Annual Meeting of the German Priority Programme
SPP 1315: Biogeochemical Interfaces in Soil

Jena, Conference Room of the Dining Hall
“PhiloMensa”,
October 09 – 11, 2013

Book of Abstracts
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General Information

Venue: Conference Room of the Dining Hall “PhiloMensa”

PhiloMensa is one of the two University’s cafeterias in downtown Jena. It was designed in 1929/30 by Neufert Ernst and Otto Banning in collaboration with the Bauhaus-Universität Weimar, the latter being not only associated with creativity and internationality, but also being known for linking theoretical knowledge with industrial practices. The building has been extensively restored in the mid-1990s. Currently, PhiloMensa offers 700 indoor seats and a nice garden with plenty of outdoor benches. The upper floor of the building occasionally serves as a conference room for a variety of symposia and meetings.

Internet Access:
User name and password will be provided at the venue.

List of Participants:
In order to receive full reimbursement from the German Research Foundation (DFG, Deutsche Forschungsgemeinschaft), please sign the list of participants daily.

Evaluation Form:
We kindly ask all the participants of the priority programme to fill out the evaluation form (provided at the Venue) by Thursday noon.
Programme
**PROGRAMME OF THE ANNUAL MEETING**  
**09-11 OCTOBER 2013, JENA**  
**CONFERENCE ROOM OF THE DINING HALL**  
**“PHILOMENSA” (PHILOSOPHENWEG 20)**

| Wednesday, October 09 |  
|-----------------------|---|
| **13:00-13:15** | Welcome |
| Kai U. Totsche |  

### Afternoon Session

**Joint Experiments Oral Presentations I**  
*Chaired by: Friederike Lang*

<table>
<thead>
<tr>
<th>13:15-13:45</th>
<th>Artificial Soil Incubation</th>
<th>Geertje J. Pronk</th>
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<tr>
<td>13:45-14:15</td>
<td>Hierarchical Structure of Biogeochemical Interfaces in Soil to Predict Transport of Reactive Chemicals in Soil</td>
<td>Thomas Ritschel &amp; Jannis Tzavaras</td>
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<td>14:15-14:45</td>
<td>Joining Two Imaging Techniques to Evidence the Effect of O2 Micro-Patterns on Metalaxyl Dissipation in Soil</td>
<td>Sascha Oswald</td>
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<td>14:45-15:15</td>
<td>The Soil-Litter Interface: A Hot Spot for Biogeochemical Interactions</td>
<td>Christian Poll</td>
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<td>15:15-15:45</td>
<td><strong>Coffee Break</strong></td>
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**Joint Experiments Oral Presentations II**  
*Chaired by: Christoph C. Tebbe*

<table>
<thead>
<tr>
<th>15:45-16:15</th>
<th>An Integrative Multidisciplinary Approach to Elucidate Structure and Function of Worm-Derived Biogeochemical Interfaces in Soil</th>
<th>Marcus A. Horn</th>
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<td>16:15-16:45</td>
<td>Interaction of Bacteria with Minerals at BGIs in Soils</td>
<td>Anja Miltner</td>
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<td>16:45-17:15</td>
<td>Effect of Phenanthrene and Hexadecane on the Release and Transport of Mobile Organic Matter in Maturated Soil</td>
<td>Katharina Reichel &amp; Doreen Babin</td>
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<td>17:15-17:35</td>
<td>Physicochemical Restructuring of Biogeochemical Interfaces: A Joint Experiment Linking Properties to Processes</td>
<td>Gabrielle E. Schaumann</td>
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<td>17:35-19:10</td>
<td><strong>Poster Session I: Individual Projects (odd numbers)</strong></td>
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| 19:10 | Dinner |  

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<tr>
<td>9:00-9:30</td>
<td>Evolved Cooperations Oral Presentations</td>
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<td>Chaired by: Geertje J. Pronk</td>
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<td>9:00-9:30</td>
<td>MCPA Adsorption by Goethite (α-FeOOH)</td>
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<td>9:30-9:55</td>
<td>Stabilization of Microbial Biomass in Soils: Implications for SOM Formation, Xenobiotic Degradation and Residue Formation</td>
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<td>9:55-11:30</td>
<td>Poster Session II: Individual Projects (even numbers) with Coffee</td>
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<td>11:30-12:30</td>
<td>Lunch</td>
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<td>Thematic Groups Oral Presentations</td>
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<td>Chaired by: Susanne K. Woche &amp; Thilo Streck</td>
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<td>12:30-12:50</td>
<td>TG1: Formation, Maturation and Dynamics of Biogeochemical Interfaces</td>
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<td>Anja Miltner</td>
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<td>12:50-13:10</td>
<td>TG2: Linking BGI properties with Phenomena and Processes</td>
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<td>Gabriele E. Schaumann</td>
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<td>13:10-13:30</td>
<td>TG3: Bridging Scales: Conceptual Understanding of Interface Properties and Functions at different Scales</td>
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<td>Kai U. Totsche</td>
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<td>Thomas Baumann &amp; Hans-Jörg Vogel</td>
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<td>13:50-14:10</td>
<td>TG5: Computational Chemistry and Advanced Physicochemical Characterisation: Quantitative Reconstruction and Modeling of BGl5 Properties and Interactions</td>
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<td>Daniel Tunega</td>
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<td>14:30-15:00</td>
<td>Coffee Break</td>
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<td>15:00-16:30</td>
<td>Workshops &amp; Discussions</td>
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<td>Workshop A: Towards the Grand Goal</td>
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| 16:30-17:30  | Workshop B: Joint Publications and Dissemination  
*Chaired by: Kai U. Totsche* |
| 17:30-18:00  | *Coffee Break*                                                       |
| 18:00-18:30  | Workshop C: The Final Symposium 2014  
*Chaired by: Joanna Hanzel* |
| 18:30-19:30  | Workshop D: Feedback from the Reviewers  
*Chaired by: Kai U. Totsche* |
| 19:30        | Dinner                                                               |

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**Friday, October 11**

**Morning Session**

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<th>Time</th>
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| 8:30-10:00   | Workshop E: Joint Experiments: Continuation and Final Work  
*Chaired by: Kornelia Smalla* |
| 10:00-10:30  | *Coffee Break*                                                       |
| 10:30-11:30  | Workshop F: Thematic Groups: Present, Future and Dissemination  
*Chaired by: Gabriele E. Schaumann* |
| 11:30-12:00  | Evaluation: SPP Reviewer Panel, SPP Members and Coordinator         |
| 12:00        | **The End**                                                          |
From the Coordinators Corner:
Highlights, Impact and Outreach of SPP1315 “Biogeochemical Interfaces in Soil”

Kai U. Totsche, on behalf of the “coordinating team” members Thilo Rennert (2007-2011) and Joanna Hanzel (2012-2014)

After now almost 6 years of joint research, it is time to balance the investments and what has been accomplished within the SPP1315. What are the “highlights”, what is the impact and is there an outreach of SPP1315? Of course, there is. Yet, it is not the mere statistics and bibliography, e.g., the number of original research papers and the publication of meanwhile four special thematic issues. Much more impressive are the people that made the SPP such an enjoyable and refreshing experience. At first, naturally, the PhD students and postdoc researchers, who had to carry the loads of putting in action the research plans of the projects. Chapeau also to the PIs: They not only took part in the sometimes controversial discussions but contributed to thematic groups and engaged themselves in the joint experiments. And, last but not least, our obeisance to the reviewers: Of course, they had the extremely difficult, unenviable and unrewarding job to select those projects that got funding within the priority program. But they also involved themselves actively in the discussion and contributed to our symposia and workshops to help make them a success.

Although the priority program funding format of the DFG does not provide the coordinator with tools to force the group in a certain direction, fortunately the structuring along thematic groups and the launching of joined experiments was the “strategy” to the – at least from the coordinators corner – success of the SPP. With this unique and commendable structure, the SPP developed in a vivid, curious and creative “band of researchers” that set out successfully to conquer the field biogeochemical interface science.

We still have roughly one year to go – the official ending of the funding but not of the research will be our final symposium next year in Leipzig – yet, I'm convinced that we will continue this fruitful cooperation not only for the remainder of the SPP running time but extend it in the future with other projects either offspring of or inspired by the work and atmosphere of SPP1315. Thank you all for this inspiring time!
Oral Presentations
Joint Experiments
The properties and development of biogeochemical interfaces in soils are determined by the type of mineral and organic surfaces available. The artificial soil incubation experiment was developed and carried out in order to gain insight into the effect of different components on interface development in a system with well-defined initial conditions. So-called ‘artificial soils’ were composed of different mixtures of the model materials quartz, montmorillonite, illite, ferrihydrite, boehmite and charcoal, manure as organic carbon substrate and a microbial inoculant from a natural Cambisol. The artificial soils were incubated for 3, 6, 12 and 18 months in the dark at 20°C at a constant water content of 60% of the maximum water holding capacity. Samples were distributed to a total of 11 different groups within the priority program and characterized for physical and chemical properties and microbial community development. Furthermore, some samples were incubated with different organic chemicals (e.g. phenanthrene, hexadecane) to determine sorption, degradation of chemicals and the effect of these chemicals on the microbial community. The parameters measured can be divided into characterisation of composition, structure, surface properties, microbial abundance and diversity, and artificial soil functioning, at different levels of resolution. In this presentation we summarise the results from this experiment and start building towards an integration of the various approaches of interface characterization.
Hierarchical structure of biogeochemical interfaces in soil to predict transport of reactive chemicals in soil

Thomas Ritschel¹, Jannis Tzavaras², Marc-Oliver Göbel³, Susanne K. Woche³, Katharina Reichel¹, John Maximilian Köhne², Hans-Jörg Vogel², Jörg Bachmann³ and Kai U. Totsche¹

¹Institute of Geosciences, Department of Hydrogeology, Friedrich Schiller University, Jena, Germany
²Department of Soil Physics, Helmholtz Centre for Environmental Research GmbH (UFZ), Halle, Germany
³Institute of Soil Science, Gottfried Wilhelm Leibniz University, Hannover, Germany

The reactive transport and transformation of organic chemicals (OC) in soils impact soil ecological and filter functions. A quantitative understanding of the processes and rates that control the distribution and persistence of OC is a mandatory prerequisite for the prediction of their fate in soils. Yet, "predictive models" to a large extent rely on parameters that have been obtained from "fitting" procedures with no predictive capabilities. Therefore, a desire not only in fundamental soil science would be to have a strategy that allows for independent quantitative reconstruction of properties. Our joint experiment on "Hierarchical structure of biogeochemical interfaces in soil to predict transport of reactive chemicals in soil" contributes to this ambitious goal. Results from pore scale model simulations suggest that highly irregular spatial distributions of reactive sites may strongly affect the macroscopic flow and transport patterns of OC, i.e. their breakthrough behavior. In natural soils, a spatially heterogeneous distribution of reactive interfaces can be expected to be more likely than a homogeneous distribution. Another issue that will be addressed is the availability/accessibility of reactive surfaces for mobile reactive substances. Even though some OC have a high sorption affinity to mineral surfaces, in natural porous media, these surfaces can be located inside aggregates, at grain-grain contacts, or in domains which do not participate in water flow. A quantification of the available surface is therefore a crucial step.

To study the decisive properties of a porous medium and its constituents and to get a mechanistic understanding of solute transport, we launched a joint column experiment to independently predict the reactive transport of target compounds. We started our experiments with well-defined granular mixtures of SPP artificial soil materials (i.e., quartz sand with silt, illite and/or iron oxides) and subsequently are going to study natural soils with sandy and loamy texture from Fuhrberg and Scheyern. For any given soil column, the starting point is the quantification of the pore structure of freshly packed columns for pore sizes > 0.1 mm using micro-computed tomography (μ-CT) followed by image analysis (group of Vogel, Halle). The 3D structure is then evaluated with the pore network model (PNM) to get effective continuum scale parameters (i.e. dispersivity). This allows for the prediction of a conservative tracer breakthrough without using any fitted parameters. The columns are then transferred to Jena for experiments, run in both closed and open flow mode, for investigating chemical fate and transport dynamics at variable saturated flow conditions (group of Totsche, Jena). A two-layer design with an organic source layer and a mineral reception layer is used in some columns (see joint experiment establishment of BGI, Reichel et al.). The solutes under study include NaCl as conservative tracer and acetate, phosphate, MCPA and vanillic acid as reactive chemicals (experiments still ongoing). After completion of the solute transport experiments, the columns are sliced. From each slice, subsamples are tak-
en for measuring interface properties at different scales, including i) adhesion forces and 3D-microtopography (>5nm resolution) using atomic force microscopy (AFM, Jena), ii) aggregate structure (SEM, Jena), iii) pore structure (μCT, 10 μm resolution), and iv) contact angles (<1 mm resolution) using the sessile drop method (SDM) (group of Bachmann, Hannover). In this way we aim at creating a 3D map of reactivity spots in the soil column, superimposed on its physical pore system geometry. If this can be achieved, the transport and breakthrough behavior of reactive chemicals can be predicted without any continuum scale parameter fitting.

In the past year, our joint experiment started by focusing on the technical realization of each of the experimental steps and the adaptation of the PNM. A method for the sub-sample extraction was developed and successfully tested on artificial soil material. Test soil columns have been investigated with SDM, SEM and AFM. Recent column experiments with goethite coated quartz lead to a first estimate of the availability of reactive surfaces under natural packing conditions and allow for the reconstruction of sorption isotherms.

Algorithms were developed and implemented in a software with a visual interface for matching 2D microscopy images with 3D μCT images (group of Vogel, Halle). As a result, any measuring point can be located in the μCT image, as long as the sample shows a clearly identifiable pore structure. Transient flow dynamics have been successfully implemented in the PNM. The infiltration process with time dependent pressure and water saturation calculation is now yielding consistent results which still need to be experimentally verified. A capillary rise simulation has been applied to the PNM as well.

The closed flow column design was adapted to quantify aromatic compounds in column effluents online with fluorescence or UV/VIS spectroscopy and factor analysis. These fast and nonconsuming methods result in a high time resolution of breakthrough data and the closed mass balance is beneficial for the quantification of sorbed substances. This allows for a detailed comparison of prediction and measurement. In order to improve the determination of small-scale wetting properties an in situ preparation technique combined with high resolution contact angle measurements was developed.

Further steps are the implementation of solute transport under transient conditions and the inclusion of different contact angles for various pores in the PNM. Another open challenging task is to quantitatively implement the already measured data on physical-chemical heterogeneity in the pore network. Moreover, extraction of subsamples from aggregated soils, combined with matching of measurement points in μCT, proved to be difficult. These tasks will be addressed in the remaining time of the project.
Joining two imaging techniques to evidence the effect of O\textsubscript{2} micro-patterns on metalaxyl dissipation in soil

Sascha Oswald\textsuperscript{1}, Nicole Rudolph\textsuperscript{1}, Sebastian Zühlke\textsuperscript{2}, Sebastian Gottfried\textsuperscript{2} and Michael Spiteller\textsuperscript{2}

\textsuperscript{1}Institute of Earth and Environmental Science, University of Potsdam, Potsdam, Germany
\textsuperscript{2}Institute of Environmental Research of the Faculty of Chemistry, Dortmund University of Technology, Dortmund, Germany

The soil-root interface is a highly heterogeneous system in terms of pH and O\textsubscript{2} distribution. This is not only producing niches with different levels of pesticide turn-over, but also applies to some degree to seemingly homogenous systems in the laboratory. Thus, also experiments aiming to control these influences and study pesticide kinetics under given pH or O\textsubscript{2} conditions suffer from a large uncertainty of the “real” pH/O\textsubscript{2} at a certain position. Here, we combined two imaging techniques, that is MALDI imaging and optical fluorescence imaging, to map pH and oxygen in a plant-soil system after treatment with the fungicide metalaxyl and following analysis of metalaxyl concentrations (Gottfried et al., 2013). By this approach we can show directly, that the pH has an influence on enantioselective dissipation of the acetonilide metalaxyl (from an applied racemic mixture, the R-enantiomer dissipates faster than the S-enantiomer in areas with high pH). Furthermore, we could show directly that sorption of metalaxyl to the root depends on O\textsubscript{2} concentration. The sum of the results indicates a great power of combined imaging approaches to examine soil-root interfaces as well as compartmentalized dissipation processes of organic pollutants in general.

References
The soil-litter interface: A hot spot for biogeochemical interactions

Christian Poll\textsuperscript{1}, Holger Pagel\textsuperscript{2}, Franziska Ditterich\textsuperscript{1}, Aurelia Gebala\textsuperscript{1}, Karolina Nowak\textsuperscript{3}, Anja Miltner\textsuperscript{3}, Marc Pinheiro\textsuperscript{4}, Laure Vieublé-Gonod\textsuperscript{4}, Thilo Streck\textsuperscript{2} and Ellen Kandeler\textsuperscript{1}

\textsuperscript{1}Institute of Soil Science and Land Evaluation, Soil Biology, University of Hohenheim, Stuttgart, Germany
\textsuperscript{2}Institute of Soil Science and Land Evaluation, Biogeophysics, University of Hohenheim, Stuttgart, Germany
\textsuperscript{3}Helmholtz Centre for Environmental Research - UFZ, Department of Environmental Biotechnology, Leipzig, Germany
\textsuperscript{4}INRA AgroParisTech, Thiverval-Grignon, France

The soil-litter interface is an important biogeochemical interface where carbon enters the soil. Whereas most studies focused on the flow of litter C into the soil and its microbial utilisation, much less attention was drawn to possible consequences of C transport on soil processes not directly connected to litter C turnover. Our joint experiments use the herbicide MCPA as a model compound to study microbial-physicochemical interactions during soil organic matter decomposition at the soil-litter interface. Transport of litter compounds was identified as important process, which regulates the activity of the MCPA degrading community at the soil-litter interface. The increased bacterial and fungal MCPA degradation might be explained by complex regulation mechanisms of MCPA degradation: (1) At the cellular level by co-substrate availability and laccase abundance, and (2) at the microhabitat level by interaction between MCPA degraders and organo-mineral surfaces as well as transport processes. These hypotheses were addressed in new experiments focusing on the effect of laccase on MCPA degradation, the contribution of different degrader communities to MCPA degradation and the importance of transport processes at the soil-litter interface. Finally, we developed a mathematical model, which integrates biological and physical processes to improve our understanding of the microbial regulation of MCPA degradation in this microhabitat.
The Joint Earthworm Column Experiment (TG4/TG6): An integrative multidisciplinary approach to elucidate structure and function of worm-derived biogeochemical interfaces in soil

Marcus A. Horn1, Jörg Bachmann2, Thomas Baumann3, Marko Bertmer4, Werner Borken5, Harold L. Drake1, Marc-Oliver Göbel2, Joanna Hanzel6, Katja Heister7, Alex Jäger4, Matthias Kästner8, Michael Kersten9, Faisal Khan9, Ingrid Kögel-Knabner7,10, Max Köhne14, Christian Metz3, Ralf Mertel1, Anja Miltner8, Yamuna Kunhi Mouvenchery11, Aniela Mundinger1, Reinhard Niessner, Pavel Ondruch11, Sascha Oswald12, Anja Ramm1, Thomas Ritschel6, Nicole Rudolph12, Gabriele E. Schaumann11, Michael Spiteller13, Stefan Strohmeier5, Kai U. Totsche6, Cordula Vogel7, Hans-Jörg Vogel14, Veronika Will1 and Sebastian Zühlke13

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7Chair of Soil Science, Department Ecology and Ecosystem Management, Technische Universität München, Freising-Weihenstephan, Germany
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9Institute of Geosciences, Johannes Gutenberg University, Mainz, Germany
10Institute for Advanced Study, Technical University of Munich, Garching, Germany
11Department of Soil and Organic Chemistry, Institute for Environmental Science, University Koblenz-Landau, Landau, Germany
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Earthworms represent the dominant macrofauna in many soils. The burrowing activity of earthworms creates a network of macropores in soil that have a nutrient rich lining. Burrow wall surface area might represent up to 1.2 m² m⁻³ soil, highlighting the potential importance of such structures for sorption and transport, soil aeration, biotransformations, and plant root growth. Earthworms enhance the degradation of certain herbicides like 4-chloro-2-methylphenoxyacetic acid (MCPA). Burrows represent ‘hotspots’ for the microbial degradation of MCPA. Thus, an experiment with a model soil aggregates from Scheyern was set up to address the effect of the earthworm Aporrectodea caliginosa on (1) MCPA-derived CO₂ fluxes, (2) the distribution of stable aggregates, pore sizes as well as oxygen, (3) redox potential, (4) dead organic matter, (5) nano-scale surface properties including composition of microaggregates, (6) transport and preferential flow paths, (7) contact angle and wettability, (8) surface hydration and biofilm formation, (9) spatial distribution of MCPA and its metabolites, as well as (10) active microbial transformers of MCPA and their distribution. Seven treatments were be set up: Soil columns with earthworms and [¹²C]- or [¹³C]MCPA, soil with [¹²C]- or [¹³C]MCPA only, soil with worms only, and soil only. Soil columns were destructively sampled fol-
lowing µCT measurements when app. 60% of the MCPA in MCPA-supplemented columns was depleted. Earthworms produced complex macropore networks. MCPA disappeared in the presence and in the absence of earthworms. Cast was deposed on the soil surface and inside burrows. µCT and ¹H NMR Relaxometry indicated that cast and burrow material was highly compacted compared to bulk soil. ¹H NMR Relaxometry indicated that water mobility was lower in cast and burrow material than in bulk soil. Cast and burrow material were less hygroscopic than bulk soil. Contact angle measurements indicated a reduced wettability of cast material compared to bulk soil and burrow material. XPS analyses indicated a higher C-to-N ratio and a C enrichment in cast compared to bulk soil. RAMAN spectroscopy identified a compound that has a low amount of C-H compared to C=C and C=O bonds at the burrow wall surface. 78 and 60% of MCPA-derived [¹³C] were recovered in [¹³C]O₂ from treatments with and without earthworms, respectively. Chloromethylphenol was detected as a degradation intermediate of MCPA. PLFA-SIP indicated that gram negative bacteria in the stationary phase assimilated [¹³C]MCPA primarily in burrow wall material rather than bulk soil. Transcription of genes encoding oxygenases initiating MCPA conversion (i.e., tfdA, r/sdpa, cadA) was primarily stimulated by MCPA. Transcriptional activities essentially declined with soil depth and distance to burrow walls in the presence of MCPA. Detected transcripts were likewise indicative of gram negative bacteria. The collective results indicate that earthworms enhance the mineralization of MCPA by creating burrows and thus aerated biogeochemical interfaces in soil with physico-chemical properties distinct from those of bulk soil.
Interactions of bacteria with minerals at biogeochemical interfaces in soils

Anja Miltner\textsuperscript{1}, Jan Achtenhagen\textsuperscript{1}, Marc-Oliver Göbel\textsuperscript{2}, Gabriele E. Schaumann\textsuperscript{3}, Do-reen Babin\textsuperscript{4}, Kornelia Smalla\textsuperscript{4}, Jörg Bachmann\textsuperscript{2} and Matthias Kästner\textsuperscript{1}

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\textsuperscript{3}Institute of Environmental and Soil Chemistry, University of Koblenz-Landau, Landau, Germany
\textsuperscript{4}Institute for Epidemiology and Pathogen Diagnostics, Julius Kühn Institute, Federal Centre for Cultivated Plants, Braunschweig, Germany

Occurrence of soil wettability after drought periods is a known phenomenon, but it is still not well understood. Recently, it has been shown that microbial residues are an important constituent of soil organic matter, thus imprinting their chemical and physical properties on it. It has also been shown that microorganisms change their surface properties in response to environmental conditions. In particular, they get more hydrophobic if they grow under water stress. It is unclear, however, how these alterations of their surface properties are imprinted on soil surface properties and thus control the properties of biogeochemical interfaces in soil, which would then in turn feedback on the environmental conditions for microbial growth. This question is studied in a joint experiment in laboratory systems with increasing complexity. In a first step, a bacterial strain, \textit{Pseudomonas putida} mt-2, was exposed to osmotic stress by growth in the presence of NaCl. We observed the interactions of stressed and unstressed cells with different soil minerals (quartz of different purity and grain size, kaolinite), and the contact angle of the associations was analysed as a key surface property. We found that stressed bacteria had a significantly higher contact angle than unstressed cells. The attachment of bacteria or bacterial fragments significantly increased the contact angle of quartz. The extent of the effect depended on the bacterial surface coverage on the minerals, but it was significant already at rather low coverages (<10%). The different surface properties of the bacteria induced by stress were reflected in the contact angle of the cell-mineral associations. Both cell fragments and the cytosol proved to be more efficient in increasing the contact angle of quartz, probably because they spread over a larger area. On the other hand, the degree of attachment of bacteria to surfaces was not clearly determined by chemical interactions or surface charge; but may be a function of bacterial functionality. Thus, the properties of the microbial biomass residues are indeed reflected in the surface properties of the biomass-mineral associations. The existence of biomass-mineral associations is also supported by AFM-nanothermal analysis of young soils. The next steps in a future project to be applied for will be (1) to study the process in more complex systems including real soil materials instead of pure minerals and bacterial communities instead of pure cultures and (2) to complement the information on the surface and material properties by analysing the surfaces more thoroughly for their biological, chemical and physical characteristics. Analysis of the biogeochemical interfaces by sophisticated and complementary methods such as contact angle analysis at different scales (sessile drop method and ESEM), analysis of the chemical composition of the surfaces by XPS and their characteristics by a variety of AFM methods, including AFM-PFQNM, AFM-nTA and functionalised tips, will allow us to elucidate how and to what extent microbial residues contribute to the formation of hydrophobic soils.
Joint Experiment 7

Effect of phenanthrene and hexadecane on the release and transport of mobile organic matter in matured soil

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Biogeochemical interfaces (BGIs) in soils are “hot spots” of microbial communities and turnover of organic substances. We hypothesize that the model compounds and additional carbon sources phenanthrene (PHE) and hexadecane (HEX) influence microbial communities, which in turn may affect the release of mobile organic matter (MOM), including biocolloids, and the properties of BGIs in matured soils. We explored the release of PHE and HEX using a new experimental approach employing two-layer columns (10x12 cm) filled with matured soil originating from a Luvisol (Scheyern, Germany; Ah, 5-20 cm). The upper layer (2 cm) served as source layer (SL) and was either spiked with PHE (0.2 mg g⁻¹) or HEX (2.0 mg g⁻¹). The lower layer, further called “reception layer” (RL, 10 cm) only contained the Luvisol soil material. The experiment was carried out under unsaturated flow conditions with two replicates per treatment (control columns were left un-spiked). Columns were irrigated with artificial rain water for one month (1-1.5 pore volume day⁻¹) with several flow interrupts (FI) of different durations (1-52 days) to allow reactions at BGIs. Physicochemical and chemical parameters (pH, EC, turbidity, TOC/DOC, anions/cations, PHE, HEX and their metabolites) and the microbial community composition were analysed in effluent samples and in soil slices with different distances to the SL obtained at end of the flow period.

The release of MOM from the columns was in general controlled by non-equilibrium. Total organic carbon (TOC) and dissolved organic carbon (DOC) differed by a factor of 1.2 after the flow interrupts. During flow, no TOC/DOC-difference was observed. PHE had only a slight effect on MOM release, which was observed after the long FI of 26 days. First results of the currently running columns spiked with HEX showed a similar behavior. Turbidity and hydrodynamic diameter, two parameters that relate to suspended particles and colloids, were unaffected in the PHE treated columns. Yet, HEX substantially increased these parameters.

In all effluent fractions of the PHE experiment, diverse and heterogeneous bacterial communities were found. This proves the assumption that microorganisms are mobile in a soil under studied flow conditions. By denaturing gradient gel electrophoresis (DGGE), depth distribution of the bacterial communities associated with the immobile solid phase indicated high similarities among different depth layers and treatments. In response to BET, some DGGE bands exhibited increasing intensity or disappeared, especially in fingerprints of Betaproteobacteria and Actinobacteria. Abundances of genes involved in the anaerobic and aerobic degradation of PHE, as well as a few bacterial populations in DGGE fingerprints were shown to be depending on the distance to SL in PHE-spiked columns.

Chemical analysis of PHE at the solid phase showed a slight displacement of the model substance at the boundary SL to RL and the concentration decreased downstream across the entire column. Small contact angles (6.6 ± 5.2 °) were determined in all Luvisol ma-
aterials indicating good and rapid wettability of the surfaces. Slightly higher contact angles (17.5 ± 3.7°) were observed in lowest RL slice of the PHE spiked Luvisol. Our results suggest that single microorganisms and even communities can be transported under unsaturated flow conditions. First indications point to the fact that the additional carbon source will impact not only the activity of special microbial taxa, but also the mobilization and transport of these microorganisms. The fact that microbes will be mobilized and passively transported to downstream compartments will help to understand the processes that result in the inhabitation of pristine surfaces, thereby resulting in the formation of new biogeochemical interfaces.
Physicochemical restructuring of biogeochemical interfaces – a joint experiment linking properties to processes –

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Summary: Linking properties of biogeochemical interfaces (BGI) to processes implements that BGI properties are measurable and accessible during experiments and can be predicted for various field conditions. It is further important to judge the stability of BGI properties in the field as well as during ongoing experiments. In addition, differences in sample preparation, storage or handling during individual experiments have a not fully understood effect on BGI properties. This includes knowledge on kinetics and effects of swelling processes within the solid-liquid interphase occurring during sorption experiments. Sample preparation and storage can have significant impact on BGI properties, for example on soil wettability (Diehl et al. 2009), kinetics of DOM release (Schaumann 2000; Schaumann et al. 2000), and sorption of organic chemicals (Schneckenburger et al. 2012). Knowledge of the effect of different drying temperatures and storage durations on BGI properties is furthermore required in order to be able to merge results of diverse experiments. Therefore, members of the Thematic Group 2 have conducted a joint experiment to test the stability of BGI properties towards the physical and physicochemical influences mentioned above.

Multivalent cations are suggested to influence the supramolecular structure of SOM via inter- and intra-molecular interactions with SOM functional groups. In this study we tested the combined effect of multivalent cations, temperature treatment, and isothermal aging time on SOM matrix properties. Samples from a peat and a mineral soil were either enriched with Na, Ca, and Al or desalinated in a batch experiment. After treatment at different temperatures (25°C, 40°C, 60°C, 105°C) and after different periods of aging at 19°C and 31% relative humidity, we investigated the samples with regard to the degree of protonation of acidic functional groups of SOM, the physicochemical matrix stability and the thermal stability against combustion. Furthermore, contact angles and sorption properties of the samples using organic chemicals as sorbates were determined. Additionally, several properties of water dispersible colloids and amounts of exchangeable cations were analyzed.
Our hypotheses were that (i) multivalent cations stabilize the OM matrix physically and chemically via cation bridges between charged functional groups of SOM, that (ii) temperature treatment disrupts these stabilizing structures, but (iii) aging leads to a successive increase in matrix stability. Although the results show that sample treatment affects stability and matrix rigidity, a direct and immediate cation-specific effect on matrix rigidity was not observed. Only after 8 weeks of aging, differences between samples treated with different cations started to evolve. According to the matrix rigidity and the thermal stability the samples were subdivided into two groups. Na- and Ca-treated samples and control samples reveal lower thermal stability and lower matrix rigidity than those treated with H and Al. Aging generally increased matrix stability. The same effect, but faster, was observed upon temperature treatment at 40°C. Temperature treatment at higher temperature led to two types of irreversible changes: (1) the loss of the WaMB transition at 60°C and higher, i.e. the loss of the matrix stabilisation via water molecule bridges, and (2) an endothermic process, which is most probably caused by melting of semicrystalline poly(methylene). These processes may change the binding status of organic chemicals, as well as colloidal and surface soil properties of soil.

With increasing valence of the dominant cations, SOM contains less and larger easily mobilized colloids probably due to cation cross-links or due to enhanced aggregation caused by reduced surface charge. The altered SOM offer more or better accessible sorption sites for hydrophobic xenobiotics. But in contrast to our hypothesis, hydrophilic sorption, as well as wettability, was not significantly affected by these changes. Increasing temperature as well as aging has a major impact on surface properties resulting in increasing surface hydrophobization with increasing solid–water contact angles and decreasing sorption of hydrophilic substances, while systematic temperature effects on easily mobilized colloids and on hydrophobic sorption could not be detected.

Conclusions: The synthesis of our results shows that aging and, even more intense, temperature treatment results in structural changes in SOM leading to a reorientation of polar moieties to inner surfaces. The relation between contact angle, physicochemical matrix structure and sorption characteristics furthermore clearly documents that sorption is a sensitive measure indicating changes in SOM physicochemical properties. The variability of sorption rates and coefficients emphasizes the relevance of biogeochemical interface properties on fate and mobility of xenobiotics and natural organics.

It is remarkable that the effects of cation treatment are significantly lower than those of temperature treatment in the soils and for the temperature range tested. This suggests that the structures formed with the multivalent cations induce stability, but other structures, like WaMB and physical network links are effective at least in the same size of order and can even overbalance pure cation effects. This becomes clear from the consideration that only a low percentage of the organic carbon is linked to carboxylic or phenolic groups, and other intermolecular interactions including van der Waals interactions may become relevant solely because they outnumber the cation binding interactions. Whichever structure is stabilizing the physicochemical OM network, it is remarkable that such rearrangements induced by heat, drying, cation treatment and sample storage are not instantaneously reversible in contact with water. Modified surface properties maintain their characteristics for important processes as it was shown for sorption of water and organic compounds. The dynamics of rearrangement is an important key process for the modelling of surface specific processes and to understand the functioning of the solid-liquid interface in real three-phase systems.
Publications arising from the joint experiment


Publications related to the joint experiment (State: 20.9.2013)


Publications to be submitted in 2013

Joint publications of the joint experiment


Oral Presentations
Evolved Cooperations
MCPC adsorption by goethite ($\alpha$-FeOOH)

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This contribution details on results of a joint experiment within the framework of SPP TG5 “Computational chemistry and advanced physicochemical characterization: Quantitative reconstruction and modeling of BGIs, their properties and interactions”. Fe oxide surfaces host BGIs which control sorption and retardation of many agrochemicals in soils. The interaction between the dominating (110) goethite surface and the modern wide-spread herbicide 4-chloro-2-methylphenoxyacetic acid (MCPC) was studied on a molecular level by means of first principles calculations based on density functional theory (DFT) using the PBE exchange-correlation functional approach. Structural and energetic features of the surface complexes were evaluated using a periodic slab model for the goethite surface. Our investigations showed that the (110) goethite surface formed by three types of hydroxyl groups offers a variety of optimized structures for hydrogen bond formation with the polar adsorbent. Binding energies and bond lengths for the interaction of these three hydroxyl groups with the MCPC carboxylic group in its various states (protonated, deprotonated, outer-sphere, inner-sphere) were calculated. A major breakthrough was made by introducing a protonated surface for this type of modeling. Equally low binding energy was found for a bidentate outer-sphere complex formation and a monodentate inner-sphere complex formation with the protonated MCPC anion, with oxygen sharing between the MCPC carboxylate and a singly-coordinated surface hydroxyl group with a release of one H$_2$O molecule for the latter surface complex. The outer-sphere bidentate complex is stabilized by O$_{\text{Carb}}$⋅⋅⋅µ$_3$OH and H$_{\text{Carb}}$⋅⋅⋅OH hydrogen bonding between the MCPC carboxylate and two surface hydroxyl groups, one triply-coordinated and one singly-coordinated, accompanying by a proton transfer for the latter. All other complexes calculated are higher in a relative energy with a less probability to determine the surface complexation process. The two most probable structures were used to constrain for a CD-MUSIC surface complexation model the charge distributions according to the Brown bond valence concept. The adsorption constants of the two surface complexation reactions were ultimately fitted with experimental batch equilibration data. These adsorption constants enable us to perform 1D transport modeling of MCPC in a soil column using the PHREEQC code. The modeling results are to be verified by experimental breakthrough curves derived in cooperation with TG3 and TG4.
Stabilization of microbial biomass in soils: Implications for SOM formation, xenobiotic degradation, and residue formation

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Soil organic matter (SOM) plays an important role in soils as carbon source and the habitat of soil microorganisms; its quality and quantity affect soil microbial activity. SOM also strongly interacts with mineral surfaces and affects physical soil properties such as wettability, water retention and thermal properties. The amount and composition of SOM determines soil quality, but SOM formation and stabilization are not yet sufficiently understood. The carbon from any degradable organic compound divides into parent compound, metabolites, CO₂, and microbial biomass. This distribution must be considered for assessing the fate of a given compound and the carbon flow in soil. Recent results identified microbial biomass as a significant source for SOM. By incubating ¹³C-labelled bacterial and fungal cells in soils and tracing the fate of the label of bacterial biomass components, it could be shown that a high percentage of the biomass carbon (in particular from proteins) remains in the non-living SOM. These residues were visualized by scanning electron microscopy (SEM) as fragmented bacterial cell walls debris of 200-500 nm size in various stages of decay and fragmentation. Similar fragments developed on initially clean and sterile in situ microcosms during exposure in groundwater, thus providing clear evidence for their microbial origin during growth and colonization.

The role of this process during early pedogenesis has been demonstrated using samples from a chronosequence in the Damma glacier forefield. SEM micrographs of these samples showed that the number of cell wall fragments attached to the mineral surfaces increased with increasing soil age, together with the C and N contents, the abundance and diversity of soil microorganisms and the contact angle of the soil material.

This process is not only relevant for the transformation of natural but also of anthropogenic compounds. If bacteria grow on pollutants as carbon source, they will incorporate the pollutant-derived carbon into their biomass. This biomass will later be stabilized in SOM and thus contribute to NER formation. This has been demonstrated in studies on the biodegradation of several isotope labeled pesticides and pharmaceuticals in soil, where the contribution of microbial biomass residues to non-extractable residues (NER) in soil was quantified. The high amount of label found in biomolecules (fatty acids, amino acids) indicated that virtually all of the NER was made up by microbial biomass residues. NER of less degradable xenobiotics, however, can also be formed by immobilization of the intact parent compound or its primary metabolites. Examples and a scheme for the environmental risk assessment of NER differentiating xenobiotic, either entrapped (type I) or covalently bound (type II), and biogenic residues (type III) will be presented.

A significant contribution of microbial cell envelope fragments to SOM formation and their stabilization by interaction with mineral surfaces thus provides a simple explana-
tion for the development of the small patches of organic materials observed in soil electron micrographs. It also suggests that microstructures of microbial cells and of small plant debris provide the molecular architecture of SOM attached to particle surfaces and represent water absorbing biopolymers. The suggested origin and macromolecular architecture of SOM is consistent with most observations on SOM, e.g. the abundance of biomarkers, the low C/N ratio, the water repellency, the stabilization of biomolecules, and the formation of bioNER from pesticides.

References
Oral Presentations
Thematic Groups
Biogeochemical interfaces play an important role for all processes occurring in soils. A thorough understanding of their formation, maturation and dynamics in soils is therefore crucial to understand soil processes and functions. In this respect, the particular properties of biogeochemical interfaces have to be taken into account. Biogeochemical interfaces can be found at very different spatial scales, ranging from nm (e.g. sorbed molecules at particle surfaces) to dm (e.g. soil horizons) and even Gm (earth surface), and relevant processes cover a similarly wide range of time scales from fs to millenia. The functions of biogeochemical interfaces are similarly manifold. They provide habitats for soil (micro)organisms, supply nutrients, buffer waste products and thus are a platform for (micro)biological activity. The objectives of Thematic Group 1 are (1) to study the role of different soil components for the formation of biogeochemical interfaces, (2) to identify relevant processes and (3) to elucidate the controls of biogeochemical interface properties. Two examples are highlighted to present the activities of this Thematic Group. Firstly, the formation of biogeochemical interfaces has been studied in artificial soils, i.e. synthetic mixtures of soil minerals, organic matter, and a microbial inoculum. The mineralogical composition of the clay fraction in these mixtures was varied in a systematic way to study the influence of soil mineralogy on biogeochemical interfaces. In a joint effort of a number of groups samples from this experiment were investigated for a wide variety of parameters related to structure, composition, surface properties, function and microbial activity during biogeochemical interface formation. Results of this endeavour will be published in a joint paper which is currently being prepared. A second joint experiment will investigate the interrelationships between microbial growth conditions and biogeochemical interface properties. Recently, it has been shown that microbial biomass residues contribute significantly to SOM formation. They will therefore be an important constituent of biogeochemical interfaces. It has also been shown that the surface properties of bacteria are affected by their growth conditions, e.g. water availability. This could be an important mechanism leading to decreased wettability of soils after drought periods. The joint experiment will investigate how surface properties of bacteria as affected by water stress are reflected in soil-microbe associations and soil organic matter. Biological processes as well as chemical and physical soil properties will be studied in laboratory systems with increasing complexity. It is planned to continue these activities after the end of the priority program. The activities of Thematic Group 1 therefore give insights into the formation and maturation of biogeochemical interfaces and reveal processes occurring at biogeochemical interfaces as well as their properties and functions.
TG2: Linking BGI properties with phenomena and processes

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The biotic and abiotic properties of BGIs shape transformation rates to a large extend. Vice versa turnover processes and fluxes of organic matter highly influence the biotic and abiotic properties of BGIs. Thus there is a close link between properties of BGIs and processes, which undergoes continuous changes in time and space. This led to the concept of “hot spots and hot moments”. If a steady state of BGI properties and processes will be reached and which conditions promote this stadium is not clear.

The objective of project partners in TG2 is to obtain a mechanistic understanding on the link between properties of biogeochemical interfaces (BGI) and processes and phenomena controlled by biogeochemical processes. Main focus will be given on aspects addressing the temporal dynamics and spatial distribution pattern of BGIs. Processes of interest include transport as well as transformation of organic chemicals. Major properties are related to the abiotic architecture of BGI (including surface properties and porosity) as well as biotic parameters (microbial community structure function and activity).

The objective of TG2 is to carry out the synthesis and to link approaches from the different disciplines with the order to obtain a mechanistic understanding. The steps are: (i) Identification of leading properties governing processes, (ii) Understand the mutual feedback between properties and processes and (iii) understand the relations between biological and physicochemical factors and processes: Which properties control which type of process and which processes control which type of property and to unravel the hierarchy of the interaction network.
**TG3: Bridging scales: Conceptual understanding of interface properties and functions at different scales**

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The Grand Goal of SPP 1315 is to develop a unified and generic mechanistic framework to understand and predict the governing role of biogeochemical interfaces for the processing of organic chemicals in soils (Totsche *et al.*, 2010). One fundamental challenge is thereby to link the processes that are operative at the local scale, e.g. the molecule or an individual organism scale, to the phenomena active at the continuum, i.e., the pedon scale in a mechanistic way. The particular objectives of thematic group 3 are therefore to gain quantitative understanding of the interplay, interdependencies, and feedbacks of soil physical, soil chemical and soil biological processes across scales and to relate structural and structural properties to the processes and finally to soil functions. In a pioneering paper by Vogel and Roth (1993) the “scaleway” concept has been proposed to predict flow and transport in structured materials independent of scale or specific type of structural organization. It is based on a reconstruction of the macroscopic structure of the material present at a chosen scale of interest in terms of different structural-functional units, while all microscopic heterogeneities within the individual units are replaced by effective parameters. The ingredients required are “a representation of the structure, a process model at the scale of interest, and corresponding effective material properties.” They exemplified operability of the approach employing transport of a conservative solute through an undisturbed soil core. The application of this approach to reactive transport in natural soil materials has so far not been undertaken. Among others, this will require to consider solutes undergoing non-equilibrium and non-linear interactions with the immobile solid phase interfaces. Yet, it must also consider biological activity that may not only result in degradation of the solutes but also affect the hydraulic active structure by changing the wettability of interfaces. One aspect of outstanding importance is to prove that all relevant processes operative at the chosen scale can be represented by effective parameters, i.e., that microscopic heterogeneities are dissipative and therefore average out at the scale of interest, so that only the macroscopic structure matters. Totsche (2010) indicated an approach to calculate “effective sorption” on the macroscopic scale taking explicitly into account the microscopic heterogeneities to allow for the quantification of the continuum scale phenomena of retardation. Bachmann and coworkers (Bachmann *et al.*, 2013) presented a technique to directly measure the wetting properties of undisturbed soil surfaces. This contributes to the assessment of effective material properties on the continuum scale. Based on these findings, two joint experiments are under way (*Hierarchical structures-Quantitative reconstruction and Establishment of BGI under flow condition*) within SPP1315 that not only provide the experimental observations to validate the “extended scaleway” approach, but also to identify and contribute to the solutions of fundamental problems, that, e.g., lie in the fact, that information obtained on the relevant material properties are available at different scales and not all techniques developed so far are operative in three-dimensions or are non-destructive. Nevertheless, progress has been made both in experimental and instrumental techniques (Rennert *et al.*, 2012) and in the theoretical pervasion (Planned...
The independent prediction of reactive solute transport in natural porous media based on the knowledge of the explicit structure and an extended assessment of material properties without the need for “parameter fitting” seems now to be in reach.

References
Totsche KU. 2010. From Atome to Pedon: Linking processes to phenomena and function, extended abstract (4 pages) 19th World Congress of Soil Science, Soil Solutions for a Changing World, 1 – 6 August 2010, Brisbane, Australia. Published on CDROM.
Biogeochemical interfaces are transient in space and time, thus rendering batch tests under equilibrium conditions and without spatial restrictions are inadequate to predict the overall behavior. To open this black box and to look at the spatial architecture of biogeochemical interfaces sophisticated chemical and biological imaging methods are required. Ideally, these methods would provide a high spatial and temporal resolution while still maintaining a large imaging region, high chemical sensitivity and selectivity, and little sample preparation. Within the framework of the SPP 1315 a variety of analytical methods with imaging capabilities have been applied, starting with e.g. secondary ion mass spectrometry or atomic force microscopy with nanometer resolution and ending with antibody-based imaging techniques with mm-voxel resolution. Although the maximum sample size was set to a cubic decimeter, there was little overlap between the spatial resolution of the methods. Some of the techniques deliver pixel or voxel integrated information, like e.g. CT or MRI, thus capturing the heterogeneity continuously in space. Other techniques loose information between discrete but highly resolved measurement areas. It is a challenge to combine different approaches such that information can be transferred between various scales to generate a comprehensive picture of the architecture of biogeochemical interfaces. Imaging techniques used within the SPP 1315 provide different levels of physical and chemical information, pore topology, rigidity of interfaces, molecular vibrations or elemental composition, to name a few. Many of the techniques have been developed or significantly improved during the projects. In some cases a consistent information chain has been established between complementary methods, while in other cases there is still a gap between the information provided. Within the SPP the current focus is on the spatial architecture of BGIs. However the reactor function of soil is also governed by their temporal dynamics, i.e. the aging and recreation of reactive zones. Hence, another challenge is to profit from the developed imaging techniques to gain information also on this aspect. A promising avenue along this line is to evaluate the time scale of internal mixing based on the evaluation of local biogeochemical gradients. The developed techniques provide some valuable tools for this purpose. There is an enormous development of spectro-microscopic and tomographic methods worldwide. Within our SPP, especially the joint experiments provide significant insight how to integrate different techniques to reveal the complexity of biogeochemical interfaces in soil.
Thematic Group 5

TG 5: Computational chemistry and advanced physico-chemical characterization: Quantitative reconstruction and modelling of BGIs, their properties and interactions

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Understanding the basis and mechanisms at molecular level represents an important contribution to a complex characterization of biogeochemical interfaces (BGIs) and processes in soil. Within the frame of the TG5 molecular modelling methods were brought together with advanced experimental techniques in order to contribute to better understanding features of BGIs and their compositional and structural complexity, heterogeneity, and interactions. Using advanced computational modelling methods to model biogeochemical interfaces in soil represents one of the important and new approaches in soil science. One of the challenges is bridging and linking molecular and higher (e.g. microscopic) scales of complex and heterogeneous BGIs systems investigated by molecular simulations and experimental techniques. On one side this requires using sophisticated design of representative molecular structures representing BGIs and application of multiscale molecular modelling approach and combination of a broad scale of modelling methods and techniques. On the other side this process requires using modern experimental techniques operating at micro- to nanoscales, selection of proper model systems for experimental studies, and preparation of suitable experiments. Important task represents linking of modelling and experimental outputs. Current spatial and temporal scales in molecular modelling, which are manageable in a realistic computational time, are up to tenths of nanometers and microseconds. Molecular simulation methods are helpful in exploring basic mechanisms and elementary steps which cannot be investigated experimentally at present. They support experiments by explanation and interpretation of experimental observations and sometimes are the only “solution” if experiments are too expensive or impractical.

In this presentation we give a brief overview of achievements within the frame of TG5. On several examples we illustrate the progress achieved in the group in the characterization of BGIs and their components. The examples will comprise

• interactions of organic species (e.g. MCPA, PAHs) with soil components (soil minerals, SOM)
• role of water and cation bridges in the SOM stabilization, hydration and wettability of SOM
• wettability of mineral and organo-mineral surfaces

These examples are presented in a relation to successful collaborations of the molecular modeling group with several experimental groups involved in the TG5. They will also show the current state of knowledge, but they also demonstrate that there are still challenges to be overcome in order to comprehensively understand functioning of BGIs.

We will, therefore, discuss practical limitations of the featured approaches and the potentials, limitations and the further development in linking molecular modeling and experimental studies of BGIs.
TG 6: Soil microbial ecology: Explore community's role for BGIs as "architect and actor" - elucidate transformation of organic chemicals (period: October 2012-October 2013)

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The year 2012/13 started after a very stimulating and successful international conference in March 2012 (Dornburg) (Life in Microhabitats of Soils - Microbial Ecology of Biogeochemical Interfaces) that was initiated as an outgrowth of ongoing discussions of TG6. A major contribution of TG6 is the special issue "Microbial ecology of biogeochemical interfaces – diversity, structure and function of microhabitats in soil" just published in FEMS ME (IF: 3.563) with seven original papers from the SPP1315. The primary goals of TG6 over the years have been and are to join efforts to improve our understanding of the role of microbial communities in soil and their impact on the formation and properties of Biogeochemical Interfaces (BGIs) and their relevance for fate of selected xenobiotics (MCPA, phenanthrene, hexadecane, and 2,4 dichlorophenol) in water-unsaturated soil. Discussions within the group over the past six years led to the idea that in soil next to primary particles, hierarchical structures exist that consist of BGIs which are formed by larger organisms such as earthworms or plants, e.g. rhizosphere, detritusphere, and drilosphere. These can be summarized under the term ‘Biogeochemical Spheres’ (BGS). Several joint experiments were performed and analyzed in 2012/2013: The central experiment on long term matured artificial soils and their response to the addition of maize litter and phenanthrene (Schloter, Smalla, Kandeler, Kögel-Knabner, Heister, Tebbe), the detritusphere (Kandler) and the drilosphere (Horn). Beyond these joint experiments, members of seven projects of the SPP1315 (Hanzel, Horn, Kolb, Drake, Tebbe, Kästner, Schloter, Kandler and Totsche) wrote a joint review on the BGS concept, which is presently prepared for a resubmission. The review article deals with the currently fragmented knowledge on microbial diversity and their dynamics in these BGS and identifies methodological bottlenecks (e.g., combination of computer tomography and single-cell based methods) which deserve further development. Thus, the goal to achieve an improved link between microbial communities and their spatial arrangement in BGSs will be perused.
Poster Presentations
Isotope effects to characterize the molecular interactions of organic contaminants with soil components

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The aim of this project is to combine sorption processes of organic substances with compound-specific stable isotope analysis (CSIA). If naturally occurring stable isotopes are measured in natural and model systems, such isotope fractionation has the potential to provide mechanistic insight into the prevailing sorption processes. The approach is based on the hypothesis that the two most important molecular interactions governing sorption processes are van-der-Waals interactions and hydrogen bonds. Every molecule or substance interacts via van-der-Waals interactions. In addition, hydrogen bonds may become important if H-bond donor or H-bond acceptor functionalities meet. Available evidence suggests that van-der-Waals interactions cause an inverse isotope effect in organic chemicals if they partition from a condensed phase into the gas phase. In contrast, a normal isotope effect is observed if hydrogen bond interactions become dominant.

To this end, we pursue an approach starting with simple model systems. Purge and trap, a dynamic headspace technique, is used to investigate the partitioning of the substances between water/air (nitrogen) and hexadecane/air (nitrogen), respectively. From these experiments isotope effects are obtained that are determined by a combination of van-der-Waals/hydrogen bond interactions and van-der-Waals interactions alone, respectively. Subsequently, experiments addressing organic matter/water partitioning will follow to use the observable isotope effects as a diagnostic tool that offers a new handle to characterize the interactions of organic compounds with biogeochemical interfaces such as organic matter or mineral surfaces.
Stability of bacteria in soil: Organo-mineral interactions and cell status as important factors

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Soil organic matter (SOM) has a complex chemical structure, which - despite high efforts in the past - is widely unknown. Existing models for SOM genesis consider plant material as the main source. However, recent studies point to an important impact of microbial residues on SOM formation: chemical analyses show that microbial compounds accumulate during litter degradation, and investigations by means of scanning electron microscopy indicate that cell envelope fragments are highly abundant in soils. These fragments seem to contribute to a large extent to SOM formation.

The mechanisms which are responsible for the protection against degradation are not yet elucidated. The interactions with mineral and metal oxide surfaces may play a significant role. In general, these interactions have far-reaching consequences for soil properties and functions and are an often described mechanism for SOM stabilization. We hypothesize, that the organo-mineral interactions, in particular incrustation of organic material by sesquioxides lead to a better protection against degradation and that cell fragments are degraded slower due to their structure. These hypotheses were tested in an experiment with radio labeled microbial biomass.

In this experiment, we tested the degradation of 14C-labeled Escherichia coli cells and cell fragments. Both materials were incubated alone and incrusted by coprecipitation with two different metal oxides/hydroxides (ferrihydrite and boehmite) in closed soil systems. The systems were incubated at different levels of oxygen to investigate the effect of changes in oxygen content. As an indicator for degradation, the formation of 14CO2 was monitored using liquid scintillation counting (LSC), while the residual activity in soil was measured by combustion using a biological oxidizer and subsequent LSC analysis.

We found that incrustation into the minerals decreased the mineralization of both the intact cells and the cell fragments by about 60% (ferrihydrite) and 50% (boehmite). This indicates a strong protection of the biomass (both, intact or as fragments) by the interaction with the sesquioxides. In addition, cell fragments were mineralized to a lower extent than intact cells. Cell fragment mineralization was 20% lower than mineralization of intact cells. This suggests that the cell envelopes are more recalcitrant than the bulk cell carbon, resulting in selective enrichment of cell envelope material during degradation of microbial biomass in soils. The effect of the different oxygen conditions on mineralization was negligible.

The results of the degradation experiments thus confirmed our hypotheses. Our study demonstrates both the relatively higher stability of the cell envelope material compared to the bulk biomass and the importance of organo-mineral interactions as a mechanism for soil organic matter protection.
Microbial communities and phenol mineralisation potential of soil particle size fractions

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Soil features diverse biogeochemical interfaces, due to various minerals and organic matter of different quality. These surfaces as represented by particle size fractions (PSF) can provide habitats for structurally different microbial communities. Neumann et al. (2013) showed that these particle-specific communities respond differently to fertilisation treatments. To explore and compare such distinct communities and their potential to mineralise phenol, soil variants from the Askov Long Term Experiment (DK), which share the same particle size distribution and pH value but differ in organic matter content and fertilisation treatment, were separated into a particulate organic matter (POM) containing sand-sized fraction (63 – 2000 µm), coarse silt (20 – 63 µm), fine silt (2 – 20 µm), and clay (< 2 µm) by mild sonication, wet sieving and centrifugation, as described by Neumann et al. (2013). Abundance determination and fingerprint analyses of Bacteria, Archaea, and Fungi from PSF-extracted DNA were conducted by qPCR and terminal restriction fragment length polymorphism (T-RFLP), respectively. To investigate the mineralisation of ¹⁴C-phenol, PSF were mixed with sterile quartz. ¹⁴CO₂ was determined by liquid scintillation counting. The sand-sized fraction contained 10⁸ gene copies g⁻¹ fraction of Bacteria, as well as 10⁶ and 10⁵ for Archaea and Fungi, respectively. These numbers increased with decreasing particle size up to 3-4 orders of magnitude in clay. Generally PSF from manured soil showed higher microbial abundances. The PSF harboured distinguishable communities and fertilisation treatment also shaped community structure, but these factors were not equally: While Bacteria and Fungi were clustered primarily by PSF, for Archaea fertilisation treatment was the main driver. Phenol mineralisation rate was negatively correlated with microbial abundances of the PSF, with the exception of coarse silt, where the lowest amount of phenol was mineralised. The time until mineralisation almost finished differed in the same pattern, from 3 days in clay up to 5 weeks in coarse silt. PSF from manured soil mineralised up to twice as much phenol. Our study demonstrates that PSF contain distinct microbial communities with different potentials to mineralise phenol depending on phylum and fertilisation treatment.

References
Studying the enzymatic influence on the formation of bound residues of $^{14}$C-metalaxyl in soil: The use of immobilized laccase

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The fate of xenobiotics and the formation of non-extractable residues (NER) in soil depend on various biological and physico-chemical factors. Especially, exocellular phenoloxidases and peroxidases as representatives of the oxidoreductase family in soil, may contribute to NER formation by oxidative coupling reactions during humification, which lead to the formation of covalent bonds between organic xenobiotics and the soil organic matter (SOM) or their sequestration. The selective influence of immobilized laccase as prominent member of the phenoloxidase family was studied in sterile soil ($\gamma$-irradiation, 25 kGy). Laccase was immobilized using alginate gel and CuSO$_4$ (0.15 M) which resulted in beads showing a diameter of 0.5 cm. These beads were mixed with sterile soil (treated with $^{14}$C-metalaxyl) in a polyamide bag; the bag was placed within an identical amount of sterile soil (treated with an identical amount of $^{14}$C-metalaxyl but without immobilized laccase) and both were incubated for 10 days at 19 °C in the dark. After exhaustive extraction (water and methanol) the soil was divided into its humic matter fractions (non-humines, humines, humic acids, fulvic acids) to quantify and examine the distribution of the NER and to compare it with preliminary results of our group. We could demonstrate that Laccase immobilized in alginate significantly increased the amount of NER in the soil. This proves the enzymatic influence of exocellular oxidoreductases on NER formation of $^{14}$C-metalaxyl in soil by covalent linkages to the humic matter fractions. In comparison to preliminary results we can conclude that the presence of living microbes or immobilized enzymes result in different amounts and distributions of NER among these fractions.
The soil-litter interface as potential seed bank of alkane degrading bacteria

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The soil-litter interface (detritus sphere) is the contact area between plant biomass and soil surface which is characterized by high nutrient and carbon fluxes. This is exceptional in the often oligotrophic soil habitat. Alkanes derived from decaying plant material account for a steady hydrocarbon input into soil and may explain the ubiquitous microbial alkane degradation potential. The impact of plant litter composed biogeochemical interfaces (BGIs), however, on a specific ecosystem functions, i.e. alkane degradation, is largely unexplored. To address this question, we modeled a soil-litter interface by incubating uncontaminated sandy soil microcosms with maize litter. The effects of the plant-derived alkanes on the alkane degrading bacterial community were studied by culture-dependent and –independent methods. Cell enumeration by Most Probable Number-assay indicated elevated numbers of alkane degraders pointing to an enhanced alkane degradation potential in soil in response to BGI formation. Elaborate isolation experiments in conjunction with molecular fingerprinting analyses of alkane degraders, revealed spatio-temporal community changes with a steadily increasing richness of alkane degrading isolates. In total, 395 alkane degraders were isolated, which were affiliated to forty distinct operational taxonomic units (OTUs, genera or families). Ten OTUs were yet unrelated to alkane degradation and five OTUs represented putative new bacterial genera. These results point to an unexpectedly high phylogenetic distribution of the alkane degradation capacity in soil, which may be fostered by the formation of a soil-litter interface. Moreover, many of the isolates obtained were not detectable with molecular fingerprinting. This points to the existence of an alkane degrading rare biosphere in uncontaminated soil and the presence of specialized hydrocarbon degrading bacteria. The BGI may thus play a significant role in soil function maintenance by contributing to the formation of a seed bank of alkane degraders (Giebler et al., 2013).

References
Fungal-bacterial teams during the colonization of artificial soils

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Various soil aging experiments in the priority program indicated that with increasing soil age, the impacts of soil composition, i.e. heterogeneity of biogeochemical interfaces (BGI), and soil maturation become more prominent fostering accordingly matured community compositions and niche formation. Here, we investigated the role of fungi and the interactions with bacteria in four two year aged artificial soils during the degradation of plant litter.

The soils contained quartz sand and silt and either montmorillonite or illite or mixtures of montmorillonite and charcoal or illite and ferrihydrite. These mixtures were inoculated with a natural microbial inoculum (water-extracted from a Luvisol) and subsequently aged for two years. Afterwards, they were amended with maize-potato litter (1 % (w/w)) and incubated for 7, 21 and 63 days. The microbial communities were analyzed using quantitative PCR (qPCR) and terminal restriction fragment length polymorphism analysis (T-RFLP) and fungal ribosomal intergenic spacer analysis (F-ARISA), targeting phylogenetic marker genes for bacteria and fungi, respectively. A network modeling approach should subsequently reveal co-colonization of fungi and bacteria in the different soils based on co-occurrence patterns derived from an integrative analysis of the individual fingerprints.

After two years of aging no soil type dependent differences of fungal abundance were observed, whereby the addition of plant litter generally increased the ITS gene copy numbers. Likewise, no strong stimulation of fungi was observed over time. In contrast, soil-dependent patterning in the fungal community fingerprinting was observed after two years of aging. Whereas the two illite-containing soils did not differ significantly from each other, indicating only minor influences of ferrihydrite, the addition of charcoal evoked a strong community divergence from soil with only montmorillonite. Moreover, the fungal community in the charcoal-containing soil was more similar to these of illite soils. However, most communities strongly converged after litter amendment. Solely charcoal-containing soil displayed only minor changes in response to the plant material. Bacterial communities also showed soil type-dependent patterns after aging to some extent, but here all communities strongly diverged after litter addition (for details see abstract of Tanuwidjaja et al.).

Statistical co-occurrence analyses showed distinct associative and avoidance relationships of fungal and bacterial fragments which were accordingly influenced by soil composition. This indicates significant BGI-specific fungal-bacterial interactions during soil colonization. Shared niche preferences and helper-effects (e.g. preferential dispersal along mycelia (“fungal highways”), hence, might foster soil type dependent community patterns in different soil types.
Soil composition and maturation as drivers of functional microbial communities and their response to disturbances

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The huge structural heterogeneity of soil is believed to foster an enormous microbial diversity, and soil biogeochemical interfaces (BGIs) are assumed to be hotspots of microbial diversity and activity (Totsche et al., 2010). Due to the eons of pedogenesis it is, however, difficult to infer main factors shaping microbial diversity and ecosystem functioning in different soils. We therefore studied temporal changes of the diversity of alkane degrading bacteria during the maturation of eight different artificial soils, and analyzed their response to disturbances induced by supplementing an additional soil-litter interface as a nutrient rich BGI with high alkane turnover.

The artificial soils contained either single components or mixtures of montmorillonite, illite, charcoal, ferrihydrite or boehmite in addition to quartz sand and silt as structural elements (Pronk et al., 2012). These were inoculated with a microbial inoculum and aged for three (T3) or twelve months (T12). Subsequently, they were incubated with winter wheat litter on the surface for further two weeks (T3+L and T12+L, respectively). Quantitative PCR (qPCR) and terminal restriction fragment length polymorphism analysis (T-RFLP) targeting a functional marker gene (alkB coding for the alkane monooxygenase, key enzyme in bacterial alkane degradation) were expected to reveal quantitative and qualitative differences in the community composition of alkane degraders during maturation of the different soils and responses to disturbances.

Generally higher alkB gene copy numbers were detected in T3 compared to T12 in the different soils. However, the communities at T12 responded much stronger to litter amendment (ΔT12+L/T12 higher than ΔT3+L/T3). Concomitantly, stronger community shifts were detected after litter amendment for twelve than for three months aged soils with converging community compositions in response to substrate availability. In general, the alkane degrading communities of different soil types increasingly diverged with ongoing aging and influences of different soil components (e.g. charcoal and ferrihydrite) were detected at the different stages of soil development.

Hence, our data suggest that the development of functional communities is strongly coupled to the composition and the state of maturation of artificial soils. Moreover, with increasing age, these impacts become more prominent suggesting matured community compositions and niche formation. In the older soils the substrate supply might be limited after one year of aging. By addition of new substrate the communities were able to strongly react and converging community shifts may point to a microbial “memory effect” of the starving twelve months artificial soils, while the potential to degrade alkanes is reactivated.
References
BGIs are a driving force for the establishment of microbial communities: Influence of plant litter and soil composition on the establishment and structure of bacterial communities

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Due to its heterogeneity soil is one of the most complex ecosystems where microorganisms can live. It consists of a multitude of microhabitats and biogeochemical interfaces (BGIs) that strongly influence the microbial ecology. In this experiment, we investigated the effect of plant litter addition and soil composition on the colonization and development of bacterial communities in different artificial soils and a natural soil. The four artificial soils consisted of quartz sand, silt and (i) montmorillonite, (ii) illite, (iii) montmorillonite and charcoal or (iv) illite and ferrihydrite. All artificial soils were inoculated with microorganisms extracted from a Luvisol and sterile manure and matured for two years to allow BGI formation (Pronk et al., 2012). The aged artificial soils and one natural Luvisol were mixed with equal amounts of ¹⁵N and ¹³C labelled maize and potato litter and incubated in the dark up to 63 days at constant temperature of 14°C and soil moisture of 60 % mWHC. Controls without litter were treated in the same way. Soil samples were taken 0, 7, 21 and 63 days after the plant litter addition. Bacterial community abundance and structure in soils with different composition were analysed on DNA and mRNA level using quantitative PCR (qPCR) and terminal restriction fragment length polymorphism analysis (T-RFLP). The 16S rRNA gene copy numbers were similar in natural and artificial soils. Despite the litter addition an increase in 16S rRNA gene copy numbers in natural soil was not detected. In comparison to 16S rRNA the 16S cDNA copy number values were significantly higher in all soils. In all artificial soils incubated with plant litter transcript values were higher than those in control soils. The increase of transcript values followed immediately after the litter addition, whereas in the natural soil the increase was delayed for 7 days. This implies that the easily available nutrients have a stronger influence on the activity of bacterial communities than the BGIs. T-RFLP analysis of 16S rRNA gene suggests that the bacterial community structure is dependent on soil composition as well as on time and litter addition. In contrast, T-RFLP of 16S cDNA revealed a different active community in the Luvisol compared to the artificial soils, while no significant difference was observed among the artificial soils. Taken together the data indicate that the mineral composition of artificial soils has an impact on the overall bacterial community composition but not on the active community. Moreover, the positive effect of released nutrients is delayed in the Luvisol where already complex BGIs exist, which might have reacted with nutrient particles.
References
Investigation of organo-mineral association in an artificial soil experiment using $^{15}$N and $^{13}$C labeled litter

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Soils are complex and dynamic systems composed of minerals, organic matter (OM) and microorganisms as solid constituents. The mineral-OM-microorganism interactions in soil influence the formation of organo-mineral associations as reactive interfaces. Clay minerals, iron oxides and charcoal are considered as major constituents affecting the formation of these interfaces in soil. The analyses of the complex interaction between minerals, organic and microbial components in soil are hampered by the huge influence of different environmental conditions and the usually unknown initial conditions. Therefore, artificial soil systems offer a valuable approach where the formation and interactions of soil properties and processes can be studied in a well-defined system.

The aim of our study was to examine the effect of different mineral compositions and charcoal on the formation of organo-mineral associations after OM addition to an already established artificial soil system.

For this purpose, 35 g of artificial soil (<2 mm) was mixed with 0.35 g $^{13}$C and $^{15}$N labeled litter (<200 µm) and incubated over 63 days. The artificial soils were produced in a long-term incubation experiment over 842 days. Four different compositions (montmorillonite (MT), illite (IL), montmorillonite + charcoal (MT+CH), illite + ferrihydrite (IL+FH)) and in addition a natural topsoil (Luvisol) were used for the incubation. The experiment was performed in three independent replicates per composition under defined conditions at 14 ºC and a water holding capacity of 60%. Samples were taken directly after litter addition and then after 7, 21 and 63 days. The isotopic nitrogen and carbon composition of the bulk soil and the soil fractions were monitored using an isotope ratio mass spectrometer after a combined density and particle-size fractionation.

Our results show that $^{13}$C is mineralized relatively quickly, whereas $^{15}$N remained constant. The immediate enrichment in the small-sized fractions indicates a rapid development of newly formed interfaces. The highest $^{15}$N and $^{13}$C concentrations in organo-mineral associations after 63 days were observed in the clay-sized fraction. First results point to a different effect of the clay minerals illite and montmorillonite on the formation of organo-mineral associations.
Does the quality of particulate organic matter influence the formation and functioning of soil microaggregates?

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Aggregation is a key process for the formation of biogeochemical interfaces (BGIs) and may control properties and functioning of BGIs in soil. Silt-sized soil aggregates are known to play an important role in storage and stabilization of soil organic matter (SOM) and in retention of organic pollutants. Virto et al. (2008) showed that OM occluded in stable micro-aggregates was more processed than the OM stored in bigger (less stable) aggregates. We hypothesize that the propensity of particulate organic matter (POM) to induce aggregate formation increases with degradation.

To test this hypothesis we synthesized artificial soil-aggregates by shaking quartz, goethite, kaolinite, and POM in 0.01 M KCl at pH 4. Differently processed POM was derived from Oi and Oa horizons of a podzol. All primary materials as well as the formed mineral-organic aggregates were characterized by SEM, and analytical centrifugation. Additional the POM was characterized by FTIR and C and N concentrations were determined. Afterwards the formed aggregates were subjected to density fractionation combined with ultrasound application (energy 400 J ml⁻¹). Three different fractions were derived: free POM, POM occluded in aggregates, and OM sorbed to mineral surfaces. Additionally sorption experiments with ¹⁴C-labeled MCPA and phenanthrene were conducted.

Density fractionation and sedimentation analyses indicate that mineral-organic associations were formed in presence of both types of POM. In contrast to literature (Haberhauer et al., 1998) the results from FTIR analyses reveal that the Oi-POM contains a higher amount of hydrophilic functional groups. The more hydrophilic Oi-POM showed a larger propensity to form aggregates with the minerals than the less hydrophilic Oa material (Oi = 92 w% of Corg mineral-associated; Oa = 58 w% of Corg mineral-associated). The C/N-ratio of Oa-POM is more or less similar in all density fractions, while the C/N-ratio of the Oi-POM differs strongly among the different OM fractions. The lowest C/N-ratio indicating advanced degradation was found in the OM fraction sorbed to mineral surfaces, supporting our hypothesis. Results of sorption experiments will be presented during the meeting.

References

Clay mineralogy shapes microbial habitats and macroaggregates during a long-term artificial soil incubation experiment

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Natural soils are complex systems with various interactions between mineral surfaces, organic matter (OM) and microorganisms shaping highly heterogeneous habitats. These so-called biogeochemical interfaces are important for different ecosystem functions. To unravel the effect of OM addition on soil properties, artificial soils were established under lab conditions for more than 2 years. Five different artificial soil compositions varying in content or presence of clay minerals (illite, montmorillonite), metal oxides (ferrihydrite, boehmite) and charcoal, respectively, were spiked with microorganisms from a Luvisol, and sterile manure. After 562 days, a second manure addition was conducted to simulate a natural OM input. Total community DNA was extracted and abundance (qPCR) and structure (denaturing gradient gel electrophoresis) of 16S rRNA genes were analyzed before, after second manure addition and at the end of the incubation time (842 days). Additionally, the total organic carbon (OC) and nitrogen (N) contents, the formation of macroaggregates (> 2mm), the particle size distribution of OC and N and the CO₂ respiration were determined. In response to OM addition, clearly elevated CO₂ respiration rates and bacterial abundances were detected, indicating a priming effect and a pre-establishment of microhabitats before OM addition. Similar changes in bacterial communities of all artificial soils were observed and fast responders were identified belonging to genus Pseudomonas. Although the OM input altered the bacterial community, the clay minerals represented the main driver of the microbial community over the long term. The compositions with montmorillonite showed more macroaggregates than mixtures with illite at the end of the incubation, which was induced by the additional organic substrate. Consequently, clay minerals were identified as key players for the microbial and structural development of these soil-like systems during a long-term incubation.
A new microscale sampling device and first results of a colloid tracer experiment

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To elucidate microscale processes at biogeochemical interfaces in soil appropriate sampling techniques are needed. We present a new sampling device to obtain soil material from thin layers (down to 0.1 mm) of small soil cores in stainless steel sampling rings (d=5.6 cm, h=4 cm). The soil sampling ring is fixed with a custom-made frame and by means of a stepping motor the inner soil core is then pushed stepwise through the sampling ring and cut with a sharp blade to sample defined layers. This technique will be used to sample soil from microcosm experiments of studies at the soil-litter interface in the future. For the first time, however, we applied the new device to sample soil cores of a colloid tracer experiment. Fluorescent microspheres with a negative surface charge (d=1 and 2 µm) were used as model colloids to study the transport of bacterial cells in soil. A layer (h=3 mm) of colloid enriched soil (10⁸ colloids (g soil)⁻¹ concentration of colloids) was placed on packed soil cores (d=5.6 cm, h=3 cm). The soil cores were placed on ceramic plates to maintain a suction of -63 hPa (pF 1.8) at the lower boundary and they were irrigated with 0.01 M CaCl₂ solution at a rate of 1 mm h⁻¹. After 0.5, 1.5 and 2.5 pore volumes the soil cores were sliced in 1 mm layers using the new microscale sampling device and the concentration of fluorescent colloids as well as bromide (used as conservative tracer) was determined. These data will be used to estimate the parameters of a colloid/ bacteria transport model by inversion. The transport model will be linked with the recently developed PECCAD model to simulate the transport of specific pesticide degraders at the soil-litter interface. Here, we present first experimental results of the colloid tracer experiment.
Succession of Soil Microbial Communities and Enzyme Activities in Artificial Soils


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More than 80-90% of microorganisms are attached to mineral surfaces or mineral-organic complexes. The initial adsorption of bacteria on clay minerals, which is strongly influenced by environmental factors, is an important pre-requisite for the survival and function of soil microorganisms. Until today, less is known about the colonization and succession of different soil minerals by microorganisms. Furthermore, the effect of soil mineral composition on the microbial community structure has been rarely explored. Hence, we hypothesised that (1) early microbial colonization and succession of reactive surfaces will be explained by life history strategies and/or nutrient availability (r- and K-strategists) and (2) the complexity of mineral composition in artificial soils will change the structural diversity of colonizing microorganisms.

In order to test these objectives eight different artificial soils with the same soil texture (42% fine sand, 52% silt and 6% clay), but with different mineral composition were used. The materials consisted of quartz + (a) one mineral component (montmorillonite; illite; ferrihydrite), (b) two mineral components (montmorillonite + illite; montmorillonite + charcoal; illite + ferrihydrite; illite + boehmite), (c) three mineral components (illite + ferrihydrite + charcoal), sterilized organic manure (carbon source) and a microbial inoculum from an Eutric Cambisol (Ultuna, Sweden). The soils were incubated 3, 6, 12 and 18 months under constant temperature (20°C) and water conditions (60% of maximum water holding capacity) in the dark. Microbial community composition was measured by quantitative PCR and structural diversity was determined using phospholipid fatty acid (PLFA) extraction.

Discriminant analyses of PLFAs showed that the microbial community structure changed over a period of 18 months towards similar communities at the end of incubation, which could be probably explained by nutrient limitation. Molecular analyses for the different mineral component systems showed similar results: One mineral vice versa three mineral components changed the complexity of bacterial community composition only under high nutrient status at the beginning of the experiment. Betaproteobacteria (r-strategists) were replaced by acidobacteria (K-strategists) in artificial soils over a period of 18 months.

This study showed that microbial colonization and succession on mineral surfaces is affected by mineral properties and nutrient availability.
Soil composition controls microbial response to plant litter and phenanthrene in matured artificial soils

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Previous studies showed the influence of the soil mineral composition and charcoal on the initial development, establishment of bacterial communities and their response to the model pollutant phenanthrene (Ding et al., 2013; Babin et al., 2013). In a follow-up artificial soil experiment we addressed the questions how long-term, soil composition-driven microbial communities respond to phenanthrene and whether the addition of plant litter affects this interaction. Artificial soils were composed by adding an identical inoculant from a natural Luvisol to 4 soil compositions differing in the type of clay mineral (illite, montmorillonite) and presence of charcoal or ferrihydrite (Pronk et al., 2012). After more than 2 years of maturation, artificial soils amended with or without litter were spiked with phenanthrene. Total community DNA, extracted from samples taken 0, 7, 21 and 63 days after phenanthrene spiking, was studied by 16S rRNA gene and ITS fragment-based analyses.

Pyrosequencing and denaturing gradient gel electrophoresis (DGGE) revealed that the type of clay mineral was the main factor shaping the bacterial community composition. Actinobacteria, Bacteriodetes, and Alphaproteobacteria were more abundant in soils containing illite whereas montmorillonite-soils exhibited more Gammaproteobacteria and Firmicutes. Influence of ferrihydrite or charcoal was seen on lower taxonomic levels. Pyrosequencing and DGGE data showed, consistently, a stable soil composition effect on Bacteria in all treatments. After phenanthrene spiking, bacterial communities in soils containing only montmorillonite revealed higher dissimilarities to other artificial soil compositions as seen by pyrosequencing. For instance, a high number of sequences affiliated to the genus Kocuria was found in artificial soils composed solely of montmorillonite, whereas Arthrobacter was enriched in all other phenanthrene-spiked soils. Adhaeribacter, Devosia, and Luteimonas were common positive responders to the litter addition. Pontibacter was found to be increased only in the presence of montmorillonite and Cellvibrio in soils containing illite. Bacillus presented a genus highly sensitive to the soil composition and treatment. In the combined treatment of phenanthrene and litter, increased bacterial 16S rRNA gene copy numbers but a decreased number of phenanthrene responders were observed. Changes in the fungal DGGE fingerprints in response to phenanthrene were only detected in the presence of litter. In conclusion, a long-term driving influence of the soil composition on the structure and response of microbial communities was discovered.

References

Modelling MCPA turnover and microbial dynamics at the soil-litter interface

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The detritusphere (soil close to the soil-litter interface) is characterized by a high availability of litter-derived organic substrates stimulating microbial growth and activity. It is a hotspot of carbon (C) turnover and degradation of pesticides. To improve our understanding of the regulation mechanisms, which are responsible for stimulated degradation of the herbicide MCPA (2-Methyl-4-chlorophenoxyacetic acid) at the soil-litter interface, we applied the recently developed PECCAD (PEsticide degradation Coupled to CArbon turnover in the Detritusphere) model (Pagel et al. 2013) with the data of a detailed microcosm experiment. We prepared ¹⁴C-MCPA (50 mg kg⁻¹) amended soil cores and set up three experimental treatments: 1) maize litter (control), 2) MCPA and 3) MCPA + maize litter. The litter was placed on top of the soil cores and the microcosms were incubated at 20 °C for 23 days. We analysed MCPA and different C pools (soil and CO₂) for total concentration as well isotopic composition (¹³C, ¹⁴C). We measured three molecular markers (tfdA, 16SrRNA and 18SrRNA genes) to estimate the abundance of bacterial MCPA degraders, total bacteria and fungi in soil. The PECCAD model was calibrated using these data by means of a multi-objective Pareto analysis.

In the detritusphere we observed increasing concentrations of dissolved organic matter (DOM) and accelerated degradation of MCPA. Litter stimulated the microbial community as reflected by increased abundances of tfdA, 16S rRNA and 18S rRNA genes in the detritusphere. The PECCAD model could match the observed C dynamic and the model was able to simulate accelerated MCPA degradation at the soil-litter interface. Both, experimental results and PECCAD model simulations, confirm that enhanced microbial growth and activity at the soil-litter interface is responsible for accelerating MCPA degradation. The model simulations indicate that, in addition to specific bacterial degraders also unspecific fungal enzymes might be substantially involved in MCPA degradation at the soil-litter interface.

References
Chitin hydrolysis in an aerated agricultural soil and associated known and novel chitinase genotypes

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Chitin, consisting of alternating β-1,4-linked N-acetylglucosamine (GlcNAc) residues, is an abundant biopolymer in soils, which are ‘hot spots’ of production and degradation of chitin (Gooday 1990). Aerobic and anaerobic soil microbes can degrade chitin by initial hydrolyzation via exo- and endochitinases to N,N’-diacetylchitobiose ([GlcNAc]₂) and longer oligomers of GlcNAc. An alternative degradation pathway involves prior deacetylation to chitosan and the subsequent hydrolyzation to chitobiose ([GlcN]₂) and longer oligomers of glucosamine (GlcN). The preferred pathway of chitin hydrolysis in soil microbial communities has yet not been resolved. In an aerated soil, oxygen distribution is highly heterogeneous, and dynamic on the micro- to millimeter scale due to different porosity in- and outside of soil aggregates and complex interactions in ‘Biogeochemical Interfaces’ (Totsche et al., 2010). Therefore, different redox processes, such as fermentation or oxygen respiration, can simultaneously be active when chitin is degraded. The aim of this study was to resolve the preferred pathway of chitin hydrolysis and to assess the responses of chitinolytic taxa and the processes associated with chitin, chitosan, [GlcNAc]₂, GlcNAc, and GlCN hydrolysis under oxic and anoxic conditions. Chitin was degraded under oxic and anoxic conditions in agricultural soil slurries, whereas chitosan was not substantially degraded. Thus, hydrolysis of chitin was preferred to the pathway that starts with deacetylation to chitosan. All N-sugars were aerobically degraded by aerobic respiration, ammonification, and nitrification to carbon dioxide and nitrate. When oxygen was absent, fermentation products (acetate, butyrate, propionate, hydrogen, carbon dioxide) and ammonia were detected. Thus, likely butyrate and propionic acid fermentation were along with ammonification responsible for anaerobic chitin degradation. TRFLP analysis showed that different bacterial chitinase genotypes positively responded to chitin supplementation under oxic (TRFs 54bp, 114bp and 264bp) and anoxic (TRFs 137bp, 188bp and 264 bp) conditions. These genotypes affiliated with a novel genotype, Beta-, and Gammaproteobacteria, and Planctomycetes. In total, 42 chiA genotypes were detected. Twenty genotypes were novel at an amino acid sequence dissimilarity of ≥50%. Thus, a large and previously unknown diversity of chitinolytic bacteria occurs in the investigated temperate agricultural soil.

References
Multi-imaging approach to simultaneously map spatio-temporal dynamics of oxygen, pH, and water patterns in soils

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Survival of plants depends on the availability of water, pH, and oxygen. *Vice versa* root activities and related microbial processes impact the interrelated distribution of these vital parameters. Despite the importance of soil water, pH, and oxygen for whole ecosystems, non-destructive monitoring of their interrelated dynamic distribution is still technically challenging. To overcome this limitation, we developed a novel inexpensive multi-imaging approach which permits *in situ* observation of dynamic patterns in soils at high temporal and spatial resolution. Fluorescence imaging coupled with neutron radiography was subsequently applied to different environments, i.e. root-soil-system with living plants and heterogeneously structured soil-systems.

Fluorescence sensors were attached to the inner-sides of quasi 2-D boron-free glass containers filled with an artificial quartz sand mixture. For the root-soil system, heterogeneous structures were built by layers of finer grained quartz. To mimic microbial oxygen demand, pyrogallol was infiltrated during experiments. For the root-soil-system, a fine grained layer was built in the horizontal centre of the slab to limit diffusion of atmospheric oxygen into the lower compartment. One lupine plant (*Lupinus albus* L.) was grown in each container. After the growing period and after infiltration of pyrogallol time series of fluorescence oxygen imaging and neutron radiographies were taken.

The structured soil-system indicates a strong relationship between oxygen transport and water content, where oxygen diffusion coefficients were reduced by factor 1000 when shifting from gas-phase to water-phase and increasing water content resulted in decreasing oxygen concentration. The root-soil-system showed an influence of root age on water and related oxygen distribution. Increased root water uptake and respiration rates due to higher root length density resulted in faster and intensive formation of oxygen depletion zones around the 25 days old root system. Furthermore, we observed a strong coupling between soil water content and pH values, i.e. high water content in the upper part diluted the root exudates but with decreasing water content acidification increases. Besides strong spatial and temporal variability, we detected variations of root surface pH, rhizosphere pH and this is related to root age.

With our coupled imaging set up we were able to monitor the dynamics of oxygen, pH and water content with a high spatial and temporal resolution. First, this includes oxygen, pH and water content distribution including respiration, acidification and transpiration driven pattern in natural porous media. Secondly, we mimic microbial induces oxygen depletion and showed importance of soil structure on oxygen diffusion. Our experimental set up provides the possibility to visualize the parameters under aerobic conditions. This experimental set up and the simultaneous visualization of oxygen, pH and water content is a novelty.
Influence of microbial products on the structure-chemistry and chemodynamic of covalently immobilised residues of xenobiotics in soil derived organo-clay complexes

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Aging of xenobiotics in soil leads to a significant proportion of non-extractable residues (NER). They have a high environmental relevance, since they influence bioavailability and, thus, (eco)toxicological properties of contaminations. Binding of NER to soil organic matter are induced by abiotic and biotic reactions. It has been shown that biological binding are influenced by both active microorganisms and extracellular enzymes (Bollag et al., 1983). Distinguishing microbial activated biodegradation from extracellular enzyme activated transformations including subsequent formation of NER is a challenging task. To achieve this, the chiral fungicide metalaxyl (unlabeled) was incubated for 92 days in soil under natural as well as sterilized conditions. The sterilization method has been proven to inhibit microbial activity but not to alter extracellular enzyme activity (Botterweck et al., 2013). Stereochemical properties of organic chiral compounds, and therefore also of metalaxyl, are highly influenced by environmental processes, in which microbial activity is involved. Such effect has been shown in a previous SPP 1315 project revealing stereoselective incorporation of the diastereomers of 353-nonylphenol during the formation of NER [3]. Furthermore, several studies pointed to a stereoselective biotic degradation of metalaxyl in aerobic soils with pH > 5 with selective depletion of the metalaxyl (−)-(R)-enantiomer (e.g. 4). However, knowledge on the stereochemical effect of NER formation on metalaxyl has not been studied so far. Besides quantitative analysis using GC/MS we also applied enantioselective analysis using chiral-GC/MS on extractable fractions of non-sterilized and sterilized soil. Metalaxyl (MX) and its primary metabolite metalaxyl acid (MX-A) from the water soluble fraction as well as solvent-extractable proportions from separated sand, silt and clay subfractions have been quantified and linked with the enantiomer fraction (EF). First results show a significant depletion of the (−)-(R)-enantiomer during an incubation time of 10 to 92 days for both sterilized and non-sterilized samples. This accounts not only for the water soluble fraction but also for the particle associated extractable fraction. Hence, a high chiral selectivity of the active microbes and/or extracellular enzymes in the soil has been demonstrated. The parallel formation of metalaxyl acid showed an inverse enantiomeric fraction than the extractable parent compound. Interestingly, the combination of quantitative data with chiral data revealed an equal enantiomeric distribution in the total extractable fractions after 92 days of incubation under sterilized as well as non-sterilized conditions. In summary, all results clearly demonstrate the considerable role of extracellular enzyme activity in the enantioselective degradation process of metalaxyl.

References
Imaging Mass Spectrometry: Localization of Metalaxyl on root Surfaces

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State-of-the-art mass spectrometric systems allow researchers to gain more information about their samples than mere amount of one particular compound of interest. We explored the localization of metalaxyl directly on root surfaces. In a proof of principle study we developed the sample preparation and measurement parameters to sensitively detect metalaxyl in situ. In this case important insight into dissipation processes can be gained and correlation with other imaging techniques might be possible. Additionally, enantioselective behavior of metalaxyl and its acidic metabolite was studied under variation of sundry physicochemical soil parameters.

References

Sorption and Degradation of Fenhexamid

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Besides degradation sorption is an important factor for the fate of organic compounds. Fenhexamid is known to build non extractable residues (NER) within short time period. The dependency of strong sorption in context to pH as well as soil moisture variation will give new insights into fast NER formation. Studies with differentially \(^{14}\text{C}\)-labeled fenhexamid enable evaluation of metabolic breakdown and binding positions.

For variation of soil parameters it was observed that soil moisture is positively correlated with mineralization and negatively with NER formation. A high pH value effectuates mineralization and coincidently increased NER formation. The carbonyl-labeled fenhexamid is a good subject to mineralization whereas the level of NER formation is higher for phenyl-labeled fenhexamid. This indicates that the carbonyl moiety is degraded and released easily while the phenyl moiety plays an important role in NER formation. ESR spectrometry gives hints that a radical reaction mechanism is involved in NER formation.

References
In-situ analysis of pore scale processes at biogeochemical interfaces

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Biogeochemical interfaces (BGI) in soil control the fate of organic chemicals and the functioning of soil as a filter to protect groundwater resources. Biogeochemical interfaces are transient in space and time, thus rendering batch tests under equilibrium conditions and without spatial restrictions inadequate to predict the overall behavior. Instead, the concentration gradients of organic chemicals have to be measured and the spatial and temporal dynamics of the BGI themselves have to be monitored. Processes at BGI can be visualized and quantified using microfluidic structures mimicking the pore topology of the soil, so called micromodels. In combination with Raman microspectroscopy chemical information can be retrieved from a micromodel experiment with a spatial resolution on the order of 1 µm² and a temporal resolution in the s-range. To increase the sensitivity, silver nanoparticles have been added to the water phase flowing through the micromodel to make use of the amplifying surface-enhanced Raman effect. Currently chemical gradients of moderately lipophilic substances have been acquired with a limit of detection of $10^{-8}$ mol/L (see Fig. 1). Challenges to overcome include the interactions between silver nanoparticles and target analytes which might alter the mass transfer rates, and the settling of nanoparticles in the channel.

Fig. 1: Gradient of crystal violet at an octanol water interface

As high resolution acquisition comes with a limited field-of-view (FoV) and, e.g., the growth of a biofilm outside of the FoV alters the flow pattern, the flow velocity has to be monitored using fluorescent latex beads and single particle tracking (Fig. 2). For a fast
measurement of well-defined variables, like the pH-value or the oxygen concentration, thin film polymers with encapsulated sensor dyes are chosen.

When looking at microbial growth in porous media, not only the development of a biofilm changes the flow paths and the accessibility to the microbes, but also the development of locally confined gas bubbles, as with *P. denitrificans*. Here, the growth rate is correlated with bacterial activity and the results indicate different bacterial densities in pore bodies and pore throats (Fig. 3).
X-ray Photoelectron Spectroscopy (XPS) as a means for chemical characterization of changes in the wetting properties of biogeochemical interfaces (?)

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Sorption and desorption as well as colloid deposition and detachment all are BGI (biogeochemical interfaces) processes. BGIs consist of multiple compounds (inorganic, organic) with a chemical composition more or less different from that of the underlying particle. Crucial for all BGI processes are the wetting properties. BGI thickness extends up to the µm scale (Rennert et al., 2012), however, the wetting properties are determined solely by the kind and orientation of the functional groups of the outmost 1 nm (Ferguson and Whitesides, 1992). To relate BGI wetting properties and chemical composition, common techniques like EDX and ATR-FTIR with an analysis depth of about 1 µm are not suitable. A promising alternative is X-ray photoelectron spectroscopy (XPS). Surface bombardment with X-rays results in the emission of photoelectrons with element- and bonding state-specific binding energy (BE) whose maximum analysis depth is restricted to the top 10 nm. First attempts to relate BGI wetting properties and chemical composition have been made for three sample sets where wettability (determined as contact angle CA) changed distinctly by (i) increasing soil age (chronosequence, Damma glacier; Schurig et al., 2013), (ii) heat treatment (natural soil), and (iii) coating with defined organic functional groups (organosilane treated glass slides). Within the chronosequence CA increased with soil age, which was accompanied by increased surface C and N concentrations. The heat modified (24 h/105°C) sandy topsoil material (Lakwiese) showed an increased and more stable CA and an increased surface C concentration. The CA of the coated glass slides was a function of the functional group added. The relation to surface C here was not unique, probably due to “adventitious carbon” (C sorbed to air-exposed surfaces). However, the position of the peak maximum was shifted to lower BE, indicating a higher share of aliphatic C. Additionally, Na from the underlying glass surface may probably be used for estimation of layer thickness or surface coverage. Results so far suggests XPS as a suitable technique to relate BGI wetting properties and chemical composition especially as a diluting influence from the bulk material is minimized compared to other surface analysis techniques. However, the relations found so far have to be verified on further samples. As well, especially, the C peak has to be fitted to reveal the share of C in polar (e.g., COO⁻) and non-polar (e.g., CH₃) bonding.

References
Transport of biocolloids in a variably saturated soil aggregate

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Recent advancement in microscopic visualization and computer technology enables us to understand colloidal transport at the pore-scale. The transport of biogenic colloids (bacteria, viruses) through saturated and unsaturated porous media is of vital interest, for the assessment of risk from pathogens in groundwater, enhanced natural attenuation and bioremediation, and for the design of better water treatment systems to remove microbes from drinking water supplies. The focal point of this work is to study the mechanisms of biocolloid mobility under different flow condition by a quantitative description of the combined effects of pore geometry, pore-size distribution, and visualization of the colloidal particle tracking.

The transport mechanisms of biocolloids include physical, geochemical and biological processes. We emphasize only the physical process of advection which is the motion of the particles along the trajectories of the fluid streamlines, i.e., tortuosity of the paths whose velocity is governed by the hydraulic pressure gradient, porosity, and permeability distribution. The pressure gradients have minimal influence on the streamlines that define the pathways within the complex pore network, although these changes certainly affect the mass fluxes. Moreover, the trapping of air bubbles as a function of pore(s) radius not only minimize the water saturation but also deviate the colloid movement which affects transport parameters. Therefore, the changes of the transport velocities in combination with the pore structure heterogeneity can lead to different distribution of residence times, and therefore, are of high environmental relevance. The fully parallelized lattice Boltzmann (LB) solver for both flow and transport processes is implemented employing GeoDict software (www.geodict.com, Math2Market GmbH). Standard LB involves an explicit time iteration scheme with a constant time step, uniform grid, and local data dependencies. All simulations were performed on a high-performance computer (HPC) comprising four Interlagos processors (64 cores), and a total RAM capacity of 512 GB.

The main focus of this study is to analyze the effect of pore geometry and pore-size distribution on the transport of biocolloids in a soil aggregate. Moreover, the effect of colloidal size on the breakthrough curve (BTC) was also studied. The simulated results of BTC were supported by visualizing particle tracking along the streamlines.
Determination of interfacial properties on the small scale

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Soils are built of a vast variety of inorganic, mineral and organic components. The spatial assemblage of the textural and structural units defines a complex, hierarchically structured and extremely large biogeochemical interface (BGI). This BGI serves as reactive interphase for the entire range of hydraulic, biogeophysical and biogeochemical processes and interactions that control the multiple functions of soil. Soil water repellency (SWR) is mainly caused by organic substances of different origin and structure as induced by BGI-formation, showing the relevance of biofilms and organic coatings present at many particle surfaces. Despite the importance of SWR for hydraulic processes such as preferential flow phenomena, generation of heterogeneous moisture patterns or surface run-off generation, detailed investigations on the spatial variability of SWR on various scales have rarely been carried out. We introduce a new and easy-to-apply operation mode for measuring the spatial distribution of wettability at high resolution using a modified sessile drop method for the direct optical assessment of the contact angle (CA) on a small scale. Results reveal that the sampling and preparation technique allows the measurement of CA at the mm scale by using droplets of 1 µL volume. Direct measurement on grain surfaces of the sand fraction is possible for grain sizes >300 µm by using drop volumes down to 0.1 µL. Geostatistical evaluation showed that the measurement grid scale is below the range of spatial dependency for droplets of 1 µL volume, but not for measurements on single grains (pure nugget effect). From these findings it can be concluded that the proposed technique allows the identification of small-scale variations in wettability that may promote the synthesis of pore network modeling and pore surface properties to describe water flux and sorption mechanisms under unsaturated and saturated conditions.

References
Colloidal deposition in a water-saturated sand matrix is increased at low wettability

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In soils a variety of inorganic, organic, and biological colloids exists, including clay minerals, metal oxides and hydroxides, organic molecules as well as bacteria, viruses, and protozoa. Transport and deposition of these colloids are important phenomena in the vadose zone and play a crucial role for soil development as well as for the formation and functioning of biogeochemical interfaces. Traditionally, DLVO theory is used to explain interactions of colloids with grain surfaces. However, considering solely electrostatic and van der Waals interactions often revealed to be insufficient for explaining colloid–mineral interactions. We therefore hypothesize that inclusion of non-charge-transfer (Lewis acid-base) interactions leads to a more accurate description of colloid deposition behavior in porous media. To address this, we analyzed the breakthrough behavior of carboxylated polystyrene microspheres (model colloids) in saturated wettable and hydrophobic sand columns at different ionic strengths. Total interaction free energies calculated from zeta (ζ)-potential and contact angle data were used to explain the specific colloid breakthrough behavior. Experimental breakthrough data could be well described with the finite-element code HYDRUS-1D using a one kinetic site model with attachment and detachment kinetics. Higher colloid deposition rates found for the hydrophobic sand could primarily be explained by its small electron-donor component of surface free energy (γ_s = 1.6 × 10⁻² mJ m⁻², as compared to γ_s = 64.1 mJ m⁻² for the wettable sand), leading to strongly attractive acid–base interactions at separation distances <5 nm, but also by weaker repulsive electrostatic interactions due to a lower ζ-potential of the hydrophobic surfaces (ζ = –38 mV, as compared to ζ = –46 mV for the wettable sand, in deionized water). Increasing ionic strength reduced repulsive electrostatic interactions and generally increased colloid deposition with the effect being more pronounced in the hydrophobic matrix. It can be concluded that grain water repellency tends to increase the deposition of negatively charged hydrophilic colloids, which can be ascribed to specific acid–base interactions. These findings demonstrate the importance of acid-base interactions for explaining both wetting and adhesion phenomena and revealed the strong relationship between the wettability of a surface and its ability to interact with colloids. The fact that classical DLVO theory would fail to explain the colloid deposition behavior in our experiments stresses the importance to consider acid-base interaction particularly when dealing with differently wettable solid surfaces. However, calculated absolute values of interaction free energy should be considered only as an approximation showing general trends because surface chemical heterogeneity as detected by atomic force microscopy may bias the determination of the actual interaction energy conditions.

References
Investigation of reactive transport with miniature closed-flow column experiments and spectroscopic online analysis of effluent composition

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The study of biogeochemical interfaces is crucial to understand soil functioning (Totsche et al., 2010). The sorption of solutes and colloids to these interfaces results in the phenomenon of retardation. Besides the interactions at the sorbent-solution-interface, the sorption rate depends also on the spatial structure of the pore network (size distribution, connectivity, topology). Column experiments allow for the consideration of the structure and thus for a quantification of possible rate limitations. We focus on column experiments run in closed-flow mode. There, a typical oscillation in the "breakthrough" of solute concentration, which conveys additional information about the flow regime (dispersivity, water content, immobile water) as well as the effective interaction kinetics, can be observed (Totsche, 2001). Another major feature of the closed flow design is the conservation of tracer mass inside the column setup. Therefore, the investigation of sorption characteristics can be simplified by using mass balances.

The duration of a transport experiment using columns depends on the size of the column. The larger the size, the larger the "mobile water content" and the longer the experimental duration if one wants to employ flow rate and corresponding transport velocities that are typically observed under natural conditions. To speed up such experiments, miniaturization is one possible solution. Because of the decreased characteristic length of the column, the darcy velocity can be maintained at a low and constant level, leaving the flow regime mainly unaffected by the miniaturisation.

We conducted an experiment with artificial soil composed of quartz and goethite in a well defined grain size distribution to study the conservative (NaCl) and reactive (vanillic acid) tracer transport. The reactive tracer was chosen to probe specific reactive surfaces, which allowed for a consideration of involved sorption mechanisms and an estimation of sorbent surface coverage. The solute breakthrough was measured with a non-consuming technique (electrical conductivity, fluorescence spectroscopy). Factor analysis of fluorescence data was used for the quantification of aromatic compounds in complex background solutions. Since the reconstructed sorption characteristics are influenced by physical and chemical non-equilibrium and possible sorption sites were unavailable due to aggregate formation and immobile regions in the porous medium, we were able to estimate the amount of void volume and the availability of sorption sites of goethite.

References
Assessment of uncertainty and number of components in two-way factor analysis

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Technical improvements during the last decades lead to the application of FTIR, UVVIS and fluorescence spectroscopy in nearly every field in analytical chemistry, mineralogy and soil chemistry. The evaluation of complex spectral mixtures can be accompanied by factor analysis, which is a special kind of matrix decomposition. The well known principal component analysis approach, which forces maximal component eigenvalues, can lead to physically meaningless spectral factor loadings, so a more general factor analysis approach is advisable. There, obtained solutions for the decomposition of one-dimensional spectra are usually not unique due to rotational freedom of factor loadings. We constrained the linear regression step involved in alternating least-squares factor analysis to be non-negative (Kim and Park, 2008), which drastically reduces equivalent solutions, but does not guarantee uniqueness. So we looked for a further criterion based on the covariance matrix involved in the solution of the linear regression step and the residuals of the model. The approach is similar to the confidence interval estimation in inverse modeling. If the number of components is too small, the residuals lead a high confidence interval. If the number of components is too large, components start to get correlated, which increases the covariance matrix and therefore the calculated confidence interval. Besides that, the shape of confidence intervals helps in interpreting the component spectra and points to deviations in the underlying sample population. The measurement of effluent concentration in our newest column designs is based on fluorescence and UVVIS spectroscopy. So, a correct decision on the number of components in sample mixtures is essential for a reliable quantification.
Biogeochemical interfaces (BGIs) represent complex and heterogeneous structural phenomena developed in soils as a consequence of formation and interactions of soil constituents. They play an important role in various physical and chemical processes in soils, e.g., sorption of chemical pollutants. Methods of molecular modeling can significantly contribute to understanding basic mechanisms of soil processes. In this work we focused both on mineral and organic matter interfaces using diverse molecular modeling methods (accurate quantum chemical and molecular mechanics (force-field based, FF)) methods combined with molecular dynamics (MD).

- Cation bridges and hydrogen bonds represent important factors in the formation and stability of soil organic matter and its interaction with mineral surfaces. The role of cation bridges and their partial hydration was studied on a set of cations $\text{Al}^{3+}$, $\text{Ca}^{2+}$ and $\text{Na}^+$. The interactions with carboxylate and carboxyl groups and the concomitant proton transfer reactions induced by these interactions were characterized. The strongest effect on the local environment was observed for $\text{Al}^{3+}$ cation. The calculations reflect the amphoteric character of the hydrated aluminum complex showing in most cases its acidic character via proton transfer from the water molecules of the hydration shell to the carboxylate group, but in some cases also deprotonation of the carboxyl group. In addition, dry aluminum acts as a strong Lewis acid and initiates electron transfer from the carboxylate groups to the cation also at larger intermolecular distances. Comparison with cation bridges formed by calcium and sodium showed the pronounced activity of the triply charged aluminum cation.

- Calculations on water bridges demonstrate their capabilities to bind distant polar groups in a humic substance matrix. The trapping of naphthalene and MCPA molecule in the nanopores of humic acids was investigated by FF-MD approach and thermodynamic quantities were estimated using a potential of mean force method.

- Adsorption of organic substances on mineral surfaces such as montmorillonites, illites, goethite, and lepidocrocite was investigated. The most recent calculations have been dedicated to the interaction of polygalacturonic acid fragment with montmorillonite and to the formation of surface complexes of MCPA with goethite.

- FF-MD simulations were performed to study the interactions of water nanodroplets with the surfaces of kaolinite and iron oxyhydroxide minerals. From the shape of the droplet the contact angle has been determined in order to characterize hydrophobic/hydrophilic nature of the mineral surfaces. Organically coated tridymite surfaces as model systems for organically coated soil mineral particles were probed by water nanodroplets using FF-MD simulations. A different surface coverage was modeled in order to explain varying hydrophobicity of surfaces.
Quantification of protonation in organic molecules with UV/VIS and fluorescence spectroscopy

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Spectroscopic methods are among the most common techniques in natural sciences. The spectra measured for example with UV/VIS or fluorescence spectroscopy contain information on electron configuration of the atoms and molecules in the sample. Since many electron transitions are covered by a single measurement, it is difficult to quantify the effect of single functional groups. Even in single component systems, multiple species can be present due to different protonation, complexation or dimerisation. Factor analysis of organic compounds showed, that the shift of spectra at different pH values is caused by the superimposition of species with different protonation.

We therefore made the attempt to reconstruct the underlying spectral contribution of these species exemplified by organic model compounds. We focused on carboxylic groups, which are easily affected by pH and show strong light absorption in the UV range due to the π-electron system. We decided to use, in order of increasing complexity, simple organic acids like formic, acetic and lactic acid, citric acid with three carboxylic groups and vanillic acid or MCPA with aromatic structure.

The evaluation was done by factor analysis with a non-negativity constraint (positive matrix factorisation, Kim and Park, 2008). We adapted the algorithm to include fixed background species. This allowed us to quantitatively reconstruct species distribution from UV/VIS absorption and to distinguish between the contribution of carboxylic groups and the aromatic ring to the total spectrum. This offers the possibility to quantify organic column effluent concentrations in nearly realtime and to track the pH value without directly measuring it.
Physical aging of soil organic matter: A $^1$H solid state NMR and DSC study and a theoretical approach

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Physical entrapment and release of chemicals in soil organic matter (SOM) is strongly depending on the mobility of organic matter segments in the supramolecular SOM structure. The segment mobility depends significantly on the water content and may be explained by water molecule bridges (WaMB) that cross link binding sites via hydrogen bonding. Such WaMB lead to an increasing matrix rigidity throughout the aging process. In this study, we present experimental results of an aging experiment on samples in hermetically sealed containers that had been triggered by a heating / cooling event of 30 minutes at 110°C to initiate a relaxation process which we refer to as aging. Two soil samples, a sapric histosol with high organic matter content and a gleyic podzol with low organic matter content, were measured. By $^1$H solid state nuclear magnetic resonance (NMR) we traced the mobility changes, making use of a wide line decomposition scheme$^1$. Via differential scanning calorimetry (DSC) we observed changes in the matrix rigidity, expressing in a step transition temperature, that shifts during the aging process. Both methods observe effects within a time span of almost one year. The general observation is similar for both techniques$^2$: the $^1$H mobility is decreasing with a logarithmic time dependence in the first few days, followed by a very slow linear decrease. The changing DSC step transition temperature also follows this time dependence.

Results of the long term series are analyzed on the basis of a random field potential model, predicting that the reorientation times on the molecular level increase exponentially as observed in the experiment.

The effect of different water contents is shown and explained in the context of WaMB being destroyed by the heating event and slowly building up over a long period of time. Possible implications on the immobilization of organic chemicals in terms of a sequestration into nanovoids generated by a stable WaMB network will be discussed.

References:
Fluid and transport process in micromodel: Comparison of simulation results with the experiment

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The transport of colloids through saturated porous media is of significant interest, from the perspective of protection of aquifers, environmental risk assessment and remediation strategies. Colloids are mainly affected by the physical and chemical processes that determine solute transport, i.e., advection, diffusion, dispersion, and adsorption. Advection is the motion of the colloids along the trajectories of the fluid streamlines. This mechanism can develop dispersion of the colloids because of the heterogeneity of the fluid velocity distribution at local pores. As a consequence, the tortuosity of the colloidal path may change which have a direct effect on colloid residence times and therefore, are of vital environmental relevance. Recent advancement in microscopic visualization can provide valuable information to enhance the understanding of pore-scale transport phenomena.

In recent years, micromodels have been increasingly employed to study the fate and transport of contaminants at the pore scale. The micromodel used for this study has a physical dimensions of L=2cm, W=1cm, H=30µm, and was made of a silicon wafer, in which a heterogeneous pore network was etched. To understand the physical process at this scale, a high resolution image of the micromodel is essential. For this purpose, the micromodel was photographed row-wise with a Nikon D70, mounted on a microscope with 10x magnification, and later downscaled to 6736 x 3334 pixels (resolution: 2.999 µm/pixel) to make it computable for simulation. For the flow simulations, the fully parallelized single-phase lattice Boltzmann (LB) solver in GeoDict software (www.geodict.com, Math2Market GmbH) was implemented, which was developed for both single- and multiphase flow. Standard LB involves an explicit time iteration scheme with a constant time step, uniform grid, and local data dependencies, and is ideal for parallel computing. For the simulation of solute transport, AddiDict module integrated in GeoDict software package was utilized. All simulations were performed on a high-performance computer (HPC) comprising four Interlagos processors, each of them including 12 cores, and a total RAM capacity of 512 GB.

The focal point of this work is to study the effect of pore geometry on the transport of colloids under different flow rates in a micromodel. Two regions-of-interest (ROI’s) were chosen to analyze fluid flow velocity distribution. Also particle tracking along the streamlines was visualized. The simulated results were compared with the experiment data.
Incorporation of organic chemicals into the organic matter of a sapric histosol observed by differential scanning calorimetry

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Soil organic matter undergoes physical and physicochemical aging processes (Kucerik et al., submitted; Schaumann et al., 2013; Kunhi Mouvenchery et al., 2013) during which labile supramolecular structures are successively stabilized by water molecule bridges (WaMB). The objective of this study was to understand the hypothesized relation between physicochemical aging and sequestration of organic chemicals. Two distinct SOM compartments were addressed in this study, hydrophilic SOM in which functional groups can be bridged by WaMB and hydrophobic aliphatic regions in SOM:

- The hydrophilic SOM compartment is characterized via its matrix rigidity, which was determined via the WaMB transition temperature, T*, by differential scanning calorimetry (DSC). T* reflects the temperature at which WaMB disrupt (Schaumann et al., 2013). T* can be observed by a step in the first heating cycle of a DSC measurement, which disappears in the second, directly succeeding cycle.

- The aliphatic compartment was characterized by its melting temperature, which was also determined by DSC. The reversible endothermic event in the first and in the second heating cycle has been interpreted as a melting transition at T_M of alkyl regions in the OM (Kucerik et al., submitted; Hu et al., 2000; Chilom and Rice, 2005). We treated a sapric histosol (SH) from Totes Moor, Fuhrberg, with phenol using four different solvents (water, acetone, hexane, methanol). After solvent evaporation, samples were equilibrated for 3 weeks at 76% relative humidity. At selected points of time during 150 days, subsamples were measured by DSC (from -50 °C to 110 °C). Thermal characteristics of the samples were evaluated as a function of time. Both T_M and T* were significantly reduced upon phenol treatment, while solvent treatment alone showed only small effects. Thus, phenol affected the OM matrix with melting point depression in the aliphatic regions as most prominent effect and by initial reduction of T*. Aging increased T* stronger than T_M. Thus, phenol can disrupt WaMB and penetrate into aliphatic regions. During the successive re-formation of WaMB phenol molecules may be incorporated in the WaMB. In contrast, at least part of the melting depression in the aliphatic regions is not reversible, suggesting an effective incorporation of phenol into aliphatic regions

References


Interactions between soil organic matter, water and bivalent cations: What are the cross-links made of?

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Multivalent cations are hypothesized to cross-link segments of soil organic matter and with this, form cation bridges (CaB). The spatial distance between the OM functional groups as well as the cation size is determinant for the formation of CaB (Kunhi Mouvenchery et al., 2013). It is hypothesised that water molecules can assist multivalent cations to bridge large distances between OM molecules, either as hydration water or as bridging agents (water molecule bridges, WaMB) between cations and OM molecules via CaB-WaMB associations (Schaumann et al., 2013). A strongly held hydration sphere of cations may result in cross-links bridging larger distances than the bare cations do. Larger CaB-WaMB associations may bridge even larger distances by involving more water molecules between the hydrated cation and organic functional groups.

In order to verify this hypothesis and to separate the effect of cation charge from cation size, a soil sample taken from the organic layer of a forest soil was treated with salt solutions containing bivalent cations of varying size (Mg$^{2+}$, Ca$^{2+}$ and Ba$^{2+}$). Initially present cations were removed from the soil sample by cation exchange resin prior to cation treatment in order to exclude the effect of competing cations. After cation treatment, the samples were air-dried and equilibrated for at least three weeks in an atmosphere of 76% relative humidity. The WaMB transition temperature ($T^*$; Schaumann et al., 2013) of these sample was then measured by differential scanning calorimetry (DSC). $T^*$ reflects the change in matrix rigidity due to disruption of WaMB at $T^*$: The higher $T^*$, the more stable are the WaMB and the more rigid is the matrix held together by WaMB (Schaumann et al., 2013).

For Ca$^{2+}$ and Ba$^{2+}$, $T^*$ increased with increasing cation content. Mg$^{2+}$ formed weaker interactions within the SOM than Ca$^{2+}$ and Ba$^{2+}$. After aging for eight weeks matrix rigidity was enhanced in all samples, indicating strengthening of the existing interactions or the formation of new CaB and/or WaMB interactions. Soil treated with Mg$^{2+}$ underwent stronger structural changes than the other two sets of samples. The final matrix of the Mg$^{2+}$-treated samples was even more rigid than that of Ca$^{2+}$ and Ba$^{2+}$. Thus Mg$^{2+}$ most probably induced cross-links in the form of CaB-WaMB associations. These results thus reveal the role of water molecules in CaB formation and the role of CaB interactions in the soil aging process.

References

Can we learn about microbe-mineral interactions from the liquid-liquid partitioning of bacterial isolates?

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Surface properties of microbes and inorganic soil compartments, especially their ability to undergo certain chemical interactions (H Donor/Acceptor, Van der Waals) as well as their surface charge are expected to be a determining factor for the process of biogeochemical interface formation. In order to test this hypothesis, we performed a study on affinity of various bacterial isolates to different mineral surfaces and compared the results with those from liquid-liquid partitioning experiments. We conducted a liquid-liquid partitioning study of each bacterial suspension, using organic solvents with varying polarity. Bacterial distribution from aqueous phase into hexadecane, chloroform, diethyl ether and octanol media were assessed. Selected bacterial species were isolated from 3 different artificial soil compositions (montmorillonite, illite, montmorillonite + charcoal) spiked with or without phenanthrene. Functional tests were performed to assess the motility, biosurfactant production and phenanthrene degradation ability of the isolates. Furthermore, genomic DNA was extracted and 16S rRNA genes were sequenced to identify the isolates. Bacterial surface charge was measured as ζ-potential by dynamic light scattering. Sorption to mineral materials such as montmorillonite, illite, quartz and boehmite were conducted in batch experiments, using bacterial suspensions in 0.9 NaCl solutions. Differences in turbidity of the suspension and in the amount of organic carbon before and after sorption were determined as measures for the amount of bacteria sorbed on mineral surfaces. Nanothermal analysis using atomic force microscopy (AFM-nTA) was performed on mineral materials after sorption in an attempt to identify and visualize the adhered bacterial cells. For some isolates, a higher motility and the ability to degrade phenanthrene were shown. Among the various bacterial strains used, no significant differences were found in biosurfactant production and surface charge, but different mineral materials were adhered by individual bacteria to different extents.
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