**Online Resource to: Interaction of minerals, organic matter, and microorganisms during biogeochemical interface formation – What can we learn from artificial soils ?**

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Online resource 1: Contact angle and surface elemental composition

1. **Wetting properties**

The wetting properties as crucial parameter for biogeochemical interface functioning (e.g., sorption of polar or non-polar compounds, microbial attachment and colonization) have been determined in terms of contact angle (CA) with the sessile drop method for the 18 months maturation period, using a CCD equipped CA microscope (Goebel et al. 2013). With the exception of boehmite (CA = 0°) the mineral components had an initial CA of around 5-28°, while both the manure and the charcoal were hydrophobic (CA>90°). All mixtures were slightly water-repellent with CA <20°; i.e. with respect to wetting properties no effect of manure and charcoal addition was visible. This may have been the result of a diluting effect due to the high proportion of sand and silt-sized quartz particles. As function of maturation time, the CA either was more or less constant (compositions MT, IL and FH, Table 1, main text) or even had a tendency to decrease. However, an aging effect became apparent in the long term as composition MT and MT+CH (Table 1, main text) showed slightly increased CA (to about 20-29°) after dry storage in closed containers for about five and four years, respectively. All CA decreased within five seconds to about 0°, thus hindrance of microbial life due to fragmented water films on the particle surfaces was unlikely.

1. **Surface elemental composition: X-Ray Photoelectron Spectroscopy**

As a closed system, chemical bulk composition of the artificial soils was constant during maturation time. To check for surface-specific changes in chemical composition, X-ray photoelectron spectroscopy (XPS) served as a suitable tool. Bombardment of the surface with X-rays results in the emission of photoelectrons (PE) with element-specific binding energy (BE), allowing identification of the emitting atom (for details on XPS technology we refer to e.g. Watts and Wolstenholme 2003). Due to the inelastic mean free path of PE in solid media, the analysis depth is restricted to a maximum of about 10 nm. Quantification of survey spectra in the range between 1200 – 0 eV thus gives the elemental composition of the topmost surface layer. Before measurement, the samples are fixed on a sample  Fig. ER1-1: Surface elemental composition of artificial soil mixtures MT (montmorillonite) and MT+CH (montmorillonite + charcoal) with maturation time as derived from XPS analysis. Additionally shown is the relation between surface O and C concentration, combined for all samples tested (first row, right side).

Bar with carbon conductive tape (Agar Scientific, Elektron Technology UK Ltd., Stansted, UK; sample size about 0.25 cm2). Three spectra per sample were recorded, each comprising an area of 300 × 700 µm. XPS analysis of artificial soils MT and MT+CH (Table 1, main text) for the starting material (0 months) and 3, 12, and 18 months maturation time indeed revealed changes in the surface elemental composition (Figure ER1-1). Generally, both mixtures showed comparable features, however, some characteristic differences could be observed. Addition of charcoal resulted in higher C contents for MT+CH compared to MT over the whole maturation period, while both mixtures showed highest C concentration for the 12 months sampling. This may have been associated with the patchy attachment of OM on clay particles found by Heister et al. (2012). The O concentration mirrored the C concentration, resulting in a high correlation between C and O (*r*2 = 0.9) that has been observed before (Schampera et al. in press). Concentration of the exchangeable cations (Na, K, Ca, Mg, Al) increased with incubation time with closest correlation for K (*r*2 >0.9, P <0.05). This can be explained by cation exchange processes between soil solution (CaCl2) and montmorillonite. As the exchanged cations could not be removed from the closed system, they increasingly accumulated on the surface. While the Si concentration of MT only tended to decrease from maturation start to 18 months, the Si concentration of MT+CH showed a close negative correlation with maturation time (*r*2 = 0.8) and accordingly a close correlation with the exchangeable cations concentration (*r*2 >0.9 for Na, Ca, K, Mg and *r*2 = 0.7 for Al, respectively). The same correlative trends were indicated for MT (*r*2 0.5-0.7). This may be explained by the formation of a surface layer with increasing thickness that reduced the amount of pure montmorillonite and quartz within XPS analysis depth. In line with bulk analysis (Pronk et al., 2012) due to charcoal addition, the surface C/N ratio at the start of the experiment (0 months) was notably higher for MT+CH than for MT; accordingly only MT showed a close correlation between C and N concentration (*r*2 = 0.98). Particle wetting properties are determined by the kind and orientation of functional groups within the outmost first nm (Ferguson and Whitesides 1992). The shallow XPS analysis depth thus allows a nearly direct correlation of chemical composition and CA. In a general approach, two subpeaks were fitted to the C 1s peak, representing polar (hydrophilic) and non-polar (hydrophobic) C species. In agreement with the observed CA, the contribution of non-polar to total C species for all samples was only small (<15% of total C) (data not shown). Additionally, the accumulation of cations within the surface layer, probably as chlorides, revealed by XPS analysis might have contributed to the good wettability.

**References**

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