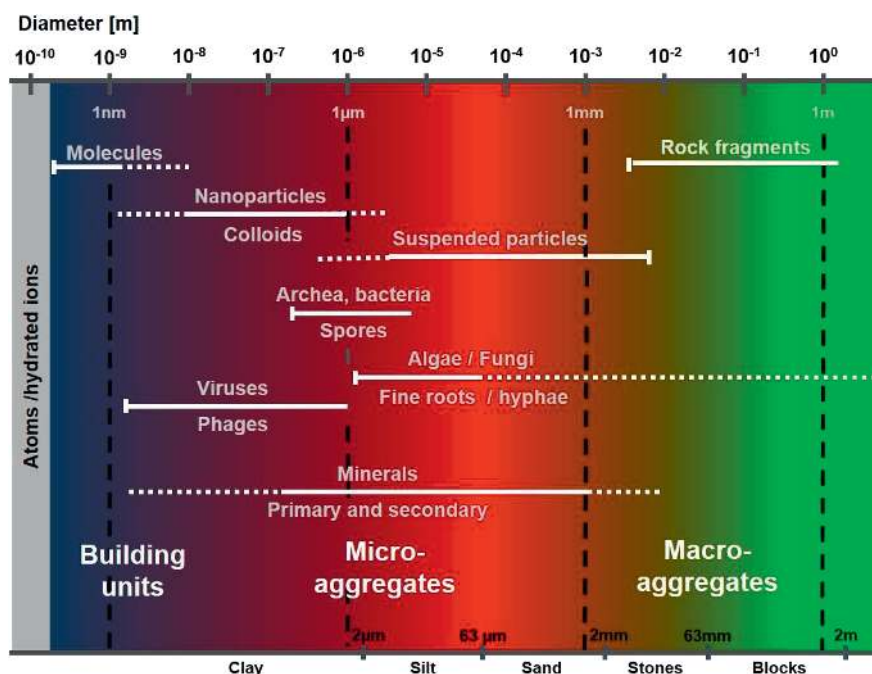
Figure 2: Size spectrum of soil components (modified from *Totsche* and *Kögel-Knabner*, 2004). The nanoparticulate, colloidal and larger particles are quartz, silicates, clay minerals, primary and secondary oxides/hydroxides of Si, Al, Fe and Mn, sulfates and carbonates. These inorganic phases span up to six orders of magnitude with the short-range ordered oxy-hydroxides such as ferrihydrite at the lower end, and quartz-grains at the upper end. Biotic components involved in the formation are unicellular microorganisms (bacteria, yeasts) and fungal hyphae. Plant and faunal debris (cell and tissue remnants) form the particulate organic matter pool and may act, like the minerals, as nuclei for the formation of building units. Humified organic matter, organic macromolecules of biotic provenience, *e.g.*, proteins, lipids, polysaccharides, as well as macromolecular mixtures like EPS and mucilage, act as gluing and agglutination agents. Pedogenic minerals, in particular the iron and manganese oxides, as well as the sulfates and carbonates, contribute to incrustation and cementation. In soils with high loads of clay minerals they form coatings and encrustations.

3.2 Type and composition of organic matter involved in microaggregate formation

Organic materials of different origin and composition have been proposed as being relevant to the association of minerals in microaggregates, as well as for sustaining the aggregate hierarchy (Tab. 1). At the scale of the microaggregate there is an enormous complexity of OC functionalities and the coexistence of various inorganic components in the organo-mineral interface, leading to the conclusion that no single binding mechanism can be accountable for the OM stored (*Lehmann* et al., 2008; *Solomon* et al., 2012). This is probably due to different OM structures being involved in microaggregate formation and stabilization, mostly of polysaccharide (*Six* et al., 2004), proteinaceous (*Kleber* et al., 2007) and lipid character (*Jandl* et al., 2004; *Liu* et al., 2013), which may form persistent organo-mineral associations.

Both organic debris (*e.g.*, *Golchin* et al., 1994; *Golchin* et al., 1996; *Jastrow*, 1996) and bacterial cells (*Chenu* and *Stotzky*, 2002) have been described as OM components that form a microaggregate core surrounded by phyllosilicates and metal oxides. By combining results on the overall composition of

soil OM using solid-state ^{13}C NMR spectroscopy with physical fractionation, *Golchin* et al. (1994) were able to differentiate between the particulate OM (POM) and clay-associated OM in microaggregates. They found that the plant residues that were isolated as occluded POM from microaggregates showed an increased degree of decomposition, indicated by a loss of O-alkyl carbon and enrichment in aliphatic carbon. This has been confirmed in subsequent studies (*John* et al., 2005; *Kölbl* et al., 2005).

Microorganisms contribute actively to the stability of microaggregates (*Cheshire*, 1985; *Lynch* and *Bragg*, 1985; *Haynes* and *Swift*, 1990). Living microorganisms can adhere to soil minerals by forming direct electrostatic bonds (*Huang* et al., 2005). The microbial cell walls involved in these bonds are frequently stable against biotic decomposition (*Chenu* and *Stotzky*, 2002), and many of them persist after the death of the bacterium (*Amelung* et al., 2008). These findings were supported by observations of high proportions of amino sugars, which are of microbial origin and which were also found to be enriched within microaggregates and fine-sized soil fractions (*Zhang* et al., 1999; *Rodionov* et al., 2001). Accordingly, *Miltner* et al. (2012) identified residues of microbial cell wall envelopes associated with microaggregates. In this regard, bacteria attached to clay particles or small microaggregates may actually serve both as a 'composite building unit' and as a nucleus for initial aggregation (see glossary).

According to *Oades* and *Waters* (1991), microaggregates < 20 μm contain little or no plant debris, but are stabilized mainly by microbial-derived materials. For the clay-associated OM in microaggregates *Golchin* et al. (1994) found a predominance of carbohydrate, aliphatic and carboxyl C, and a narrow C:N ratio. They concluded from their data in combination with results from labelling studies that this material is of microbial origin. Also *Guggenberger* et al. (1994), *Amelung* et al. (1999) and *Puget* et al. (1998) reported that microbial carbohydrates were enriched in microaggregates or fine soil fractions. Generally the OM in clay fractions isolated from a number of soils have been found to be dominated by alkyl C and/or O/N-alkyl C (*Baldock* et al., 1992; *Quideau* et al., 2000; *Chen* and *Chiu*, 2003; *Schöning* et al., 2005b). *Schöning* et al. (2005a) found an intimate association between O/N-alkyl C of soil OM and iron oxides occurring in clay fractions of A horizons in a ^{13}C NMR spectroscopic variable contact time experiment. These authors suggested that iron oxides and O/N-alkyl C are preferentially associated in soil

and that this interaction was likely to contribute to the stabilization of O/N-alkyl C. These results were in contrast to the common assumption that interactions occur mainly *via* ligand exchange of the carboxyl groups of acidic organic compounds (*Kaiser* et al., 1997; *Kleber* et al., 2007).

Amphiphilic proteinaceous compounds have also been hypothesized to be of major importance for the stabilization of OM at mineral surfaces (*Kleber* et al., 2007), as these would account for the narrow C:N ratio commonly observed in clay-associated OM. A preferential accumulation of N-rich materials was indeed found in investigations of organo-mineral association during the early stages in a natural soil chronosequence (*Dümig* et al., 2012), as well as in artificial soils developed from different mineral materials (*Pronk* et al., 2013). As the C:N ratio of fine-sized soil fractions is low (around 10–12), there must be a substantial contribution from N-containing materials, which should be reflected in the microaggregate OM composition.

Of particular importance for the formation and stabilization of microaggregates are the two gel-like, water-rich macromolecular organic mixtures, namely extracellular polymeric substances (EPS) and the mucilage produced by microorganisms and plants and some microorganisms, respectively. Mucilage is a mixture of predominantly polar glycoproteins and polysaccharides (*e.g.*, *Jones* and *Morre*, 1967), while EPS additionally harbor a significant amount of lipids and proteins, and a minor amount of nucleic acids (*Liu* et al., 2013). *Morel* et al. (1991) found a "… spectacular and immediate increase in soil aggregate stability…" of water-stable aggregates < 2000 μm in incubation experiments with mucilage. They argued that the freshly released mucilage rapidly adheres to soil particles and results in an effective protection of these aggregates against destruction by water.

Comparing microaggregate stability between rhizosphere soils and bulk soils, *Sparling* and *Cheshire* (1985) found less contribution of polysaccharides to microaggregate stability in the rhizosphere soil compared to bulk soil despite the much higher content of mucilage-polysaccharides in the rhizosphere soil. These authors speculate that this is due to "… their presence as comparatively massive plant remains and debris…" like sloughed cells, root and cell-wall debris. Such material should be expected to have "… a lesser binding action with the soil particles than the more degraded and chemically transformed components in the (bulk) soil." The reasons remain speculative, but point to the need to study the formation and stabilization processes of microaggregates in different soil microenvironments, *e.g.*, the rhizosphere, the drilosphere, and the detritusphere.

In sorption experiments with EPS on minerals, the proteinaceous fraction is commonly lost during the extraction procedure (*Flemming* and *Wingender*, 2010), which probably leads to an overestimation of the importance of polysaccharides in microaggregate formation. Related to that, the results of studies by *Omoike* et al. (2004) and *Omoike* and *Chorover* (2006) indicate EPS-derived proteinaceous, N-containing compounds to be major binding agents upon sorption to goethite. This accords with work by *McGill* and *Paul* (1976) who found

that N is mainly associated with sesquioxides rather than phyllosilicates.

A large number of studies have focused on the role of dissolved organic matter (DOM) in the formation of organo-mineral-associations and coatings on mineral surfaces by sorption or precipitation processes (*Kleber* et al., 2015, and references therein). DOM is an umbrella term for a rather poorly defined, but heterogeneous mixture of organic (macro-)molecules of diverse origin. Sources of DOM include: immobile organic matter from which it is derived by desorption and colloidal dispersion; plant residues from which it is released; or its formation *in situ* by microbes or root exudates. Of particular interest has been the formation of organo-mineral associations with the short-range ordered phases of Fe, Al, and Mn. It has been suggested that DOM rich in aromatic moieties and carboxyl groups is preferentially adsorbed onto Al and Fe (hydr)oxides *via* ligand exchange or co-precipitation (*Yost* et al., 1990; *Gu* et al., 1995; *Kaiser* et al., 1996; *Korshin* et al., 1997; *Kaiser* and *Zech*, 2000; *Kaiser*, 2003, *Eusterhues* et al., 2008; *Eusterhues* et al., 2011). These findings are in good agreement with studies that found positive correlations between Fe and Al phases and OM (*Hughes*, 1982; *Johnson* and *Todd*, 1983; *Adams* and *Kassim*, 1984; *Evans* and *Wilson*, 1985; *Skjemstad* et al., 1993; *Kaiser* and *Guggenberger*, 2000; *Kleber* et al., 2005) as well as negative correlations with OM turnover in a wide range of soils (*Veldkamp*, 1994; *Torn* et al., 1997; *Masiello* et al., 2004).

There is no consensus concerning whether the OM, sorbed or co-precipitated from solution in soils or horizons rich in Fe (hydr)oxides, is of plant or microbial origin. Nevertheless, the composition of DOM resembles that of clay-associated OM in mineral soils (*Kaiser* and *Guggenberger*, 2000), with a high degree of lignin side-chain alteration and a dominance of microbial hexoses in the carbohydrate spectrum (*Guggenberger* et al., 1994; *Kiem* and *Kögel-Knabner*, 2003; *Spielvogel* et al., 2008). Similarly, a large proportion of the mineral-associated soil OM in Fe oxide rich subsoil horizons has been found to be composed of low molecular weight molecules, most probably water soluble, with a high content of labile carbohydrates (*Rumpel* et al., 2010).

Organic matter in soils does not only contain plant debris and compounds of microbial origin, but also fairly stable C, usually assigned to black carbon (BC) (*Skjemstad* et al., 2004; *Roth* et al., 2012). BC is the residue from the incomplete combustion of hydrocarbons, comprising char and soot, for instance, with a continuum of different chemical properties that is mainly aromatic in nature (*Keiluweit* et al., 2010; *Kloss* et al., 2012; *Wolf* et al., 2013; *McBeath* et al., 2014; *Wiedemeier* e al., 2015). Charcoal, produced during anthropogenic and natural fires, varies widely in its chemical characteristics and is likely to be important for the formation of organo-mineral complexes. In addition, aged charcoal particles with oxidized, reactive surfaces (*Brodowski* et al., 2005; *Archanjo* et al., 2015) are thought to act as binding agents capable of stabilizing aggregates (*Brodowski* et al., 2006; *Nishimura* et al., 2008). Increased nutrient retention and positive effects on bacterial diversity have been reported for newly formed microaggregates after the addition of charcoal (*Ding* et al., 2013). It

is assumed that its high microporosity yields favorable environments for microorganisms and that the hydrophobicity of the charcoal increases sorption (*Ding* et al., 2013). In experiments with artificial soils, it has not been possible to demonstrate a correlation between charcoal and microaggregate formation (*Pronk* et al., 2012; *Vogel* et al., 2014). The enrichment of charcoal-carbon in (natural) microaggregates could thus also reflect the recalcitrance of BC rather than the direct involvement of BC residues as agents for microaggregate formation.

3.3 Role of (micro)organisms in the provision of microaggregate gluing agents

One of the first studies on the role of microorganisms in the provision of gluing agents was the work of *Martin* (1945). In this pioneering study he showed that fungi and bacteria brought about marked aggregation of silt and clay particles: "Up to 50 percent of the aggregation effect of the fungus was brought about by substances produced by the cell material, and the remainder was due to the binding influence of the fungus mycelium. The soil bacillus cell, on the other hand, produced 20% of the aggregating effect, and substances produced by the cells accounted for 80%". While fungi are predominantly involved in the formation of macroaggregates due to their hyphal structure, which physically enmeshes soil particles and microaggregates, bacteria are of particular relevance for the formation and stabilization of microaggregates (*Christensen*, 2001; *Six* et al., 2004; *Davinic* et al., 2012). Although there are many investigations into microbial gluing agents and their effect on soil aggregation, only a few specifically address their role for microaggregate formation. Microbial products and their interactions with soil particles, such as clay minerals, polyvalent metals, and other organic materials or organo-metal complexes, promote the crosslink between individual building units, particularly in microaggregates < 20 μm (*Christensen*, 2001). This is in agreement with the few observations that bacteria are predominantly detected in this size fraction (*Monrozier* et al., 1991; *Stemmer* et al., 1998; *Hemkemeyer* et al., 2014). Soil microorganisms use EPS for cell attachment to mineral surfaces due to the richness in functional groups, specifically carboxyl, amide, and phosphoryl groups (*Beveridge* et al., 1997; *Omoike* and *Chorover*, 2006). Yet, the adsorption of EPS to mineral surfaces fosters the aggregation of mineral particles (*Puget* et al., 1998; *Cheshire*, 1977; *Davinic* et al., 2012). Such mechanisms are considered to be of particular importance in the formation of composite building units and small microaggregates in mineral surface horizons having high microbial activity (*Cambardella* and *Elliott*, 1993). The addition of OM to soils stimulates microaggregate formation by enhancing microbial activity and hence the production of EPS, which aids binding of soil particles (*Chotte*, 2005; *Chenu* and *Cosentino*, 2011). As pointed out by *Golchin* et al. (1996) and *Kallenbach* et al. (2016), a great diversity of microbial compounds is produced by the microbial community also from low-molecular weight substrates such as occur in the rhizosphere. Glomalin, a glycoprotein released by arbuscular mycorrhizal fungi, has been considered to have a role as a gluing agent (*Rillig* and *Mummey*, 2006; *Chotte*, 2005) similar to EPS and mucilage.

However, the many possible binding and stabilization mechanisms of the biotic glueing agents, as well as their relevance to microaggregate formation, remain little understood.

4 Mechanisms of microaggregate formation

Several mechanisms for the formation of soil microaggregates have been proposed, with either mineral or organic (and sometimes even biotic) components assumed to form their core (Tab. 2). Pursuing earlier findings of *Schloesing* (1902), *Sideri* (1936), and *Emerson* (1959), *Edwards* and *Bremner* (1967) suggested that microaggregates form by interactions of polyvalent metal cations and organic ligands with mineral surfaces, either *via* adsorptive interactions or co-precipitation (*Tombácz* et al., 2004; *Eusterhues* et al., 2008; *Eusterhues* et al., 2011). The nature and binding strength would then depend on the type and the surface area of the mineral particles (*Kaiser* and *Guggenberger*, 2003; *Guggenberger* and *Kaiser*, 2003; *Sollins* et al., 2009). Recently, it has been shown that oxide surfaces in particular contribute to this process (*Kiem* and *Kögel-Knabner*, 2002; *Kleber* et al., 2004; *Eusterhues* et al., 2005; *Kaiser* and *Guggenberger*, 2007; *Mikutta* et al., 2007). Alternatively, microaggregates are considered to form when organic debris is surrounded by fine mineral particles (*Tisdall* and *Oades*, 1982; *Six* et al., 1998; *Cambardella* and *Elliott*, 1993; *Golchin* et al., 1994; *Jastrow*, 1996). The encrustation of clay particles around OM can lead to the formation of very stable clay-OM microstructures (< 20 μm) (*Oades*, 1993; *Six* and *Jastrow*, 2002). Composite building units and microaggregates smaller than 20 μm may be stabilized by materials of microbial or faunal origin, including polysaccharides, hyphal fragments, bacterial cells or cell microcolonies, all of which have been found to be encrusted with clay particles (*Oades* and *Waters*, 1991). Recent findings point to the binding of OM *via* both sorption and entrapment of small organic particles in silt-sized microaggregates < 50 m (*Virto* et al., 2008). Neither process is exclusive and they might occur simultaneously.

Asano and *Wagai* (2014) have suggested that in allophanic Andisols the micron to submicron-sized aggregates are built from 'presumed building blocks' composed of organo-mineral-metal mixtures. The authors coined the term 'presumed building blocks' when they developed their conceptual model for an aggregate hierarchy in Andisols, simply because they were unable to isolate them. Based on their findings, *Asano* and *Wagai* (2014) deduced that nano-sized composites are present that are rich in N-rich organic matter. These composites are resistant to maximum dispersion by sonication, and tend to be more dispersed and enriched upon stronger dispersion levels. The findings further suggest that these presumed building units acted as effective (probably persistent) binding agents.

Formation of the composite building units and small microaggregates < 20 μm has also been attributed to other abiotic mechanisms such as the precipitation of Fe- and Al-oxides or hydroxides (*Duiker* et al., 2003). Hydrolytic precipitation of, *e.g.*, Fe^{3+} may cause microaggregation by co-precipitation of OM and flocculation of clay (*Tombácz* et al., 2004; *Eusterhues* et al., 2008). In principle, both OM–mineral as well as

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Table 2: Processes involved in the formation, stabilization, destruction, and turnover of microaggregates.

Category	Process	Actors and agents (examples)	(Potential) role for microaggregates	Importance for soil groups
Biological processes	Inhabitation, colonization	Bacteria, archea, fungi	Surface alteration and coating, production and provision of gluing agents (EPS, mucilage), complexation and association, wettability	All soils
	Agglutination	Bacteria, archea, fungi, fine roots	EPS- and mucilage production, stabilization through gluing agent, wettability	All soils
	Biodegradation and consumption	Bacteria, archea, fungi OM-feeding fauna	Reductive destabilization and destruction	All soils
Biophysical processes	Bioturbation	Soil dwelling fauna, earthworms	Mechanical displacement and stress (tensile and compressive), redistribution	All soils
	Bioadmixing	Soil dwelling fauna Earthworms, Termites	Mechanical mixing and stress (tensile and compressive), aggregation in earthworm cast, formation and stabilization	All soils
	Pore-dilatation	Roots, soil dwelling fauna, earthworms	Mechanical displacement and mechanical stress (tensile and compressive), pore space and geometry alteration and expansion	All soils
	Bio-transport and -translocation (including 'digging')	Soil dwelling fauna, earthworms, termites	Redistribution, displacement, import / export of MA and cross soil compartment transfer	All soils
Physical processes	Freezing-Thawing	Water (soil solution)	Mechanical displacement, redistribution, mechanical (tensile and compressive) stress, geometrical reorientation, formation and stabilization	Cryosols, temperate soils
	Shrinking- swelling	Swelling clay minerals, Solution composition, ionic strength and pH	Mechanical displacement, redistribution, mechanical stress (compression), geometrical reorientation, formation and stabilization	Soils with expanding clay minerals
	Capillary forces	Water (soil solution).	Capillary cohesion, water menisci, stabilization (partial water saturation), destabilization (Slaking)	All soils
	Advection	Water (soil solution), permeability and pore space properties	Transport, relocation of dissolved and colloidal materials, relocation of suspended materials, import/export and cross soil compartment transfer	All soils
	Diffusion	Water (Soil solution), permeability and pore space properties	Relocation of dissolved materials, intra-microaggregate substance transfer	All soils
	Tillage, harvest	Agricultural machinery	Possible destruction and relocation	Agricultural soils
	Inundation including ponding and flooding	Water (soil solution, precipitation or flood water)	Slaking, disintegration, reductive destabilization and destruction	Upland and floodplain soils

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Table 2. Continued.

Category	Process	Actors and agents (examples)	(Potential) role for microaggregates	Importance for soil groups
Chemical processes	Adsorption	Solution and gas Phase components	Surface coating, formation of OM-associations, formation and stabilization	All soils
	(Co-)precipitation	Solution composition, ionic strength and pH	Formation of OM-associations, cementation, formation of nuclei and building units	Acid subsoils, acid to neutral topsoils
	Oxidation	Aeration state and duration	Oxidation and formation of building units, encrustation, exterior surfaces	Aerated soils
	Reduction	Water-saturation state and duration	Reductive destabilization and destruction of building units, internal surface, micro-pores	Hydromorphic soils, floodplain soil
	Complexation including ligand exchange	Soil solution, organic and inorganic ions, ionic strength and pH	Stability and surface alteration	All soils

mineral–mineral interactions initiate the buildup of composite building units and, thus, the processes of microaggregate formation (Fig. 3). Yet, in the majority of research papers, authors did not discuss their findings in the context of microaggregate formation and stability. Rather, they focused on the OM-mineral interactions, the formation of the organo-mineral-associations as composite building units of the microaggregates, the stabilization of OM, or protection against microbial attack. *Asano* and *Wagai* (2015) revealed that the sonication-resistant, nano-sized organo-mineral composites acted as a 'persistent binding agent' for microaggregate formation, at least in andic soils. They further showed that these composites were enriched in microbially-processed OM. *Lehmann* et al. (2007) found that different organic carbon species are not only adsorbed to mineral surfaces, but are entrapped within microaggregates, so that they are in close contact with mineral surfaces and physically protected against enzyme attack. The concept suggested by *Lehmann* et al. (2007) starts with the formation of organic coatings on clay minerals, followed by the physical occlusion of the organic coating by a second mineral. They propose that microaggregation as a result of organo-mineral interactions helps to protect OM coatings, as well as any intra-aggregate organic debris, against biological degradation through physical inclusion. However, the commonly observed patchy distribution of organic material on mineral surfaces (*Mayer* and *Xing*, 2001; *Chenu* and *Plante*, 2006; *Hatton* et al., 2012; *Vogel* et al., 2014) is in contrast to Lehmann's concept, as organic coatings are not frequently observed in soils. *Mödl* et al. (2007) and *Heister* et al. (2012) observed that even a patchy coating of, *e.g.*, goethite with selected organic materials may be sufficient to form silt-sized microaggregate structures. *Tisdall* (1996), based on electron microscopy work by *Foster* (1983) and *Dorioz* et al. (1993), suggests that the formation of microaggregates is initialized by the alignment of clay particles around bacterial cells. After cell death and lysis, the microaggregate stabilized by microbial materials, especially polysaccharides, remains stable. *Tisdall* (1996) points out that root exudates have a similar effect. In addition, she maintains that the pressure exerted by roots or bacteria when growing in the soil leads to a reorientation of the mineral material, which also promotes aggregation in clay microstructures. *Chenu* and *Plante* (2006) report that many of the so called 'clay particles' are in fact nanometer- to micrometer-sized microaggregates in which OM is encrusted with minerals. They concluded that these very small microaggregates are major sites of OM stabilization, both by adsorption and by entrapment of OM.

Adsorption is relevant for the cohesion of microaggregates through interactions of mineral surfaces and OM, but a large proportion of OM is entrapped in stacks of clay layers (*Oades*, 1984; *Chenu* et al., 2009). *Barré* et al. (2014) discuss the problem concerning the association of phyllosilicates with iron oxides, which makes it difficult to differentiate between the roles each component might have, especially in Oxisols dominated by kaolinite-oxide microaggregates. Generally, the OC content is lower in soils dominated by kaolinite compared to soils with 2:1 minerals and clay-sized aggregates that show OC entrapment contain preferentially 2:1 minerals (*Chenu* et al., 2009). These results are further corroborated
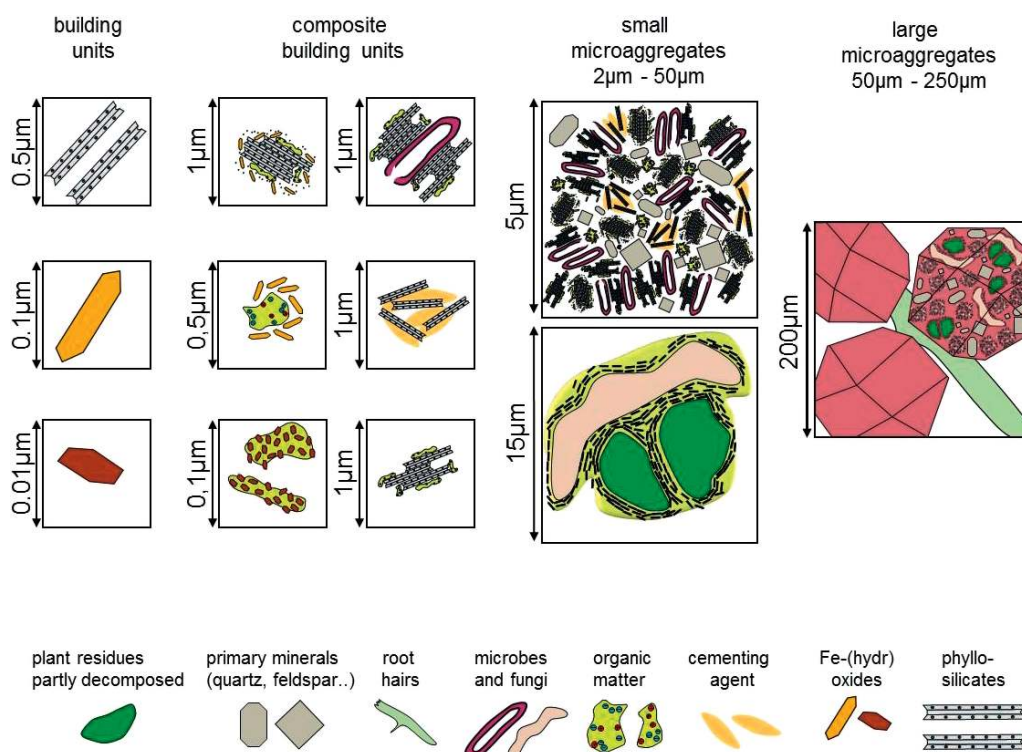
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Figure 3: Hierarchy of building units and microaggregates in soil. Components of microaggregates are primary minerals (quartz, feldspars, *etc*.), microbes, plant and microbial debris and the fine-sized mineral building units (exemplified here as phyllosilicate, goethite, and ferrihydrite). The composite building units are commonly found examples, but do not reflect the full range. The various components that are part of microaggregates span more than five orders of magnitude and are aggregated in a hierarchical manner. The formation is dependent on the presence of water and is affected by changing milieu conditions (*e.g.*, change in pH or redox). Note that water, solutes, and the organic molecules (proteins, polysaccharide, etc.) have not been included due to their very small size. Presumed and evidenced processes of formation and stabilization are given in Tab. 2. Inspired and drawn to scale from *Tisdall* and *Oades* (1982) and *Chenu* et al. (1998).

by studies showing that silt-sized microaggregates are enriched in 2:1 minerals (*Virto* et al., 2008; *Fernández-Ugalde* et al., 2013).

In volcanic ash soils, short-range ordered allophane (*Parfitt*, 1990a; *Parfitt*, 1990b) and long-range ordered tubular imogolite are the major clay-sized minerals available for interactions with OM. Both minerals have a large specific surface area (700–1500 m^2 g^{-1}) and positive as well as negative charges (*Parfitt*, 1990a; *Parfitt*, 1990b) that support strong sorption of oxianions and OM. Up to 63% of the OC in allophanic soils were found in the clay fraction (*Parfitt* and *Henmi*, 1982; *Churchman* and *Tate*, 1986; *Asano* and *Wagai*, 2014) and thus associated with the building units of microaggregates. Most sorption studies, however, have used humic acids as a surrogate for OM. Ligand exchange has been suggested to be the major mechanism of humic acid adsorption to allophane surfaces, thereby increasing the negative charge (*Parfitt* et al., 1977; *Perrott*, 1978; *Yuan* et al., 2000).

In acidic subsoils, organic matter-associations with short-range ordered ferrihydrite seem to be especially important (*Kaiser* and *Guggenberger*, 2000; *Kaiser* et al., 2002; *Eusterhues* et al., 2003; *Wiseman* and *Püttmann*, 2005), but

there is also evidence for its having a major role in acid to neutral topsoils (*Kiem* and *Kögel-Knabner*, 2002; *Hiemstra* et al., 2010b). However, this is based mainly on indirect evidence, as the natural oxides are nanometer-sized (*Eusterhues* et al., 2005; *Kiem* and *Kögel-Knabner*, 2002; *Hiemstra* et al., 2010a) and, therefore, can hardly be observed by electron microscopy and, more importantly, cannot be analyzed for their elemental composition by means of energy dispersive x-ray analysis (SEM-EDX). The interaction between OM with ferrihydrite may also occur *via* co-precipitation. *Schwertmann* et al. (2005) demonstrated in a ^{57}Fe-Mössbauer spectroscopy study that up to 10% of the OC forms C-O-Fe bonds with the organic material. ^{13}C NMR spectroscopy used in that study also suggested that the main interaction between the iron oxide and the OM occurred *via* the O-alkyl C. *Eusterhues* et al. (2008) found a strong interference of mineral-associated OM with crystal growth leading to smaller ferrihydrite crystals, increased lattice spacings, and more distorted Fe(O,OH)$_6$ octahedra. Whereas adsorption results in a discrete, patchy accumulation of OM at mineral surfaces, co-precipitation (depending on the metal:carbon ratio) leads to a more homogeneous composition with the inorganic phase being more effectively embedded in an organic matrix (*Mikutta* et al., 2009; *Mikutta* et al., 2014; *Eusterhues* et al., 2014).

One may note that short-range ordered phases of aluminium and even manganese may be equally important in the formation of microaggregates or composite building units. The lack of information on the role of such phases is simply due to the circumstance that they are not in the research focus at present, but may provide a research demand in the near future.

4.1 An updated status of organo-mineral associations in the system of aggregates

The sharp differentiation between organo-mineral associations and microaggregates, like those presented by, for example, *Christensen* (2001), is no longer compatible with recent findings as pointed out by, among others, *Chenu* and *Plante* (2006) and *Asano* and *Wagai* (2014). All those mechanisms and processes so far discussed, and that have been suggested as having a role in the formation and stabilization of organo-mineral associations, thus essentially help us to explain and understand the formation and properties of microaggregates. We hypothesize that the processes and interactions that stabilize microaggregates differ from those that stabilize macroaggregates. The fact that macroaggregates are less stable and tend to disintegrate more easily than microaggregates points to different processes and mechanisms being involved than those operating at the scale of macroaggregates and their stabilization.

4.2 Role of surface properties on initial aggregation of soil microaggregates

For the aggregation of mineral particles or OM-coated mineral particles, the composition of the exterior surface regions of organic-coated particles is more decisive than the bulk composition of the reaction partners. Because the quantity, composition, and properties of aggregate building units vary with pedogenesis, they are likely to promote differences in the formation mechanisms of microaggregates.

Clay minerals have negative charges on their basal surfaces due to isomorphic substitution in tetrahedral or octahedral layers, but variable charges at their edges. These edges are probably available for forming quite strong interactions with organic moieties (*Haberhauer* et al., 2001). Phyllosilicate minerals in soils are highly variable in composition, layer structure, particle size, surface area, and charge. Their common association with other, often poorly crystallized but highly reactive minerals can be explained by their formation in the highly heterogeneous and dynamic soil environment (*Churchman*, 2010b). Oxide minerals carry variable charge and their charge characteristics, as well as that of their reaction partners, are controlled by the environmental conditions, with the pH being the main factor. Soil oxides exhibit high points of zero charge, which in turn enables sorption of negatively charged OM or reaction with permanently negatively charged clay minerals under most field conditions with a pH lower than that of zero charge (*Kleber* et al., 2004; *Eusterhues* et al., 2005; *Kaiser* and *Guggenberger*, 2007). Negatively charged OM can also be bound directly to clay minerals *via* bridges with multivalent cations (*von Lützow* et al., 2006; *Kleber* et al., 2015).

Nearly all mineral particles in soil have a rough surface, with steps, kinks, holes and nanopores at weathered surfaces (*Basile-Doelsch* et al., 2015). This becomes specifically evident in Andosols and other allophane-rich soils. The highly porous allophane nanoaggregates and microaggregates allow high amounts of OM to be adsorbed. This OM is effectively protected within a 'nanolabyrinthic', *i.e.*, a highly tortuous network of pores in the range of 100–500 nm and even smaller pores < 100 nm (*Filimonova* et al., 2011; *Huang* et al., 2016). *Filimonova* et al. (2016) suggested a coupled adsorption mechanism of OM onto allophane that requires both the narrow pores and the surface OH-groups and Lewis acid centers (coordinately unsaturated Al^{3+} cations) of nanoparticulate Fe oxyhydroxides, mostly ferrihydrite and Fe-substituted allophane. Such mechanisms of entrapment of OM in micropores have also been described for non-allophanic soils. *Mayer* and *Xing* (2001), *Kaiser* and *Guggenberger* (2003), and *Chenu* and *Plante* (2006) concluded that most OM was stabilized in soils by close associations with clays in very small microaggregates, either through adsorption or by entrapment. In several studies, OM was found entrapped within pores rather than adsorbed as coatings by minerals (*Wan* et al., 2007; *McCarthy* et al., 2008). The elevated surface structure at the opening of the micropores allows for a more stable positioning of organisms; within the lumen of the micropores organic residues appear to be physically protected as organisms and their enzymes cannot reach into these spaces (*Kaiser* and *Guggenberger*, 2003; *Nunan* et al., 2003). *Lugato* et al. (2009) observed spatial dependencies between labile OC and micropores, thus, pointing towards a special preservation area in micro-aggregated bulk soil samples. *Jiang* et al. (2014) found an increase of the interface roughness for soil colloids due to the contributions of metal oxide nanoparticles.

Earlier studies often attributed the capacity for OM storage in soil aggregates to either the amount of iron oxide minerals or phyllosilicate clay minerals present in soils. However, recent results suggest that fresh OM amendments are specifically enriched at the rough surfaces of minerals (*Vogel* et al., 2014). By using NanoSIMS these authors have shown that the attachment of OM to mineral surfaces occurs presumably in patchy structures on clay minerals, whereas there is only little sorption of homogeneously distributed OM onto Fe oxides. Further, by combining NanoSIMS and isotope tracing, newly introduced, labeled and pre-existing OM can be distinguished and the location of the new OM relative to already present organo-mineral clusters can be ascertained. Results from these studies provide evidence that only a limited proportion of the clay-sized surfaces may contribute to the interaction with OM and thus help us to understand the confounded results regarding the contribution different mineral and organic components make to the formation of microaggregate structures in soils. Moreover, data from this study have shown that the surface topography seems to be important for OM stabilization when fresh OM is added to the soil.

Variable-charge minerals tend to have a higher affinity for carboxyl-rich aromatic substances than for polysaccharide- or protein-type OM (*e.g., Kaiser* et al., 1996; *Chorover* and *Amistadi*, 2001; *Kaiser*, 2003). Individual structures, such as polygalacturonic acids or tannins, however, were found to be

much less efficient in coating goethite, for instance, than complex mixtures in DOM, and only the latter have been able to aggregate the goethite minerals (*Mödl* et al., 2007). On the other hand, microbial or plant-derived polysaccharides and proteins, as present in EPS and mucilage, may also become fractionated upon sorption to minerals with respect to their organic P and N components, thus creating variable surface compositions of the mineral-organic associations formed (*Mikutta* et al., 2011). The multitude of aggregate forming materials and the interaction with organic substances may lead to a submicron-scale patchy distribution of OM on soil microaggregates as observed, *e.g.*, by *Heister* et al. (2012) and, in addition, a high complexity of OM functionalities (*Solomon* et al., 2012).

4.3 Microaggregate formation by physical processes

Microaggregate formation is further aided by hydration–dehydration reactions (*Denef* et al., 2002), which allow the individual reaction partners to approach each other physically. Wetting–drying cycles seem to be of particular importance, because smaller soil particles are moved by capillary forces, *i.e.*, by the action of water menisci. With increasing numbers of these wetting–drying cycles, the smaller particles become re-oriented in an energetically more stable arrangement (*Horn* and *Dexter*, 1989), resulting in a particular spatial organization of the solid phase and pore space. Water menisci forces can also lead to shrinkage and hence to the rearrangement of particles. Although microaggregates are mostly considered to be very stable, rigid units, not usually exhibiting shrinkage, *Reatto* et al. (2009) found for a Ferralsol that microaggregates, that it did exhibit shrinkage behavior which decreased with the age of the soil. This suggests that the hydraulic stress history is an important factor in microaggregate stability and structural dynamics and may directly link to soil water retention and hysteresis. However, the issue of the shrinking–swelling properties of microaggregates remains a debatable point as direct measurement techniques are still lacking. The same is true for the influence of mechanical stresses, for example, those related to root penetration of micro-scale structures. In this case, imaging based techniques such as digital image correlation (*Peth*, 2010a; *Peth* et al., 2010b; *Keyes* et al., 2016) are likely to provide a better insight into the micro-mechanical processes involved in the formation of microaggregates in future studies.

Apart from the nucleation and growth of a solid phase from an oversaturated solution, microaggregate formation out of the building units requires transport prior the interaction. Surprisingly, there is virtually nothing available in the literature that focuses on the role of translocation and transport, other than water menisci, for the formation of microaggregates. The obvious fact that diverse aggregate forming materials of different provenance and origin can be found in one single soil microaggregate implies that these materials must have approached and contacted each other by translocation processes, *e.g.*, diffusion or advection when suspended within fluids, mechanical displacement by roots, or by being linked to and mediated by biota (*e.g.*, biotransport, bioturbation). In Ferralsols, for example, termites have been suggested as

being actors involved in the formation of microaggregates < 300 μm, while earthworms have also been thought to be involved in the formation of macroaggregates (*Balbino* et al., 2002). Diffusion is an ubiquitous and omniactive translocation process, and is, perhaps, the most important for dissolved and smaller colloidal species in the liquid phase and for the processes of adsorption, complexation, and co-precipitation. The larger the aggregate forming materials and the building units are, the greater the energy required to move them in space. Thus, larger energies and stronger forces become more and more important as the size of microaggregates increases. But these mechanical and transport aspects of microaggregate formation and stabilization have to date been largely ignored and thus remain unexplored.

5 Stability and turnover of microaggregates

Six et al. (2004) summarized the five major factors influencing soil aggregate and OM dynamics that have been identified since the 1950s. They are: soil fauna, microorganisms, roots, inorganics, and physical processes. The stability and turnover of microaggregates seems to be dependent on changing environmental conditions, *e.g.*, in moisture, pH, redox-potential, ionic strength, and mechanical load. Thus, physicochemical and chemical interactions like electrostatic and even covalent bonds rather than mechanical interactions seem to be important for the formation of microaggregates. However, studies on microaggregate stability and the controlling factors are scarce. If one follows the aggregate hierarchy concept (*Oades* and *Waters*, 1991), which implies that microaggregates are formed within macroaggregates, any process that destroys macroaggregates and liberates microaggregates may also have consequences for the stability of the microaggregates themselves (*Fultz* et al., 2013). For well-aggregated soils, *Baumgartl* and *Horn* (1991) found higher shear resistance, measured by a direct aggregate shearing test, which highlighted the importance of the spatial arrangement of the solid phase on aggregate stability. A useful parameter characterizing aggregate stability is tensile strength, defined as the force per unit area that is required to break an aggregate under tensile stress along preexisting planes of weakness which may be microcracks or pores (*Hallett* et al., 1995; *Blanco-Moure* et al., 2012). A failure under tensile stress may occur naturally in soils, for instance, upon drying where aggregates break down into smaller aggregate subunits (*Amézketa*, 1999). Most studies on the tensile strengths of aggregates have focused on macroaggregates, while, to the best of our knowledge, no data are available on the tensile strengths of microaggregates. Such data would be important in assessing the mechanical (shear forces) and hydraulic (pulling forces of water menisci) effects on microaggregate turnover or breakdown.

Data on water stability of aggregates show that with decreasing diameter of the aggregates the stability increases and that microaggregates are more stable than macroaggregates (*Golchin* et al., 1994; *Tisdall*, 1996). According to *Wittmuss* and *Mazurak* (1958), microaggregates < 74 μm were specifically stable compared to larger aggregates. *Leifeld* and *Kögel-Knabner* (2003) found that small particles specifically contribute to the formation of microaggregates and attributed this to the stronger physicochemical bonding.

Once again, when we focus on the subunits and building units of microaggregates, the findings on the stability and turnover of organo-mineral associations must be used as a proxy for microaggregates.

The microbial decomposition of aggregate-associated OM might lead to aggregate disintegration and thus initiate aggregate turnover (*Six* et al., 2000a). *Al-Kaisi* et al. (2014) found that aggregate stability and moisture content are highly correlated with OC content, and the decay rate of both, macro- and microaggregates is highly influenced by the intensity of tillage. Also, the removal of Fe oxides (and OM) upon microbial Fe^{3+} reduction and coupled OM desorption (due to Fe oxide dissolution and pH increase) leads to aggregate instability and, thus, initiates turnover. In a short-term (14-day) laboratory inundation experiment with soil materials from upland soils, *De-Campos* et al. (2009) found decreased aggregate stability with decreasing redox-potential. This correlated with an increase of redox-sensitive elements (Mn and Fe), alkaline metals (Ca, Mg, and K), and DOC in the solution. Cultivated soils were more affected by decreasing aggregate stability than uncultivated soils. *Lehtinen* et al. (2014) investigated microaggregate stability in different soil orders. They found that stable microaggregates in the range of 63 μm to 250 μm were positively correlated with oxalate-extractable Fe and Al, as well as with soil OM content. High inputs of easily degradable OM have been shown to result in a rapid consumption of readily available electron acceptors like dissolved oxygen and nitrate, thus, favoring again the utilization of Fe(III) and Mn(IV) oxides. Such redox processes can therefore destabilize the structure of microaggregates and release smaller colloids, nanoparticles, organic matter and redox sensitive elements from eventually short-range ordered minerals that used to serve as the cementing agents (*e.g., Thompson* et al., 2006; *Jaesche* et al., 2006; *Buettner* et al., 2014; *Fritzsche* et al., 2015). In line with these findings, *Jiang* et al. (2015) found that organically bound P was released from water-dispersible colloids after reductive removal of Fe, resulting in size shifts of water-dispersible nanoparticles.

Alternating redox, moisture, and pH conditions, as found, *e.g.*, in floodplain soils, seem to have only minor effects on the release of redox sensitive elements, as *Fritzsche* et al. (2015) reported for a field study. This points to a stronger resilience of floodplain soils against temporary variations in these conditions than soils that are rarely water-saturated as for example in the soil of the above-mentioned study of *De-Campos* et al. (2009). Yet, *Henderson* et al. (2012), who studied the release of phosphorous from agricultural soils under forced anoxic conditions in a lab experiment, found an increased release of colloid-bound and nanoparticulate-bound phosphorous upon anoxic incubation. They attributed that observation to the reductive dissolution of the iron-oxides cementing the nanoparticulate and colloidally bound phosphorous within the microaggregates. This release was even more pronounced for seasonally saturated soils than for well-drained soils. These studies suggest that changes of pH or redox conditions beyond a certain threshold, and that make the system tip to instability, are more important for the destabilization of micro-aggregates than just the alternating conditions itself.

Increased OM desorption and colloid mobilization has also been found during alteration to more alkaline conditions (*Thompson* et al., 2006), a process which is also likely to impact the stability of microaggregates. Likewise, charge reversal and charge repulsion effects that result from sorption of solutes to minerals may cause destabilization of micro-aggregates (*Ilg* et al., 2008).

A particular process that may affect microaggregate stability is the heating of soil during vegetation fires. Such heating is usually confined to the top few centimeters of the mineral soils because of the low thermal conductivity of both the mineral fraction and the air in the pore space. As reviewed by *Mataix-Solera* et al. (2011), low severity fires do not produce changes in aggregate stability, and the increase reported in some cases is attributed to increased water repellency (*Goebel* et al., 2011). The effects of high severity fires vary from disaggregation as a consequence of the OM loss, to strong aggregation, if a recrystallization of minerals such as Fe- and Al-oxyhydroxides occurs after exposure to high temperatures. *Thomaz* and *Fachin* (2014) report a threshold at 550°C in a laboratory study, where a sharp change in aggregate stability and diameter occurred. At temperatures between 250°C and 550°C, they observed OM depletion associated with a decrease in aggregate stability. A further temperature rise to 650°C enhanced aggregate stability, despite a loss of soil carbon, attributed to a thermal fusion of minerals. *Albalasmeh* et al. (2013) suggested that aggregates are destroyed even under low fire intensity as a result of mechanical stresses induced by rapidly escaping steam from soil pores undergoing rapid heating. Recent results from *Mastrolonardo* et al. (2015) suggest that in soils experiencing a fire, aggregates are partly broken up, promoting the release of occluded OM. From these results it seems that vegetation fires, if reaching the mineral soil, can have a strong impact on soil aggregate stability, modulated by temperature and exposure time. At present it is not clear if there is a fire-induced effect on soil microaggregates as specific information about fire effects on microaggregates could not be found in the literature. Nor are there any studies on the recovery of soil aggregation after fire exposure. However, it can be hypothesized that recovery of aggregation depends on OM input driven by re-vegetation and input of charcoal (see above).

Accounts of methods that directly measure the turnover of aggregates are rare. An interesting approach has been developed by *De Gryze* et al. (2006), which relies on the use of tracer compounds foreign to soils, like rare earth oxides. With the help of particulate tracers in microaggregate sizes, macroaggregate turnover can be quantified (*Plante* et al., 1999). As summarized by *Chenu* and *Cosentino* (2011), these studies have shown there to be broad and overlapping ranges of turnover times of between 4 and 95 days (*Plante* et al., 2002) and between 9 and 30 days (*De Gryze* et al., 2006) for macroaggregates, while in the latter study microaggregates turned over more slowly, though still within a range of 17 to 88 days. These data are obviously not consistent with the much longer turnover rates of the OM stored in different aggregate size classes, in which turnover times of up to 300 years were reported for OM stored in microaggregates (see below). Generally, only a few studies on microaggregate turnover exist

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and these need to be extended to different soils and to *in situ* conditions (*Chenu* and *Cosentino*, 2011).

Most studies into microaggregate stabilization generally focus on the role of microaggregates and micro-aggregation for the stabilization and sequestration of soil OM or the release of DOM and carbon dioxide. In a similar manner, the cementing role of carbonates has received only limited attention, possibly due to difficulties in analytically distinguishing it from OC when only very small sample amounts are available. We are not aware of any study that specifically links potential inorganic disaggregation and aggregation processes to the turnover of soil microaggregates. Thus, a fundamental understanding of the processes and factors that control the turnover, resistance and resilience of microaggregates and the link to the properties is still lacking.

It is also worth noting that no studies have investigated temporal changes of microaggregates together with their properties, like pore volumes and connectivity, as well as elemental patterns at outer surfaces or within the interior. This includes addressing the question whether new microaggregates form from decaying microaggregates or whether they always build-up by interactions among primary constituents. This knowledge is indispensable for a mechanistic modeling of the underlying processes, which has to overcome the current parameter fitting approaches of merely descriptive linear turnover rates (*Malamoud* et al., 2009; *Stamati* et al., 2013).

6 Modeling microaggregate formation and turnover

In their review, *Six* et al. (2004) point out that a quantification of the dynamic interrelation between the major influencing factors involved in micro-aggregate formation—as stated above—is clearly necessary. In their perspective, this lack of quantitative studies may be due to the plethora of possible interactions, the different scales on which the mechanisms operate, and the heterogeneity of the porous system. As already outlined above, notable research has been done on the links of soil OM dynamics with the stability and structure of soil microaggregates. Although strong links have been

shown to exist, a quantitative understanding—in the form of a mathematical model—of the interplay and the identification of the key factors is still lacking. In line with that, only a few approaches have modeled OM dynamics and the formation of soil aggregates in a deterministic, mathematical way. Most of them have been aimed at studying carbon balances at the field scale or have even been done in connection with earth system models, but have not considered detailed small-scale processes (*Campbell* and *Paustian*, 2015). For instance, several works (*e.g.*, *Kuka* et al., 2007; *Malamoud* et al., 2009; *Segoli* et al., 2013; *Stamati* et al., 2013) present multipool soil carbon model concepts to quantify the carbon mass content of the various pools (see Fig. 4 for an example of such a multipool concept and Fig. 5 for a simulation of the temporal evolution of the corresponding masses after fresh matter input, from *Segoli* et al., 2013). The temporal evolution of the pools is mostly described by systems of ordinary differential equations including first order kinetics. All related empirical parameters are gained by parameter fitting for the purpose of performing numerical simulations on specific sites. This limits the explanatory potential of such approaches for other sites and conditions. *Malamoud* et al. (2009) present the mechanistic approach Struc-C, which is based on the Rothamsted Carbon model RothC (*Coleman* and *Jenkinson*, 1996): the formation of aggregates is related to biology *via* the input of fresh OM, to chemistry *via* the decomposition of fresh OM, and to physics *via* the complexation of clay with soil OC. Likewise, in the soil carbon, aggregation, and structure turnover model CAST of *Stamati* et al. (2013), three size classes of aggregates are considered as containing different components (pools) including, *e.g.*, microbial mass, which results in a more complex system of ordinary differential equations. In both approaches the formation of aggregates is related to physical properties in terms of porosity using simple relations based on spherical packing. *Segoli* et al. (2013) couple the rate of formation and breakdown of macro- and microaggregates with the dynamics of OM in these aggregate fractions. Thus, the measurability of the turnover rates is emphasized. A modeling approach to investigate soil structural dynamics based on soil mechanics and rheological properties is presented in *Or* and *Ghezzehei* (2002). They consider the re-joining of aggre-
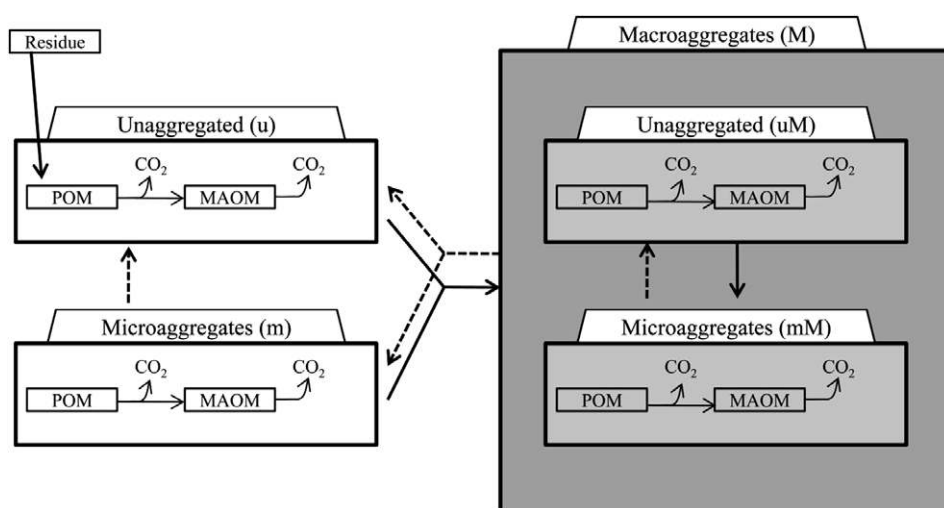

Figure 4: Conceptual multipool model of soil aggregate dynamics coupled with soil organic matter dynamics. POM: particulate organic matter, MAOM: mineral associated organic matter (Reprinted from Ecological Modelling, Vol. 263, M. Segoli, S. De Gryze, F. Dou, J. Lee, W. M. Post, K. Denef, J. Six, AggModel: A soil organic matter model with measurable pools for use in incubation studies, 1–9, Copyright (2013), with permission from Elsevier.).
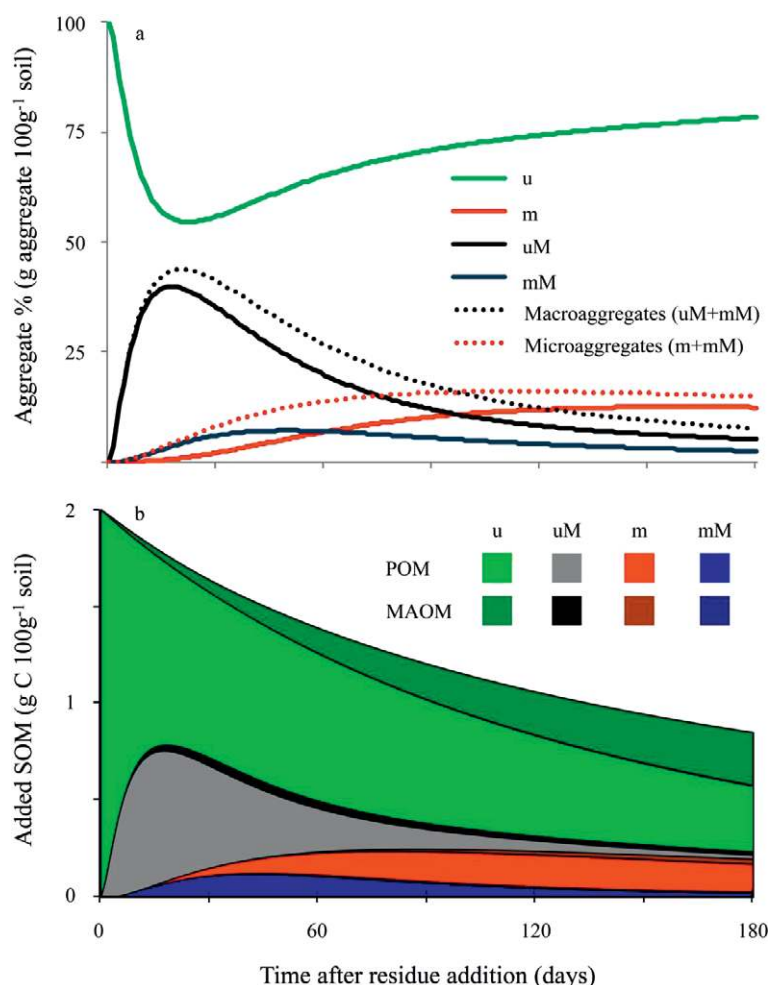
Figure 5: AggModel daily predictions for (a) soil aggregates, and (b) cumulated added SOM within soil aggregates, during a half-year simulation following the addition of 2 g C 100 g^{-1} soil to an unaggregated soil. u = Unaggregated soil external to macroaggregate; m = Microaggregates external to macroaggregates; mM = Microaggregates within macroaggregates; uM = non-microaggregated soil within macroaggregates (Reprinted from Ecological Modelling, Vol. 263, M. Segoli, S. De Gryze, F. Dou, J. Lee, W. M. Post, K. Denef, J. Six, AggModel: A soil organic matter model with measurable pools for use in incubation studies, 1–9, Copyright (2013), with permission from Elsevier.).

gates by external and internal forces, including capillary forces in an ideal geometric setting.

It is well known that bacteria and fungi play a fundamental role in the formation, stabilization and destruction of soil microaggregates (*Crawford* et al., 2012). A quantitative and mechanistic understanding of the possible feedback loop between the soil structure and the microbial activity is thus mandatory for the understanding of aggregate formation, the persistence of microaggregates, and their functioning, *e.g.*, as a habitat. Only a few papers address the relationship between microbial growth and activity and the structure of a soil (*Young* and *Crawford*, 2004; *Crawford* et al., 2012; *Ebrahimi* and *Or*, 2014; *Ebrahimi* and *Or*, 2015), where *Ebrahimi* and *Or* (2015) also address aspects of nutrient availability and hydration effects on microbial communities in aggregates. Essentially, only one research work provides a

quantitative modeling approach to validate the theoretical concept of the self-organized 'soil-microbe system' (*Crawford* et al., 2012). Using a model of the feedback loop between the aggregation and the microbial activity and diversity, the qualitative behavior showed that only in cases where bacteria and fungi were present did the simulated aggregation result in an increased porosity. While the results of this simulation exercise are striking and the consequences far reaching, the explanatory and predictive power remains limited, as neither the governing parameters that control the aggregation, nor the 'physics' behind the functional relationships are mechanistically understood. Nevertheless, such data could help to identify new priorities for the development of mechanistic models and aid an opening up of new avenues for dedicated and theory-guided experiments and explorative instrumental studies. As the processes that control microaggregate formation and turnover in porous media take place at a range of spatial scales—starting from the interactions of individual molecules to interactions of molecules with minerals, colloidal interactions, and the action and interplay of associations with micro-organisms—a modeling approach should also account for processes on different spatial scales within a multiscale approach. Mathematical up-scaling [*e.g.*, volume averaging, *Whitaker* (1999); homogenization, asymptotic analysis, *Hornung* (1997)] can account for such processes on small scales resulting in an averaged model description on the macro-scale. However, one has to face the challenge of balancing accuracy, solvability, computational speed, and benefit of the model.

7 Microaggregate properties and functions

7.1 Pore system

The spatial arrangement and size distribution of intra-aggregate pores play an important role for the physical protection of OM against decomposition (*Ananyeva* et al., 2013). Currently, we have a rather vague qualitative understanding of how soil pore space architectures influence biological, physical and geochemical processes within soil aggregates and it is not known to what extent their dependency on soil pore networks triggers local mineralisation processes. *Juarez* et al. (2013) stated that "…soil microbial communities live in the soil pore network and therefore the access they have to organic substrate, oxygen and water depends on how this network is structured." Evidently there is some effect of the spatial separation of substrate and decomposers which may protect small particles of OM in micropores (*Chenu* and *Plante*, 2006). For instance, *Kinyangi* et al. (2006) found that POM is occluded in pores with diameters of between 2 μm and 5 μm suggesting an interaction between the physical function of microaggregate infrastructures and long-term carbon stabilization in microaggregates. Possible

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reasons for this are that aggregation results in physical barriers between decomposers and the substrate, *i.e.*, OM. Moreover, the adsorption of organic compounds within the inner pore space of aggregates is strongly controlled by transport.

While the internal structures of macroaggregates have been examined in various studies focussing on the effect of land management (Fig. 6; *Peth* et al., 2008a; *Peth* et al., 2008b; *Peth* et al., 2010b; *Wang* et al., 2012; *Zhou* et al., 2012; *Naveed* et al., 2014) and of shrinking-swelling soils (*Ma* et al., 2015), investigations on microaggregate architectures are absent. The only study we are aware of, that has attempted to resolve the architecture of soil microaggregates, is one on Oxisols by *Rabbi* et al. (2015). Using a conventional industrial scanner they found that the achieved resolution of 5.2 μm for scanning 125–250 μm microaggregates was not 'ideal' for visualizing pores in microaggregates, and that scanning small microaggregates (< 53 μm) was not operationally possible. Assuming that OM, which is a key factor in aggregate forma-

tion and stabilization, may be locked up in pore diameters < 2–5 μm, microaggregate structures have to be investigated at a much better level of resolution that goes well into the submicron scale.

Due to the difficulty in conducting direct physical measurements at the scale of microaggregates, modeling will play an important role in testing the relationships between structure and function. For example, *Khan* et al. (2012) have used a lattice Boltzmann model to simulate the permeability of a soil aggregate and have compared the results with the empirical formula of *Kozeny-Carman*, which relates permeability with porosity and the specific surface area, and found a good agreement between the two methods. In another study, *Pot* et al. (2015) used Lattice–Boltzmann simulations to predict the 3-dimensional distribution of gas and water filled pore spaces in soil aggregates showing a very good match with the gas and water configuration measured by synchrotron-based X-ray microtomography. However, understanding the formation, evolution and stabilisation of microaggregate structures requires a combination of spatially explicit pore-scale modeling approaches to account for the interplay between physical, biological and chemical processes.

7.2 Wetting properties and water retention

Retention of water in soils is largely controlled by the pore diameters, which is a function of soil structure. As indicated in the previous paragraph, it is possible to derive water retention functions from image-based data using mathematical morphology (*e.g.*, *Delerue* et al., 1999). As stated by the Young–Laplace law (*Bear*, 1972), wetting properties need to be known to determine the relationship between capillary diameter and hydraulic potential required to fill or empty a pore. For the macro-scale, this assumption of full wettability may be valid for many situations, but, especially when we consider micro-scale surfaces, wetting properties may be spatially very heterogeneous. As a result, current data on the pores of aggregates have mainly been obtained for macroaggregates or even pedons (*e.g.*, *Urbanek* et al., 2007), but not yet for microaggregates.

Sorbed organic material influences the wetting properties of aggregate surfaces, which is usually quantified in terms of contact angle (CA). Depending on the kind and orientation of the OM functional groups exposed to the pore space, the particle can be wettable (CA = 0°; mainly polar functional groups,
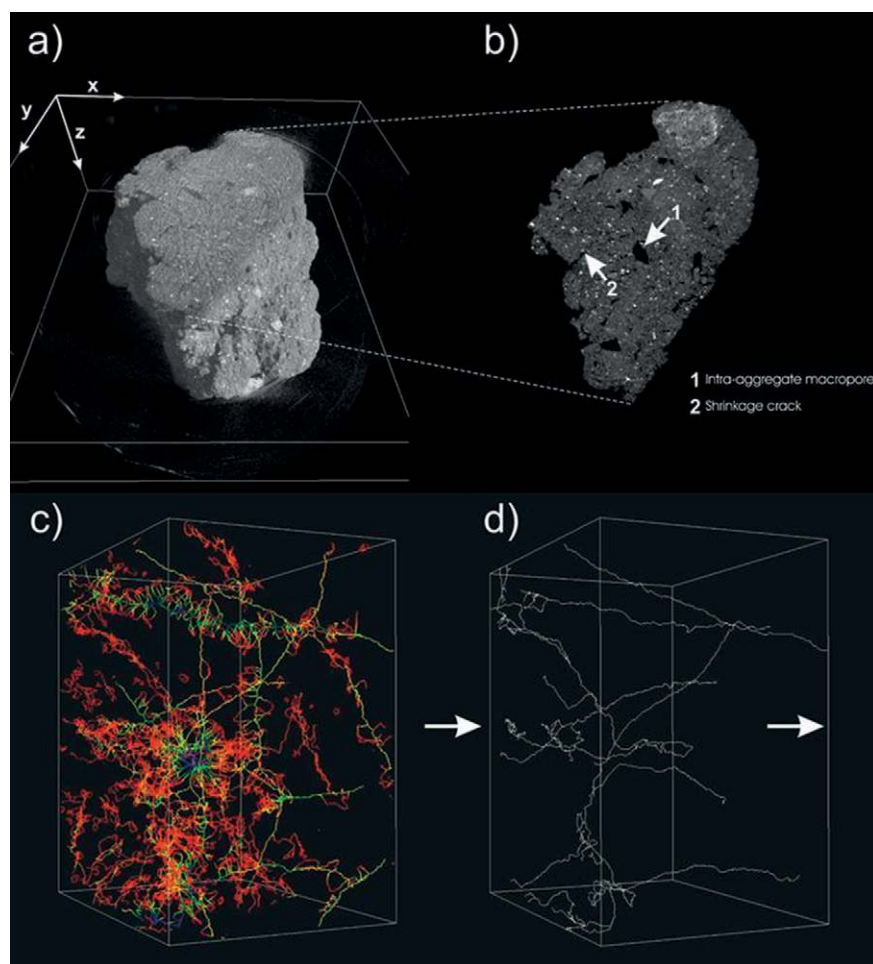

Figure 6: (a) Reconstructed three-dimensional view of a 5 mm diameter soil aggregate. (b) cross-sectional view of an image slice showing (1) intra-aggregate macropores, and (2) shrinkage cracks. (c) A brick-shaped subvolume where the pore skeleton has been extracted showing the 3D architecture of the pore network. Colors indicate channel widths with red colors representing narrow channels and purple colors representing wide pore channels. Connectivity between opposing interfaces are shown in (d) with shortest possible connections from left (inlet) to right (outlet). Taken from *Peth* (2010a).

e.g., COO⁻), subcritically water repellent (CA > 0° and < 90°; polar and non-polar functional groups), or hydrophobic (CA > 90°; mainly non-polar functional groups, *e.g.*, $-CH_2-CH_3$), emphasizing OM quality as decisive with respect to wetting properties (*Woche* et al., 2005; *Bachmann* et al., 2003). Recent molecular modeling studies revealed that surface coverage of hydrophobic substances on reactive mineral surfaces might strongly influence contact angles (*Šolc* et al., 2015). *Zhuang* et al. (2008) speculated that the OM-induced wetting properties might influence the water retention behaviour of microaggregates, representing an important soil function. The wetting properties strongly depend on the concentration and type of OM located at the exterior (1 nm; *Ferguson* and *Whitesides*, 1992) of the interface, again pointing to the importance of the surface composition on soil reactivity. Sorption of DOM to initially wettable quartz sand was found to increase the contact angle (*Lamparter* et al., 2014), and the attachment of microbial residues or biomass to minerals can also strongly alter the wetting properties of exposed surfaces. The distinct contact angle increase with increasing soil age within the *Damma* glacier chronosequence, for instance, could be correlated with the increasing coverage of particle surfaces by cell envelope fragments (*Schurig* et al., 2012).

7.3 Microaggregates and the microbial habitat

Microorganisms are unevenly distributed in the soil matrix, indicating that some regions are more favorable and more in reach for microbial life than others (*Grundmann*, 2004; *Nunan* et al., 2007; *Young* et al., 2008; *Vos* et al., 2013). The microorganisms in soil are assumed to live attached to surfaces most of the time, where they occur as single cells, microcolonies or small biofilms (*O'Donnell* et al., 2007; *Or* et al., 2007b). Early microscopic studies revealed that bacteria occur embedded in particles as well as within open pores (*Grundmann*, 2004; *Foster*, 1988). Later, it was reported that bacteria are preferentially found in micropores of < 10 µm diameter (*Ranjard* and *Richaume*, 2001). In such pores, bacterial cells are protected against adverse environmental influences such as desiccation, pH fluctuation or predation (*Stotzky* and *Rem*, 1966; *Bitton* et al., 1976; *Elliott* et al., 1980; *England* et al., 1993). This applies in particular to very small pores of 1–5 µm diameter. However, such small pores can also restrict microbial activities due to diffusion limitation and thus substrate availability, while larger pores (15–60 µm) are less protective, but better support microbial activity (*Chenu* and *Cosentino*, 2011; *Ruamps* et al., 2011). Microscopic analyses of colonization patterns in relation to microaggregate structure are rare, but in a recent study, *Raynaud* and *Nunan* (2014) analyzed inhabitation patterns on internal and external surfaces of aggregates based on microscopic images of several hundred thin sections of soils. Though not focusing on microaggregates, they observed an average cell-to-cell distance of ca. 12.5 µm in the soil matrix, which implies that individual cells interact with a rather small number of other individuals (on average 120 neighboring cells within a distance of 20 µm).

Besides the microscopic analysis of microbial cells within the soil matrix, molecular analyses of microbial communities of size- or density-fractionated soil samples revealed coloniza-

tion preferences. Bacteria and microbial activity are predominantly located in microaggregates or associated to the clay fraction (*Ranjard* and *Richaume*, 2001; *Poll* et al., 2003; *Fansler* et al., 2005; *Saviozzi* et al., 2007; *Neumann* et al., 2013; *Nie* et al., 2014). In contrast, fungi occur more abundantly in association with macroaggregates (*Kandeler* et al., 2000; *Kihara* et al., 2012). Differences in the microbial community composition were not only reported for different aggregate size fractions, but also for the aggregate interior *versus* the outside, indicating that specific bacterial taxa have habitat preferences that are linked to the morphological, chemical and physical properties of the interior and exterior interfaces of microaggregates (*Ranjard* et al., 2000; *Poll* et al., 2003; *Mummey* and *Stahl*, 2004; *Mummey* et al., 2006; *Davinic* et al., 2012; *Neumann* et al., 2013; *Hemkemeyer* et al., 2014). However, consistent patterns among studies showing that specific bacterial taxa preferentially colonize macro- *versus* microaggregates or the silt *versus* the clay fraction are not yet very evident. Also, strong differences were not necessarily detected for the dominant soil colonizing taxa, but rather for some low abundance taxa (*Davinic* et al., 2012). The fact that soils with different properties were used in these studies and fractionated by different methods contributes to the difficulty in drawing general conclusions about possible habitat preferences. A disadvantage of the molecular methods commonly applied in such studies is the rather large amount of sample material, which limits the possibility of performing studies with high spatial resolution. Nevertheless, the analysis of individual macroaggregates by molecular methods in combination with enzyme activity assays has been successfully performed and has revealed that differences in enzymatic activity are reflected in microbial community composition (*Bailey* et al., 2013a; *Bailey* et al., 2013b). Similarly, genomic single-cell studies are now possible (*Lasken* and *McLean*, 2014), demonstrating that microbial analyses down to the scale of individual microaggregates, and at even finer scales, should be feasible in combination with microscale sampling approaches.

The influence of environmental parameters on microorganisms in soils is largely scale dependent (*O'Donnell* et al., 2007). Among the important parameters at the small scale are particle surface properties, the pore network structure and the water content of a soil (*O'Donnell* et al., 2007; *Kravchenko* et al., 2013; *Wang* et al., 2013; *Ebrahimi* and *Or*, 2015). Thus, the composition of microaggregates and the arrangement of the building units as well as their specific properties will affect bacterial colonization. Different soil components, such as minerals, metal oxides, OM of different composition (including charcoal), have been reported to influence the community composition of microorganisms in soils (*Carson* et al., 2009; *Davinic* et al., 2012; *Babin* et al., 2013), besides the more frequently discussed factors, such as soil pH, availability of water, oxygen and nutrients, which are mostly analyzed at large spatial scale. Bacteria are, for example, known to occur preferentially in association with OM or clay particles. Aggregates with higher OC contents have been shown to have higher levels of activity among OM decomposing enzymes (*Qin* et al., 2010; *Lagomarsino* et al., 2012; *Nie* et al., 2014). These findings point to the fact that microaggregates may provide a favorable habitat for micro-

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organisms. Yet, in a recent study with an Eutric Cambisol, *Blaud* et al. (2014) found no difference in bacterial community structure for different organo-mineral soil fractions that correspond to small and large microaggregates, but rather strong differences with the particulate organic matter (POM). They infer that only the POM provided distinct microhabitats for bacterial communities, which are presumed to vary with the state of POM decomposition. However, microaggregates contain rather low amounts of new and easily accessible OM, so that bacteria within microaggregates may largely depend on OM that reaches the cells *via* diffusion through voids and pores rather than on the stabilized OM present within micro-aggregates (*e.g.*, *Skjemstad* et al., 1993). Thus, bacteria residing in the inner part of a microaggregate may be rather limited in carbon. Recent studies suggest that much of the mineral-associated OM in microaggregates is actually of microbial origin, either in the form of microbes or in the form of microbial by-products (*Plaza* et al., 2013; *Pronk* et al., 2013), indicating an efficient microbial recycling of OM.

Besides OM, clay content affects bacterial life in and on microaggregates (*Carson* et al., 2009). Aggregation experiments with artificial soils revealed that mineral type affects microbial community composition most strongly during the initial phase of soil aggregation, while OM quality appears to be of higher relevance at later stages (*Babin* et al., 2013; *Ding* et al., 2013; *Hemkemeyer* et al., 2014). Associations of microbial cells with clay particles are already known from early microscopic studies (*Hattori* et al., 1976; *Foster*, 1988; *Kabir* et al., 1994), and were later described as 'clay hutches'. They were proposed to represent a specific habitat for individual or a few bacterial cells (*Lünsdorf* et al., 2000; *Dechesne* et al., 2007). Clay particles may actually protect bacterial cells from unfavorable environmental conditions (*Chenu* et al., 2001), but conversely, they can also limit diffusion processes and thus nutrient supply. It currently remains unclear whether these cell-clay associations are indeed favorable for bacteria or not.

As bacteria are assumed to live attached to surfaces most of the time (*O'Donnell* et al., 2007; *Or* et al., 2007b), surface properties of microaggregate building units can be expected to influence the attachment of bacterial cells and may serve as a further explanation for differences in the bacterial community composition in terms of its dependence on soil and microaggregate composition (*Ding* et al., 2013). Surface characteristics, such as hydrophobicity, roughness and charge density, can be assumed to influence attachment directly and indirectly. Indirect effects occur by affecting the distribution of water and the thickness of surface water films (*Doerr* et al., 2000; *Or* et al., 2007a). Detailed studies analyzing the attachment of bacterial species to soil particles are largely missing, in particular at a level of resolution appropriate to single cells.

While the localization of bacteria in the soil matrix and in association with soil microaggregates has been addressed in studies based on different experimental approaches, detailed studies analyzing microbial activity associated with different building units in and on microaggregates down to single-cell resolution are rare. It is still a challenging task to determine the metabolic capabilities and activity of microorganisms reli-

ably within aggregates and pores (*Gupta* and *Germida*, 2015; *Bach* and *Hofmockel*, 2014), but such analyses are needed in order to gain insights into the habitat function and localization of microbial activity associated with microaggregates and in relation to the pore network. This will reveal whether and where microaggregates harbor hot-spots of microbial activity, protective habitats for bacterial cells to endure unfavorable conditions as inactive cells, or habitats that are dead-end roads for bacterial cells, *e.g.*, once they are trapped in a clay hutch within a microaggregate, decoupled from nutrient and gas flow. Pores provide the basis for connectivity of a micro-habitat as they enable the flow of water and nutrients and diffusion of gases to sustain microbial activity and enable the connection of spatially separated bacterial microcolonies so allowing interactions to occur (*Vos* et al., 2013). Of particular importance is the moisture content of a soil or, more specifically, the matrix potential. This determines the thickness of water films on surfaces and, thus, the level to which pores are filled with water, which in turn controls diffusion processes and thus nutrient and gas supply. Moreover, water films on soil surface particles support bacterial movement and enable their dispersal (*Or* et al., 2007b; *Young* et al., 2008). The discontinuity of pore systems and surface water films on soil particles results in the spatial separation of microhabitats and can cause (steep) gradients of nutrients, pH, or gas concentrations at small spatial scales (*Or* et al., 2007b). This serves as one explanation for the high bacterial diversity observed in soil, which is based on coexistence in spatially separated distinct habitats (*Dechesne* et al., 2008; *Young* et al., 2008; *Long* and *Or*, 2009; *Carson* et al., 2010; *Vos* et al., 2013; *Ebrahimi* and *Or*, 2015). A step forward in connecting pore network characteristics and hotspots of microbial activity would be to study intra-aggregate habitats, in terms of their physical structure, simultaneously with the spatial localization of OM by means of non-invasive techniques such as X-ray microtomography. While this is a straightforward task for studying pore networks, it remains difficult to locate OM and even more so (metabolically active) microbial cells within the pore space and soil matrix. Attenuation to X-rays is of too little contrast with respect to other soil constituents. The use of osmium-tetroxide as an OM-specific staining agent can enhance the contrast of OM in X-ray CT scans to obtain the distribution of OM in relation to the pore space (*Peth* et al., 2014). The spatial distribution of potential microbial hotspots associated with OM could thus be deduced from the micro-scale location of OM.

7.4 Microaggregates and biogeochemical cycles

Nearly 90% of soil OC in surface soils was found to be located within aggregates (*Jastrow* et al., 1996) with 20–40% of OC as intra-microaggregate OC (*Carter*, 1996). In most temperate surface soils OM quality decreases with decreasing aggregate size, as indicated by a decrease of the C:N ratio and declining abundance of plant residues from macro-to microaggregates (*Gregorich* et al., 2003; *Skjemstad* et al., 1993; *Balesdent*, 1996; *John* et al., 2005). Consequently, microaggregate OM is on average older and in a more decomposed state than macroaggregate OM. Stable isotope tracer studies have been successfully used to study the fate of OM in different soil fractions, and the results supported the

aggregate hierarchy model established by *Tisdall* and *Oades* (1982). Turnover times were between about 15 and 50 years for OC stored in macroaggregates and between 100 and 300 years for OC in microaggregates (*Angers* and *Giroux*, 1996; *Besnard* et al., 1996; *John* et al., 2005; *Puget* et al., 2000; *Six* and *Jastrow*, 2002; *Lobe* et al., 2011). The highest reported turnover times were in the lower centennial range (200–320 years) and were found in the smallest aggregates < 20 μm. *Angers* et al. (1997) observed a redistribution of ^{13}C from macroaggregates to microaggregates with time, which clearly indicates that OC occlusion in microaggregates only happens after occlusion at the macroaggregate scale.

The turnover of OM is intimately associated with the stability of the microaggregates themselves. Observations of enhanced OM mineralization following disruption of aggregates have shown that occlusion in aggregates has a retarding effect on soil OM decomposition (*Goebel* et al., 2009; *Mueller* et al., 2012). Protection will be greatest for soils with a high proportion of labile OM (*Goebel* et al., 2009), where aggregate stability is high and aggregate turnover is low, making aggregation the stabilization mechanism that is potentially most susceptible to disturbance.

As the OM located at the aggregate surface is more accessible to oxygen and microbial decay, it is possible that along gradients across aggregates, C is depleted at the edges, as, *e.g.*, has been shown for macroaggregates (*e.g.*, *Sexstone* et al., 1985; *Amelung* and *Zech*, 1996; *Bachmann* et al., 2008). High recent depositions of OM at the surfaces of small particles might, however, also invert these gradients (see, *e.g.*, *Amelung* et al., 2001; *Kaiser* and *Guggenberger*, 2003). Obviously, the bioaccessibility of C and N in the soil and at the surface of aggregates for decomposition and deposition may have a large affect on the spatio-temporal patterns of OM at the microscale.

Nothing is yet known about the variation of mean residence times of OM across the aggregate level, or of the role of their surface accessibility for OM decay and deposition. It is worth noting that the gradients and patterns of OM in soil microaggregates are not only influenced by aggregate formation and life time: OM may also be degraded in the aggregates, and OM of different age may be involved in the re-formation of microaggregates. Attempts to model soil C sequestration capacity have largely failed to include effects of structural protection within soil aggregates (*von Lützow* et al., 2008). The approach adopted by *Kuka* et al. (2007) was to scale carbon turnover as a function of pore size within microaggregates. A true understanding of the coupling of microaggregate architecture to soil OM dynamics requires the amount of C and the turnover rates to be known at each subsite in a microaggregate.

Together with C, the cycling of N, P and S is also affected by microaggregation. It is well known that organic N is accumulated together with OM in microaggregates. Generally, the accumulation of organic N and P is more intensive than that of OC, as can be deduced from the lower C:N and C:P ratios in microaggregates (*Elliott*, 1986; *Monreal* et al., 1995; *Angers* et al., 1997). *Wang* et al. (2016) similarly describe

that microaggregates are enriched in P and S compared to the bulk soil. C:N:P ratios of 75:9:1 in small microaggregates of a Mollisol (*Elliott*, 1986) are quite close to the stoichiometry of the soil microbial biomass which generally have C:N:P ratios of between 60:7:1 and 42:6:1 (summarized by *Spohn* and *Chodak*, 2015). This observation has two implications with respect to microaggregate-associated OM. First, the OM is possibly to a large part microbially derived, as corroborated by *Lehmann* et al. (2007), who emphasized the importance of microbial metabolites associated with mineral surfaces within microaggregates. Second, as reported by *Manzoni* et al. (2012) and *Spohn* and *Chodak* (2015), the carbon use efficiency of microorganisms is much higher at narrow carbon to nutrient ratios than at wide ones. This may provide an additional explanation for the high apparent stability of microaggregate-associated OM to microbial decomposition (*i.e.*, low mineralization rates). Stoichiometric studies concerning carbon use efficiency at the level soil microaggregates may help to disentangle the mechanisms of OM stabilization in microaggregates.

In a laboratory study, *Sey* et al. (2008) quantified emissions of the greenhouse gases nitrous oxide (N_2O), CO_2, and methane (CH_4) from a sandy-loam soil and found that microaggregates produced more CO_2 than macroaggregates, pointing to the fact that microbial activity was higher in microaggregates. Compared to macroaggregates and bulk soil, the microaggregates were responsible for 95% of the total N_2O production at 80% water saturation. While denitrification was the dominant process in the microaggregates, nitrification was dominant in the macroaggregates and bulk soil and made up 97–99% of the N_2O production in those fractions. These data suggested that "…oxygen diffusion into and around microaggregates was constrained, whereas macroaggregates remained oxic at 80% WFPS [water-filled pore space]". With increasing water saturation, methane production in aggregates increased (1.1–6.4 ng CH_4-C kg^{-1} soil h^{-1}).

The biogeochemical processes functioning at the microaggregate scale coupled with advective and diffusively controlled solute transport will also determine element cycling in soil. We therefore consider that micro-aggregation also has major impacts on the cycling of major and trace elements in soils, such as, *e.g.*, Ca, K, Si, Fe, Al, and Mn. It seems that this has to a limited extent been covered for those elements where the cycling is strongly associated with C, *i.e.*, N, P and S. We are not aware of any studies that have addressed the effect of micro-aggregation on element cycling in soils for elements that are not strongly coupled to the C cycle. One can speculate that the different building units of microaggregates as well as the amount of coverage of mineral surfaces with OM and the resulting cation and anion exchange capacity may affect the storage and release of these elements in soils.

8 Conclusions and outlook

The basis for almost all soil based ecosystem services is the soil's unique ability to process and accumulate inputs of energy and matter, collect, retain and redistribute water, while simultaneously storing gases, and harboring an incredible biological diversity across all major trophic levels. Although

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soil properties and functions are to a large degree controlled by the formation of an aggregate structure, still very little is known about the rates and underlying deterministic or stochastic controls that act on soil microaggregate formation in space and time. Up to now, microaggregate structure and development has been investigated with respect to three aspects: (1) the overwhelming number of studies deals with OM stability and turnover with specific focus on carbon and, to a minor extent, nitrogen; (2) flow and transport of fluids and mechanical stability related to soil resilience; (3) and, more recently, but with increasing intensity, the role of aggregates for the formation of microhabitats and the biogeography and diversity of microbial communities. We lack studies that link functional traits (*e.g.*, connectivity, tortuosity and heterogeneity of the 3D pore space) across scales with microaggregate formation and turnover. Most approaches used to explore the pore network operate on the millimeter scale. Adapting these approaches for studying soil microaggregates and linking it to its properties and turnover in a quantitative, deterministic way remains to be done.

We need to expand studies on C and N in microaggregates to the biogeochemical cycling of other elements such as P and S, but also the pedogenic oxides of Fe, Al, and Si. And we need to link these processes in a 3D space or even better in a 4D spatiotemporal context, with *in situ* observations of microaggregate turnover and related pore-scale dynamics. Related assessment techniques are still in their infancy or require large-scale equipment with previous invasive sampling and fractionation. Progress may thus be expected from the joint application of tomographic and spectro-microscopic techniques on intact microaggregates and sophisticated mapping strategies. It will then be possible to image the three-dimensional structure at a high spatial resolution, while mapping the chemical and the mechanical properties of the surfaces, which are important for interactions, adhesion and fluid flow. Although still in its infancy, the 3D-mapping of the spatial distribution of soil microorganisms inhabiting the interior space of soil microaggregates will be another important step forward.

The development of competitive theoretical approaches cast into mathematical simulation tools would boost progress in our fundamental understanding of: (1) the formation of microaggregates; (2) their functions as habitat, for carbon storage, and for water retention; (3) the interplay of microbial activity and diversity in concert with these functions. Up to now, no approaches have been available that could link fluid flow and the reactive chemical transport of major elements, *i.e.*, Fe, Si, C, and N, with the microbially-mediated build-up and decay of aggregates and surface coatings. The modeling of the (mathematically speaking) '*full problem*', *i.e.*, the integration of soil microaggregate formation and turnover with biogeochemical cycling, would require the combination of the different modeling approaches being developed for fluid flow and biogeochemical transport, microbial community structure and diversity together with the concepts of the formation of aggregates and soil structure. Such models may not only be used to test hypotheses, but could also be used to analyse and identify the governing processes and factors and their sensitive ranges and, thus, open the doors for analytic and prognostic

scenarios. Using these approaches applied to the research avenues outlined above will allow for the complete representation of soil microaggregates together with their resident microorganisms and the corresponding spatial patterns of their chemical and mechanical properties. This in turn will bring us closer to understanding and managing soil functionality, based on the properties and processes controlled in microaggregates as the smallest functional soil structural units.

9 Glossary

A number of terms in this review are widely used in the scientific community but with different meanings because a generally accepted, unique and formalized definition is lacking. To avoid misunderstanding, we provide this glossary.

Microaggregate forming materials

Microaggregate forming materials comprise all mineral, organic and biotic components that are involved in the formation, cohesion and stabilization of (composite) *building units*. Microaggregate forming materials may act as nucleus, gluing agent or cementing agent.

Building units (syn. building blocks)

The building units of soil microaggregates comprise all single particles and composite structures smaller than about 2 μm. They may consist of organo-mineral associations, minerals devoid of organic matter, as well as organic compounds such as plant and microbial remains.

Composite building units

Building units of soil microaggregates that comprise composite structures smaller than about 2 μm made of more than one microaggregate forming material.

Cementing agent

Cementing agents comprises all inorganic substances (*e.g.*, Fe- and Al-oxides, calcium carbonates, sulfates) responsible for cementing and embedding the building units that form a soil microaggregate. The properties of cemented subunits tend to be rigidity and brittleness.

Classes of soil microaggregates

Microaggregates are subdivided into three size classes (Fig. 3, Tab. 1): Building units (**smaller than about 2 μm**), including the composite building units; small microaggregates (**between about 2 μm and 20 μm**) and large microaggregates (**between about 20 μm and 250 μm**).

Gluing agent (syn. agglutination agent)

Gluing agents comprises all organic substances (*e.g.*, polysaccharides, proteins, extracellular polymeric substances) responsible for the agglutination of subunits forming a soil microaggregate or a composite building unit. The **property of** building units that are **held** together by gluing agents **is that they** tend to be more flexible.

Hierarchic aggregate system

A conceptual understanding of aggregated soils being composed of macroaggregates that are built from microaggregates, which themselves are formed from diverse (composite) building units and microaggregate forming materials. The concept is based on the operational definition of hierarchical features by a step-wise dispersion of soil aggregates upon increasing dispersion energies (*Tisdall* and *Oades*, 1982).

Pore size classes

Two different definitions of pore size classes are relevant for this **review: the** IUPAC system (IUPAC: International Union of **Pure** and **Applied Chemistry**; *IUPAC*, 1996); **and that** used **in practice** by soil scientists to describe the pore-size distribution of soils (Tab. 3). **In** soil science (*Hartge* and *Horn*, 2016) **pore** size is defined as **the** equivalent pore diameter of **ideal capillary** pores, **while** the IUPAC system refers to **the** actual **size of** pores found in chemical compounds. If not stated **otherwise**, the IUPAC system is used throughout **this paper.**

Shear strength

Aggregate mechanical resistance against breakdown due to shear **stresses.**

Soil aggregates

Soil aggregates are composite soil structures made of numerous aggregate forming materials. Soil aggregates can be classified into macro- and microaggregates. Macroaggregates comprises all soil aggregates **> 250** μm, whereas soil microaggregates denote all compound soil **structures < 250** μm.

Soil texture

To classify the soil based on its physical texture the textural classification system proposed by the United States Department of Agriculture (USDA) is used.

Tensile strength

Aggregate mechanical resistance against breakdown due to tensile **stresses.**

Table 3: Pore size-classes according to soil science and IUPAC.

	Denotation	Size (nm)	Size (μm)	Where in Microaggregates
IUPAC	Micropores	< 2	< 0.002	Internal pore space of, *e.g.*, ferrihydrite or zeolite, interlamella pore space of phyllosilicates
	Mesopores	2–50	0.002–0.05	Internal pores of aggregate forming material
	Macropores	> 50	> 0.05	Pore space between building units
Soil Science	Fine	< 200	< 0.2	Intra-micro-aggregate
	Medium	200–10000	0.2–10	Intra-aggregate pore space
	Coarse (small)		10–50	Mechanical fissures and biopores (fine root)
	Coarse (wide)		> 50	Cracks, biopores (roots, earthworm)

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