

**Co-Evolution of soils and organic substances:  
Links between soil forming processes and the  
stabilisation of organic substances**

2nd - 4th March 2011, Landau / Pfalz - Germany

Conference guide and abstracts



## Conference topic

Soil forming processes such as weathering, formation of secondary minerals and aggregation control the stability of soil organic matter and of synthetic organic substances in soils. Soil forming processes are involved into the formation of organo-mineral associations, occlusion of organic matter, fixation of biomolecules or the formation of bound residues.

On the other hand, the accumulation of organic matter contributes to soil formation and affects other soil forming processes like aggregation or the formation of minerals. Thus, interactions between soil formation and the stabilisation of organic substances being in the centre of our workshop are of high relevance for resulting soil properties as well as for the fate of pedogenic matter and synthetic organic molecules in soils. Soil organisms affect these interactions as they transform and decompose organic matter and influence other soil forming processes (aggregation, weathering).

We will focus on the link between recent methodological innovations from physics and chemistry and new concepts and results from soil chemical, soil biological and mineralogical research. We hope that concepts on the mechanisms of organic matter stabilisation will inspire the research concerning the formation of soil bound residues and vice versa.

## Organising committee

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<b>Time</b>	<b>Wednesday 2 March, 2011</b>	
13:00	Registration	
13:30	Opening & welcome	
<u>Session 1: Changes of quality and quantity of organic matter along with soil development</u>		
14:00	<i>Peter Buurman</i> (Keynote)	<i>Co-evolution of soils and soil organic matter – a soil scientists' view</i>
14:45	Daniela Sauer et al.	Soil development in climatically different periods in S Italy
15:05	Felix Heitkamp et al.	The modifying effect of lime bands on the partition-ning of soil organic matter into pools of different stability in a long-term fertilization experiment
15:30	Coffee break	
16:00	Christian Heller Jutta Zeitz	Stability of SOM in mires and peatlands depending on parent material and soil forming processes
16:20	Christian Siewert Jiří Kučerík	Clay and water binding as a fingerprinting base for detection of virgin soils
16:40	Antonio Nebbioso et al.	Humeomics for a structure-bioactivity relationship of Humic Substances
17:00	1 <sup>st</sup> poster session	
18:00	Dinner	
19:30	Icebreaker: Wine tasting „Weingut Schunck“	

<b>Time</b>	<b>Thursday 3 March, 2011</b>	
<u>Session 2 + 3: Processes of co-evolution</u>		
09:00	<i>Ingrid Kögel-Knabner</i> (Keynote)	<i>Processes of initial soil organic matter formation</i>
09:45	Anja Miltner et al.	SOM genesis - Microbial biomass as a significant source
10:05	Karin Eusterhues et al.	Fractionation and stabilization of soil organic matter due to reaction with ferrihydrite
10:30	Coffee break	
11:00	Thilo Rennert et al.	Geogenic CO <sub>2</sub> affects mineral and organic soil constituents on a mofette site
11:20	Ruth Ellerbrock et al.	Analyzing effects of polyvalent cations on long-term composition of stable soil organic matter fraction
11:40	Markus Graf Friederike Lang	Soil formation and stabilisation of soil organic matter in riverine floodplains
12:00	Lunch	

14:00	<i>Claire Chenu</i> (Keynote)	<i>Insights into the physical stabilisation of soil organic matter at the microscale</i>
14:45	Makiko Watanabe Nobuo Sakagami	Status of sclerotia of <i>Cenococcum geophilum</i> as structured SOC from studies in Harz mts., central Germany
15:05	Sandra Spielvogel et al.	Soil type specific stabilization of cutin- and suberin -derived compounds in SOM pools with different functions and turnover times
15:30	Coffee break	
16:00	Daniel Tunega et al.	Interactions of organic pollutants with soil components investigated by means of molecular modelling
16:20	Thomas Wutzler et al.	Modelling the soil organic matter profile development
16:40	Heinz Friedrich Schöler et al.	The abiotic degradation of soil organic matter
17:00	Pellegrino Conte et al.	Use of char from industrial thermo-chemical processes to improve soil quality
17:20	Discussion session on the basis of impulse statements	
	2 <sup>nd</sup> poster session	
18:30	Dinner	

Time	Friday 4 March, 2011	
Session 4: Relevance of co-evolution for the retention of xenobiotics in soils		
09:00	<i>Joseph J. Pignatello</i> (Keynote)	<i>Insights into dynamic events taking place during sorption of xenobiotics by natural organic matter and black carbon</i>
09:45	Tatjana Schneckenburger et al.	Influence of water-induced SOM alterations in peat on sorption behaviour of xenobiotics
10:05	Anastasia Shchegolikhina Bernd Marschner	Effects of cation saturation and aging on extractability of nonylphenol and phenanthrene from soils
10:30	Coffee break	
11:00	Jaane Krüger Friederike Lang	Restructuring of mineral-organic associations upon drying: Processes and relevance for the sorption of MCPA and phenanthrene
11:20	Tanja Müller et al.	Instantaneous reduction of sulfadiazine extractability after spiking to soil
11:40	Final discussion & concluding remarks	
12:45	Lunch	
14:00	Excursion	

## **Co-evolution of soils and soil organic matter – a soil scientists' view**

*Peter Buurman*

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To consider co-evolution of soil and SOM, circumstances for the formation of both must be similar. This virtually excludes (the study of) co-evolution of SOM in very old soils, such as Oxisols. SOM composition is very strongly related to vegetation (up to 50% of chemical variation), and therefore climate change interferes with the concept of co-evolution: every change of climate and vegetation induces a new phase of development that may be completely independent of the previous one. Topsoil and subsoil have different dynamics (MRTs), and the question arises whether they are in equilibrium with each other. The same considerations should be applied for free and mineral-bound SOM. If the mineral-bound fraction forms early in the soil formation process, its <sup>14</sup>C 'age' may reflect age rather than MRT, while in free fractions it reflects MRT. Can we find out whether this happens?

The general increase of MRT with depth in a soil profile is also reflected in the fraction of stable (non-oxidizable) carbon. In Ferralsols and Acrisols of Colombian Amazonia, this fraction may increase from 10% of total C in topsoils to 70% in subsoils, but the fraction appears to change rapidly upon change of land use. This suggests that co-evolution of SOM and soil development is a labile system.

Some soils need to pass a certain stage of development before they reflect their present SOM chemistry. This is clearly the case in Andosols and Podzols, where the earlier stages of formation are essentially different from the mature ones. In podzols, morphology allows a detailed sampling of different kinds of organic matter. A Brazilian podzol sequence clearly shows a relation between hydrology and chemical composition of E and B horizons. Contrary to podzols of temperate climates, the well-drained types may have a considerable microbial SOM fraction in the E horizon, due to decay of the upper-B horizon.

Strong aggregation stops the co-evolution of occluded SOM and the soil, because the chemical evolution of the occluded, and the free and extractable fractions moves in a different direction.

As a whole, co-evolution of SOM and soil is difficult to trace in advanced stages of soil development because SOM has a long memory, and some fractions adapt more rapidly to changed circumstances than others. In young stages of soil development, development of soil properties and vegetation may evolve simultaneously, so that each stage reflects vegetation development rather than an intrinsic evolution of the SOM fraction.

notes:

## Processes of initial soil organic matter formation

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Knowledge on the initial phase of soil organic matter formation is scarce, as most investigations are carried out in mature soils. The presentation will summarize information on the early stages of soil organic matter formation resulting from laboratory incubation experiments as well as field chronosequence studies. The accumulation of soil organic matter may be controlled by the type of particle surfaces present and the assemblage of organic matter with mineral particles. This was studied with artificial soils which were produced in a long-term biogeochemical laboratory incubation experiment that used clay minerals, iron oxides and charcoal as major model components. Already after 6 months of incubation the artificial soils exhibited different properties in relation to their composition. Retreat of glaciers resulting in the exposure of pristine glacial till to atmospheric weathering conditions provides a unique set-up to understand how mineral weathering and soil formation control SOM accumulation. We studied the accumulation of SOM after retreat of the Dammaglacier in the Central Alps, Switzerland, where the proglacial area offers a time sequence from three classes of surface age (ca. 15 yrs, 60 – 80 yrs, 110 – 140 yrs), and mature soils outside the proglacial area older than 700 years. The OM loading of the clay fractions increases from 44 mg g<sup>-1</sup> in the young soils to 190 mg g<sup>-1</sup> in the 110 - 140 year old soils and to 323 mg g<sup>-1</sup> in the mature soils. This leads to decreasing specific surface areas of the clay fraction as determined by N<sub>2</sub>-adsorption (BET approach). A strong correlation is found between increasing ferrihydrite contents (determined as oxalate-soluble iron) and increasing OM contents of the clay fraction with soil formation. H<sub>2</sub>O<sub>2</sub> resistant OC also increases with soil age, again strongly correlated with increasing amounts of ferrihydrite in the clay fraction. This implies a major role of ferrihydrite for the stabilization of OM during initial soil formation in these acid soils. Formation of organo-mineral associations starts with the accumulation of O/N-alkyl C in the proglacial area, which is in line with hydrolysable neutral sugar contents of the clay fractions. Accumulation of alkyl C is detected at a later stage only in the mature soils. These results clearly demonstrate the specific role of soil minerals for the early phase of SOM accumulation.

notes:

## **Insights into the physical stabilisation of soil organic matter at the microscale.**

*Claire Chenu*

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The importance of the soil forming process of soil structure development in soil organic matter stabilization has been recognized and extensively studied in the last two decades. While the protection of organic matter in macroaggregates was first considered, the attention is now focused on finer spatial scales of soil structure: protection of soil organic matter in sand-sized, silt-sized and even clay-sized aggregates. Such structures are associated with older organic matter, seem to offer protection over decades or more, and are meaningful regarding the ecology of microbial decomposers of soil organic matter.

This presentation addresses several questions concerning the physical protection of soil organic matter at the microscale, based on studies developed on silty soils under temperate conditions.

What is the relative importance of microaggregation in silt-size aggregates versus adsorption to clay size minerals in SOM storage and stabilisation? We used parallel fractionation methods with different dispersion intensities combined with HF demineralisation to estimate adsorbed OM. We found that 34-64% of TOC was stored within silt-size aggregates in a Haplic Luvisol and 34-40% in a Plinthic Cambisol and the relative importance of silt size aggregation and adsorption on OM storage and age depended on depth and soil type.

What is the turnover rate of silt-size microaggregates? The rate of young OM incorporation in microaggregates and the turnover rate of C suggest that their turnover would be of a few years at most. It shows that even at fine spatial scales, the turnover of SOM cannot be decoupled from that of soil structural units.

Have mineral amendments an impact on C stabilisation in the long term, via changes in soil structure? We used a long term bare fallow experiment, where the organic matter is older than 80 years, that includes treatments improving (e.g.  $\text{CaCO}_3$ ) or degrading (e.g. KCl) soil structure, to quantify the additional – or not- preservation of organic matter.

The “aggregate based approach” as developed here, is compared to a “pore based approach” of the physical protection of organic matter at the scale of microorganisms.

notes:

## **Insights into Dynamic Events Taking Place During Sorption of Xenobiotics by Natural Organic Matter and Black Carbon**

*Joseph J. Pignatello*

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Sorption controls the fate and effects of organic xenobiotics in soils and sediments by regulating the fraction that is mobile or bioavailable. The predominant sorbents of most organic compounds in soils and sediments are the natural soil organic matter (SOM) and black carbon (BC) fractions. Of the many hundreds of studies published on sorption in these materials, most have focussed on correlations between sorption strength and solute structure or bulk properties of the sorbent. The paradigm of the sorbent historically has been that of a passive matrix. Only a minority of studies have attempted to examine what really happens at the microscopic scale, and fewer still on the dynamics of sorbent structure (and solute structure, in some cases) during the sorption/desorption process. This lecture addresses questions related to sorption specificity, physical alteration of the sorbent during the sorption/desorption process that feeds back on sorption/desorption, and speciation shifts in the solute induced by the solid.

Sorption nonlinearity in SOM—indicative of sorption site heterogeneity—is typical, even for nonpolar compounds, and even for purified humic acid materials. Using spin probes and  $^{13}\text{C}$ -NMR for a peat soil and a lignite coal we have shown that sorption is remarkably non-specific with respect to functional group identity of the C; this likely means that functional groups are well-mixed at the nanometer scale, and that sorption specificity probably exists as a consequence of the physical structure of the solid. We have proposed that nonlinearity is due in part to the presence of voids within the solid (unrelaxed free volume) that serve as preferential “adsorption” sites. We have shown that sorption causes inelastic expansion of the solid matrix, which, in turn, leads to creation of new void volume. This phenomenon is a cause of true hysteresis, which we have termed ‘pore deformation hysteresis.’ Matrix flexing appears also to be a secondary process contributing to sorption or desorption retardation. Matrix swelling takes place in charcoal BC, as well. Accumulating circumstantial evidence links the swelling/shrinking cycle that takes place during sorption/desorption to physical entrapment of a small fraction of the sorbate in pores. This may be one explanation for the formation of bound residues. Finally, examples are given of solute speciation shifts induced by adsorption of ionizable compounds to BC.

notes:

## **Soil development in climatically different periods in S Italy.**

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Detailed reconstructions of palaeo-vegetation and palaeo-climate in S Italy for the Late Pleistocene, based on pollen from lake sediments, have been published in the past decades.

The pollen record of Lago Grande di Monticchio shows for 127.2-115.8 ka forest with *Quercus* and Mediterranean taxa; for 115.8-109.5 ka forest with *Abies*, *Alnus* and *Betula*; for 109.5-107.6 ka high abundance of *Betula* and steppe taxa; for 107.60-90.65 ka temperate deciduous forest; for 90.65-87.98 ka *Artemisia* steppe; for 87.98-82.73 ka temperate deciduous forest; for 82.73-59.00 ka fluctuation, then *Artemisia* steppe; for 59.00-25.90 ka alternation between steppe (stadials) and wooded steppe (interstadials); for 25.90-14.30 ka steppe (Last Glacial Maximum). Questions of the ongoing work presented here are: Which soil features are related to Mediterranean climate, and which correspond to steppe environments during glacial periods? Can we find steppe soils in S Italy? Soil profiles were described and analysed on sequences of marine terraces in S Basilicata and Calabria. In addition, buried soils in an alluvial fan in Calabria were included. Soils on marine terraces, formed during the Last Interglacial period, are reddish-brown and show distinct clay coatings. Soils on older terraces become more reddish with age, whereas soils on loess and Holocene sediments are brown and show no or very thin clay coatings. Dark paleosols in the alluvial fan with evidence of high palaeo-bioturbation reflect periods of steppe environments. Such soils have been preserved only where they had been buried before the climate shifted again to a typically Mediterranean one. Otherwise, their characteristically high amounts of organic matter were probably rapidly decomposed and the soils changed into reddish-brown Mediterranean soils.

notes:

## **The modifying effect of lime bands on the partitioning of soil organic matter into pools of different stability in a long-term fertilization experiment.**

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Effects of fertilizer type (e.g. organic vs. mineral) and rate on total stocks of soil organic carbon (SOC) in cropland soils are well known from data of long-term experiments, predominantly on loamy soils. Samples were taken from plots of the fertilization experiment (strip plot design,  $n = 4$ ) at Darmstadt, Germany, founded in 1980. The soil was classified (FAO 2006) as Ferric Arenosol (Eutric). Treatments were (a) application of farmyard manure at high ( $140 \text{ kg N ha}^{-1}$ ; FYMH) and (b) low rate ( $60 \text{ kg N ha}^{-1}$ ; FYML) and application of mineral fertilizer with cereal straw incorporation at (c) high (MSIH) and (d) low rate (MSIL). We tested (i) how fertilizer type and rate affected the partitioning of C into pools of different stability and (ii) how spatial heterogeneity affected the results. Applying a simple model with first order kinetics and two pools (turnover times of very labile and labile pools: 17 and 462 days, respectively) on mineralization data ( $10^\circ\text{C}$ , 55% water filled pore space, 266 days) revealed, that only the fertilizer rate affected the labile pool, whereas a calculated intermediate pool was affected by fertilizer type and showed higher C storage in the FYM soils. Density fractionation ( $\rho=2.0 \text{ g cm}^{-3}$ ) showed that higher recalcitrance of SOC in the FYM treatments induced higher SOC stocks. Light fraction C (LFC, apparent turnover time calculated after C3/C4 vegetation change: 21-32 years) was in the order  $\text{MSIL} = \text{MSIH} < \text{FYML} < \text{FYM}$ . The general high proportion of LFC on SOC (45-55%) indicated the relatively low importance of C-stabilization on particle surfaces. Using Ordinary Kriging, a map revealed the specific distribution of pH induced by shell-derived lime bands across the experimental area. The pH interacted strongly with microbial biomass C and respiration and showed interaction with the treatment for these indices. After 266 days, cumulative C mineralization in the FYMH treatment for example, was about  $2 \text{ t ha}^{-1}$  at pH 6.8 but 25% less at pH 6.1. Furthermore, the proportion of organic C in the heavy fraction was weakly positively related to pH. Overall, the effect of fertilizer type and rate on C-partitioning was modified by spatial distribution of lime-bands in the sandy soil of the Darmstadt experiment.

notes:

## **Stability of SOM in Mires and Peatlands depending on Parent Material and Soil Forming Processes.**

*Christian Heller, Jutta Zeitz*

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Mires and peatlands play an important role in the global carbon cycle due to their high organic soil contents, caused by waterlogged conditions. The C-vulnerability of these soils depends- among other external environmental factors- on the quality of the substrate, i.e. its potential for decomposition and mineralization.

The quality of peatland soils can be described in terms of so-called 'horizon-substrate-combinations' (HSC), according to the German soil classification system (KA5). These HSC describe the parent material (here: 'peat-forming plant') in combination with its soil forming processes (e.g. degree of decomposition, level of drainage and degradation) and cover a wide range of different substrate qualities (e.g. Sphagnum-derived vs. Carex-peat, drained vs. undrained peat etc.).

An exact differentiation, with special notice to substrate quality and C-vulnerability within the great number of different peatland soils and substrates (WRB-classification: Histosols), has not been made so far. Particularly, the question of how strong the peat forming- plant and/or the soil-forming processes influence the C-vulnerability of different peat soils, is our great research interest.

Previous investigations identified statistically significant HSC depending on the peatland area size, and specified them for the four most important mire and peatland types in Germany. In the present study, geographical positions of these specific HSC were allocated, and peat samples were taken to the laboratory and analyzed.

Some SOM fractionations, to characterize the C-vulnerability of different peat substrates, are now in progress. Therefore we estimate the readily mineralizable SOM by hot-water-extraction and a much more resistant pool by acid hydrolysis. In addition, some incubation-experiments were made to measure the CO<sub>2</sub>-production. First results will be given, methodical problems will be pointed out and discussed.

notes:

## **Clay and water binding as a fingerprinting base for detection of virgin soils.**

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Monitoring of soil changes is an important issue for sustainable soil use, protection and remediation. It should include a possibility to distinguish soils from carbon containing mineral substrates, gardening moulds, composts and artificial soils by intrinsic soil features formed during long term processes in ecosystems.

For this purpose, we tried to create a reference base using virgin soils, not affected by human activities, originating from different regions and climatic zones. These data were compared with samples collected from sites which were exposed to different land use. This fingerprinting approach was derived from gen-biology, supposing soil formation as a product of co-evolution during history of Earth. Experiments were focused on the detection of bound water loss depending on the increase of temperature in order to consider

1. theories about water binding on clay surfaces as a starting point for the evolution of genes in the first stage of life on Earth,
2. the importance of water supply for interactions between organisms and their environment on terrestrial conditions,
3. the reflection of water supply in similar soil type formation in regions with distinguishing organism communities (vegetation and fauna) and organic matter composition.

Obtained results confirmed literature data about water binding on clay in soils and correlations between clay content and thermal mass losses at temperature around 125 °C. Further, it was also confirmed the influence of clay on humus accumulation by correlations of the clay content with thermal mass losses around 525 °C. Mass losses recorded both at 125 °C and 525 °C can be used for detection of the clay content (Siewert, 2004).

Those clay-related dependences imply their mutual relationship. Surprisingly, this connection is valid only for soils but not for other samples such as carbon containing substrates; in artificial and black carbon containing soils this correlation significantly disturbed. We conclude the water binding by clay and/or organic substances could be a possible starting point for the development of methods useful for unravelling of intrinsic soil properties.

notes:

## **Humeomics for a structure-bioactivity relationship of Humic Substances.**

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Humic Substances (HS) represent a class of naturally occurring organic compounds and are commonly found in soils, sediments and natural bodies. They have an effect on environment's physical-chemistry and biology, influencing quality and fertility of soil. The heterogeneous and complex nature of humic components represents the main difficulty against the chemical characterization and structure elucidation. Recent findings support the hypothesis that HS are organized in supramolecular architecture: simple molecules held together by weak bonds, allowing for characterization of single compounds with appropriate analytical methods, such as NMR and mass spectrometry (MS). A humic acid (HA) from a volcanic forestal soil (Allic Fulvudand) was analyzed with such approach. Analysis showed in organosoluble fractions a content of linear aliphatic and, to a lesser extent, aromatic compounds. In hydrosoluble fractions several compounds with a chemical formula similar to saccarides suggested by high content of oxygen and nitrogen atoms are detected. In the final residue quantitative assessment shows aromatic (mostly quaternary)>aliphatic>carbonyl molecules in order of abundance. From NMR relaxation time measurements, a more rigid architecture is attributed to this material with respect to the starting HA. Mass spectrometry revealed formulas with great oxygen substitution and unsaturation, attributed to the NMR signals in sp<sup>2</sup> carbon region. MS analysis of the final residue showed for fatty acids an increase from the first to the tenth HPSEC fraction in the ratios between 1) short and long chained homologues and 2) hydrophilic and hydrophobic homologues, suggesting a correlation between chemical composition and hydrodynamic properties. A comprehensive description of all components of HS, defined as "Humeomics" would bring an important achievement for research in agrarian and environmental chemistry.

notes:

## **SOM genesis - Microbial biomass as a significant source**

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SOM plays an important role for soil fertility, and C sequestration in soil organic matter (SOM) is discussed as a means to mitigate the global increase of the atmospheric CO<sub>2</sub> concentration. SOM formation and its interaction with soil forming processes, are, however, not yet understood sufficiently for the development of proper management options. Recently, microbial biomass residues have been identified as a significant source for SOM. We therefore studied the fate of microbial biomass in soil by incubating <sup>13</sup>C-labelled bacterial cells in a soil and traced the fate of the <sup>13</sup>C label of bacterial biomass in the soil by isotopic analysis. We summarise the mass balance data and visualise the microbial biomass and its residues by scanning electron microscopy (SEM). In addition, the formation of microbial residues during pedogenesis was followed by SEM and PLFA analysis of samples from a glacier forefield chronosequence. The results of the incubation experiment indicate that a high percentage of the biomass-derived carbon remains in soil for extended periods of time, mainly in the non-living part of SOM. The SEM micrographs only rarely show intact cells. Instead, organic patchy fragments of 200-500 nm size are abundant. These fragments are associated with all stages of cell envelope decay and fragmentation. Similar fragments develop on initially clean and sterile in situ microcosms during exposure in groundwater providing evidence for their microbial origin. In the glacier chronosequence, the contribution of the microbial derived material increases with proceeding soil development, underlining the stabilisation of microbial residues in soil. Microbial cell envelope fragments thus contribute significantly to SOM formation. This origin and macromolecular architecture of SOM is consistent with most observations on SOM, e.g. the abundance of microbial-derived biomarkers, the low C/N ratio, the water repellency and the stabilisation of microbial biomass.

notes:

## Fractionation and Stabilization of Soil Organic Matter Due to Reaction with Ferrihydrite

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Ferrihydrite, a poorly crystalline Fe oxyhydroxide, is known to be highly reactive towards soil organic matter (OM) and may play an important role in its long-term stabilization. In soil, ferrihydrite formation takes place in the presence of dissolved OM. This disturbs crystal growth and gives rise to coprecipitation of ferrihydrite and OM. To investigate the consequences of coprecipitation, we prepared a series of ferrihydrite-organic matter associations by adsorption as well as coprecipitation using the water-extractable OM of a Podzol forest-floor layer. The reaction products were studied by <sup>13</sup>C CPMAS NMR, FTIR, and analysis of hydrolyzable neutral polysaccharides. Liquid incubation experiments were carried out to quantify the biodegradation of the ferrihydrite-associated OM (pH 5, 68 days, inoculum extracted from the forest-floor).

Relative to the original forest-floor extract, the ferrihydrite-associated OM was enriched in polysaccharides but depleted in aliphatic C and carbonyl C, especially when adsorption took place. Moreover, mannose and glucose were bound preferentially to ferrihydrite, while fucose, arabinose, xylose and galactose accumulated in the supernatant. This fractionation of sugar monomers was more pronounced during coprecipitation and led to an enhanced ratio of (galactose + mannose)/(arabinose + xylose). Incubation experiments showed that 7% of the original forest-floor extract was mineralized after 68 days, whereas a C mineralization of ferrihydrite-associated OM (adsorbed or coprecipitated) was not detectable during the first 13 days. In the following days a slight increase was observed, but assumed to be caused by processes such as excretion, cell lysis and enzymatic hydrolysis.

The fact that the composition of coprecipitated OM differs from surface-adsorbed OM is of particular interest for our understanding of stabilization mechanisms and turnover rates of carbohydrates. Since the attachment of OM to Fe-oxide surfaces strongly reduces its biodegradation, our findings may explain why labile polysaccharides contribute significantly to the refractory C pool and why the mineral-associated soil OM often shows a high GM/AX ratio.

notes:

## Geogenic CO<sub>2</sub> affects mineral and organic soil constituents on a mofette site

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Geogenic CO<sub>2</sub> on mofette sites may be an important soil-forming factor. We studied soils (0–60 cm depth) along a transect across a mofette in the NW Czech Republic by determining soil CO<sub>2</sub> partial pressures ( $p(\text{CO}_2)$ ), contents of C, N, S, and dithionite- and oxalate-extractable Fe and Mn. X-ray diffractometry (XRD) and Fourier-transform infrared (FTIR) spectroscopy were applied to the soils' particle-size fractions. Spatially resolved Fe mineralogy was determined by scanning transmission X-ray microscopy. The CO<sub>2</sub> partial pressures largely varied along the transect (0.001–1) and were positively correlated with both the C<sub>org</sub> contents (5.5–432.9 g kg<sup>-1</sup>) and the C/N ratio (9.3–32.2). When the soil atmosphere was entirely composed of CO<sub>2</sub>, contents of pedogenic Fe oxides were low (minimum 0.5 g Fe d kg<sup>-1</sup>) and poorly crystalline. XRD and FTIR spectroscopy revealed primary and secondary minerals such as quartz, feldspars, mica, illite, kaolinite and halloysite irrespective of CO<sub>2</sub>.

A pronounced effect of CO<sub>2</sub> was found for soil organic matter (SOM), because the FTIR spectra did not reveal the usual accumulation of alkyl C and lipids of microbial origin in the clay fraction. This indicates hindered microbial synthesis and/or hindered degradation of plant-derived aliphatic species. In comparison to the clay-plus-silt fractions, we neither detected more organo-mineral associations, nor microbially formed polypeptides, nor pectin in clay fractions at high  $p(\text{CO}_2)$ . This points to relatively unaltered particulate OM in the clay fraction. At high  $p(\text{CO}_2)$ , the FTIR band indicative of lignin became detectable and that indicative of aryl ketones in lignin was positively correlated with  $p(\text{CO}_2)$ . Thus, microbial formation of SOM and degradation of lignin is hampered under a CO<sub>2</sub> atmosphere. Preliminary Fe-K edge XANES data indicate that precipitated Fe(III) oxyhydroxides, predominantly ferrihydrite, are located on the surfaces of macropores, e.g., former root channels. In contrast, the bulk soil matrix was depleted in Fe, and the primary Fe form was Fe(II) present in clay minerals.

notes:

## **Analyzing effects of polyvalent cations on long-term composition of stable soil organic matter fraction**

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Soils from long term field experiments can be used to study effects of fertilization or crop rotation on composition of the soil organic matter (SOM). Relative stable organo-mineral complexes (OMC) are resulting from interactions between organic matter (OM) and inorganic components such as polyvalent cations (PC). While the formation of OMC is known from coordination chemistry for well-defined systems, the applicability of these concepts for analyzing OM of complex soil has not been explored. The objective of this study is to adopt principles of coordination chemistry for a simplified description of OM interactions with PC in soil.

Soil samples from plots of long term field experiments at Halle, Bad Lauchstädt, and Rotthalmünster were analyzed for exchangeable cations, oxalate soluble elements, clay, and soil organic carbon (SOC). The composition (i.e., C=O group content) of pyrophosphate soluble organic matter (OM(PY)) was determined using Fourier transform infrared (FTIR) spectroscopy. The C=O group content in OM(PY) is not related to the contents of oxalate soluble Fe, Al, or Mn cations. A relation is obtained when considering the effectiveness (i.e., binding status and speciation) and applying principles of coordination chemistry. The relation between C=O groups in OM(PY) and “effective” PC is particularly strong for all plots except for those that received farmyard manure (FYM). The long term FYM application seems to shift the SOM composition in OM(PY) towards a ‘FYM-type’ that reflects OMC formed outside the soil within dung heaps. The relation between the contents of C=O groups in OM(PY) and “effective” PC excluding data of FYM plots is significant at the 99%-level ( $r^2 > 0.8$ ). The results suggest that the application of coordination chemistry for describing interactions between OM and PC is useful for improving explanation of the effects of PC on the site-specific composition of SOM of arable soils.

notes:

## **Soil formation and stabilisation of soil organic matter in riverine floodplains**

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Sedimentation and erosion processes are crucial for the formation of riverine floodplain soils. Sediments, which consist of former top soil material eroded in the river catchment, provide the parent material for soil formation. It is widely assumed that eroded material becomes disaggregated during transport in the river and re-aggregation is one of the soil forming processes. Aim of our study is to test this concept and to analyse the relevance of re-aggregation for soil organic matter (SOM) stabilisation.

Our study sites are situated in the floodplains of the 'Nationalpark Donau-Auen' near Vienna, Austria. We analysed sediment and soil samples from a site characterised by variable sedimentation conditions near to the main river channel (site A), a site with constant sedimentation conditions (site B, distant to the main river channel) and a site within the inactive floodplain due to dike construction in the year 1884 (site C). We carried out a modified density fractionation procedure to obtain the amount of OM bound to the following operationally defined fractions: free particulate organic matter (fPOM,  $\rho < 1.6 \text{ g/cm}^3$ ), intra-aggregate particulate organic matter (iPOM,  $\rho < 1.6 \text{ g/cm}^3$ ) and organic matter associated to mineral surfaces (MOM,  $\rho > 1.6 \text{ g/cm}^3$ ). We determined aggregate stability with stepwise increasing amounts of ultrasonic energy.

Indeed, the results from site A (near to main river channel) confirm that recently deposited material is mostly disaggregated. Opposed to that, fresh sediment on site B (distant to main river channel) is highly aggregated containing high amounts of OM in iPOM fraction. This may be due to redistribution of aggregated topsoil material within the floodplain or the fractionation of the delivered sediments during the transport within the floodplain, respectively.

Aggregate stability in top soil layers was found to increase in the following order: site close to the river (site A) > site distant to the river (site B) > site without sedimentation since the year 1884 (site C). The amount of SOM stabilised within aggregates shows an opposed trend. In summary, we can verify that undisturbed soil in the inactive floodplain show progressing aggregate formation. Flooding and input of fresh sediment impairs aggregate stabilisation but may promote the stabilisation of SOM.

notes:

## Status of sclerotia of *Cenococcum geophilum* as structured SOC from studies in Harz mts., central Germany

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Sclerotia of *Cenococcum geophilum* and related species can be easily found in natural forest soils from their black and spherical feature, ca 0.05-8 mm in diameter with a characteristic hollow structure. Elemental analysis conducted for these sclerotium grains found in Japanese Andosols revealed that Al (1.4%) was detected as the dominant metal element following C (48%), O (30%), H (3.3%). The <sup>27</sup>Al MAS NMR and X-ray diffraction analyses determined the predominant state of Al contained in sclerotia as octahedral Al, which suggested the presence of Al-humus complex. Functional carbon groups for sclerotia were characterized by the dominance of *O*-alkyl C associated with aromatic C by solid-state CPMAS <sup>13</sup>C NMR analysis (Watanabe et al., 2001; 2007).

Comparative study carried out in Harz mts. elucidated that chemical composition of sclerotia in forest soils of Podsole (Haplic Podzols), Braunerde (Albic Luvisols) and Braunerde-Podsoles (Dystric Cambisols) was dominant with C and Al, as well, and suggested that the high content of exchangeable Al in soil ( $Al^{3+} > 0.54 \text{ g kg}^{-1}$ ) may have effect on accelerating the formation of large sclerotia and the ratio of organic bonding Al ( $Al_p$ ) to amorphous Al ( $Al_o$ ) ( $Al_p/Al_o > 0.5$ ) may be one of the determining factors of sclerotium formation, regardless of soil type. While, sclerotium grains were not found from strongly acidic soils which had low content of colloidal Al ( $Al_d$ ,  $Al_o$ ,  $Al_p$ ) due to intensive clay destruction (Watanabe et al., 2004). Our precise observation carried out in *Picea abies* forest in Elend, Harz mts. demonstrated that contribution of sclerotial C to total soil C was 1.0% at maximum and tended to increase in soils with relatively low humification degree (Sakagami, 2009).

Consequently, the state of active Al and pH values were considered as definite factors for the formation of sclerotia. Since the maximum content of sclerotium grains is obtained as  $5.4 \text{ g kg}^{-1}$  in A horizon of Luvisols in Harz mts., sclerotium grains cannot be ignored as soil organic components (SOC) especially in low pH forest soils.

notes:

## **Soil type specific stabilization of cutin and suberin-derived compounds in SOM pools with different functions and turnover times**

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We analysed topsoil and subsoil samples of four soil types (Laxic Cambisol, Skeletic Cambisol, Entic Podzol, Cutanic Alisol) under European Beech to determine the effects of soil type on stabilization of aliphatic biomarkers in soil.

Total lipid biomarker stocks as well as cutin- and suberin-derived fatty acid-patterns were determined in the free light fraction (fLF), the occluded light fraction (oLF) and the mineral-associated fraction (MAF). Additionally, the stocks of characteristic cutin and suberin degradation products as well as of some microbial fatty acids have been calculated.

More than 40 % of the fatty acids in most topsoil horizons of all soil types as well as in the subsoil horizons of the Skeletic Cambisols and the Cutanic Alisols were stored in the oLF. In contrast, subsoils of the Laxic Cambisols contained the largest amount of aliphatic biomarkers in the MAF, whereas lipids of the Entic Podzol subsoils were equally distributed between the fLF and the MAF, the oLF of the Entic Podzols contained < 10% of the total lipid biomarker pool.

Density fractions of the soil types differed also significantly in their aliphatic biomarker patterns. The MAFs of Laxic Cambisol samples contained large amounts of microbial fatty acids, whereas the MAFs of Entic Podzol samples were dominated by degradation products which are characteristic for (hydroxy-)alkanedioicacids derived from suberin. The fatty acid signature of all MAFs of all soils was clearly different compared to the signature of fresh plant material or the signature of the light fractions. Our data indicate that there is a strong influence of soil forming processes on the stocks and composition of lipid biomarkers in soils.

notes:

## **Interactions of organic pollutants with soil components investigated by means of molecular modelling**

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The major objective of our work is to develop new tools based on theoretical methods for a quick first assessment of the potential behaviour of new compounds in soil interfaces based on a hypothesis that the behaviour of organic compounds on micro scale is driven by interactions of these compounds on the nano scale. Methods of computational chemistry can contribute to elucidate basic processes involved. These methods cover a large range of techniques (especially quantum chemical methods (DFT, DFTB), force-field methods, molecular dynamics (MD), and Monte Carlo(MC)). In this work an intensive study was conducted concerning sorption of polycyclic aromatic hydrocarbons (PAHs) on soil mineral goethite. Here, relatively large sorption energies were calculated. We found a relation between the surface structure/shape of the PAHs molecules and sorption energies. Linear PAHs, especially anthracene, showed the strongest sorption. The origin of adsorption is mostly in dispersion/polarization interactions between surface OH groups and  $\pi$ -electrons of PAHs. Studies of interactions of humic moieties under different chemical environment showed a clear impact of the hydrophobicity of the environment on the observed Gibbs free energies. Owing to the structural complexity and flexibility of humic substances (HS) various “nano” pores and holes can be formed in their structure. These spaces can be filled by various small molecules, e.g. water. Water molecules can form in these spaces a stable network of hydrogen bonds, thus creating “wet spots” in HS.

notes:

## Modelling the soil organic matter profile development

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The SOMPROF soil organic matter (SOM) model is presented, which explicitly models transport of SOM with depth and the development of the vertical distribution of SOM from bare ground up to current conditions. The model was calibrated for a young coniferous site (Loobos) and an old deciduous site (Hainich). The bayesian model calibration revealed that the current SOM profile could be explained reasonably well by two different dominating processes. Either recalcitrant carbon was transported downwards by diffusive bioturbation or adsorbed carbon was slowly transported downward by advective movement as dissolved organic carbon (DOC). By extending the model for the radioactive isotope lead-210 and by including observed  $^{210}\text{Pb}_{\text{ex}}$  profiles in the model calibration and by including prior knowledge about the parameters we identified the advective transport to be the dominating process at both of the studied sites. This finding suggests that adsorption of OM to minerals is an important process for SOM stabilization in subsoil.

notes:

## The Abiotic Degradation of Soil Organic Matter

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Natural abiotic degradation of soil organic matter has been the subject of many experimental studies during the last years. It was shown that the oxidation of soil organic matter by iron(III), hydrogen peroxide and chloride produces volatile halogenated organic compounds (VOX). These compounds are important trace gas components of the atmosphere. Their oxidation impacts ozone and can lead to aerosol formation. Therefore, these volatile compounds can influence both the oxidation capacity of the atmosphere and the earth's radiative budget.

Beside VOX formation, the production of polar halogenated organic compounds (POX) is also an important degradation pathway of soil organic matter. For example, chlorinated acetic acids which are relevant toxic environmental substances were confirmed in soils and sediments.

In this context the DFG Research Unit 763 HALOPROC (Natural Halogenation Processes) identified a number of volatile organic compounds such as halomethanes (e.g.  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{Br}$ ) or halogenated alkenes (e.g.  $\text{C}_2\text{H}_2\text{Cl}_2$ ,  $\text{C}_2\text{H}_3\text{Cl}_3$ ) and non-halogenated species (e.g. furans) in salty soil samples. Oxalic acid was detected as an important polar organic compound.

For a better understanding of these natural formation processes mechanistic studies were conducted using model compounds (e.g. catechol, 3,5-dichlorocatechol) as representative for structural elements of the humic substances and its reaction with iron(III), hydrogen peroxide and chloride. This kind of approach leads for example to a widely accepted elucidation of the mechanistical steps for trihalomethanes formation. In a further investigation the absence of chloride revealed that the formation of oxalic acid could be found as the major degradation product of catechol with 60%.

The results of the soil measurements are similar to those obtained with the model compounds. Therefore, the newly gained insights with model compounds appear to be applicable to soil conditions. These findings increase the understanding of the degradation pathways of soil organic matter.

notes:

## Use of char from industrial thermo-chemical processes to improve soil quality

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Char or biochar is a type of charcoal obtained from gasification/pyrolysis of biomasses. Instead of burning standing biomass from cleared forest, the resource is charred. This material is recognized to improve soil quality and fertility. However, up to now only little is known about its chemical-physical properties. The present study reports about the effects of chars obtained from industrial thermo-chemical processes (gasification for energy production) on soil quality. Namely, radish germination was monitored. Results revealed that, following char addition to soil, radish roots had different lengths depending on the nature of biomasses used to produce the different chars. High resolution solid state NMR spectroscopy revealed no differences among the chemical nature of the different chars. Conversely, low resolution <sup>1</sup>H fast field cycling NMR relaxometry showed that porosity of chars was directly related to the nature of the biomasses used for the thermo-chemical transformations.

We can conclude that not all the chars can be applied to soil to improve its quality, but a careful lab study prior to field application must be carried out in order to avoid counter-effects which can damage soil productivity.

notes:

## **Influence of water-induced SOM alterations in peat on sorption behaviour of xenobiotics**

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Water affects the physico-chemical properties of soil organic matter (SOM). Thus, sorption behaviour of xenobiotics is expected to vary depending on the water influence. Aim of this contribution was to elucidate the influence of hydration-induced alterations of SOM physicochemical properties on the sorbed amount and the sorption rates of xenobiotics.

Three polycyclic aromatic hydrocarbons (PAH) and three naphthalene derivatives were selected as model sorbates according to their ecotoxicological relevance and their different physicochemical properties. Sorption kinetics and sorption isotherms of these compounds were recorded using a peat soil that had been equilibrated at three different water contents for four different time periods. The resulting sorption parameters were related to the changes in SOM matrix rigidity, heterogeneity, hydrophobicity and estimated pore sizes that resulted from the water treatment. Furthermore, the amounts of freezable and non-freezable water were regarded. Increasing amounts of non-freezable water in the peat sample initially decreased the matrix rigidity and increased the matrix heterogeneity and hydrophobicity of SOM. Moreover, the matrix rigidity was increased at all water contents with increasing water contact times which also increased the hydrophobicity of SOM in the presence of freezable water. Even though physicochemical properties of the sorbates affected sorption to a higher extent than water-induced SOM alterations, the influence of water-induced changes of the SOM matrix on sorption was also remarkable: Increasing amounts of non-freezable water and increasing pore sizes negatively affected the fast sorption rate which was in turn positively influenced by SOM hydrophobicity. The presence of freezable water in the sample increased the slow sorption rate and the sorption hysteresis, but decreased the sorbed amount of xenobiotics. The influence of matrix rigidity on the sorption rates and the sorbed amount was ambiguous and varied with the water content. The water-induced SOM alterations significantly changed the sorbed amount of single model xenobiotics by up to 6%, the fast sorption rate by up to 100% and even increased the slow sorption rate by up to 200%.

It is concluded that water-induced alterations of SOM physico-chemical properties strongly influence the mobility of xenobiotics in the soil environment and must be considered in environmental assessments.

notes:

## **Effects of cation saturation and aging on extractability of nonylphenol and phenanthrene from soils**

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This study was carried out to assess the influence of physicochemical properties on the sequestration of hydrophobic model compounds in a sterile sandy soil. Original control and soil treated by different salt solutions (NaCl, CaCl<sub>2</sub> and AlCl<sub>3</sub>) were used in this study. The treatments aimed at altering the soil sorption properties through changed conformation of soil organic matter.

Radiolabelled (<sup>14</sup>C) nonylphenol and phenanthrene were spiked and aged for up to 287 days in sterile field moist soil microcosms. The degree of compound sequestration at various sampling times was determined by their extractability with water and organic solvents (ethanol and cyclodextrin solutions).

The amount of extractable PAH decreased with compound aging in the soil. At the first day of aging, extractability of nonylphenol and phenanthrene by water was about 7 and 4.5 % respectively. After 140 days of aging release of xenobiotics from soil with water was decreased and for some of samples this parameter reduced up to two times.

Directly after spiking the phenanthrene extractability by cyclodextrin solution from salt treated soils increased with cation valence: from 19 for Na treated soil to 27 % for Al treated material. During the aging period this difference became statistically negligible and the amount of phenanthrene released from all soils by cyclodextrin was about 8-10 % at 140 day. This shows that cation treatment possibly affected the short-term phenanthrene sorption processes, whereas physicochemical properties of soil responsible for long-term sorption during aging were not modified.

notes:

## **Restructuring of mineral-organic associations upon drying: Processes and relevance for the sorption of MCPA and phenanthrene**

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Mineral surfaces in soils are partially covered with organic matter, which may strongly affect the physicochemical properties of the minerals (e.g. surface charge) and hence affect the retention of nutrients and pollutants in soil. In natural soils organic matter is subjected to moisture fluctuations, which has been shown to induce restructuring of organic macromolecules associated with mineral phases. We hypothesise that restructuring results in decreased accessibility of negatively charged functional groups of organic molecules. Polyvalent cations may function as “bridging cations” which stabilise the networks of organic molecules and inhibit the collapse of these molecules. We expect that these processes explain the effect of drying on sorption of organic pollutants by organo-mineral associations.

To test our hypothesis we measured the zeta potential of polygalacturonate (PGA) coated lepidocrocite colloids without drying and after air-drying and rewetting at 0, 2, 4, 18, 24, 48, 168, 336 h. We conducted the experiments in presence of 10 mmol L<sup>-1</sup> K<sup>+</sup> (pH 5 and 4) and Al<sup>3+</sup> (pH 4). Additionally we conducted sorption experiments with MCPA and phenanthrene to the differently treated material.

As expected in presence of K<sup>+</sup> zeta potential of “wet” samples was more negative at pH 5 (40 ± 3 mV) than at pH 4 (-26 ± 2 mV). In contrast the “rewetted” samples showed lower surface charge (-18 ± 2 mV) which did not depend on pH. In presence of Al<sup>3+</sup> zeta potential changed to positive values (25 ± 3 mV) and no significant effect of drying could be observed. No significant change of zeta potential of “rewetted” samples could be obtained over time. So far our results confirm our hypothesis. Furthermore the irreversibility of restructuring indicates that drying induces the formation of covalent bindings between PGA and lepidocrocite.

First results from still running sorption experiments show that drying reduces the sorption of MCPA significantly. Final results will be presented.

notes:

## **Instantaneous reduction of sulfadiazine extractability after spiking to soil**

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Decreasing extractability over time is often observed for organic compounds in soil. The various processes involved are usually summarized in the term ‘sequestration’ and may include diffusion into micro-pores and soil matrix, strong chemical sorption, physical entrapment or covalent bonding.

The antibiotic sulfadiazine (SDZ) shows typical sequestration in soil. A sequential extraction method proved to be appropriate for investigating sequestration of SDZ in batch experiments. Concentration dynamics over 200 days in different extracts could be described well by a conceptual kinetic model, which implies a reversible as well as an irreversible sequestration resulting in ‘non-extractable residues’. Remarkably, experimental results along with model simulations indicated that extractability of SDZ is clearly reduced already shortly after the start of incubation. We assumed this finding to be attributed to very fast interaction processes with soil possibly relevant for risk assessment. Therefore, we performed a set of soil batch experiments focussing on the first 24 hours of incubation and tested the influence of manure and water content on the observed effect: SDZ was added in aqueous solution or dissolved in manure to soils of different water content (3% vs. 25% of water holding capacity). We used the sequential extraction method and analysed SDZ in the extracts by LC-MS/MS.

Immediately after spiking SDZ to soil, extractability was reduced in all setups confirming processes on a time scale of minutes. Only small differences in the initial SDZ distribution were observed between the various experimental treatments. However, during the following 24 hours of incubation, sequestration proceeded further. Rate constants for sequestration into a microwave-extractable fraction appeared to be fairly the same in all experiments. In contrast, simultaneously occurring additional dissipation from a CaCl<sub>2</sub> and methanol extractable fraction was clearly faster in the manure treatments compared to the water treatments, presumably as a consequence of enhanced microbial activity.

notes:

## Effects of Multivalent Cations on Soil Organic Matter

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One of the most important functions of soil organic matter (SOM) is its capability to act as ion exchanger. Variable charges originating from carboxylic and phenolic functional groups are decisive factors for a pH dependent cation exchange capacity. Their interactions with cations will determine the evolution of SOM. The wide spectrum of affinity between cations and SOM results in various options of ion binding; for example ion exchange, complexation and adsorption. Furthermore, multivalent cations can cross-link organic molecules via cation bridges (CAB), which is expected to have significant effects on biological and chemical interactions in biogeochemical interfaces. In this current contribution, we discuss an experimental approach to understand how the cations interact with soil organic matter. A Sapric peat from Fuhrberg whose organic content is more than 99 % was first desalinated and then, after pH adjustment to 3.8 and 4.1 in different experiments, treated with  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$  and  $\text{Na}^{+}$  salt solutions resulting in cation addition between 12.3 and 98.4 mmolc/kg of soil. After phase separation, drying and equilibration at 76% RH for two weeks, the treated and conditioned samples were analyzed for the effectiveness of cation addition, their ability to exchange  $\text{Ba}^{2+}$ , release of dissolved organic matter (DOM) and colloids as well as physicochemical properties. Additional experiments were conducted in order to find out to which extent solid organic matter itself is changing and to which extent the organic matter properties may change due to formation of DOM-cation precipitates. We found that cation removal induces some irreversible changes in the solid SOM resulting in a significantly reduced cation uptake, significant differences in the ability to exchange cations and the release of DOM.

These changes in organic matter quality clearly result changes in the solid soil material. Since the precipitation was very low due to the small amount of added cations, it is concluded that the quality of organic matter after cation addition is not significantly determined by the precipitated OM.

notes:

## Long term DSC and <sup>1</sup>H NMR ageing experiments - setup and first results

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Soil organic matter (SOM) is a highly complex system of various molecules interacting on different time and length scales. In our hypothesis, water molecules play a pivotal role in acting as a cross linker of organic matter compounds generating a network held together by intermolecular hydrogen bonding. This network is sensitive to external parameters and undergoes changes in rigidity and structure depending on temperature, water content and ion concentration.

Being an essential tool for understanding the long term dynamics of soil organic matter in its natural context of ageing, sequestration and degradation, DSC and <sup>1</sup>H NMR experiments on selected samples were recorded over a time period of up to three months. The study includes results for long term observation of three soils including peats that represent highly organic soil and a gleyic podzol representing a mixture of organic and inorganic soil components.

The soil samples were prepared by phase separation, drying and then storage at 76% RH to obtain a well-defined initial state with a certain water content and were then exposed to a single heating event up to 110°C for 30 minutes to destroy the water network. After that we investigated the regeneration of this water network as characterized by a change in step transition temperature occurring in differential scanning calorimetry (DSC) and changes to linewidths and intensity ratios in wideline <sup>1</sup>H NMR experiments.

The temperature of the step transition is interpreted as measure for matrix rigidity and therefore physicochemical stability of SOM. The selected soil samples showed a step transition between 60 °C and 75 °C similar to transitions observed in previous studies. The sapric peat showed after heating event an additional step transition at 35 °C this step transition temperature slowly re-increased upon isothermal storage within several months to 50 °C. The temperature of the step transition between 60 and 70 °C shifted only slightly after the heating event.

<sup>1</sup>H wideline NMR spectra of soil samples can be analysed in terms of combining a narrow fraction for mobile protons, preferably water, and a broad fraction for rigid protons, in this case organic matter and rigid water in cross-linked networks. The resulting spectra are decomposed straightforwardly applying the mathematical context of Lorentzian and Gaussian line shapes to identify respective fractions of mobility of water molecules.

Measurements over a period of three months have shown that the decrease of Lorentzian signal ratio – corresponding to higher rigidity of SOM due to water cross-links – consists of a combined exponential and linear dynamical behaviour that occurs subsequently over time ranges of hours to weeks, respectively.

The results will be used to get a more accurate description and understanding of water dynamics in SOM that should also be combined with molecular modelling approaches. Following this, investigation of the ageing behaviour of different soils and treatment with cations of different valence will be undertaken.

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## **Following organic matter accretion and transformation in top- and subsoil – A research program to measure the build-up of soil structure in alluvial soils**

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The FP7-project „SoilTrec – Soil Transformations in European Catchments“ (2010-2014) aims to develop an integrated model of soil processes that quantifies key soil functions (e.g. food and fibre production, filtering, transformation and buffering, storage of carbon and biological habitat). Key to this research agenda is the central role of soil structure, which includes the physical structure of mineral and organic matter aggregates, pore space distribution, horizonation, the distribution of carbon, mineral and solute reactivity, and the distribution in intensity and diversity of biological activity and mechanical forces.

One intensive study area (covers about 40 km<sup>2</sup>) is located in the Danube floodplain downstream of Vienna/Austria in the so called “Marchfeld”, which shows little variation in topography and climate (mean annual temperature ~ 9°C, annual precipitation ~550 mm). In a former study a soil chronosequence was established including young island soils in the Danube River, sites regularly inundated during flood events, sites disconnected from the river for about 100 years through a flood-control dike as well as sites not impacted by river dynamics for longer time periods during postglacial times. The study sites cover an age gradient from about 10 years to about 12000 years and include various land use like forests and cropland. At one site, a long-term field experiment was established in 1967 to document the fate of <sup>14</sup>C-labelled manure and <sup>15</sup>N fertilizer under different crop management systems and bare fallow.

The poster will present our sampling design along the soil chronosequence in the topsoil but also in the subsoil down to the mainly unweathered alluvial deposits, our plans to characterize the soil organic matter for modelling purposes (e.g. Roth-C) as well as a monitoring survey at the <sup>14</sup>C-labelled site using lysimeters to measure dissolved organic carbon flux.

notes:

## **Soil carbon evolution after the application of high doses of sludge in mediterranean agricultural soil: a short term experiment.**

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The application of sewage sludge to agricultural land is the main treatment method for this type of waste (Ottaviani et al. 1991). Several studies indicate that after the application of sludge, soils increase their concentration in organic matter, especially in the humic fractions which are the most persistent and difficult to degrade (de las Heras et al, 2005). However other authors (Torri et al, 2003) suggest that most organic matter is mineralized as CO<sub>2</sub>. So far little research has been done in Mediterranean climates. In addition, the nitrification process requires available sources of carbon and ammonium for microorganisms.

In an experimental station in Madrid, Central Spain, we applied a single high dose (160 t•ha<sup>-1</sup>yr<sup>-1</sup>) of three different urban sludges: aerobic and anaerobic sludge from a wastewater treatment plant, and biosolids. We monitored total organic carbon, soluble carbon, (ISRIC, 2002) and 3 fractions of carbon: labile pool 1 (sugars), labile pool 2 (cellulose) and recalcitrant carbon following Rovira and Ramón Vallejo (2007). The nitrification potential rate was measured following Fierer (2002), 3 and 6 months after application. A high increase of total organic carbon can be seen after the application of the sludge. There are differences according to the type of sludge: the biosolid treatment shows a more stable behavior in relation with the others. Differences between plots with aerobic treatment and control plots are low 6 months after application, probably because the carbon sources are more degradable than the others. Available carbon (mainly sugars) in labile pool 1 and 2 shows a common trend, with a sharp increase after application followed by a continuous decrease; after 6 months the values are close to the original in the control plots. The general trend, in terms of recalcitrant carbon, is for an increase after application and a gradual decrease over the longer term. The nitrification potential rate shows a significantly high increase in summer, and reaches values similar to the original after 6 months. These data are independent of the type of sludge and can be related to the climatic pattern; nitrification is highest when the water content is minimal under the Mediterranean climate type.

notes:

## **SOC pools and stocks in permafrost soils on the Tibetan plateau**

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A particularly sensitive area with regard to possible effects of a global climate change is the Tibetan Plateau. Approximately two thirds of the total area are affected by permafrost. Specific soil hydrological properties in permafrost regions have a major impact on soil moisture and hence on the accumulation of organic matter. Detailed investigations were carried out at two sites on the northeastern part of the Qinghai-Tibet Plateau in May/June 2009 to get a better understanding of the role of permafrost on soil organic carbon pools and stocks. Site Huashixia (HUA) is located in discontinuous permafrost and has a higher mean annual precipitation (326 mm) than the 530 km further west located site Wudaoliang (WUD, continuous permafrost, 255 mm).

Three organic carbon fractions were isolated using density separation combined with ultrasonic dispersion: the light fractions of free particulate organic matter (FPOM) and occluded particulate organic matter (OPOM) with a density  $< 1.6 \text{ g cm}^{-3}$ , plus a heavy fraction of mineral associated organic matter (MOM) with a density of  $> 1.6 \text{ g cm}^{-3}$ . The fractions were analyzed for C, N and their portion of organic C of the bulk sample. FPOM contained an average OC content of 25.2 %. Higher OC contents (32.0 %) were found in the intermediate OPOM. MOM had the lowest OC contents with 2.9 %. Due to the lower mass the easily decomposable fractions FPOM and OPOM contribute 27% to the total stocks in HUA (WUD: 22 %). POM values of 36 % occurred only in wet profiles. In HUA mean OC stocks of  $10.2 \text{ kg m}^{-2}$  were found, compared to  $3.8 \text{ kg m}^{-2}$  in WUD. Carbon stocks decreased with depth, particularly in WUD. Significant amounts of SOC were found in frozen soil horizons below the active layer.

notes:

## **Relationship between ageing, mineralisation and microbial degraders' communities of pesticide bound residues in soil.**

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Understanding mechanisms involved in the formation and the fate of pesticide non-extractable residues (NER) in soil could improve the assessment of pollution risks. The aim of this study was to evaluate the influence of NER ageing and fresh soil addition on the microbial communities responsible for their mineralisation. Soil samples containing either 15 or 90 day-old NER of <sup>13</sup>C-labelled 2,4-dichlorophenoxyacetic acid (2,4-D) were incubated with or without fresh soil for 90 days during which <sup>13</sup>C-CO<sub>2</sub> was monitored. The structure of microbial degraders' populations was determined by lipid-SIP (Stable Isotope Probing) and the NER were characterised using pyrolysis-GC-c-IRMS. Molecular analysis of NER showed chemical differences between young NER, mainly composed of 2,4-dichlorophenol (2,4-DCP), and older NER, composed of several other molecules. The addition of fresh soil had no effect on the mineralisation of the old NER or of the soil organic matter, but increased the extent and rate of younger mineralisation. The analyses of <sup>13</sup>C-enriched FAME (fatty acids methyl esters) profiles showed that the fresh soil amendment only influenced the amount and structure of microbial populations responsible for the biodegradation of young NER. By coupling biological and chemical analyses, we gained some insight into the nature and the biodegradability of pesticide bound residues.

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## Prediction of soil respiration by methods of thermal analysis

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The major factor affecting the carbon cycle in the terrestrial biosphere is soil organic matter and its biological transformation. Processes of biological transformation can be considered as a measure of the soil quality and thus it is of a great importance to find a reliable method for its evaluation. Results of Siewert (2004) indicated that there exists an interrelationship between soil total organic carbon, nitrogen, carbonate and clay contents and mass losses detected by thermogravimetry. Those parameters, however, do not reflect the activity of soil living organisms which are responsible for soil organic matter turnover. In contrast, activity of soil microorganisms mirrors soil's primary functions, composition and actual condition.

The aim of this work was the verification of previously published linear correlation between soil respiration measured as CO<sub>2</sub> evolution and mass losses determined at specific temperature intervals by thermogravimetric analysis (Siewert et al., 2011)

87 soil samples, originating from a wide range of geological and vegetation conditions such as German (33 samples), United States (21 samples) and Siberian (33 samples) national parks were investigated. Obtained results showed that highest correlations between respiration and mass losses, for all soil samples, was around 100 °C (e.g. R<sup>2</sup>=0.85 for German soils) and around 300 °C (e.g. R<sup>2</sup>=0.87 for Siberian soils) almost over the whole incubation experiment. Further, statistically significant correlations were found also around 250 °C and 450 °C.

Results of this work confirmed that combination of thermogravimetry with laboratory incubation experiments represents a great potential in development of methodical approaches useful for prediction of soil microbial activity represented by soil respiration. Further, thermogravimetry seems to be a promising tool useful for determination of soil quality and origin.

Siewert, C., Kislinger, J., Kucerik, J., Demyan, M. S. (2010): Can soil respiration be predicted by thermal analysis? *European Journal of Soil Science*, submitted.

Siewert, C. (2004): Rapid scanning of soil properties using thermogravimetry. *Soil Sci. Soc. Am. J.* 68: 1656 – 1661.

notes:

## Site and tree stand specific variations in organic matter properties from forest soils

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The quantity and quality of soil organic matter (SOM) and SOM pools, and related soil properties such as carbon sequestration and water retention are not constant. Instead, SOM exhibits considerable variations that may be amplified through a changing climate. Hence, for silvicultural management it is demanded to determine easy identifiable parameters that might be used as indicators for climate change induced susceptibility or shifts in forest soil properties.

The aim of the study presented is to identify SOM storage and stability in forest soils and its dependence on site properties and interaction with tree stand conditions. This is done at selected sites from four watersheds that represent typical forest stands in the region of Luxembourg and South West Germany. Soil parameters investigated were pH, total and available concentrations of selected elements (Al, Mn, Fe, Ca, Mg, K, Na, P) and effective CEC. Organic matter storage in soil horizons and litter layers was investigated, total and hot water-extractable C and N and respective C/N ratios were determined, and SOM stability was characterised through density fractionation of selected samples from organic layers, Ah and Bv horizons. Results of the C and N analyses and of SOM density fractionation showed differences between forest stands, i.e. Douglas fir, Norway spruce and beech, especially in the top mineral soil horizons (Ah). The distribution of total OC among the different fractions followed on average the sequence: 10% mineral fraction < 20–30% free particulate OM < 60–70% light and heavy fraction of occluded particulate OM. Differences were obvious between soil horizons but also between coniferous and broadleaf stands and were mostly related to the fraction of SOM occluded in particulate OM. This fraction was clearly smallest in soils under Norway spruce stands that also exhibited shallower Ah horizons than deciduous forest stands. Furthermore, it was indicated that the distribution over fractions partly depended on soil pH and was presumably associated with microbial activity.

notes:

## The Abiotic Degradation of Soil Organic Matter

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Natural abiotic degradation of soil organic matter has been the subject of many experimental studies during the last years. It was shown that the oxidation of soil organic matter by iron(III), hydrogen peroxide and chloride produces volatile halogenated organic compounds (VOX). These compounds are important trace gas components of the atmosphere. Their oxidation impacts ozone and can lead to aerosol formation. Therefore, these volatile compounds can influence both the oxidation capacity of the atmosphere and the earth's radiative budget.

Beside VOX formation, the production of polar halogenated organic compounds (POX) is also an important degradation pathway of soil organic matter. For example, chlorinated acetic acids which are relevant toxic environmental substances were confirmed in soils and sediments.

In this context the DFG Research Unit 763 HALOPROC (Natural Halogenation Processes) identified a number of volatile organic compounds such as halomethanes (e.g.  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{Br}$ ) or halogenated alkenes (e.g.  $\text{C}_2\text{H}_2\text{Cl}_2$ ,  $\text{C}_2\text{H}_3\text{Cl}_3$ ) and non-halogenated species (e.g. furans) in salty soil samples. Oxalic acid was detected as an important polar organic compound.

For a better understanding of these natural formation processes mechanistic studies were conducted using model compounds (e.g. catechol, 3,5-dichlorocatechol) as representative for structural elements of the humic substances and its reaction with iron(III), hydrogen peroxide and chloride. This kind of approach leads for example to a widely accepted elucidation of the mechanistical steps for trihalomethanes formation. In a further investigation the absence of chloride revealed that the formation of oxalic acid could be found as the major degradation product of catechol with 60%.

The results of the soil measurements are similar to those obtained with the model compounds. Therefore, the newly gained insights with model compounds appear to be applicable to soil conditions. These findings increase the understanding of the degradation pathways of soil organic matter.

notes:

## Element compositions of Laurel Forest Soils. Understanding element cycles between volcanic rocks, soils and plants (Tenerife, Canary Islands, Spain).

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The Laurel Forest is an important and sensitive ecosystem with particular element cycling mechanisms. The distribution is straitened to parts in the north, north-west and northeast. On Tenerife the mountains act as a topographical barrier to moist trade winds, creating a toposequence of contrasting climatic conditions (Fernández-Palacios and de Nicolás, 1995). The altitudinal climate variations are closely related to the seen soil differences. On the northern side two climosequencec have been defined depending on the age of materials. On old basaltic lava flows Vertisols, Alfisols, Ultisols and Inceptisols corresponding to aridic/ustic, udic and xeric moisture regime are found (Hernández-Moreno JM., 2005). On recent pyroclastic materials, at these same climatic levels, Inceptisols, allophanic and vitric Andisols are present (Hernández-Moreno JM., 2005). Andisols are the most characteristic soils found on Tenerife.

The present study aims to understand the geogenic element transports of different inorganic elements between volcanic rocks, soils and Laurel forest. We want to determine the geogenic and anthropogenic impacts on forest soils and *Laurus novocanariensis*. During the first fieldtrip (17.03.10 -14.04.10) 200 soil samples from 18 sample sites have been collected. At each locality, about 300 g of leafs (*Laurus novocanariensis*), 50 g roots, 1 kg of soil and about 3 kg of volcanic rocks where collected. All leafs are from male species and are all taken from the same tree heights (1,5 – 2, 5 m). All tress are located directly at the soil profile. At 5 localities we took samples from *Laurus novocanariensis* trees with different heights (1,5 – 2,5 m and 6 – 15 m) to compare the element distribution between younger and older species.

FERNANDÉZ-PALACIOS, J. M. & NICOLÁS, J. P. (1995): Altitudinal pattern of vegetation variation on Tenerife. Journal of Vegetation Science 6: 183-190.

HERNÁNDEZ-MORENO JM, et al., (2005): Compartamiento de suelos volcanicos frente al riego con aguas depuradas y desalinizadas. Influencia del yeso en la correccion de problemas de boro y sodio. Reunión Internacional sobre avances en iego localizado, 2-5 december 2002. INIA, pp 220 – 226.

notes:

## **Application of pyrolysis – mass spectrometry (Py-MS) techniques and synchrotron-based X-ray absorption spectroscopy (C- und N-XANES) to determine heat effects on soil organic matter**

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The soil organic carbon (C) and nitrogen (N) form large pools on Earth and control many ecosystem services, e.g., soil fertility, plant productivity, biodiversity and C sequestration. Global warming caused more frequent and severe vegetation fires in parts of the world, and effects on bulk soil organic matter (SOM) were studied occasionally. Analytical methods on molecular-scale and quantification of such changes are unsatisfactory because of methodological limitations in the flash pyrolysis-gas chromatography coupled to MS methods, nuclear magnetic resonance spectroscopy, and thermal and chemical oxidation so far applied to this topic. Therefore, new methods are required to gain deeper insights into molecular-structural SOM changes arising from vegetation fire heat impact.

The general objective of the research was to test further methods for the investigation of pyrolysed organic matter (PyOM) in soils. As a first step we compared XANES and various MS - based methods to characterize SOM in samples from a long term field experiment in Germany, in which plots were periodically burned, mulched or left to natural succession. Results showed a larger sensitivity of temperature-resolved pyrolysis - field ionization MS (Py-FIMS) than for other MS and XANES methods in the detection of molecular differences among the treatments. The direct comparison of the treatments showed a larger relative amount of  $m/z > 200$  and a shift of thermal release of compounds to higher temperatures for the burned plots. A principal component analysis of the Py-FIMS data separated the burned variants at two different locations from the others, suggesting sampling site independent effects. Relative enrichments of double bonded and/or aromatic C and heterocyclic N compounds in the XANES spectra of the burned plots can be explained by their heat-induced de novo synthesis. This has been confirmed in a separate controlled burning experiment in the laboratory, where the C- and N-XANES spectra also showed characteristic formations of aromatic and heterocyclic molecules in SOM.

notes:

## **Evaluation of a method for measuring labile and stable fractions of soil organic at the landscape scale**

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A large methodological set exist to partition soil organic matter (SOM) into fractions of different stability. On the one hand, there is no doubt that there is need for further research of the nature of these fractions on the molecular scale, e.g. chemical composition, interaction with minerals and decomposition kinetics. On the other hand, there is need to extrapolate the distribution of SOM among fractions to the landscape scale. Different mineralogy, topography, soil type, land-use and site history challenge fractionation methods which can be used reproducibly on very large sample numbers. Therefore, the method should be easy, fast and cheap, but results have to be interpretable. To test a method for their usefulness, very different soil samples have been analysed with a multiphase carbon determinator (MCD). The MCD was originally used to determine different carbonate species by their specific activation energies. Calibration revealed consistently three different peaks on soil samples at 260, 460 and 650°C, each held for 130-180 seconds under excess O<sub>2</sub> supply. The fractions were operationally named "labile C", "stable C" and "inorganic C". Results on organic materials showed, that C of maize leaves were totally labile, pine wood had a small portion of 13% stable C and charcoal consisted to 56 % of stable C. First results on soil samples from Germany (grassland and forest on calcareous soil), Mexico (forest with different burning histories) and South Africa (two different burned wetlands) show that 75 to 85% of C<sub>org</sub> are labile across all soils. However, recent burning resulted in higher proportions of stable C in the Mexican samples. Although the method may not result in the separation of homogenous functional pools, it may be useful in combination with other methods, such as particle size fractionation. However, this will increase the working load and diminish the usefulness on the landscape scale. Further material such as peat, light or sand fraction material from soil and standard materials and soils for black C analysis will be tested and the method will be compared to other established methods, such as oxidative treatment with H<sub>2</sub>O<sub>2</sub>.

notes:

## **Wastewater from Olive Oil Mills in Israel and Palestine: Interactions with Soil, Organic Contaminants and Mechanisms of Incorporation into soil**

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Olive orchards play an important role in Israeli and Palestinian agriculture. For the olive oil production mainly the 3-Phase extraction process is used. Thereby, water is added to the pomace to get three phases: water, oil and pomace. Besides the valuable oil, about 200,000 m<sup>3</sup> and 50,000 m<sup>3</sup> of wastewater are yearly produced in Palestinian and Israeli olive oil mills, respectively. It has a high concentration of organic material and is hardly microbial degradable. This is caused by toxic effects of some organic compounds, especially of polyphenols

In a trilateral project funded by the DFG with scientists from Israel, Palestine and Germany we will investigate wastewater-soil-interactions and the effects of wastewater organic matter on soil-agrochemical interactions. Therefore, we want to differentiate between chemical and physical bound, incorporated and adsorbed organic matter. Furthermore we will identify substances affecting water repellency, phytotoxicity, toxicity and the sorption of agrochemicals. Especially the dependence on seasonally climatic conditions, for instance on moisture dynamics, is of great interest.

The main part of the project is a field study, which will be conducted in Palestine. This poster should give an introduction in the setup of the field study and the different parameters which will be determined.

notes:

## **Evidence for calcium bridge stabilization of MCPA-soil complexes by using a novel experimental setup**

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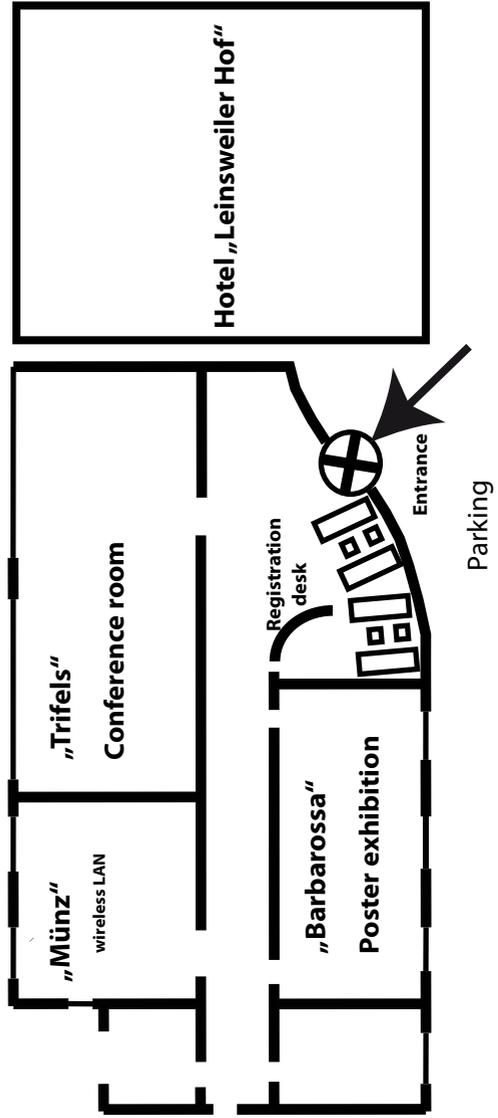
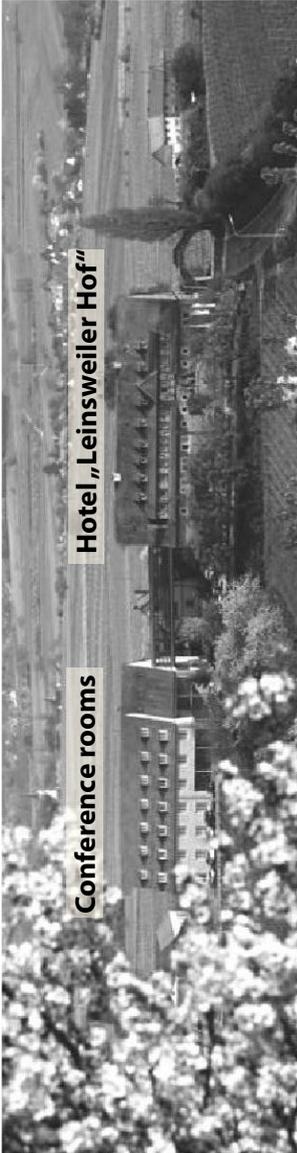
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The herbicide 4-Chloro-2-methylphenoxyacetic acid (MCPA) is an agro-chemical widely applied for broadleaf weed control. Due to its poor biodegradability, it poses risks to water sources; it readily sorbs to soil matter, both polar and apolar sorption mechanisms have been proposed for MCPA. Polar interactions can occur via its carboxy group which is deprotonated at pH values commonly occurring in natural soils. Such binding to soil surfaces can further be enhanced by forming divalent cation bridges, e.g. Ca<sup>2+</sup>.

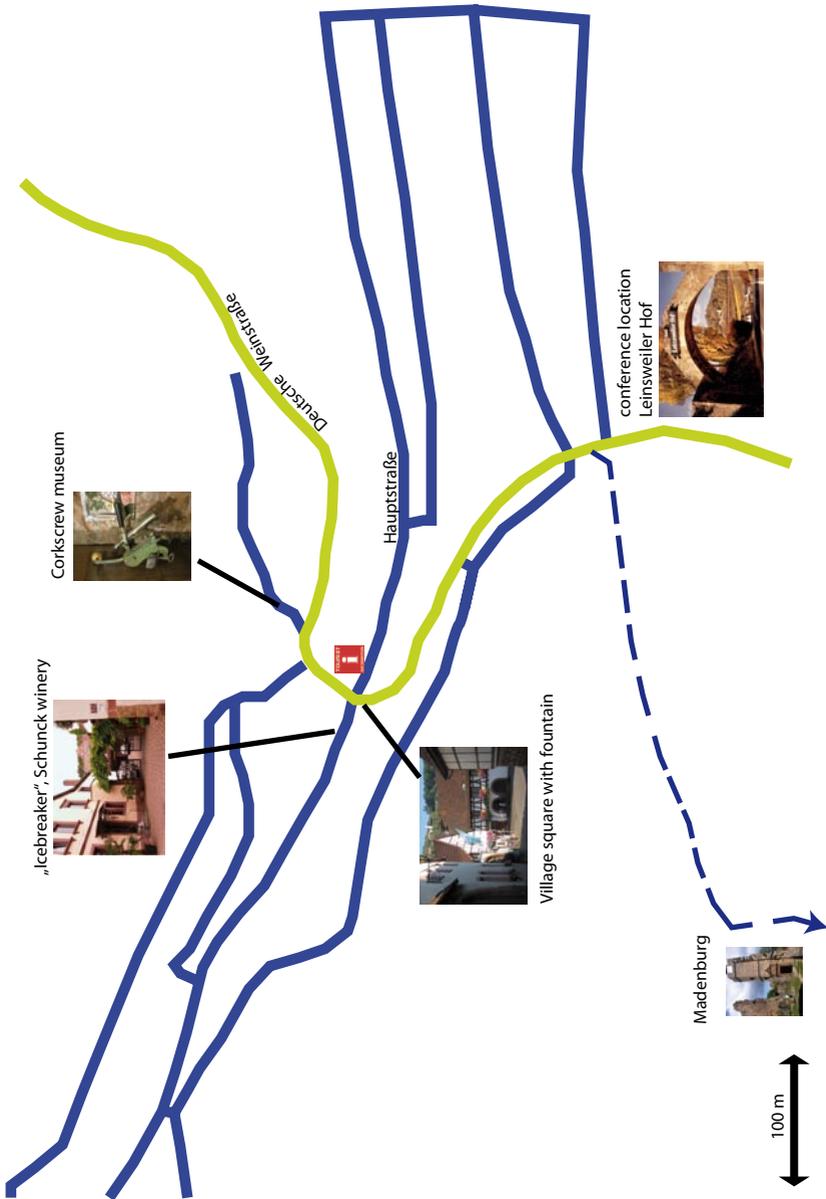
To investigate such type of polar interactions an experimental model system was set up for optimized contacting of solutions with solid surfaces: commercial carboxy-coated microscope slides showing a spongy 3D-structure (manufactured using molecular surface engineering) were contacted with MCPA. In order to enhance sensitivity, a disposable hybridization chamber, i.e. a micro-reaction chamber (a DNA analytical tool) was used. This way a reproducible and very low liquid film thickness was maintained, maximizing the surface/volume ratio. Adsorption-reaction times were extended up to several days.

The MCPA concentration remaining in solution was determined: the amount of sorbed MCPA was higher in presence of Ca<sup>2+</sup> than without Ca<sup>2+</sup>. This finding was interpreted as evidence for the Ca<sup>2+</sup> bridging between the carboxy groups of the solid and dissolved substrates, respectively.

notes:



Map of Leinsweiler village



## **Organization / Imprint**

### **Conference host**

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Institute of Environmental Sciences  
Chair Environmental and Soil Chemistry  
Fortstr. 7  
76829 Landau

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