Abstract Volume
10th Swiss Geoscience Meeting

Bern, 16th – 17th November 2012

14. Environmental Biogeosciences

Swiss Academy of Sciences
Akademie der Naturwissenschaften
Accademia di scienze naturali
Académie des sciences naturelles

UNIVERSITÄT
BERN

14. Environmental Biogeosciences.

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Swiss Commission of Oceanography and Limnology (COL)

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14.1

Lability of monomeric U(IV) species in laboratory and field experiments

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The *in situ* bioremediation of uranium is premised upon the addition of an electron donor, such as lactate, acetate, or molasses, to simulate the growth of indigenous microbes in geologic media, and cause the concomitant enzymatic reduction of soluble and mobile U(VI) to relatively immobile U(IV) species. Although the product of U(VI) reduction was long assumed to be the mineral uraninite, $UO_{2(s)}$, recent research has confirmed the presence of other, non-crystalline U(IV) species collectively called monomeric or mononuclear U(IV) (*e.g.*, Bernier-Latmani *et al.*, 2010; Boyanov *et al.*, 2011). These species can form as a product of uranium reduction by microbes (Bernier-Latmani *et al.*, 2010), biogenic Fe(II)-bearing minerals (Veeramani *et al.*, 2011), and in natural sediments (Sharp *et al.*, 2011). Alessi *et al.* (2012) showed that monomeric U(IV) associated with all of the above surfaces can be extracted with a concentrated solution of bicarbonate, while uraninite remains intact. Thus there is some evidence that monomeric U(IV) species may be more easily mobilized than U(IV) bound in crystalline uraninite.

The goal of this study was to compare uranium mobilization rates from systems containing primarily uraninite, to ones containing primarily monomeric U(IV) species under realistic groundwater conditions. To this end, monomeric U(IV) associated either with *Shewanella sp.* CO-9 or with biogenic magnetite were prepared and embedded in agarose gel pucks. The gel pucks were deployed into two groundwater wells at the Old Rifle field site in Colorado, USA to evaluate the persistence of this product under *in situ* conditions. Gels were recovered at specific time intervals, the uranium loss quantified by digestion, and U L_{III}-edge X-ray absorption spectroscopy performed to monitor changes in uranium speciation. A parallel laboratory study, using Old Rifle groundwater, was conducted to investigate the mechanism of uranium mobilization from monomeric U(IV). In particular, the impact of carbonate complexation and oxygen-dependent oxidation were evaluated for monomeric U(IV) and UO_2. The results from both the laboratory (Figure 1) and field studies confirmed that monomeric U(IV) was more easily remobilized than uraninite. Additionally, monomeric U(IV) mobilization mediated by carbonate was also documented in addition to oxidation. Thus, the consideration of monomeric as a contributing species in the subsurface may be critical in generating accurate predictive models of uranium transport. Future studies quantifying the rate loss kinetics of monomeric U(IV) will be important in informing these transport models.

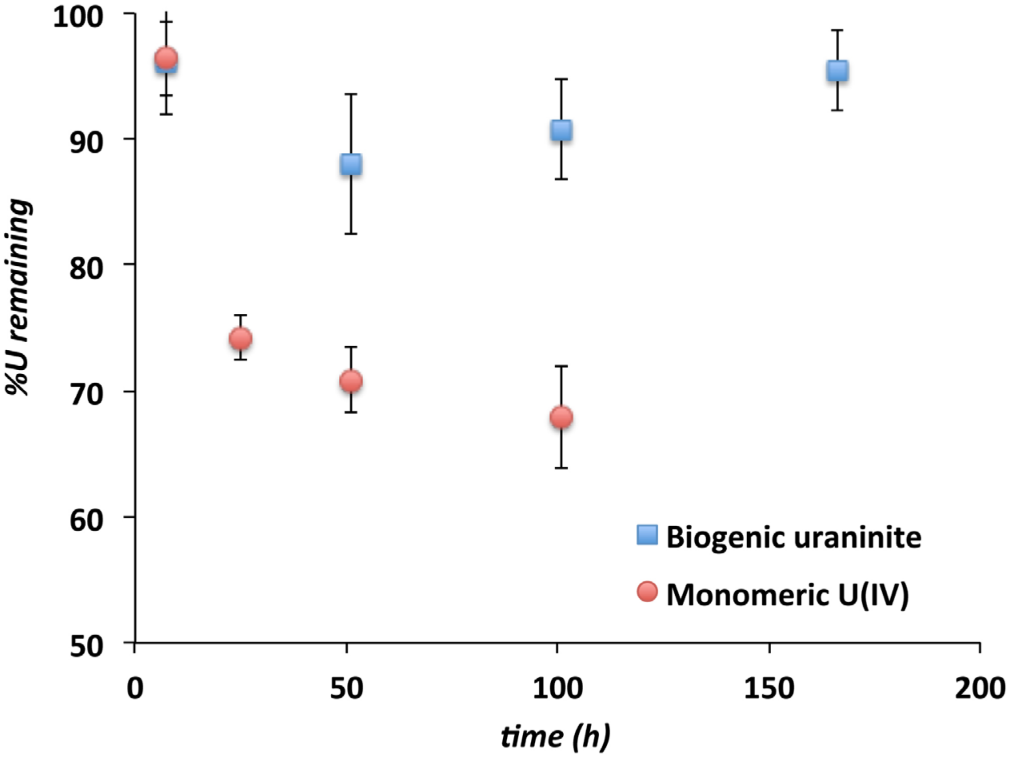

Figure 1. Uranium removal from *Shewanella sp.* CO-9 cells containing primarily monomeric U(IV) species versus cells containing primarily biogenic uraninite, in anoxic groundwater from Rifle, CO.

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14.2

Plant-soil microbe interactions for nutrient acquisition in peatlands: responses to climate warming and vegetation change

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Ombrotrophic peatlands or bogs are nutrient-poor ecosystems that are strictly dependent on atmospheric inputs. As a result, they present a good model for understanding the effects of climate change on interactions between plants and soil microbes. Here, we investigated the seasonal dynamic of biogeochemistry and interactions between soil microbes and vascular plants in four Swiss peatlands along an altitudinal gradient that simulated a natural gradient of soil temperature. Along this gradient, the peatlands were also characterised by a differences in cover of the main plant growth forms, with decreasing abundance of ericaceous species with increasing altitude. Peat microbial biomass carbon (C) and nitrogen (N), soil enzymatic activity, organic and inorganic exchangeable N, microbial community structure, as well as polyphenol and dissolved organic C (DOC) concentration in pore water, were periodically assessed during the plant growing season.

We found a significant difference in the seasonal trend of C:N ratio in microbial biomass in relation to both altitude and the abundance of ericaceous species. In particular, we observed that, at lower altitude, soil microbes immobilized less N, suggesting a higher competitive ability of plants for N acquisition. Decreasing polyphenol concentration in pore water with altitude was reflected in a lower amount of exchangeable organic N in peat, which is consistent with the capacity of polyphenols to retard N release from decomposing organic matter. We also found a positive relationship between vascular plant production, which decreased with altitude, and DOC concentration in pore-water. Spectroscopic measurement of DOC showed a higher release of labile C compounds at lower altitude, which points to a primary role of root exudates in affecting DOC quantity and quality. The stoichiometry of the main hydrolytic enzymes involved in the degradation of C and N compounds differed along the altitudinal gradient in relation to the structure relative dominance of fungi and bacteria in the soil microbial community structure.

Our data suggest that the presence of important aboveground-belowground feedback in terms of nutrient acquisition, which can potentially destabilize the ability of peatlands to act as C sinks if vascular plants become more competitive than peat-forming mosses with increasing soil temperature.

14.3

Endospore-forming bacteria as an indicator of pollution in sediments of Lake Geneva

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Treated wastewater and runoff-water is released by the outlet of the sewage treatment plant of Vidy (Lausanne) directly into the Lake of Geneva via a pipe located 300m from the shore. Even if this water is properly treated with modern technologies, we can observe an accumulation of micro pollutants into the sediments, and in particular of trace and heavy metals. The main objective of this project is to investigate how these elevated concentrations of metals affect both abundance and diversity of prokaryotes in the sediments. A special emphasis was given to endospore-forming bacteria, which could use sporulation as a survival strategy to resist in highly contaminated areas. This study could have implications for understanding the role of endospore-forming bacteria in the environment, their potential as bioindicators of pollution in sediments, as well as in terms of improving bioremediation processes.

Lake Geneva is the largest freshwater lake in Western Europe. Since several decades this lake has been the subject of close environmental monitoring. Different studies from the Forel Institute (Pote et al., 2008; J-L Loizeau et al., 2004) indicate that the sediments of the Vidy Bay contain high level of trace and heavy metals (TM/HM). This is mainly due to the rejection into the bay of runoff surface water, but also the treated wastewater from the city of Lausanne and its suburbs (412'000 equivalent inhabitants). Even if the concentration of TM/HM in the rejected water is low, over time those accumulate in the surrounding sediments. Endospore-forming bacteria (EFB) are well known for their ability to resist to harsh environmental conditions over long periods of time (Vreeland et al., 2000). When conditions are not optimal, endospore formation is triggered. Spores are resistant structures intended to protect and conserve the genetic material of the organisms until the conditions become suitable for vegetative growth (Nicholson, 2002). We hypothesized that thorough the formation of endospores, EFB have an advantage to tolerate and prevail in environments with high pollutants load. However, so far, the effect of pollutants on the prevalence of endospore-forming bacteria is unknown. Therefore, this study aims at evaluating an eventual link between endospore-forming species and the load of trace and/or heavy metals in the environment using as model polluted sediments from Lake Geneva. In addition, considering the fact that recent studies have demonstrated that some redox activities are active at the surface of endospores (Junier et al., 2009; Rosson and Nealson, 1982), a better understanding of the role of this special group of bacteria in polluted areas could lead to improved bioremediation processes in the future.

Two MIR submersibles could be used to monitor the surface of the sediments and to select the more interesting coring zones around the rejection pipe of the wastewater treatment plant of Lausanne. A first set of four cores was retrieved from precisely selected areas by using the robotic arm of the submersible. In order to have more contrasted heavy-metal concentrations, two additional cores were retrieved from a boat during a second sampling campaign. Two depths (0-3 and 3-9 cm) were analyzed independently. The physicochemical analyses show that four out of 12 samples analyzed are clearly separated from the others based on higher TM/HM contents. Multivariate analyses of the physicochemical data and the composition of the bacterial community assessed by 16S rRNA gene pyrosequencing, show a strong link between the prevalence of endospore-forming species and the TM/HM content of the sediments. As a good correlation is also observed between TM/HM and nutrients (represented by C.org and N.total vectors), it is not clear if the first set of physicochemical factors is sufficient to explain the prevalence of EFB in the community of these four particular samples.

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14.4

Biogeochemical analysis as a tool to isolate extremophilic Archaea

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We studied a microbial snottite biofilm in an abandoned pyrite mine in the Harz mountains. The organisms that build up the biofilm grow at pH about 2.3 and sulfate concentrations of up to 200 mM. The microorganisms are dependent on the oxidative dissolution of pyrite as the primary energy and on CO_2 as the primary carbon source. The microbial community is mostly composed of bacteria, predominantly by the genera *Leptospirillum* and *Acidithiobacillus* (Ziegler et al. 2012) which are mostly present in the vicinity of the oxygenated zone. Surprisingly, the respiratory activity of aerobic organisms lead to a large anoxic zone beginning roughly 700 µm away from the outer surface. In this inner anoxic area Archaea are present and comprise a large part if not even the majority of the community. Recent metagenome analysis of the snottite biofilm revealed that deep branching Euryarchaeota and species closely related to so far uncultured ARMAN ("Archeal Richmond mine acidophilic Nanoorganisms", J. Baker et al. 2006) build the archaeal community. Based on our oxygen and pH measurements and further cryo-laser ablation inductively-coupled plasma mass-spectrometry (LA-ICP-MS), ICP optical emission spectrometry (OES) and X-ray absorption near edge structure (XANES) analyses we designed a medium for enrichment cultures which also included 20 mM ferric iron as electron acceptor, casein as well as hydrogen and carbon dioxide in the gas phase. Using CARD-FISH and PCR of the 16S rDNA we could show an enrichment of so far uncultured Achaea from the class *Thermoplasmatales*. After prolonged incubation time, even ARMAN could be detected and transferred several times. Surprisingly, the enrichment was not possible until autoclaved biofilm material was added as an additive to our cultures. At the moment we focus on establishing pure cultures of the enriched *Thermoplasmatales* and we further try to isolate the growth supporting substance of the biofilm.

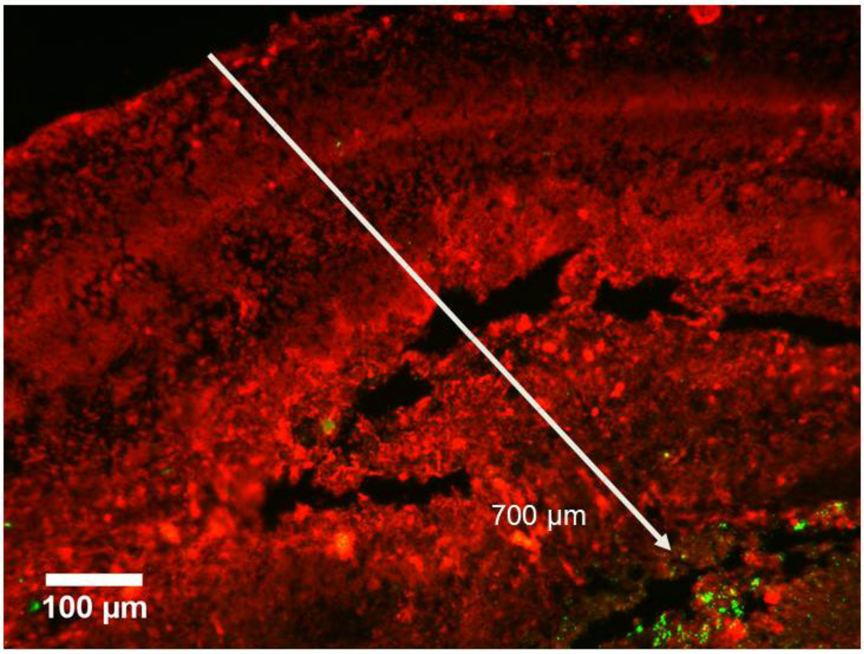

Figure 1. CARD-FISH of a cross section of the biofilm. Bacteria (EUB 338-I) in red (Alexa 546) are evenly distributed across the whole biofilm. Archaea (ARCH 915) in green (Alexa 488) are only present in the inner, anoxic part.

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14.5

Biogenic copper and metal sulphide colloid formation in a contaminated floodplain soil

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The fate of metal contaminants in riparian soils is strongly affected by periodic variations in (ground)water level. Associated changes in soil redox state and metal speciation may result in the release of metals into surface and groundwater. In laboratory microcosms, we studied the dynamics of Cu, Hg, Cd and Pb in a contaminated riparian soil over up to 5 weeks of soil flooding. Pore water was withdrawn directly into an anoxic glovebox after certain time intervals and analysed for dissolved and colloidal concentrations of major and trace elements. Colloidal Cu and Hg dominated the pore water dynamics of Cu and Hg and peaked shortly after flooding before the onset of sulphate reduction. X-ray absorption fine structure (XAFS) spectroscopy revealed metallic Cu colloids, which incorporated small amounts of Hg. Transmission electron microscopy (TEM) showed that metallic crystals were always associated with bacteria. Upon sulphate reduction these crystals transformed into hollow Cu-rich metal sulphide particles that also incorporated Hg, Cd and Pb. In parallel, freely dispersed, mixed Cu-Pb-Cd-Hg sulphide colloids with sizes from a few nanometres to ~300 nm formed directly in the pore water. Other metals did not precipitate as sulphides because most biogenic sulphide was bound in poorly soluble Cu_xS. These results demonstrated that metallic and metal sulphide colloid formation may be an important mechanism leading to trace metal mobilization in periodically flooded soils.

To identify the bacteria that were involved in the formation of Hg-substituted Cu metal crystals, denaturing gradient gel electrophoresis (DGGE) analysis was performed as a first approach. Clearly visible bands were excised and sequenced, revealing mainly species of the genus *Clostridium*. A clone library also demonstrated the dominance of the genus *Clostridium* and other gram-positive bacteria in pore water samples of maximal Cu concentration. We previously proposed that metallic Cu crystals are formed via a Cu(I) efflux from bacteria followed by Cu(I) disproportionation and metallic Cu growth on the surface of bacteria (Weber et al., 2009). Typical Cu efflux pumps are Cu P-type ATPases (CopA), which can shuttle the Cu(I) outside of the cell. We therefore isolated spore-forming bacteria by a pasteurisation step and cultivated them on plates for subsequent 16S rRNA gene sequencing and to test the isolates for CopA gene. 16S rRNA gene sequence analysis of the isolates showed that they were all closely related to *Clostridium beijerinckii*, *Clostridium roseum* or *Clostridium acetobutylicum*. A new primer was designed on the basis of the genome of *C. beijerinckii* to test the isolates for the CopA gene. Positive amplification indicated that the isolates have the gene CopA. The isolates will now be tested for their ability to form metallic Cu during growth. Considering that many typical fermenting soil bacteria are from the genus *Clostridium*, metallic Cu formation (with Hg substitution) may be a widely occurring reaction in periodically flooded riparian soils.

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14.6

Signatures of ancient deep microbial activity and applications in the search for life on Mars

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Recent microbial activity in rocks down to significant depths is a well-known fact (e.g. Balkwill 1989; Moser et al. 2005). But how can such deep microbial activity be recognized in geologically old (fossil) cases? After destruction of all live/organic/biochemical material, the recognition of an involvement of biology in the origin of mineral assemblages or geochemical signatures must remain indirect, relying on so-called biosignatures.

Recognizing former biological activity is crucial to understand low-T geochemical processes in terrestrial rocks as well as to search for possible ancient live on other planets, e.g. Mars. The rates of deep subsurface microbial activity in many environments is extremely low (Røy et al. 2012) and signatures from such processes have a low probability to be recognizable. High rates of microbial activity can develop in situations of strong chemical disequilibria and high energy flux, however.

Classical examples for such situations at the Earth's surface are hot springs. In deep environments, strong disequilibria can result from relatively short-term geological perturbations, e.g. the interaction of oxidizing groundwater with sulphide-rich ore-bodies, or the mixing of near-surface and deep groundwater. Signatures from resulting microbial blooms have a much higher potential to be preserved than those from low-level activity due to associated high cell densities and high rates of mineral precipitation.

Examples of microbial signatures that can be related to microbial blooms are subsurface filamentous fabrics (SFF) from the oxidation zone of ore deposits, porous volcanic rocks and redox boundaries in red beds (Hofmann et al. 2008). Redox disequilibria are typically related to infiltration of oxidizing groundwater, but may also include radiolytically conditioned pore fluids containing H_2 (Lin et al. 2005). The formation of some low-T mineral deposits and microbial blooms may be closely linked because both processes are a result of strong redox disequilibria.

As a lesson, in the search for life on Mars, geological situations that represent ancient redox disequilibria in subsurface situations should be considered as promising targets. SFF are easily recognizable in certain cases due to a macroscopic expression of the filamentous fabric resulting from mineral encrustation.

So-called moss agate consisting of filamentous microbial mats transformed into goethite, enclosed in transparent chalcedony. Sample from Mongolian basalts. Field of view is approx. 3 cm.

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14.7

NanoSIMS study of trophic interactions in the coral-dinoflagellate endosymbiosis

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Tropical and subtropical reef-building corals generally form a stable endosymbiotic association with autotrophic single-celled dinoflagellate algae, commonly known as "zooxanthellae", which is crucial for the development of coral reef ecosystems. In the present work, the spatial and temporal dynamics of trophic interactions between corals and their dinoflagellates was investigated *in situ* and at a subcellular level in the reef-building coral *Pocillopora damicornis.* Transmission electron microscopy (TEM) and quantitative NanoSIMS isotopic imaging of tissue ultra-thin sections (70 nm) were combined to precisely track the assimilation and the fate of ^{15}N-labeled compounds (ammonium, nitrate and aspartic acid) within each symbiotic partner of the coral-dinoflagellate association. Among our main results, we found that (i) both dinoflagellate algae and coral tissue rapidly assimilate ammonium and aspartic acid from the environment, (ii) however only the dinoflagellates assimilate nitrate, (ii) nitrogen is rapidly and temporary stored within the dinoflagellate cells into uric acid crystals, and (iii) the algae endosymbionts translocate nitrogenous compounds to their coral host. This study paves the way for exploring in details the wide range of metabolic interactions between partners of any symbiosis in the biosphere.

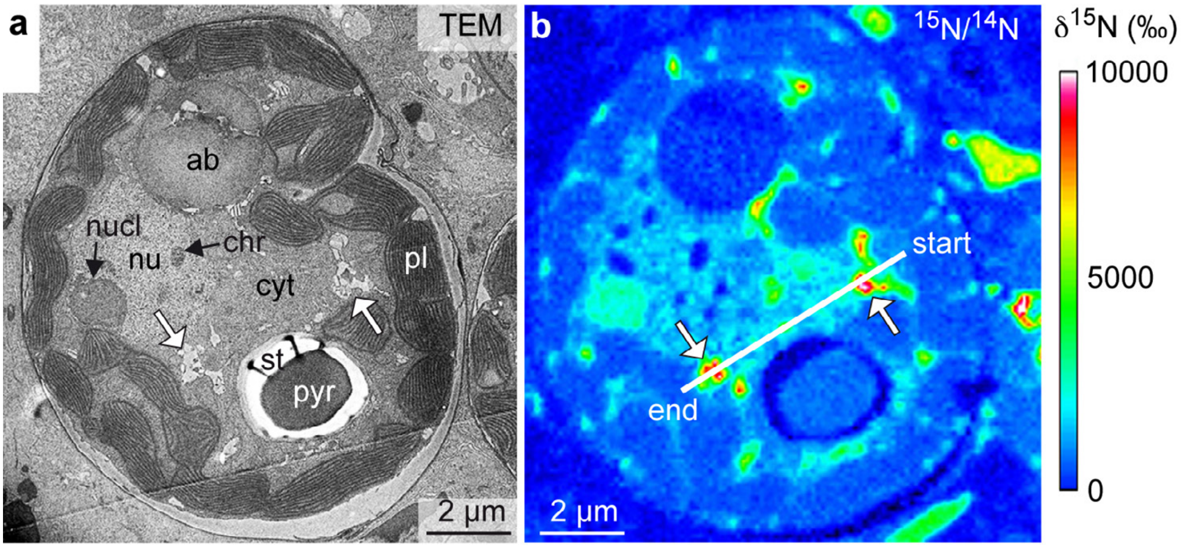

Fig. 1. Nitrogen incorporation and storage by the dinoflagellate endosymbionts of the reef-building coral *P. damicornis*. (a) TEM micrograph and (b) corresponding NanoSIMS isotopic ^{15}N/^{14}N image of a dinoflagellate cell after 90 min of exposure to ^{15}N-labeled ammonium. Highly enriched hotspots of ^{15}N enrichment are spatially correlated with uric acid crystals within the algal cell (white arrows). ab = accumulation body; chr = chromosome; cyt = cytoplasm; nu = nucleus; nucl = nucleolus; pl = plastid; pyr = pyrenoid; st = starch.

14.8

Isotope effects during nitrogenous gas production by microbes in anaerobic environments

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Measuring the nitrogen (N) isotope ratios in NO_x has proven to be an excellent tool to track N transformations in freshwater and marine ecosystems. Organo-heterotrophic denitrification, the bacterial reduction of NO_x (NO_3^- + NO_2^-) to N_2O and N_2 during organic matter degradation in oxygen deficient waters and sediments was traditionally considered as the primary metabolic pathway of marine or lacustrine N loss, and as the main factor controlling the isotopic composition of oceanic N. In many aquatic systems, other pathway of N_2 and N_2O production may be comparably important (e.g., sulfide-dependent denitrification, nitrifier-denitrification, anaerobic ammonium oxidation). In this contribution, I will present data that highlight the N isotope effects (or their absence) for some of these N sinks in various natural environments and in laboratory experiments, and I will discuss the observed N isotope signatures in the context of their use to identify N cycle reactions and quantify N fluxes in aquatic environments.

14.9

Micro-spectroscopic arsenic speciation in a highly contaminated, mining-affected river floodplain

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Many rivers worldwide are polluted with trace elements originating from past or present mining. Even after closure and remediation of the mines, highly contaminated floodplains often remain as a source of contaminant release into river and ground water. Arsenic (As) has a high potential for mobilization under reducing conditions, e.g., during soil flooding, but this strongly depends on the speciation of As among other factors.

The speciation and micro-scale distribution of As, Fe and Mn and other elements in alluvial soils and sediments along the river Ogosta in NW-Bulgaria was studied by micro-X-ray fluorescence (µ-XRF) spectrometry, micro-X-ray absorption fine structure spectroscopy (µ-XAFS) and bulk-XAFS.

“Chemical imaging” using hard X-ray micro-spectroscopy was used to visualize the distribution of major As and Fe species in the soils. Disturbed and undisturbed soil samples were collected along transects ranging from the river bed through the lower and upper floodplains, taking special precautions to minimize oxidation. All samples were analyzed for soil pH, mineralogy, elemental composition, and ascorbate-extractable As, Fe and Mn. Additionally, selected soils were size-fractionated to explore the elemental composition, mineralogy, and As speciation as a function of particle size.

Soil As concentrations in Ogosta floodplain ranged between 40 and 37,400 mg kg^{-1}. Highly As-contaminated soils were also enriched in Fe, Mn, S, Pb, Sb, and other trace elements. Bulk and micro-XAFS, combined with ascorbate-extractions, revealed that most As was present as As(V) sorbed to poorly-crystalline Fe(III)-oxyhydroxides, with smaller amounts of As bound in primary As-bearing minerals, such as arsenopyrite. The fine particle size fractions <5 and 5-20 µm were strongly enriched in As (up to 93,000 mg kg^{-1}) as compared to the corresponding bulk soils. These size separates contained only traces of arsenopyrite and exhibited very high ascorbate-extractable As and Fe contents, reaching molar Fe/As ratios of <5. Our results suggest that As and Fe in these soils should be readily bioavailable for microbial reduction upon soil flooding.

14.10

Authigenic carbonates as dynamic microbial ecosystems: expanding views of methane cycling in the deep sea

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Sulphate-dependent anaerobic oxidation of methane (AOM) is the dominant sink for methane along continental margins and seafloor methane seeps, oxidizing significant fraction of methane in anoxic sediments prior to its release to the hydrosphere (Reeburgh, 2007).

The alkalinity generated during this process frequently results in the precipitation of δ^{13}C-depleted authigenic carbonates, which vary in morphology, size, and mineralogy, ranging from micritic cements and cm-sized concretions to massive ‘chemoherm’ structures, mounds, and pavements that can cover hundreds of square meters.

These methane-derived structures often persist long after the flux of methane subsides, with remnant methanotrophic biomarkers recovered from paleo-seep carbonates dating back to the Paleozoic (Birgel et al. 2008). While these authigenic carbonates have long served as important indicators of methane seepage, they are frequently discussed as passive recorders of prior seep activity, rather as than an active and dynamic microbial habitat.

Here we will present recent evidence that deep-sea authigenic carbonates are living and actively evolving ecosystems, capable of supporting methanotrophic microorganisms that live endolithically within the carbonate matrix. Using a combination of molecular analyses, stable isotope labelling experiments and nanoscale secondary ion mass spectrometry (nanoSIMS), we demonstrate that authigenic deep sea carbonates 1) host abundant aggregations of methanotrophic archaea and sulphate-reducing bacteria, 2) are actively oxidizing methane 3) are capable of growth and incorporation of methane into biomass 4) provide a unique habitat and food source for seep-associated meio- and macrofauna.

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14.11

Increased nitrate availability in the soil of a mixed mature temperate forest subjected to elevated CO_2 concentration (canopy FACE)

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In a mature temperate forest in Hofstetten, Switzerland, deciduous tree canopies were subjected to a free-air CO_2 enrichment (FACE) for a period of eight years. The effect of this treatment on the availability of nitrogen (N) in the soil was assessed along three transects across the experimental area, one under *Fagus sylvatica*, one under *Quercus robur* and *Q. petraea* and one under *Carpinus betulus*. Nitrate, ammonium and dissolved organic N (DON) were analysed in soil solution obtained with suction cups. Nitrate and ammonium were also captured in buried ion-exchange resin bags. These parameters were related to the local intensity of the FACE treatment as measured from the ^{13}C depletion of dissolved inorganic carbon in the soil solution, because the CO_2 used for the treatment was depleted in ^{13}C (Schleppi et al., 2012).

Over the eight years of the experiment, the CO_2 enrichment reduced DON concentrations, did not affect ammonium, but induced higher nitrate concentrations, both in soil solution and in resin bags. In the nitrate captured in the resin bags, the natural abundance of the isotope ^{15}N strongly increased. This indicates that the CO_2 enrichment accelerated net nitrification, probably as an effect of the higher soil moisture resulting from the reduced transpiration of the CO_2 -enriched trees. It is also possible that N mineralisation was enhanced by root exudates (priming effect) or that the uptake of inorganic N by these trees decreased slightly as the result of a reduced N demand for fine root growth. In this mature deciduous forest we did not observe any progressive N limitation due to elevated atmospheric CO_2 concentrations; on the contrary, we observed an enhanced N availability over the eight years of our measurements. This may, together with the global warming projected, exacerbate problems related to N saturation and nitrate leaching, although it is uncertain how long the observed trends will last in the future.

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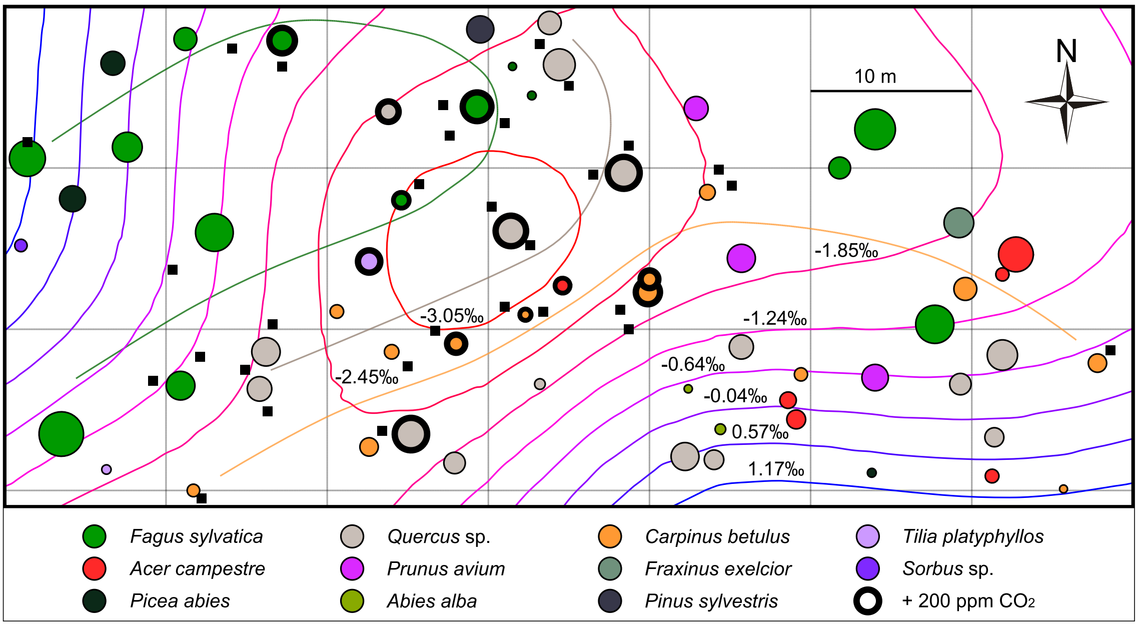

Figure 1. Map of the difference between summer and winter δ ^{13}C in the dissolved inorganic carbon (DIC) of the soil solution (contours as distance-weighted least-square estimates). Small squares represent the sampling locations (suction cups and ion-exchange resin bags) along 3 transects (dashed lines). The position of the trees is indicated by circles, whose size is proportional to the breast-height diameter, but enlarged 4 times compared to the map. Thick circles indicate treated trees.

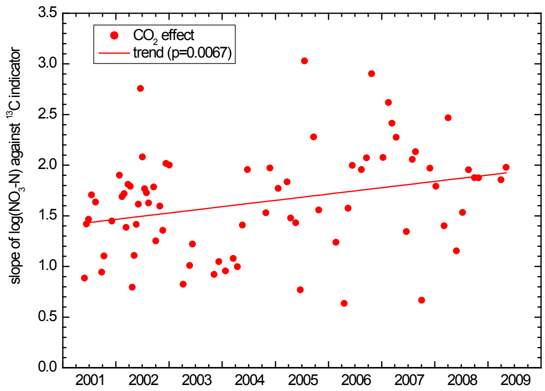

Figure 2. Effect of the CO$_2$ treatment on nitrate-N concentrations in the soil solution. For each point in time, the indicated effect is the slope of log(NO$_3^-$-N) against the ^{13}C-based indicator (defined between 0 and 1).

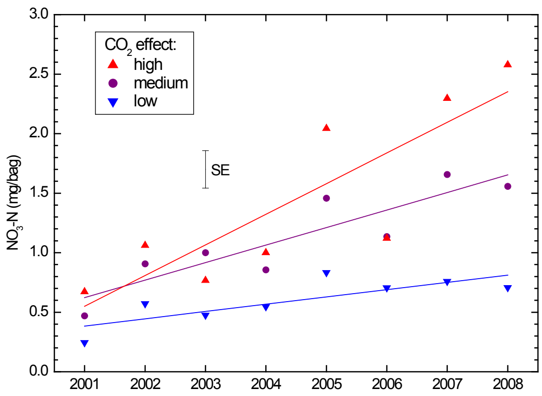

Figure 3: Nitrate N in resin bags after six months in the soil. The locations of bags are grouped in low, medium or high, according to their exposure to the CO$_2$ treatment as measured by the depletion in ^{13}C of DIC.

14.12

Biological controls on the product of microbial U(VI) reduction

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Stimulation of indigenous microbes to mitigate subsurface uranium contamination through reductive immobilization of U(VI) to U(IV) is a promising method of remediation. The product of microbial uranium reduction is often reported as uraninite (UO$_2$), a sparingly soluble crystalline U(IV) species. However, recent laboratory and field-scale remediation experiments reveal the prevalence of non-crystalline U(IV) known as monomeric U(IV) in the microbial product. This product is less desirable as it is considerably less stable than uraninite. It is therefore imperative that we understand the mechanism of monomeric U(IV) formation in order to favor UO$_2$ formation. The work presented here utilizes scanning transmission X-ray microscopy (STXM) to provide direct evidence of a biological response modulating the chemical nature of the U(IV) product. Our key mechanistic insight is that monomeric U(IV) is formed by enzymatic U(VI) reduction in the extracellular polymeric matrix (often referred to as extracellular polymeric substances or EPS) whereas UO$_2$ is formed at the cell surface. Thus, the cellular localization of the U(VI) reduction step appears to determine the ultimate chemical characteristics of the product. The presence of EPS fundamentally alters the U(IV) product of microbial U(VI) reduction. This finding implies that there is a form of biological control on the product of microbial U(VI) reduction not previously recognized.

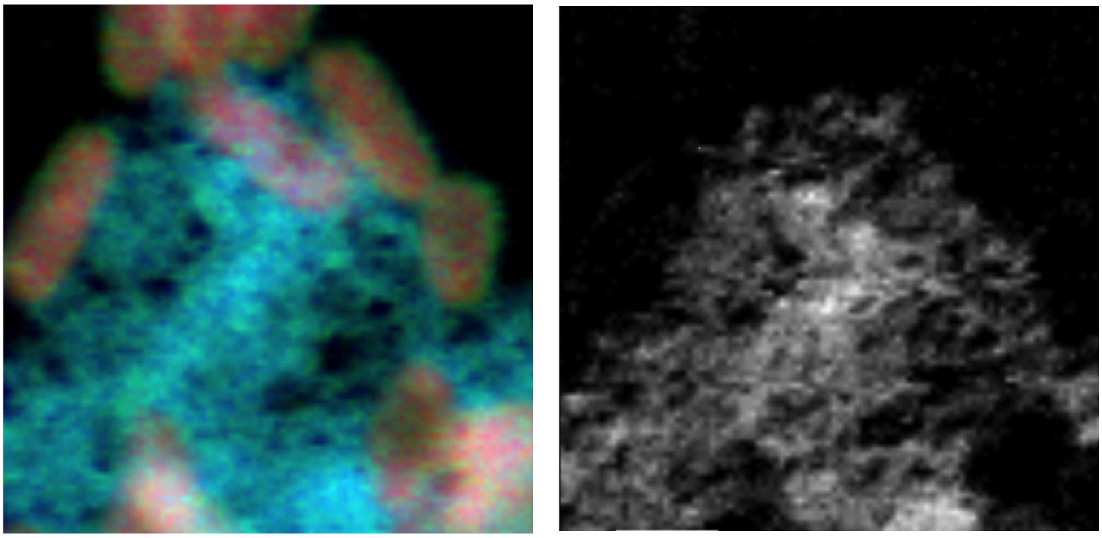

Figure 1. Monomeric U(IV) STXM maps. (a) Carbon speciation map where protein is red, lipid is green and polysaccharide is blue. EPS is clearly visible as extracellular mix of green and blue, forming cyan. (b) Uranium map of the same region demonstrating co-localization with EPS. Scale bar: 1 µm.

14.13

Synthetic δ -MnO_2 as a model for biogenic Mn oxides: Ni and Co adsorption

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Biogenically produced manganese oxides are ubiquitous in the environment and greatly influence the environmental fate of nutrients and contaminants via sorptive, redox, and/or electrostatic mechanisms. The large metal-sorption capacity of layer-type Mn minerals arises from the negative surface charge created by Mn(IV) vacant sites in the MnO_2 layers and compensated by adsorbed countercations. The sorption reactivity and coordination geometries of adsorbed metals depend on factors such as pH, surface loading, and the presence of competing ions. For example, extended X-ray absorption fine structure (EXAFS) spectroscopy showed that Ni binds to biogenic Mn oxides predominantly via coordination at vacancy sites as a triple-corner-sharing complex (Ni-TSC), but increasing pH and surface loading favours the coordination via Ni incorporation (Ni-Inc) into the MnO_2 sheet (Pena et al, 2010).

In addition to sorption at vacancy sites, metal adsorption can occur potentially at the particle edges (Manceau et al, 2007) and on the bacterial cells and extracellular polymeric substances (biomass) responsible for mineral precipitation (Pena et al, 2011). Based on these studies, surface loadings close to or greater than vacancy content should favour metal partitioning between the vacancies, the particle edges and the functional groups of the biomass. Thus, in biogenic Mn oxides, the presence of organic functional groups associated with the biomass complicates the determination of the coordination modes of metals at the particle edges.

The goal of this project is to understand the reactivity of MnO_2 particle edges. We approach this question through sorption studies using a chemically synthesized d-MnO_2 free of any organic material and through competitive sorption experiments on both δ-MnO_2 and biogenic MnO_2. We studied adsorption of Ni and Co at the surface of δ-MnO_2, a close analog of biogenic Mn oxide with similar structural characteristics and a vacancy content of up to 6% (Villalobos et al, 2003). We investigated the adsorption mechanism of Ni by δ-MnO_2 as a function of pH and surface loadings using a combination of wet chemistry methods and EXAFS spectroscopy. In addition, we tested whether we can minimize the number of surface complexes formed on MnO_2 by blocking the vacancies with a high-affinity metal (Co). We compare these data to the Ni/Co adsorption at the surface of the biogenic birnessite produced by *Pseudomonas putida* strain GB-1 and discuss the possibility of using δ-MnO_2 as an model for reactivity studies of biogenic Mn oxides.

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14.14

Zooming in on trace metal bioavailability to phytoplankton in surface waters

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Trace metals (TMs) play a central role in the aquatic ecosystems. TMs interact with a broad spectrum of biotic and abiotic components via dynamic interrelated processes. As a result they exist in various forms with different reactivity and biological availability. The present study zooms in on the TM bioavailability to phytoplankton in surface waters, which are subject of natural variability and multiple sources of stress. It can be anticipated that the physical stressors such as solar radiation and enhanced TM concentrations will operate additively, however there is a paucity of systematic knowledge on the underlying processes, as well as lack of adapted methodologies for exploration of their combined effects. In such a context, an array of novel and powerful technologies was used to determine how the interacting effects of TMs, variable solar radiation and dissolved organic matter (DOM) alterations will impact the phytoplankton population in surface waters.

Experiments were performed in specially designed radiation system consisting of microcosm and solar simulator units. Solar radiation intensity was varied to represent the dose received by the phytoplankton in a euphotic zone corresponding to the clear sky day of winter and summer at mid-latitude for Europe. Cd, Cu and Pb concentrations were varied in the wide range from 10^{-9} to 10^{-5} mol/L, representative for the natural and polluted surface waters. The effect of solar radiation intensity on the DOM structure and characteristics and thus DOM capacity to bind TMs were studied in parallel. Green microalgae *Chlamydomonas reinhardtii* and *Chlorella kesslerii* were used as representative phytoplankton species. Bioavailability was characterized by measuring cellular metal contents, algal population structure, esterase activity, and membrane integrity and lipid peroxidation by using flow cytometry.

Obtained results demonstrated that the variability of solar radiation intensity affects TMs bioavailability by influencing both TM speciation, via photo-transformation of DOM in the medium, and by affecting the vital cellular functions of phytoplankton. Increased sunlight intensity resulted in an alteration of the algal cell population structure and growth inhibition. Cell bleaching, membrane damage, oxidative stress and increased lipid peroxydation were pronounced at higher radiant dose. Similar effects were also observed in algae exposed to high concentrations of Cd, Cu or Pb. Combined action of the enhanced solar radiation and high metal concentration was found to operate synergistically. In addition, sunlight of increasing intensity degraded DOM, thus resulting in increase of the free metal ion concentrations in medium and cellular metal content. The findings of the present study are discussed from biogeoscience view point in a context of changing environment.

Acknowledgement - The authors thank Swiss National Science Foundation for the financial support.

14.15

Dynamic Fe precipitation by Fe(II) oxidation in water

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The oxidation of Fe(II) at biogeochemical redox interfaces results in the formation of nanoparticulate Fe(III)-precipitates that act either as immobilizing sorbents or colloidal carriers for contaminants and nutrients.

In earlier work on Fe oxidation products in neutral aqueous suspensions, we concluded that nanoparticulate amorphous Fe(III)-phosphate is the first precipitate that forms during Fe(II) oxidation in the presence of phosphate (P). At initial dissolved P/Fe ratios less than ~0.55, the precipitation of Fe(III)-phosphate is followed by the precipitation of amorphous to poorly crystalline Fe(III)-(hydr)oxides (depending on silicate/Fe ratio). In recent work, we studied the dynamics of precipitate formation during Fe(II) oxidation in aerated phosphate-containing solutions (bicarbonate-buffered to pH 7.0) in more detail by investigating a larger range of initial P/Fe ratios and by performing time-resolved experiments. Precipitates collected during and after complete Fe(II) oxidation were characterized by a suite of complementary techniques, including X-ray absorption spectroscopy and transmission electron microscopy.

Our new results confirm the initial formation of an amorphous Fe(III)-phosphate with a P/Fe ratio ~0.5 even in solutions with lower P/Fe ratio, but also show that in solutions with initial dissolved P/Fe ratios less than 0.55, initially formed Fe(III)-phosphate is transformed into a precipitate with higher degree of Fe(III) polymerization during continuing Fe(II) oxidation in P-depleted solution. At initial dissolved P/Fe ratios less than ~0.2, initially formed Fe(III)-phosphate is completely transformed into a ferrihydrite-like precipitate. However, even at low dissolved P/Fe ratios, Fe-phosphate may dominate locally at spatial redox interfaces where low O_2 concentrations limit the extend of Fe(II) oxidation.

In future work, we will further explore Fe precipitation dynamics during Fe(II) oxidation and the aging of fresh precipitates, also with respect to the influence of silicate and Ca and implications for trace elements such as As.

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14.16

Robust method for quantitative trapping of volatile organic selenium and sulfur species

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Selenium (Se) is of key importance to human health but its global biogeochemical cycle is largely unknown and unstudied. Chemical analogies between Se and sulfur (S) have recently led to the hypothesis that volatile Se compounds could be formed similarly to the biogenic gas dimethylsulfide.

This compound is naturally produced in the oceans by certain types of phytoplankton and plays an essential role in the Earth's biogeochemical cycles. However, in order to measure the production of these gaseous compounds in low concentrations, both in the lab and in the field, a trapping and pre-concentration method is required that is reproducible and preserves information about speciation.

We tested a liquid chemotrapping method that uses concentrated nitric acid as a trapping medium, based on an earlier developed method (Winkel et al. 2010). The naturally relevant organic Se and S volatile compounds dimethylselenide (DMSe), dimethyldiselenide (DMDSe), dimethylsulfide (DMS) and dimethyldisulfide (DMDS) were injected in a set up consisting of three nitric acid impingers in series. The trapping liquids were analyzed by ICP-MS (for total Se and S) and HPLC-ICP-MS (for speciation determination).

First results indicate that the trapping recoveries for DMSe (92% ± 2%), DMDSe (50% ± 7%), DMS (96% ± 4%) and DMDS (73% ± 6 %) are high and that results are reproducible. The largest amount of inject S and Se (>90%) is retained in the first trap. Furthermore, information on the speciation of all volatile Se and S compounds is retained via the formation of oxidized derivatives: dimethyl sulfoxide (DMSO) and dimethyl selenoxide (DMSeO) for DMS and DMSe, and methyl sulfonic acid (MSA) and methyl seleninic acid (MSeA) for DMDS and DMDSe, respectively.

The presented method is quantifiable and reproducible and will be applied to trap Se and S compounds in experiments with phytoplankton cultures. Due to its simplicity and robustness this method can potentially be applied to qualitatively and quantitatively study Se and S volatilization in a wide range of natural environments.

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P 14.1

Soil organic matter dynamics: bridging the gap between Rock-Eval pyrolysis and chemical characterization (CPMAS ^{13}C NMR)

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Being a source of mineral nutrients, organic matter contributes to soil chemical fertility and acts on soil physical fertility through its role on soil structure. Soil organic matter (SOM) is a key component of soils. Notwithstanding this paramount importance of SOM, information on its chemistry and behaviour in soils are still incomplete. Numerous methods are used to characterize and monitor OM dynamics in soils using different approaches (Kogel-Knabner, 2000). Two of the main approaches are evaluated and compared in this work. Rock-Eval pyrolysis (RE pyrolysis) consists of the description of SOM general evolution using its global thermal stabilities. The second tool (^{13}C CPMAS NMR) aims to give precise and accurate chemical characterization information of OM.

The RE pyrolysis technique was designed for petroleum exploration (Lafargue et al., 1998) and because of its simplicity, it has thus been applied to a variety of other materials such as soils or Recent sediments (Disnar et al., 2000; Sebag, 2006). Recently, RE pyrolysis became a conventional tool to study OM dynamics in soils. In RE pyrolysis, a peak deconvolution is applied to the pyrolysis signal in order to get four main components related to major classes of organic constituents. These components differ in origin and resistance to pyrolysis: labile biological constituents (F1), resistant biological constituents (F2), immature non-biotic constituents (F3) and a mature refractory fraction (F4) (Sebag, 2006; Coppard, 2006). Main advantages are rapidity and repeatability of this technique to give a general view of OM properties and stocks. However, do the four major classes used in the literature reflect a pertinent chemical counterpart?

To answer this question, we used ^{13}C Nuclear Magnetic Resonance Spectroscopy in the solid state (^{13}C CPMAS NMR) to collect direct information on structural and conformational characteristics of OM. NMR resonances were assigned to chemical structures according 5 dominant forms: alkyl C, O-alkyl C, aromatic C and phenolic C and carbonyl–carboxyl C. Moreover, in order to avoid the influence of pedogenesis, we decided to use “less complex OM”, *i.e.* compost samples already studied in a previous work (Albrecht, 2009).

Significant and high correlations are observed between classes, or indices, from RE pyrolysis and main classes of organic matter detected by NMR *e.g.* F1 and labile / easily degradable components (alkyl C et O-alkyl C); F3/F4 and humified OM (aromatic C and phenolic C); R index (contributions of bio-macromolecules) and phenolic and aromatic C; I index (related to immature OM) and labile / easily degradable components (alkyl C et O-alkyl C).

This work confirms interests of RE pyrolysis in soil science (notably with used of R/I index ratio). The next step consists of using more complex samples such as bulk soil samples.

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P 14.2

Biogeochemical cycling of trace elements in a tropical montane rain forest in Ecuador

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Many trace elements are essential micronutrients for plants and microorganisms. However, nearly all trace elements become toxic when they occur in high concentrations. Therefore it is of interest to study trace element fluxes in ecosystems to reveal imbalances and possible effects on ecosystem functioning.

We calculated trace element budgets for important micronutrients (e.g. Cu, Cr, Ni and Zn) and for purely toxic trace elements (e.g. Pb, Cd) in a small catchment in remote montane rainforest in South Ecuador, which developed on trace element poor bedrocks. All relevant ecosystem solutions (rainfall, throughfall, litter leachate, soil solution in 15 and 30 cm depth and surface runoff) and litter fall were sampled for one hydrological year (2001/2002) in monthly resolution. Water fluxes for the different compartments were directly measured or taken from the literature (Boy et al., 2008). Additionally organic and mineral soil horizons were sampled. Samples from organic horizons and litterfall were digested in HNO_3 under pressure and digests were measured together with solution samples by ICP-MS. Element composition of mineral soil and local bedrock samples were analysed by using RFA. Element budgets were calculated from element concentrations and water/litterfall fluxes. Dry deposition was calculated according to Ulrich (1983).

Especially Cd, Cu and Zn showed high deposition rates, despite the remote location of the catchment. The fluxes between the different compartments were comparatively high, while Cu and Zn were concentrated in the aboveground part of the cycle and retained in the organic layer. In the opposite, Cr input to the catchment was comparatively low and high fluxes occur only within the soil system. The mass balance at the catchment scale indicates retention for all of the investigated metals, reflecting the enrichment of metals in the ecosystem. The high input and the enrichment of trace metals might on the long-run effect the ecosystem by supplying micronutrients to the naturally poor system (low bedrock and soil concentrations) and especially extremely trace element poor habitats e.g. for epiphytes and lichens. On the other hand increasing concentrations of toxic trace elements e.g. in the organic layer might affect organic matter turnover by sensitive microorganisms.

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P 14.3

The oxalate-carbonate pathway: at the interface between biology and geology

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The formation of calcite in otherwise carbonate-free acidic soils through the biological degradation of oxalate is a mechanism termed oxalate-carbonate pathway. This pathway lies at the interface between biological and geological systems and constitutes an important, although underestimated, soil mineral carbon sink. In this case, atmospheric CO_2 is fixed by the photosynthetic activity of oxalogenic plants, which is partly destined to the production of oxalate used for the chelation of metals, and particularly, calcium. Fungi are also able to produce oxalate to cope with elevated concentrations of metals. In spite of its abundance as a substrate, oxalate is a very stable organic anion that can be metabolized only by a group of bacteria that use it as carbon and energy sources. These bacteria close the biological cycle by degrading calcium oxalate, releasing Ca^{2+} and inducing a change in local soil pH. If parameters are favourable, the geological part of the pathway begins, because this change in pH will indirectly lead to the precipitation of secondary calcium carbonate (calcite) in unexpected geological conditions (Figure 1). Due to the initial acidic soil conditions, and the absence of geological carbonate in the basement, it is unexpected to find C in the form of calcite. The activity of the oxalate-carbonate pathway has now been demonstrated in several places around the world, suggesting that its importance can be even greater than expected. In addition, new roles for each of the biological players of the pathway have been revealed recently forcing us to reconsider a global biogeochemical model for oxalate cycling (Martin et al., in press).

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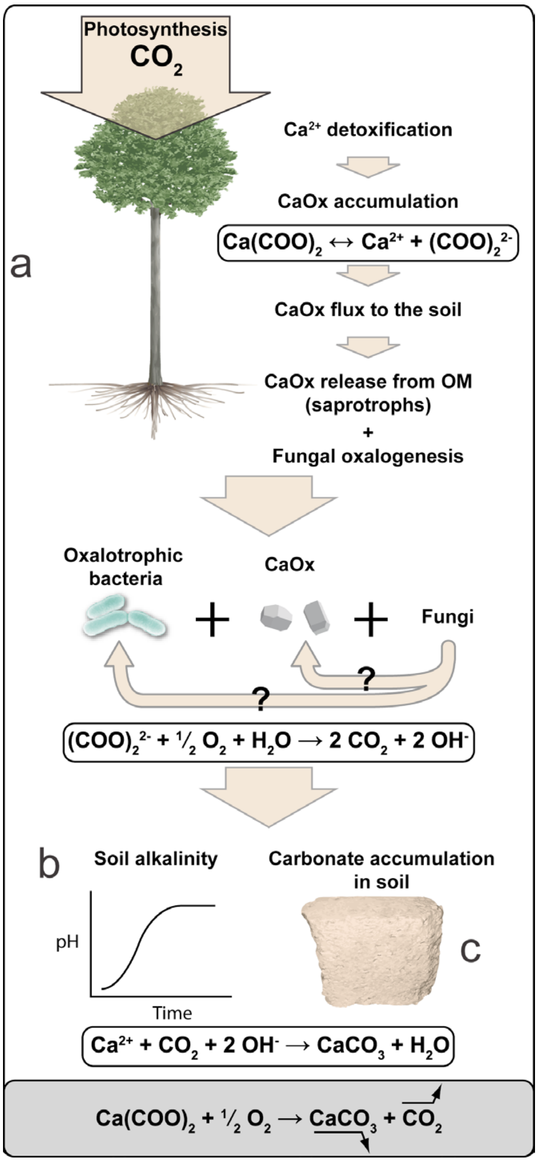

Fig. 1. Schematic representation of the oxalate–carbonate pathway showing the main biological players and the chemical reactions involved (modified from Aragno and Verrecchia, 2012). The unknown contribution of fungi as calcium oxalate producers and the role of their interaction with bacteria are indicated by a question mark. CaOx = calcium oxalate. a = processes leading to the formation of CaOx in the plant and fungi, oxidation of CaOx by bacteria and arrows indicating the unknown contribution of fungi; b = effect of oxidation of CaOx on soil pH over time; c = final product of the oxalate–carbonate pathway. The reactions leading to the formation of calcium carbonate are indicated below.

P 14.4

Influence of plant diversity on polycyclic aromatic compounds and their metabolites in temperate grassland soils

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Polycyclic aromatic hydrocarbons (PAHs) and their polar oxygenated (OPAH) and nitrated (Nitro-PAH) derivatives are generated by incomplete combustion of fossil fuels. Furthermore, OPAHs and Nitro-PAHs can be formed in the atmosphere and in soils by photochemical and microbial transformation of PAHs. OPAHs and Nitro-PAHs are more mutagenic and carcinogenic than their parent-PAHs. Plants can influence the concentrations of organic pollutants in soil by scavenging them from the atmosphere and fixing them in soil "filter effect", releasing enzymes that degrade organic compounds and favoring PAH-degrading microbes associated with plant roots (Dietz et al., 2001; Van Aken et al., 2010). The use of mixtures of plant species for clean-up of soil contaminated with parent-PAHs "phytoremediation" has been frequently reported, but the effect of such procedures on metabolites such as OPAHs and Nitro-PAHs has not been reported (Meng et al., 2011). It is known that plants frequently do not release suitable enzymes to mineralize parent-PAHs completely. Hence, accumulation of intermediate products is a possibility (Van Aken et al., 2010). It can be assumed that the nature and extent of transformation of organic pollutants (PAHs, OPAHs & Nitro-PAHs) in soil differs amongst different plant species because of differences in the morphology, enzymes they exude and number/kind of microbes associated with their roots. The objective of this study was to understand how plant diversity and plant functional group composition influences the accumulation/transformation of parent-PAH/OPAHs and Nitro-PAHs in temperate grassland soils.

To achieve this we analyzed the concentrations of PAHs, carbonyl-OPAHs and Nitro-PAHs in soils from the Jena Biodiversity Experiment plots. In the Jena Experiment, the composition of plant cover has been manipulated to create a gradient in plant species richness and number of plant functional groups. The experimental design consists of 82 plots with plant mixtures of varying species numbers (1, 2, 4, 8, 16 and 60 species), functional group diversity (1, 2, 3 and 4) and plant functional group identity (grasses, legumes, tall herbs, small herbs) composition (Roscher et al., 2004, Bandowe and Wilcke, 2010). The influence of plant diversity (species number, functional group number, presence or absence of specific functional groups: grasses, legumes, small herbs and tall herbs) on the concentrations of parent-PAHs, carbonyl-OPAHs and Nitro-PAHs was explored with the help of Univariate ANOVA followed by posthoc tests.

The concentrations of Σ28 PAHs (471-2289 ng/g), Σ15 carbonyl-OPAHs (123-405 ng/g) and Σ7Nitro-PAHs (42-337 ng/g) in Jena soils were comparable to those of other urban sites in Europe. Plots with higher species number had significantly higher 1-naphthaldehyde concentrations (F=4.358, p=0.013). Increases in functional group number only caused a significant increase in concentration of 6H-benzo(cd)pyrene-6-one (F=3.302, p=0.047). The functional group identity seems to play a more important role in transformation of PAHs, OPAHs and Nitro-PAHs in soil than species richness and number of functional groups. The presence/absence of legumes and small herbs had different effects on the different compound groups. The concentration of 2-methylnaphthalene was higher when legumes were present (F=4.309, p = 0.05). The concentration of 6H-benzo(cd)pyrene-6-one (F=7.104, p=0.02), several individual Nitro-PAHs: 2-nitrobiphenyl (F=4.98, p=0.04), 3-nitrofluoranthene (F=5.35, p=0.03), 2,7-dinitrofluorene (F=4.88, p=0.04) and Σ7Nitro-PAHs (F=6.803, p=0.02) were lower in the presence of legumes. This is an indication that the legumes either directly release enzymes to their root zone capable of degrading Nitro-PAHs and 6H-benzo(cd)pyrene-6-one or the presence of legumes enhances microbial activity in their rhizosphere, mainly because of the improved nitrogen supply. Presence of small herbs decreased concentrations of anthracene but increased those of 1-nitronaphthalene and 6-nitrochrysene. This could mean that 1-nitronaphthalene and 6-nitronaphthalene are formed by enzymes associated with small herbs while anthracene is biodegraded. This knowledge might help to develop and improve phytoremediation for soils contaminated with atmospheric pollutants like PAHs, OPAHs and Nitro-PAHs.

Figure 1: Jena Biodiversity Experiment Site (*www.the-jena-experiment.de)*

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P 14.5

Biologically induced vs. biologically influenced mineralization of carbonates from a hypersaline microbial mat, Pernambuco Lagoon, Brazil

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In microbial mats, microbes mediate the formation of laminated structures, most commonly composed of carbonates, a process defined as organomineralization. It includes (i) biologically-induced mineralization resulting from the interaction between biological activity and the environment; and (ii) biologically-influenced mineralization which is defined as passive mineralization of organic matter (biogenic or abiogenic in origin), whose properties influence crystal morphology and composition (Dupraz et al., 2009). Cell walls, sheaths and extracellular polymeric substances (EPS) are currently thought to be the main templates involved in mineral formation that may be partially preserved in the geological record. This study focuses on organomineralisation in a living hypersaline non-lithifying microbial mat from Lagoa Pernambuco, Brazil. Microscopic, spectroscopic and microelectrode studies of the microbial mat provided information on the microbial population and the biologically-influenced vs. biologically induced mineralization processes, specifically the formation of Mg-calcite and dolomite, which are present in different horizons of the microbial mat.

Chemical imaging of biological materials is advancing our understanding of biochemical processes and the role of microbes in mineral precipitation. Using NanoSIMS, we aimed to link microbial metabolism to molecular structures and produce a detailed view of the role of these organisms during the formation of the carbonate cortex in ooids. Coordinated NanoSIMS-microscopy studies make it possible to obtain simultaneous information on the mineralogy, structure compositions, and petrographical context of the different organomineral layers. Mapping of O, S, Si, Ca, Mg and C/N was accomplished at specially targeted sites bringing unique information about the relationship among these elements.

Results highlight photosynthesis, exopolymer degradation and sulfate reduction, which play important roles in element cycling in specific layers of microbial mats and which have a crucial role in amorphous Mg-Si and $CaCO_3$ precipitations. Moreover, this study reports viruses that become mineralized and it discusses their potential on mineralization and preservation.

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P 14.6

Effects of P, Si and Ca on composition, structure and As uptake of fresh and aged Fe precipitates

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The oxidation of Fe(II) in aerated water leads to the formation of amorphous to poorly-crystalline Fe(III)-precipitates. Such precipitates control the cycling of major and trace elements in a wide range of redox-dynamic environments, but also play an important role in engineered systems, such as drinking water treatment for As removal from anoxic As-rich groundwaters.

Previous work has shown that the composition and structure of fresh Fe(III)-precipitates from Fe(II) oxidation strongly depend on the concentrations of phosphate (P), silicate (Si) and Ca in solution. However, systematic quantitative information is still limited with respect to:

- effects of Si and Ca on the composition and structure of fresh Fe oxidation products over a range of P/Fe ratios
- changes in composition and structure of different precipitates with aging
- effects on uptake and solubility of co-transformed As.

To fill this knowledge gap, we perform batch experiments on Fe oxidation, precipitation and precipitate aging in bicarbonate-buffered solutions at pH 7.0. At initial dissolved P/Fe ratios from 0 to 2, we investigate the effect of the Si and/or Ca on the composition and structure of fresh Fe precipitates (sampled after 4 h, i.e., complete Fe(II) oxidation) and on the uptake of arsenate (initially 500 µg/L As(V)). The same types of precipitates will also be analyzed after aging in their synthesis solution for 30 d at 40°C.

First results confirm that the presence of Ca substantially enhances P and As(V) uptake by fresh precipitates formed at high P/Fe ratios. Si on the other hand seems to markedly slow down precipitate crystallization at low P/Fe ratios. These results will be complemented with data for aged precipitates, as well as with results from precipitate characterization by Fe K-edge X-ray absorption spectroscopy and transmission electron microscopy.

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P 14.7

Evidence for a life-influenced Dead Sea during the last glacial-interglacial cycles

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The ICDP Dead Sea Deep Drilling Project aims to reconstruct the paleoclimatic and paleoseismicity records of the Levant region. Within this frame, a geomicrobiogical investigation is undergoing in a 450m-long core retrieved from the deepest part of the hypersaline modern Dead Sea. One goal of this investigation is to constrain the microbial influence on the precipitation of authigenic minerals.

Lake level fluctuations during the two last glacial-interglacial cycles have allowed the development of microbial life in both the water column (Oren & Shilo, 1982) and the sediments (this study). While today's hypersaline conditions hardly favor the development of sustained life in its water column, preliminary geomicrobiological results argue for an impact of microbial life on the water and the sediments of the Dead Sea and its predecessors.

Although formerly thought to be abiotically driven (Barkan et al., 2001), it has been acknowledged that algal blooms have influenced the carbon cycle in the Dead Sea and its precursors (Kolodny et al., 2005). New carbon isotopic data from Holocene and Pleistocene aragonite corroborate this interpretation, additionally supported by C/N ratios indicating lacustrine algae as the main source of OM. It appears that these variations have been driven by relative changes in the contribution of photosynthetic activity, aerobic and anaerobic organic matter decomposition, as well as changes in evaporation and rainfall that have triggered numerous water column turnovers.

Furthermore, SEM investigations of modern microbial mats associated with aragonite laminae along the emerged Dead Sea shores show a co-occurrence of EPS and aragonite needles possibly arguing for an additional mode of precipitation. These EPS may act as a template for aragonite nucleation and needle growth. Carbonate ions may also be released by SRB degradation of EPS in the sediment allowing aragonite precipitation, which could further explain the negative shifts in aragonite $\delta^{13}C$. Authigenic pyrite is commonly found within these laminae supporting an active biologic S cycle.

Ongoing processes in the newly emerged Dead Sea shores provide plausible explanations for the observed lithological patterns and microbial imprint in the retrieved sedimentary core. These data may further help understanding the occurrence of aragonite within laminated and non-laminated sediments as well as of native sulfur concretions and framboidal pyrite. Finally, the combined dataset of this unique hypersaline system witnesses the high variability of the carbon cycle throughout time.

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P 14.8

Are the spectacular speleothems of Asperge biogenic?

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Asperge Cave is 7 km long, 126 m deep and it is located in the region of the "Montagne Noire" - Hérault (Fr). The cave opens in Cambrian terrains at the contact between the "Calcaire marmoréen massif, cristallin de La Garrigue" (marble) and the "Schistes et calcaires phylliteux" (schist) (Alabouvette et al., 1982).

Pits and meanders of the Asperge Cave develop within marble and schist, and limited zones of the cave present groups of concretions formed by bouquets of acicular-, coralloid- and bulb- shaped aragonitic speleothems (Fig. 1). Thanks to the spectacular morphology and colors of these concretions, Asperge has been proposed as UNESCO World-Nature-Heritage (IUCN, 2007). Speleothems with shapes as those found in Asperge are not unique and have been described elsewhere in the world (e.g. in Hidden Cave, New Messico (Hazel et al., 2007)). Hazel et al. (2007) suggested that morphologies such as u-loops might be the result of a biological process. However, this hypothesis remains quite speculative. Testing it is the goal of our study.

Here we present preliminary results of a series of field observations, mineralogical-chemical and microbiological analysis of the Asperge concretions. Yeast Extract Agar plates were used to sample the living organisms from different location of the cave. Various bacterial and fungal species that need to be classified have been successfully isolated from the speleothems. We speculate that these organisms might play a central role in the formation and the shaping of the concretions.

With this contribution we aim to emphasize the importance of biology in apparently inhospitable underground environments. Speleothems thus far regarded as abiotic concretions might instead be the product of yet unknown living organisms.

Figure 1. The spectacular speleothems of the "Galerie des grandes aragonites bleues" in Asperge Cave (Fr)

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P 14.9

Stratification of active methanogenic consortium along the Holocene record of Laguna Potrok Aike, Patagonia

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Methane and carbon dioxide within anoxic lake sediments are the final products of organic matter degradation. The biogenic production of these end members depend on both the refractoriness of the organic sources and the metabolic pathways used by the microbial consortia. During early diagenesis, fermentation and reduction processes can gradually convert primary inputs into simpler molecules, which can sometimes mask the initial signals of the bulk organic fraction (Freudenthal et al. 2001; Lehmann et al. 2002). Moreover, in anaerobic habitats, a stepwise degradation of complex organic compounds takes place via hydrolysis, fermentation or acidogenesis, acetogenesis and methanogenesis (Garcia et al. 2000). McInerney et al. (2008) have shown the occurrence of competitive and syntrophic relationships between microbes depending on local physical and chemical conditions. For example, methanogens can bond to chemoheterotrophic bacteria in low nitrate and sulfate environments producing methane at various stages. While methyl fermentation seems to be a favored pathway in freshwater environments (Whiticar et al. 1986), acetogenesis appears to dominate in cold environments (Kotsyurbenko 2005). Thus, the total amount of methane measured in the sediments depends on complex interactions between sedimentary substrates (Conrad et al. 2010), bacterial activity and metabolic pathways (Whiticar 1999). Furthermore, microbial assemblages tend to evolve toward energy conservation at depth, (Schink 1997), while developing at the same time the ability to use refractory substrates (McInerney et al. 2009). However, until recently geomicrobiological investigations of methane-bearing lacustrine sediments have been limited to their most surficial portion.

We investigated the microbial methanogenic population along the uppermost 10 meters of sediments of Lake Potrok Aike, a subsaline maar located in southern Patagonia. To determine its impact on the sediments we measured methane content and its relative carbon isotopic composition (Fig. 1A). Different microbial substrates were identified and characterized by analyzing their bulk organic fraction and pore waters chemistry. Variable degrees of sediment colonization were observed in relation to organic sources refractoriness. Living microbial activity in the sediments was first assessed using in situ ATP detection, and microbial populations further quantified via cell counts. DGGE and archaeal clone libraries allowed defining their overall diversity and a phylogenetic tree was further established based on retrieved sequences of methanogens. Bacteria dominated the microbial assemblages while methanogenic populations appeared strongly stratified within the sediments. Phylogenetic attributions revealed that species such as *Methanolinea* (Imachi et al. 2008) and *Methanoregula* (Bräuer et al. 2011) are tolerant to Potrok Aike's cold and subsaline conditions (Fig. 1A). The predominance of *Methanomicrobiales* shows that CO_2 reduction has been the major pathway leading to methane production (Borrel et al. 2011), although the highest methane content measured in the sediments appears to be associated with *Methanosarcinales* (Fig. 1A). Methane isotopic values in shallow sediments were similar to those of the bulk organic fraction (approximately -24 ‰), but much more negative at depth (approximately -65 ‰ to -68 ‰). The concomitant presence of *Syntrophus*-related sequences (Jackson et al. 1999) suggests that syntrophy could gradually lead to more negative $\delta^{13}C_{CH4}$ values.

Figure 1B shows a proposed stepwise model that summarizes the main stages of organic matter degradation.

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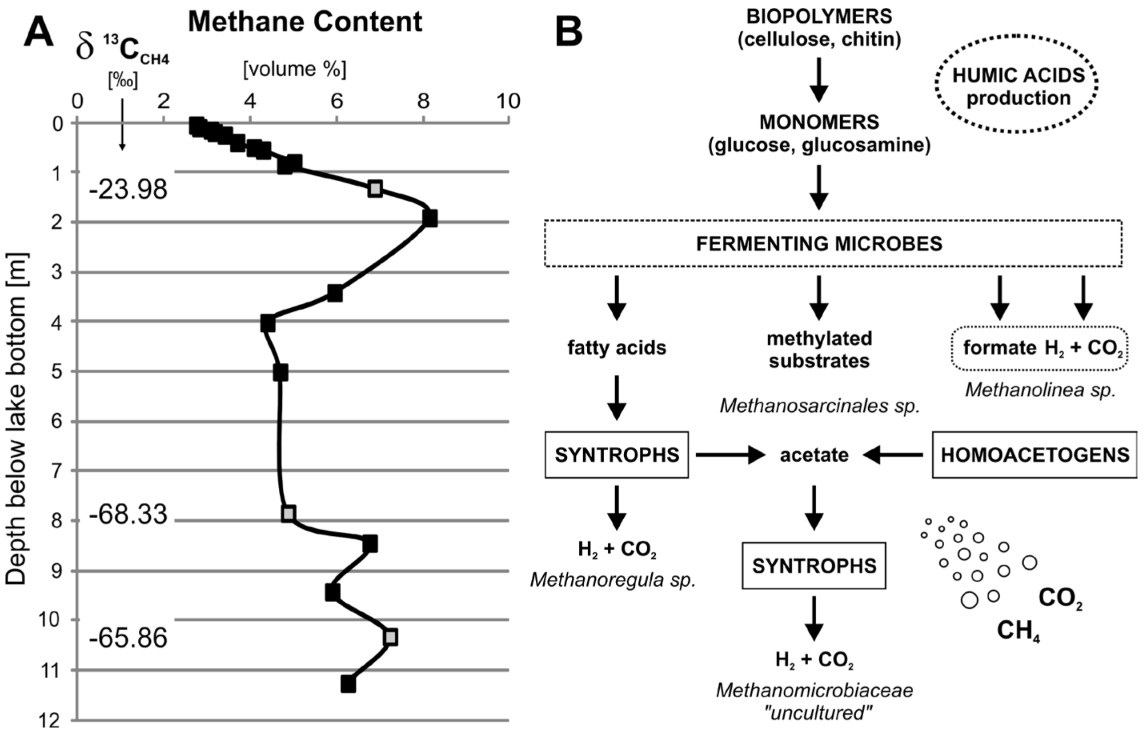

Figure 1. A) Methane content and its corresponding carbon isotopic values. B) Model showing the stepwise organic matter degradation with hydrolysis, acidogenesis and acetogenesis while methanogenesis can take place at different degradation stages. Methanogens are placed on the diagram with respect to their substrate and depth.