ASSOCIATION OF SOIL MINERALS AND ORGANIC MATTER AND THEIR IMPACT ON pH_0 VALUE

Penyatuan Mineral Tanah dengan Bahan Organik dan Dampaknya pada Nilai pH_0 tanah

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ABSTRACT

Clay and organic colloids are two factors that control major, if not all, chemical, physical and biological processes and soil properties but maintaining soil organic matter content under tropical conditions is difficult. The objectives of this review are to explore association between minerals and organic substances, mechanisms underlying the stabilization of soil organic matter, and their implication on pH_0 of soil variable charge component. The modes of interaction in clay-humus complexes may occur through anion and ligand exchange to the crystal edges, cation or water bridge to basal surfaces, H-bonding to the siloxane or gibbsite sheet by van der Waals forces attraction (physical bonds), entrapment in crystal pores and intradomain regions, and adsorption in interlayer spaces. Organic matter preservation was related to amount of clay fraction, type of clay mineral present and aggregate formation. High preservation occurs in soils having high clay content, the presence of 2:1 minerals and amorphous minerals (allophane and imogolite), and a larger aggregate size. Current knowledge indicates that the mechanisms of soil organic matter stabilization are: (i) chemical recalcitrance involves elemental composition, the presence of functional groups, and molecular conformation of organic substances against decomposition by microbes and enzymes; (ii) chemical stabilization occurs through adsorption of functional groups to clay mineral surfaces and amorphous sesquioxides; (iii) physical protection involves organic substances being protected by clay fractions in soil pores, especially mesopres (2-50 nm) that limits the accessibility of microbes and enzymes. Soil organic matter is powerful in masking reactive mineral surfaces and generating soil negative charge, which is revealed by the low value of pH_0.

Keywords : Organo-mineral association, organic matter preservation, soil pH_0

ABSTRAK

Koloid mineral liat dan organik adalah dua faktor utama yang mengendalikan hampir seluruh proses dan sifat kimia, fisika dan biologi tanah tetapi mempertahankan kandungan bahan organik tanah pada daerah tropis adalah sangat sulit. Tujuan dari review ini adalah mengungkapkan penyatuan antara mineral tanah dan bahan organik, mekanisme kestabilan bahan organik dalam tanah dan implikasinya pada nilai pH_0 muatan tidak permanen. Modus keterkaitan humus-liat kompleks terjadi melalui pertukaran antara anion dan ligand pada ujung mineral, kation atau molekul air penghubung antar permukaan mineral, ikatan hidrogen pada lapisan siloksan atau gibsit karena daya tarik gaya van der waals, terperangkap dalam pori antar kristal dan daerah antar domain, dan terjerap dalam ruang antar lapisan mineral. Kestabilan bahan organik dalam tanah dapat dihubungkan dengan banyaknya fraksi liat, tipe mineral dan pembentukan agregat. Kestabilan yang tinggi terjadi pada tanah yang berkadar liat tinggi, adanya mineral 2:1 atau mineral amorpus (alofan dan imogolit) dan agregat yang berukuran besar. Mekanisme kestabilan bahan organik dalam tanah, menurut pengetahuan saat ini, adalah (i) rekalsitran secara kimia yang dipengaruhi oleh unsur penyusunnya, adanya grup fungsional, dan konformasi molekul bahan organik menolak dekomposisi berbagai mikroba dan enzim; (ii) stabilisasi secara kimia melalui jerapan grup fungsional pada permukaan mineral liat dan seskuioksida amorf; (iii) proteksi bahan organik secara fisik oleh fraksi liat dalam pori tanah, khususnya pori meso (2-50 nm) yang membatasi aksesibilitas berbagai mikroba dan enzim. Bahan organik tanah mempunyai kemampuan mencolok dalam menyelimuti permukaan mineral tanah yang reaktif dan menciptakan muatan negatif yang ditunjukkan oleh nilai pH_0 yang rendah.

Kata kunci : Penyatuan mineral-organik, kestabilan bahan organik, pH_0 tanah

The role of soil organic matter (SOM), unquestionably, has been widely recognised as a major key to maintain soil functions. This function includes production of food and fibre and maintenance of environmental quality by acting as a filter and buffer for water, air, nutrients and toxic elements (Doran and Parkin, 1996). In soils, clay-humus interaction plays an important role in many soil processes, such as mineral cycling and weathering, profile development, and aggregate stabilisation (Theng, 1982). A

comparison of the residence time of organic C in soils can be made by comparing the *turnover time*, defined as the amount of organic C in the soil divided by the net annual addition (Oades, 1989). The turnover rate of SOM is modified by temperature, water regime and clay content (Parton *et al*., 1987).

Carbon storage in soils is mainly related to primary and secondary organo-mineral complexes (Christensen, 1996). The primary organo-mineral complex refers to association between SOM and clay, silt and sand fractions. Furthermore, the secondary organomineral complex refers to the soil structure as defined by the degree of aggregation of primary organomineral complexes. The organic matter in soil, which is not recognised under a light microscope as possessing the cellular organisation of plant material is called humus (Oades, 1989).

Clay and organic colloids are two factors that control major, if not all, chemical, physical and biological processes and soil properties. The interaction of clay fraction and SOM is believed to dictate turnover rates of various organic matter pools. Parton *et al*. (1987) divided SOM into three pools: an active pool where soil C and N consist of live microbes and microbial products; a slow pool where C and N are physically protected or in chemical forms with more biological resistance to decomposition; and a passive pool where C and N are chemically recalcitrant and may be also physically protected.

According to Oades (1995) the active SOM is usually present in the largest particle size fractions of soils and is composed of carbohydrates, proteins, polyphenols (e.g. lignin) and alkyl groups. In addition, Franzluebbers and Arshad (1997) stated that the active C pool mainly consists of soil microbial biomass C, C mineralization and macroaggregate (> 0.25 mm) protected SOM. Carbon mineralisation as measured by CO_2 evolution decreased with increasing clay content in whole soil, suggesting that the potential turnover time of SOM was greater in coarse textured soils than in fine textured soils (Hassink and Whitmore, 1997; Franzluebbers and Arshad, 1997; Anda *et al*., 2005). Turnover time of C in clay, silt and sand is 59, 6 and 4 years, respectively (Christensen, 1996).The minimum turnover times of active pool, slow pool and passive pool are 0.5, 10, and 500 years, respectively (Parton and Rasmussen, 1994).

Sanchez *et al*. (1989) stated that the active SOM pool could play a major role in nutrient release and perhaps could be estimated by microbial biomass determination; the slow SOM pool may play a major role in the stabilization of macroaggregates, while the passive SOM pool may be largely inert as a nutrient release source, but may play a major role in the binding of primary soil particles.

The turnover and preservation of SOM are very important issues due to their impact on carbon sequestration, soil quality and crop production, especially in Indonesia as a tropical area where high annual rainfall and temperature cause intensive weathering processes and cation leaching, resulting in soils with low activity clays. Ultisols and Oxisols that occupy the Indonesian archipelago of 45.8 and 14.1 million ha, respectively (Puslitanak, 2000) belong to low activity clay or poor soil quality

The interaction between organic matter and mineral fractions of soils to form organo-mineral complexes may be responsible in controlling soil quality because it could improve soil physical, chemical and biological properties. Hence, the objective of this essay is to explore association between minerals and organic substances, mechanisms underlying the stabilization of soil organic matter and their implication on pH_0 of soil variable charge component. In order to approach this objective, the discussion starts with the chemistry of organic matter, followed by interactions between soil minerals and organic matter to form organo-mineral complexes, and reaction of organo-mineral complexes with respect to soil pH_0.

CHEMISTRY OF SOIL ORGANIC MATTER

Chemical characterization of SOM involves the use of alkaline and acid solutions to extract SOM tightly bound to soil inorganic colloid. These extractants could extract 20 to 60% of SOM and the extreme pH values during extraction may produce artifact (Morobey, 1981 cited by Monreal *et al.*, 1995). Reactivity of SOM was mainly controlled by a type of functional groups. Various techniques have been used to assess chemical structure and functional groups of SOM. At present, the most reliable technique to characterize SOM properties is the use of a cross-polymerization and magic-angle spinning (CPMAS) solid ^{13}C nuclear magnetic resonance (NMR) as the nondestructive method which does not alter chemical composition, making it an ideal technique for studying the nature of the organo-mineral complexes (Oades, 1989). The chemical shift (δ) in the spectrum caused by absorption or release of energy from electrons around the nucleus under applied magnetic field is expressed in parts per million (ppm) relative to a suitable reference compound, usually tetramethyl silane (Si(CH$_3$)$_4$) (Oades, 1989). Thus, the shift in terms of applied field, or frequency, expressed in ppm is taken as zero for (Si(CH$_3$)$_4$). For chemical grouping in humus during ^{13}C NMR analysis, the chemical shifts in the spectrum range from 0 to 200 ppm. According to Sollins *et al.* (1996) a ^{13}C NMR analysis technique allows quantification of relative amount of O-alkyl (-C-O-C-), aromatic ($\Diamond$), carboxyl (-COOH) and alkyl (-C-C-C-) carbon in soils. An example of the functional groups in the spectra obtained from ^{13}C NMR is shown in Figure 1.

Parfitt *et al.* (1999) divided the spectra into four chemical shift (δ) ranges, assigning the signals in each range to carbon in specific functional groups. First, signals in the (δ) = 0 - 60 ppm were assigned to alkyl carbon, including carbon in amino acid site chains, alicyclic carbon in resin acids, and carbon in structures derived from cutins and suberins. Second, signals in the

(δ) = 60-95 ppm were assigned to O-alkyl carbon, i.e. oxygen-substituted carbon in alcohols and ethers, including cellulose, hemicelluloses, and other polysaccharides. Third, signals in the (δ) = 95-165 ppm were assigned to aromatic carbon, including that in condensed tannins, hydrolysable tannins, and lignins. Fourth, signals in the (δ) = 165-220 ppm were assigned to carbonyl carbon, including secondary amide carbon in proteins, carboxylic carbon in hydrolysable tannins and carboxylic carbon in resin acids.
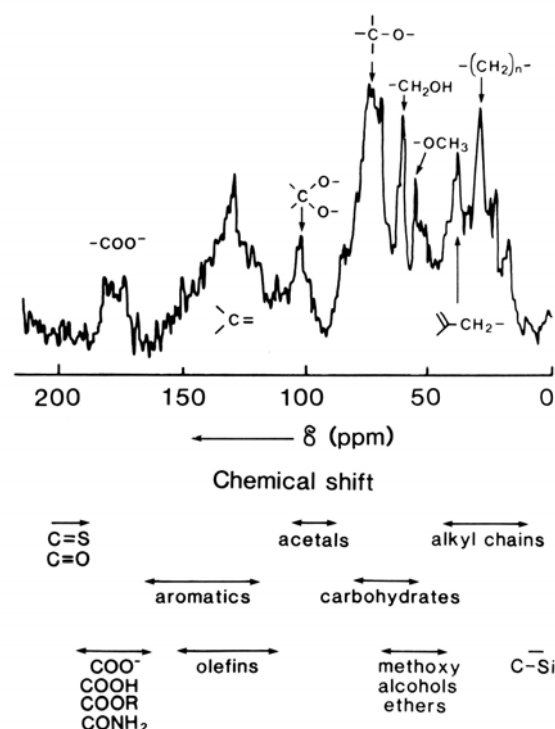

Figure 1. The ^{13}C NMR spectra showing various functional groups of a humic acid (Newman *et al.*, 1980 *in* Oades,1989)

Monreal *et al.* (1995) characterized SOM in whole soil and particle size fractions by CP MAS ^{13}C NMR and by Py-FIMS and reported that between 46 and 72% of the soil organic C mass consisted of aliphatic structures and between 17 and 23% of aromatic structure.

INTERACTION OF SOIL MINERALS AND HUMIC SUBSTANCES

It has been deduced that the probable modes of interaction in clay-humus complexes are: anion and ligand exchange to the crystal edges, cation or water bridge to basal surfaces, H-bonding to the siloxane or gibbsite sheet by van der Waals forces attraction (physical bonds), trapping in crystal pores and intradomain regions, and adsorption in interlayer spaces (Francois, 1990 cited by Stevenson, 1994). All types of bonds involved in clay-humus complexes formation are shown in Figure 2.
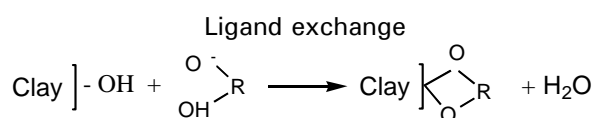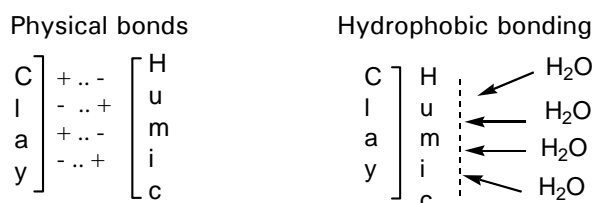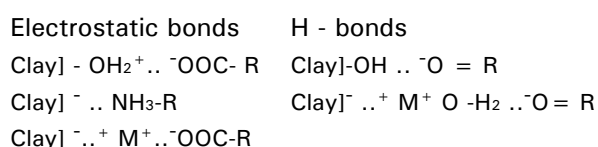
Electrostatic bonds

$Clay] - OH_2^+ .. \ ^-OOC- R$

$Clay] \ ^- .. NH_3\text{-}R$

$Clay] \ ^- ..^+ M^+ ..^-OOC\text{-}R$

H - bonds

$Clay]\text{-}OH .. \ ^-O = R$

$Clay] \ ^- ..^+ M^+ O \text{-}H_2 ..^-O = R$

Physical bonds

Hydrophobic bonding

Ligand exchange

Figure 2. Possible types of bond involve in interactions between humic substances and minerals (Francois, 1990 *in* Stevenson, 1994)

Alteration and stabilization of SOM involve various terms which need to be defined. These terms include stabilization, destabilization, synthesis, condensation and interaction which are briefly given here based on Sollins *et al*.

(1996) and for more detail, the readers should consult this reference. Organic matter stabilization refers to a decrease in the potential loss caused by respiration, erosion or leaching. The inverse of stabilization is destabilization that indicates the increased loss of SOM by respiration and leaching. Furthermore, synthesis includes all processes by which simple precursor molecule become linked to form larger molecules, such as poly-aromatic, polysaccharides, nucleic acids, proteins and lipids. When synthesis occurs outside cells, it is referred to as condensation. In addition, interactions refers to the inter-molecular interactions between organic and either inorganic substances or other organic substances that alter the rate of degradation of those organics or synthesis of new organics.

The major mechanism involved in organic and mineral interaction is adsorption which is defined as "the accumulation of a substance or material at an interface between the solid and bathing solution" (Sposito, 1989; Scheidegger and Sparks, 1996). Adsorption is a two dimensional process and does not include three-dimensional processes such as surface precipitation and diffusion into the crystal. According to Scheidegger and Sparks (1996) if the retention mechanism at surface either two or three dimension process is not known then the term sorption which is defined by Sollins *et al*. (1996) as the transfer of the solute (sorbate) from solution to an existing solid phase (sorbent) is used.

The mechanism underlying stabilization of SOM is not entirely understood. Christensen (1996) reviewed organo-mineral complexes and reported that mechanisms responsible for stabilization of SOM include chemical recalcitrance, chemical stabilization and physical protection.

Chemical recalcitrance

According to Sollins *et al*. (1996) organic stabilization could be due to chemical recalcitrance (i.e. cross-lingking by bonds that are not hydrolizable). The aliphatic, cyclic and aromatic moieties of varying molecular weight and derived from residual substrate and decomposition products may be incorporated into polyaromatic structures (Christensen, 1996) which are known as the most resistant to biological degradation. Recalcitrance may also be due to inherent chemical characteristics of substrates (e.g. aromatic plant polymers, fungal melanins) (Christensen, 1996).

Chemical stabilization

The interaction between soil minerals (mainly clay fraction) and organic matter can occur due to the presence of charges on clay surfaces and hydroxyl or carboxyl groups of OM. Although some clay surfaces and organic substances bear positive charge type, generally they have a negative charge type. Therefore, repulsion forces between clay surfaces and humic substances will occur. However, the anionic character of organic acids is pH dependent and some adsorption is possible through H-bonding and van der Waals forces when pH falls below pKa of the acidic group (Stevenson, 1994).

Clays with permanent negative charge, such as smectite, are more likely to interact with humic substances in soil if Ca or Al ions are present, since these cations can form bridges between clay and humic molecules (Oades, 1989). Both entropy and enthalpy factors favour the formation of these complexes and humic substances are stabilized against decomposition (Parfitt *et al*., 1995). The type of bond between organic matter and clay depends on the type of clay minerals, surface cations, organic C species and soil moisture.

Parfitt *et al*. (1999) studied the interactions of soil organic matter with Al and allophane in Podsols using a ^{13}CNMR and found that the intense peak at 179 ppm (assigned to carbon in carboxylic acids) shifted to 177 ppm after removal of allophane using HF. This evidence led them to conclude that carboxyl groups in the organic matter are bonded to structural Al on the surface of allophane spherules. In addition, Huang *et al*. (1977 cited by Stevenson, 1994) found that the sorption capacity of soils for phenolic acids was significantly decreased by removal of sesquioxides, suggesting that the high sorption capacity of noncrystalline hydroxy Al and Fe complexes for phenolic acids was due to interaction of negatively charged carboxylate, COO$^-$ and phenol, O$^-$ groups with positively charged Al-OH$_2^{0.5+}$ and Fe-OH$_2^{0.5+}$ sites. Yuan *et al*. (2000) studied the interactions of allophane with humic acids and cations and reported that ligand exchange between a hydroxyl group attached to Al in allophane structure and a caboxylate group of the humic acid is the mechanism of this interaction.

Binding of organic anions by clay is possible when a polyvalent cation is present on the exchange complex, where the cation neutralizes the negative charge on the clay as well as the acidic group of the organic molecules to form a salt bridge (clay-M-OOCR) (Stevenson, 1994). This coordination reaction involves covalent bonding that occurs when the ligand donates electron pairs to a metal ion (Tan, 1993). This process could be assessed experimentally by addition of cations to increase sorption of organics on clay surfaces as shown in Figure 3. For example, the presence of cation bridging (Fe, Al, La, Cu, Ca, Mg, K) in montmorillonite can increase the amount of humic acid adsorbed (Figure 3). It seems that cations with higher valency such as Fe^{3+}, Al^{3+}, La^{3+} could promote more humic acid adsorption than cations with lower valency. Varadachari *et al*. (1991) found that sorption of humic acid on illite, montmorillonite and kaolinite varied with the cation added, decreasing in the order Al > Ca > Mg > K, Na. Quantitatively, the most important cations in soils are Ca^{2+} in neutral to alkaline soils and Al^{3+} in acid soils (Oades, 1988). There is substantial evidence that Ca^{2+}

acts as a bridge between clay plates, between functional groups on biopolymers, and between biopolymers, bacteria and clay surfaces (Oades, 1989). The neutral to alkaline soils such as Mollisols and Vertisols where Ca^{2+} is a dominant cation probably play a major role in preserving organic C.
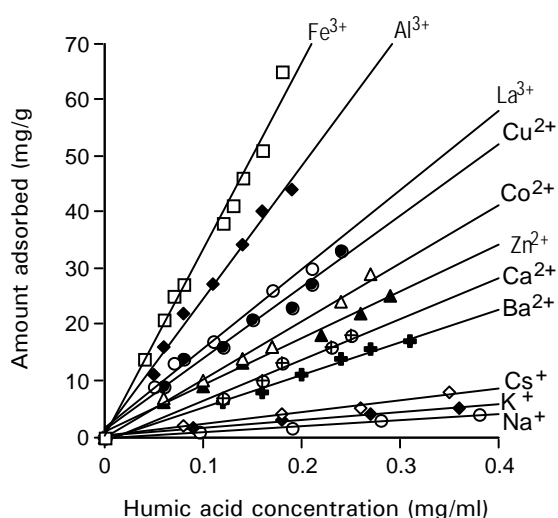

Figure 3. Isotherms for the adsorption at 293 K and pH 7 of humic acid by montmorillonite saturated with different cations (Theng and Scharpenseel, 1975)

In fact, data of 7 pedons of Mollisols from East Nusa Tenggara reported by Prasetyo *et al.* (1999) indicate that of the 16-46 me/100 g total exchangeable cations at 0-40 cm depths, 8-44 me/100 g was contributed by Ca^{2+}. Furthermore, data of 5 pedons of Vertisols from Madiun reported by Prasetyo *et al.* (1996) indicated that of the 36-70 me/100 g total exchangeable cations at 0-40 cm depths, 27-58 me/100 g was contributed by Ca^{2+}. Field evidence as indicated by dark brown colour (Hue of 10YR or 7.5YR and value and chroma of less than 3) may further support the role of Ca^{2+} in preserving the organic C.

Olk *et al.* (1995) reported humic acid bound to Ca is probably protected from chemical

and biological degradation through development of bonds to exchangeable Ca. Juste *et al.* (1975 cited by Baldock, 1989) postulated that the mechanism through which polyvalent cations alter the biological stability of humic materials involves a blockage of specific sites on the humic materials which are required by the microbial biomass to initiate the decomposition process, and a toxic effect of the polycations on the microbial biomass. In addition, they observed that for the Al^{3+}, Fe^{3+}, Zn^{2+}, and Cu^{2+} saturated humic materials a portion of the stabilization involved a toxic effect; however, no toxic effect was involved with the Ca^{2+} saturated materials.

Cation bridges are stable at high pH, which may explain the relative insolubility in NaOH of the organic matter in the fraction from 1 to 20 μm in diameter (Oades, 1989). In addition, cation bridges are supposedly destroyed by $Na_4P_2O_7$, although this has not been demonstrated unequivocally. The Ca may bridge functional groups in humic materials, thus shrinking the molecule by decreasing electrostatic repulsive forces on different strands of the "random coil," and may bridge the polymers to clay surfaces (Oades, 1989).

Anda *et al.* (2008a) used Al_p and Fe_p contents (extracted by Na-pyrophosphate), as a measure of cation bridging between SOM and soil minerals, in comparing an Oxisol having high organic C (3.4%) with other Oxisols having low organic C ($\sim$ 1.4%). They showed Al_p and Fe_p contents were much higher (31 to 108 times) in an Oxisol having high organic C compared to those in Oxisols having low organic C, leading them to conclude that organic C preservation in soils occurs through cation bridging.

Parton *et al.* (1994) attempted to quantify the effects of mineralogy during long term soil incubation for temperate and tropical soils with different clay mineralogy (smectite, kaolinite, oxidic and allophanic) and across a range of soil textures. They reported that the size of the passive pool is larger for oxidic and allophanic

mineralogy in comparison to kaolinitic and smectitic mineralogy. In addition, they stated that total SOM levels increased with increasing clay content, and the fraction of total SOM carbon in the passive fraction and the slow passive SOM turnover time increased linearly with increasing clay content. The fraction of the total C in passive SOM increased from 30 to over 50% as clay content increased from 10 to 50%.

Physical protection

The interactions of organic molecules with clay surfaces in aqueous system depend on the extent of available surface and the ability of the adsorptive molecules to displace cations or H_2O from the surface (Oades, 1989) as indicated in Figure 4. According to Theng (1979), besides acting as an aggregant, polymers can have a dispersive or protective effect on suspended solids when added in sufficient large quantity. This action is ascribed to the formation of a coat or layer of macromolecule around the solid particles, with loops and tails extending into the external solution (see Figure 4B). In addition, he noted that the organic polymers, look like long chains with flexible and polyfunctional ends. Chain flexibility and polyfunctionality further allow the polymer to adopt various shapes or conformation states at the clay surfaces and to be attached to the solid at different points (train) leaving loops and tail in solution.

Physical protection of substrates within micro- or macroaggregates occurs through physical barriers created between substrates and decomposers. Scanning electron microscope (SEM) clearly showed the organic matter that was physically protected within microaggregates (Figure 5). The coil or tail of organic matter is freely unprotected while other portions were fully encapsulated by clay particles. Hence, the
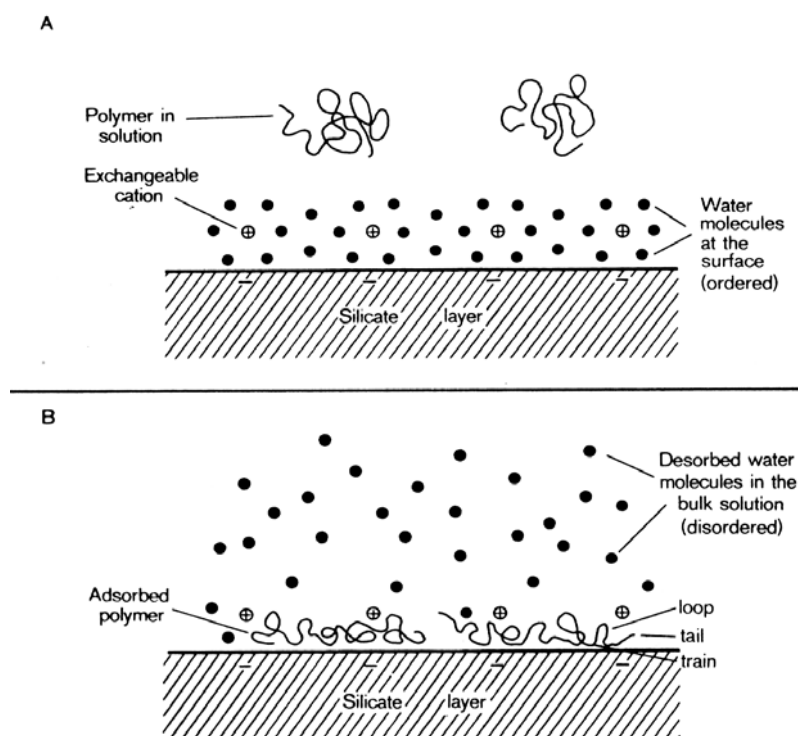

Figure 4. Adsorption of uncharged linear polymer on clay surfaces showing (A) polymer in solution with random coils, and (B) desorption of water molecules from a clay surface during adsorption of the polymer (Theng, 1979)

soil minerals of clay size fraction play the major role in protecting SOM decomposition.

Previous workers have shown a positive correlation between organic C content and clay content (Parton *et al*., 1987; Hassink and Whitmore, 1997). Recently, Anda *et al*. (2005) artificially modified soil texture where clay content was adjusted to 15, 30, 45, 60, and 75% by adding a proportion of sand (on weight basis) to a soil having high clay content. Each of these clay percentages was treated with organic C (rice straw origin) at 1, 2, 3, 4, and 5% rates. Most interestingly, their results showed a clear trend for the capacity of different clay
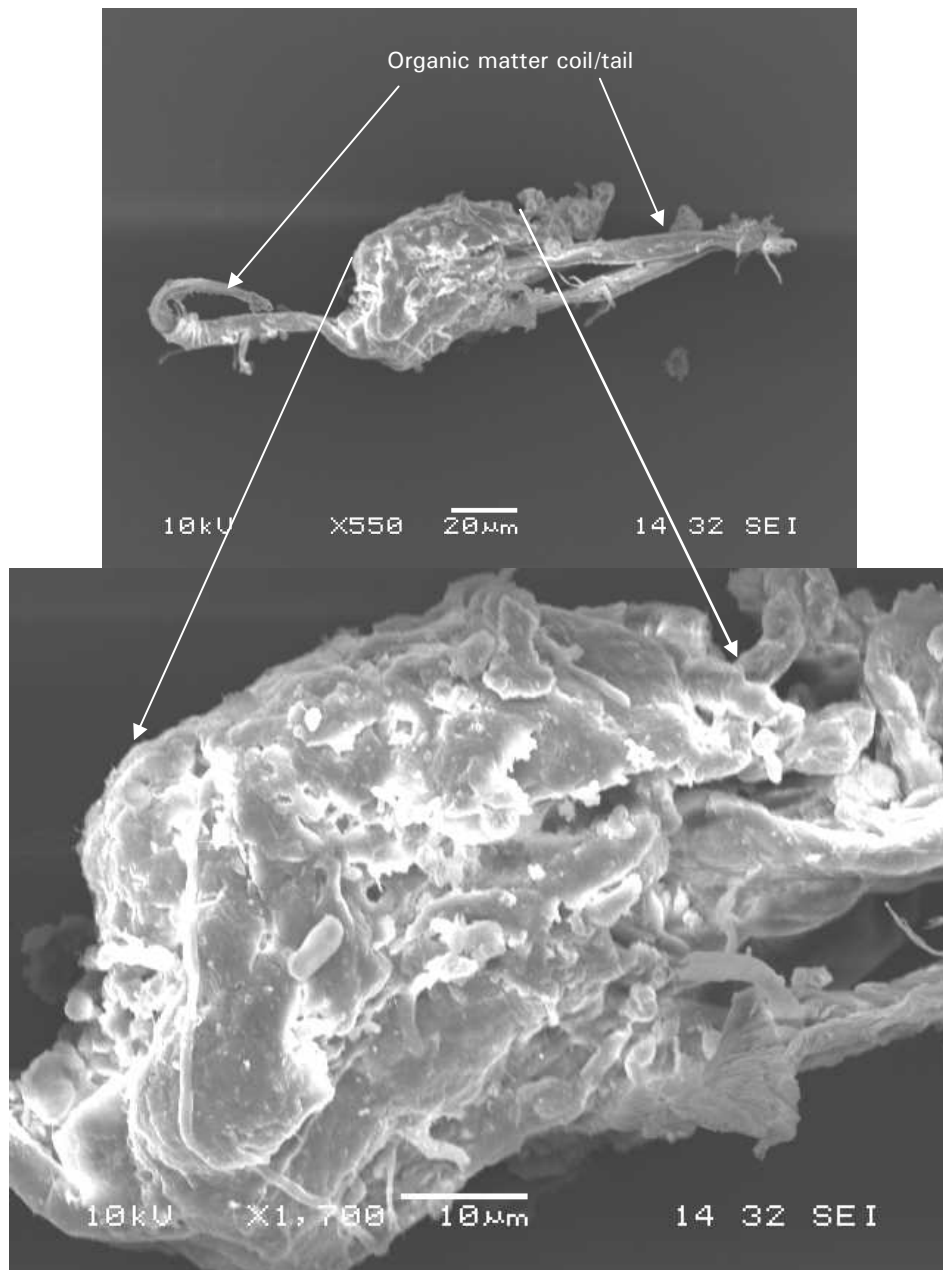

Figure 5. Scanning electron microscope showing the middle portion of organic matter was encapsulated by clay mineral particles (top picture) and enlargement of encapsulated portion (bottom picture) (Author's unpublished data)

percentages to preserve organic C content (Figure 6). The higher the clay content, the more organic C preservation at the same C application rate, confirming that the clay fraction in soils acted as an agent to preserve soil organic C through physical protection from microbial decomposers. The efficiency of stabilising active SOM into slow SOM is assumed to be a function of soil texture, with sandy soils being less efficient than fine textured soils (Parton *et al.*, 1987).

Skjemstad *et al.* (1996) using ^{13}C NMR with CP/MAS studied the chemistry and nature of protected C in Argixeroll, Haplustoll, Kandiustox and Pellustert at 0-10 cm depth and reported that the mechanism of long term protection of SOM against microbial decomposition is physical incorporation into microaggregates that are able to withstand physically disruptive forces. They also claimed that this mechanism is a dominant factor to protect SOM in strongly structured soils such as Krasnozem (Kandiustox). Anda *et al.* (2008c) studied mechanisms of SOM preservation in three heavy clay (73-82%) Oxisols under tropical conditions; they measured pore spaces

and specific surface area (SSA) with and without soil organic matter removal (using peroxide). Their results convincingly indicated that the volume of pore spaces, especially mesopores (2-50 nm), sharply increased after SOM removal. Similar situation is true for SSA. The increases in pore spaces and SSA after SOM removal suggested that SOM blocked the soil pores. In other words, under natural condition (without SOM removal), the SOM was physically protected within soil mesopores. Mayer (1994) found that the mechanism of stabilisation of organic matter is adsorption into small pores (<8-nm width) where slower condensation reactions can occur because of exclusion of faster, competitive biological reactions (hydrolytic enzymes).

In tropical Oxisols, Baldock *et al.* (1992) found alkyl C was the most dominant, indicating that alkyl C constitutes the most stable organic C. They reached this conclusion because alkyl C originated in plant and mychoryzal tissues and that microbial degradation was fastest in tropical soils. However, Capriel *et al.* (1990) suggested that inaccessibility rather than recalcitrance might be responsible for the stability of the alkyl
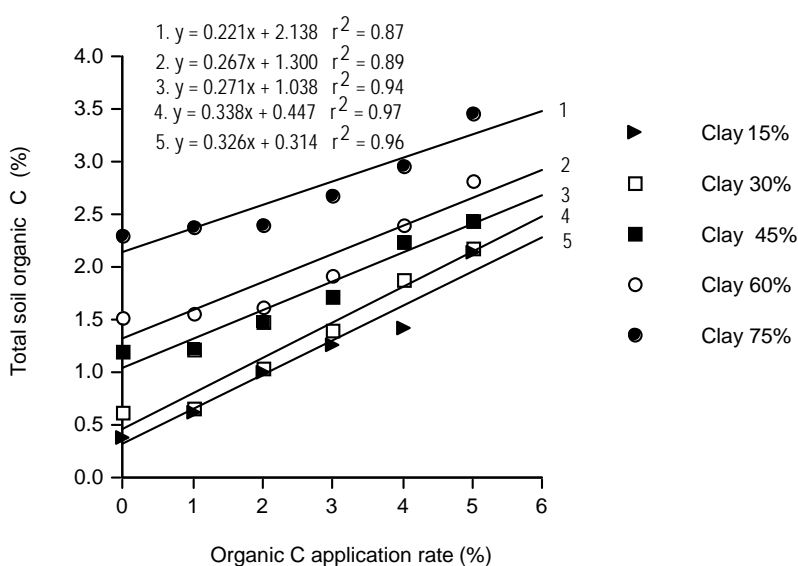

Figure with regression equations:
1. $y = 0.221x + 2.138$ $r^2 = 0.87$
2. $y = 0.267x + 1.300$ $r^2 = 0.89$
3. $y = 0.271x + 1.038$ $r^2 = 0.94$
4. $y = 0.338x + 0.447$ $r^2 = 0.97$
5. $y = 0.326x + 0.314$ $r^2 = 0.96$

Legend:
Clay 15%
Clay 30%
Clay 45%
Clay 60%
Clay 75%

Axes: Total soil organic C (%); Organic C application rate (%)

Figure 6. Correlation between soil organic C and organic C application rate for five clay percentages (Anda *et al.*, 2005)

C because the extracted alkyl C fraction had a degradability rate in between glucose and corn straw. Accessibility refers to the location of organic substances as it influences their access by microbes and enzymes (Sollins *et al.*, 1996).

Results obtained by several workers for the proportion of soil C contained in clay-organic complexes are given in Table 1. It can be seen that about 52 to 98% of the C in the soils examined was associated with clay. This evidence, again, confirms that the clay fraction of soils has high capacity to preserve organic C.

SURFACE REACTION OF ORGANO-MINERAL COMPLEXES

The main factor that controls interaction between a soil mineral (especially clay minerals) and SOM is the presence of negative and positive charges on mineral surfaces and SOM. Electrical charges in soils may be divided into permanent and variable charge components (Uehara and Gillman, 1981). Permanent charge is derived from isomorphous substitution, that is, the replacement of cations by others of nearly similar size and usually lower valency (Theng and Orchard, 1995). The substitution takes place mostly Al^{+3} for Si^{+4} within tetrahedral sheet and Mg^{+2} for Al^{+3} within octahedral sheet. These substitutions cause a net negative charge on clay surfaces. On the other hand, according to Tessens and Zauyah (1982) a positive permanent charge is the result of isomorphous substitution of Ti (IV) for Fe (III) in iron oxides. The variable charge component in soils arises on the edges of lattice clay minerals and on the surfaces of organic substances (e.g. carboxyl and phenolic groups), sesquioxides, amorphous materials such as allophane and imogolite (Figure 7).

The term variable charge was applied because the magnitude of the charge generated on mineral and organic substance surfaces depends on pH, ionic strength, nature of index ion, and metals and ligands in soil solution (Uehara and Gillman, 1980; Naidu *et al.*, 1997). The surface charge is generated by the adsorption of potential determining ions (H^+, OH^-) onto the surface. The negative variable charge is resulted through deprotonation and that positive variable charge through protonation on sesquioxides. The assessment of the presence of negative or positive variable charge in soils is usually carried out by determining a pH value where net variable charges (negative and positive) are zero, known as point of zero charge, pH_0 (Uehara and Gillman, 1980). The soils bear positive charge if the pH_0 value is higher than natural soil pH, whereas negative charge if the pH_0 is lower than natural soil pH.

Table 1. Proportion of soil organic C contained in the clay-organic complex

| Soil	Total C in soil	C in clay-organic complex
	%	% of total soil C
Renzina (Mollisols)	-	66.5
Podzol (Spodozol)	1.6	89.6
Chernozem (Mollisols)	4.4	85.2
Renzina (Mollisols)	5.8	54.3
Brown Earth (Alfisols)	3.2	68.1
Red Brown Earth (Alfisols)	2.2	71.5
Renzina (Mollisols)	5.8	68.4
Lateritic Red Earth (Oxisols)	1.7	97.8
Solodized solonetz	1.0	76.4
Solodized Brown soil	0.6	51.6

From Greenland (1965) *in* Stevenson (1994)

The importance of pH$_0$ determination is that its position on pH scale has great influence on the cation exchange capacity and anion exchange capacity of such soils (Gillman, 1985) and on the estimation of the soil net permanent charge (Uehara and Gillman, 1980). Once the net charge of variable charge component was zero, i.e. at pH$_0$, than the remaining charge was attributed to the permanent charge (Uehara and Gillman, 1981).

In Indonesia, variable charge soils could be found in Ultisols, Oxisols, Andisols and Podsols and probably some acid Inceptisols (Dystropepts). Anda (1999) measured the pH$_0$ within profiles of two Oxisols (Anionic Acrudox and Typic Kandiudox) and two Ultisols (Typic Paleudults and Typic Kandiudults). He reported that pH$_0$ values range from 3.5 to 5.7 for Oxisols and from 3.4 to 4.0 for Ultisols. Interestingly, one profile of Oxisols (Anionic Acrudox) had significantly lower pH$_0$ at soil surface (3.5) compared to pH$_0$ values in subsurface horizons (5.0-5.7). This difference is mainly due to the difference in organic C where a surface horizon has considerably higher organic C (3.3%) than the subsurface horizons (0.4-1.0%), indicating the ability of organic C to lower a pH$_0$ value by coating the mineral surfaces. In addition, the pH$_0$
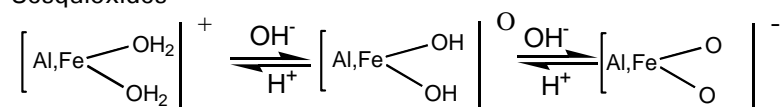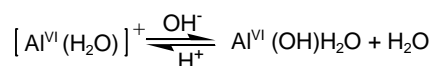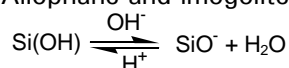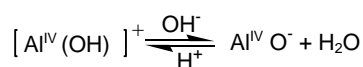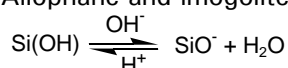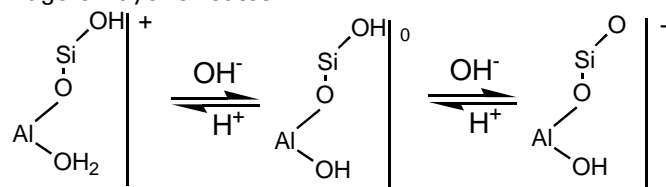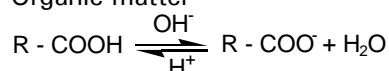

Figure 7. Mechanisms of charge generation on variable charge surfaces (after Wada, 1989 and Naidu *et al.*, 1997)

value is higher than the natural soil pH in subsurface horizons of Anionic Acrudox, indicating the soil colloids bear a positive charge.

The magnitude of pH_0 values is dependent on type of oxide present in soils. Table 2 shows the pH_0 value of Al and Fe oxides range from 5.3 to 9.4, whereas oxide of Si is much lower compared to Al and Fe oxides. This is due to SiO_2 which is a proton donor (Park, 1967 cited by Gast, 1977) causing the pH value to be lower. The high pH_0 values for Al and Fe oxides are probably due to hydroxyl groups that could be released from positive sides to the solution. Wada (1995) stated that interaction between polymeric hydroxy Al and Fe cations in Andisols having variable positive charge with humus may block carboxyl groups, which results in the development of pH dependent negative charge.

Table 2. Point of zero charge (pH_0) for soil oxides and short range order minerals

Mineral	Formula; Molar ratio	pH_0
Goethite	α-FeOOH	8.1
Hematite	α-Fe_2O_3	8.5
Gibbsite	γ-$Al(OH)_3$	9.4
Silica	$SiO_2.4H_2O$	2-3
Imogolite (natural)	$(OH)_3 Al_2O_3$ $SiOH; Al/Si = 2.0$	6.8
Allophane (synthetic)	$Al/Si = 1.74$	6.9
	$Al/Si = 1.43$	6.5
	$Al/Si = 1.15$	5.5
Ferrihydrite (natural)	$5 Fe_2O_3.9H_2O$	5.3-7.5

Source : Theng and Orchard (1995)

Anda *et al*. (2008a) studied the effect of soil organic C and iron oxides on negative charge of three Oxisols. They showed a negative linear correlation between soil organic C and pH_0. Interestingly, they found that every 1% organic C could lower a unit pH_0 value. This evidence suggests that soil organic matter was powerful in generating negative charge of highly weathered soils. Using stepwise linear regression, Gillman (1985) showed that soil organic matter accounted for 42% of variation in pH_0, and it increased to 68% when acid extractable phosphorus was included and finally to 78% following the inclusion of free iron.

The implication of all findings of mineral-SOM interaction, until the present knowledge, is the management of SOM. The SOM could be applied at high rate for soil having high clay content, since SOM was preserved through clay protection, while the soils having high sand fraction the SOM should be applied periodically to minimize SOM losses (e.g. CO_2 emission) due to rapid decomposition. At present, the great challenge is to obtain an organic matter source, having slow decomposition rates in order to increase its resident time in soils.

According to Baldock *et al*. (1992), the chemical structure of organic materials contained in the soil is controlled primarily by the chemical composition of the C inputs and the environment. Using OM sources with high polyphenolics content may promote C retention (Tian and Brussard, 1997) and counteract the rapid SOM losses in tropical climates (Shang and Tiessen, 1998). Cellulose and lignin constituents of organic matter are known to be relatively resistant against microbial degradation. It implies that organic matter sources containing high cellulose and lignin are very suitable to replenish organic matter loss and to preserve it in soils. Anda *et al*. (2008b) reported that rice husk compost (RHC) contained high cellulose with minor amount of lignin as revealed by solid CP/MAS ^{13}C NMR study. They also reported that volatile material loss was only < 6 % and the CO_2 production during mature composting was low and relatively constant, indicating RHC is resistant to microbial degradation. This suggests the promising potential of RHC to sustain C reserves, especially in tropical soils.

CONCLUSIONS

1. The association of soil minerals and organic matter involves anion and ligand exchange to the mineral edges, cation or water bridge to basal surfaces, H-bonding by van der Waals forces, entrapment in crystal pores, and adsorption in interlayer spaces.

2. The stabilization of soil organic matter (SOM) is controlled by amount of clay fraction, type of clay minerals and aggregate formation as indicated by the greater organic C preservation when the soils contain high clay content, more 2:1 minerals and amorphous minerals present, and larger aggregate sizes.

3. The mechanisms underlying SOM stabilization are: (i) chemical recalcitrance which involves elemental composition, the presence of functional groups, and molecular conformation of organic substances against decomposition by microbes and enzymes; (ii) chemical stabilization which occurs through adsorption of functional groups to clay mineral surfaces and amorphous sesquioxides involving various modes of interaction; (iii) and physical protection in which organic substances are protected physically by the clay fraction that limits the accessibility of microbes and enzymes.

4. Organo-mineral association resulted in organic matter coatings on soil minerals and is responsible for lowering pH_0 value, indicating the generation of soil negative charge.

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