

stream geomorphological variables (stream length, watershed size, drainage density, slope) in the September 2002 sampling. Multiple factor regression and principle component analysis showed strong correlations between DOC concentration and stream drainage density, stream length, watershed area, and mean % slope in the watershed. Streams with higher DOC concentration also had higher DOM M_w and molar absorptivity, but the slope of this relationship changed seasonally. Moreover, DOM M_w and molar absorptivity were negatively correlated with drainage density and the percent of the watershed in open water. Despite the high cover of wetlands in the watershed, our results show that watershed geomorphology and land cover explain more variation in DOM concentration and physicochemistry than the prevalence of wetlands alone. Hydro-geological mechanisms operating in subwatersheds of contrasting geomorphology and land cover composition likely account for these patterns in stream water DOM concentration and physicochemistry.

B31B-05 0935h

Carbon Loss From Peatlands: A UK Perspective

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Carbon budgets in UK peatlands are in the spotlight for two main reasons. Firstly the water supply industry, which in many parts of the country relies heavily on upland water sources, is concerned about increasing water colour, and secondly peatlands account for 50% of the total UK soil carbon store. It is therefore entirely relevant to ask the question whether these important long-term carbon stores are beginning to leak more carbon into surface waters, which at a certain threshold value will switch the mass balance of individual peatlands to net carbon loss. Streams draining UK peatlands are typically DOC-rich and it is not uncommon to measure concentrations and fluxes in excess of 15 mg L⁻¹ and 100 kg C ha⁻¹ yr⁻¹, respectively. We have recently measured DOC fluxes of 115-270 kg C ha⁻¹ yr⁻¹ from acidic catchments containing between 35 and 85% peat (Billett et al. 2004; Dawson et al. 2004). A full inventory of downstream carbon loss in streams draining these catchments increases riverine fluxes by 19-50% to values ranging from 137-323 kg C ha⁻¹ yr⁻¹. This includes additional measurements of POC, DIC and free CO₂. Estimates of CO₂ lost by evasion from the stream surface in two catchments suggests that significant amounts of carbon (46-141 kg C ha⁻¹ yr⁻¹) are lost via the stream-atmosphere pathway. Our work and others therefore shows that riverine fluxes from peatlands can exceed the annual long-term rate of carbon accumulation (200-300 kg C ha⁻¹ yr⁻¹). UK peatlands would appear to be prone to increased DOC loss; the potential for disturbance is large, drainage networks are often dense (with good connectivity between the soil-stream system) and climatic variability is an important driver of both seasonal and long-term flux change. At the moment it is not possible to say whether a fundamental change is taking place in UK peatlands or whether we are now simply aware of all the loss terms and measuring each term more accurately. The combination of long-term NEE measurements with a complete inventory of streamwater carbon losses is clearly a powerful way of monitoring changes in the carbon balance of peatlands. References Billett MF, Palmer SM, Hope D, Deacon C, Storeton-West R, Hargreaves KJ, Flechard C and Fowler D. 2004. Linking land-atmosphere-stream carbon fluxes. *Global Biogeochemical Cycles* 18, GB1024, doi:10.1029/2003GB002058. Dawson, JJC, Billett MF, Hope D, Palmer, SM and Deacon CM. 2004. Sources and sinks of aquatic carbon linked to a peatland stream continuum. *Biogeochemistry* (in press).

B31B-06 0950h

Carbon Cycling in a Northern Peatland

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In peatland ecosystems, actual microbial activity is lower than the potential activity as a result of both substrate and nutrient limitations. Extracellular enzymatic hydrolysis is often considered the rate limiting step for the provision of fermentative products. Terminal mineralisation to CO₂ and CH₄ is dependent upon the rate and activity of the fermenting organisms and CH₄ is additionally hindered by the presence of competitive electron accepting processes such as iron and sulphate reduction. The aim of this study is to determine the spatial and temporal patterns of potential CO₂ and CH₄ production, DOC and fatty acid dynamics across a peatland complex. The results of this study show that the history and botanical composition are equally important to the pathway of terminal mineralization of C to CO₂ and CH₄. Under standard conditions, CH₄ contributes a small portion of total C mineralised. The presence of alternative electron accepting processes such as iron reduction were not likely inhibitory and did not contribute a large portion of the CO₂ produced. However, despite small concentrations of SO₄²⁻, evidence of thiosulfate production and consumption in incubations supports the notion of sulphate recycling, resulting in competitiveness with methanogenesis. The addition of glucose and acetate resulted in a spatially variable response both within sites and between sites. Acetate additions in slurries did not stimulate potential CH₄ production in the poorer Bog site. Additions of glucose resulted in the variable accumulation and utilisation of fatty acids. The dynamics of this DOC pool are a reflective of the zone of fluctuation and mean annual water table depth. Microbial populations have a high affinity to labile sources of carbon and are influenced by the presence of alternative processes. Despite small concentrations, SO₄²⁻ can be a potentially large source of CO₂ production and CH₄ limitation in certain peat environments. Fatty acids as intermediates for terminal C mineralization are seen as key players in peatland ecosystems.

B32A CC: 524 A Wednesday 1030h

Dissolved Organic Carbon in the Biogeochemical Functioning of Systems II (joint with H, GC)

Presiding: T Moore, McGill

University; K Bishop, Swedish University of Agricultural Sciences

B32A-01 1030h INVITED

Coupling of carbon and nitrogen cycles through humic redox reactions in an alpine stream

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Humic substances are a heterogeneous class of moderate molecular weight, yellow-colored bio-molecules present in all soils, sediments and natural waters. Although humic substances are generally resistant to microbial degradation under anaerobic conditions, some microorganisms in soils and sediments can use quinone moieties in humic substances as electron acceptors or as electron shuttles in the microbial reduction of ferric iron. In turn, ferrous iron can reduce nitrate, facilitating the formation of organic nitrogen moieties. Field studies of humic electron shuttling processes can be carried out by characterizing the oxidation state of quinone moieties in humic substances at natural concentrations using fluorescence spectroscopy. We have used fluorescence spectroscopy to show that humic substances are important in electron transport reactions in coastal marine sediments and in the water columns of ice-covered lakes. Gradients in humic redox state may also occur as stream water is exchanged with water in associated hyporheic zones. We conducted a conservative tracer injection experiment in an alpine stream-wetland system located in the Front Range of the Colorado Rocky Mountains. In this system, concentrations of nitrate and dissolved organic carbon both increase with the onset of snowmelt as nitrate deposited in the snowpack is mobilized and DOC is flushed from upper

soil horizons. During the tracer experiment, we sampled wells adjacent to the stream and found that lower nitrate concentrations occurred in wells with slower hyporheic exchange and more reduced dissolved humic substances. These results suggest that humic redox shuttling may be an important process linking carbon, nitrogen and iron cycling in watersheds.

B32A-02 1050h

Redox reactions of dissolved organic matter contribute to anaerobic sulphur cycling in peatland soils

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Sulphate reduction rates in wetland soils typically account for a large fraction of the anaerobic electron flow, despite small pool sizes of sulphate in the pore waters. The studies objective was to test the hypothesis that recycling of sulphur occurs and that redox-reactions of dissolved organic matter (DOM) are involved in the recycling process. To examine the recycling process we used peat mesocosm from two peatlands in Ontario, Canada and subjected them to sulphur deposition and vertical water flow of about 2 mm/day. Depth profiles of DOC and sulphate concentrations were determined and vertical mass balances calculated. In addition we determined 34S sulphate profiles of pore waters. Batch experiments with addition of H₂S to solutions of standard peat humic acid (Pahokee Peat, IHSS) were used to determine whether H₂S was oxidized by humic acids, and what the reaction products were. Enrichment with 34S at intermediate depths, constant sulphate concentrations with depth and absence of oxygen suggested that sulphate reduction and anaerobic sulphate release concurrently occurred. In the batch experiments two apparent reactions of H₂S with DOM were observed. In the fast initial reaction, H₂S was oxidized mostly to elemental sulphur and secondarily to sulphate. Production of thiosulfate was not observed. In a slower reaction step H₂S was further consumed and the sum of dissolved inorganic forms of sulphur in the pore water decreased. This was interpreted as H₂S being incorporated into the organic substance. No systematic relationship between pH and the oxidation process was found. Overall the results suggest that dissolved organic matter is involved in an anaerobic sulphur cycle allowing for high rates of sulphate reduction in sulphate-poor peatlands.

URL: <http://www.geo.uni-bayreuth.de/hydrologie/mitarbeiter/index.php?mitid=15&lang=en>

B32A-03 1105h

The Flux and Concentration of DOC in Surface Waters in Northern Sweden is Particularly Susceptible to Changes in Winter Conditions

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In the boreal region of northern Sweden, where approximately four weeks of snow melt provides close to 50% of the annual runoff, winter conditions and the transition to spring plays a key role in controlling the flux and concentration of dissolved organic carbon (DOC). Because of the long winters in northern Sweden, with an average snow cover of 170 days per year, changes in the snow cover or amount and timing of snow melt could significantly alter the DOC dynamics during the spring flood period. We report on a study involving fifteen boreal catchments in northern Sweden monitored during the spring flood to examine the DOC variability in relation with catchment characteristics, in combination with a soil frost manipulation study. The results suggests that the amount and timing of snow melt and the extent of soil frost can have large influence on the DOC concentration in small streams and rivers in the region. Because much of the pH decline in northern Sweden during the spring flood is attributed to natural variability in DOC, a further concentration

increase during the spring could severely affect the biodiversity in many surface waters. For example, a 15% increase in the concentration of DOC during the spring flood would augment the decline in pH to an extent that could severely affect the biodiversity of many surface waters in northern Sweden.

B32A-04 1120h

Is a Universal Model of Organic Acidity Possible: Comparison of the Acid/base Properties of DOC in the Boreal, Temperate and Tropical Zones

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The acid/base properties of dissolved organic carbon (DOC) are an important feature of soil and surface waters. Large differences in the acid/base properties of DOC observed in different studies might be solely due to spatial and temporal differences. Different analytical techniques, however, may explain some of the observed differences. We used a combination of ion-exchange techniques, titration and surface water chemistry data to evaluate DOC character from two substantially different areas - the relatively pristine boreal zone of Sweden and the heavily acidified temperate zone of the Czech Republic. On average we found a significantly higher site density (amount of carboxylic groups per milligram of DOC) for the Swedish sites (10.2 microequivalent/mg DOC) compared to the Czech sites (8.8 microequivalent/mg DOC) measured in 1990s. This suggests a slightly higher buffering capacity for Swedish DOC. A tri-protic model of a type commonly incorporated in biogeochemical models was used for estimating the DOC dissociation properties. For Swedish sites the following constants were calibrated: pKa1=3.04, pKa2=4.51, pKa3=6.46, while the constants for Czech sites were pKa1=2.5, pKa2=4.42, pKa3=6.7. Despite differences in site density values, both models predict very similar dissociation and thus pH buffering by DOC in the environmentally important range of pH 3.5-5.0. Interestingly, very recent results showed an increased site density in some of the Czech sites to values of 10.4 microequivalent/mg DOC, almost identical to that valid for the boreal zone. Recent data from a tropical region of Kamerun indicate values of 10.9 microequivalent/mg DOC. These two observations suggest that the temporary heavy anthropogenic acidification in the Czech sites had a measurable influence on acid/base properties of surface water DOC.

B32A-05 1135h

Trace Metals and Nutrients at the Soil-Root Interface of Forest Soils

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The activity of roots creates a microenvironment, known as the rhizosphere, where soil properties, processes and feedback mechanisms differ substantially from those observed in the soil matrix. Due to its proximity to the site of elemental uptake by plants, the rhizosphere is viewed as a biogeochemical hotspot characterized by massive fluxes of matter and energy. In this context, the acquisition of new knowledge on the rhizosphere is crucial to increase our capacity to understand, manage and model soil-plants systems. Of particular interest to scientists is the response of the rhizosphere to perturbations of natural (e.g. climatic fluctuations) or anthropogenic (e.g. soil contamination) origin. Moreover, results from rhizosphere research help

define new approaches designed either to restrict the entrance of potentially toxic elements in crops and, hence, in the food chain or, contrarily, to increase the uptake of trace elements by plants in contaminated environments to be bioremediated. Our recent studies in forested environments have clearly established that the rhizosphere (Abies, Acer, Betula, Picea, Pinus or Populus roots) is more acidic than the soil matrix and that it is enriched in organic substances (dissolved and solid), nutrient cations (Ca, Mg) and trace metals. Indeed, the rhizosphere systematically acts as a sink for Cd, Cu, Ni, Pb and Zn, notably under bioavailable (water-soluble and salt-extractable) forms. Yet, the relative activity of free metal ions is lower in the rhizosphere, as shown for Cu⁺⁺, probably as a consequence of the higher DOC content. The corrosive environment forming in the rhizosphere, as controlled by the release of H⁺ ions and of organic acids, also impacts on mineral assemblages through an increase in the weathering of primary minerals (amphiboles, plagioclases) and the formation of secondary solid phases such as Fe and Al oxides. Some of the research avenues currently investigated by our research group include the quantification of functional links between organic carbon, microbial activity and metal speciation, the development of methodological and analytical approaches operating at the spatial scale of the rhizosphere and, the assessment of preferential hydrological fluxes along root networks.

B32A-06 1150h

Plant Species Anaerobiosis and DOC Dynamics in a Peat-Forming Wetland, New York State

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We quantified spatial and temporal patterns of dissolved organic carbon (DOC) concentrations in the shallow peat soil of a freshwater wetland (located in central New York State) and correlated the patterns with anaerobiosis in roots of the dominant plant species. Sampling was stratified in zones dominated by: lakebank sedge (*Carex lacustris*), common cattail (*Typha latifolia*), purple loosestrife (*Lythrum salicaria*) or soft rush (*Juncus effusus*). Concentrations of DOC peaked in late summer and were much greater in wet years (14.3 mg C/L) than during summer drought (5.3 mg C/L). DOC concentrations did not vary significantly as a function of plant species and were greater in subsurface peat (13.3 mg C/L at 20 cm depth) than in surface peat (8.6 mg C/L at 5 cm depth). Anaerobiosis was pronounced in cattail in the spring and autumn, in purple loosestrife in mid summer, but showed little seasonal pattern in rush and in sedge. Although recent ecological research has shown that plant species can control belowground processes, we found little evidence for plant species control of DOC dynamics in this wetland.

B33A CC: 220 C-E Wednesday 1330h

Estuarine Ecosystems and Links to Uplands Posters

Presiding: D M Peteet, NASA

Goddard Institute for Space Studies; P Louchouart, Lamont-Doherty Earth Observatory

B33A-01 1330h POSTER

The Existence and Release of Bio-effective Silicon in the Estuary Sediments

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Silicon is an essential element for the living body. A moderate amount of silicon in seawater has a stimulative function to oceanic primary productivity. The excessive silicon may lead diatom to propagate rapidly. The red tide that the diatom is in the majority have

relation to the bio-effective silicon released from sediment. To reveal the existence and release of the bio-effective silicon with various species in the estuary sediments is of great significance for understanding the mechanism of inducing red tide and controlling red tide harm. The existent species and release behaviors of bio-effective silicon in sediment columns collected from the Peal River estuary in China where the red tides occur frequently are studied. The results show that the concentrations of various species silicon below 15cm depth of sediment column decline obviously. It is suggested that the bio-effective silicon in surface sediment can be released due to the variations of aquatic dynamics condition and physicochemical features of seawater. The results of simulated tests indicate that the release of exchangeable silicon in sediment bears mainly a relation to aquatic dynamical action. The release of silicon combined with carbonate is controlled by pH. The reduction reactions occurring in the redox interface of sediment can promote the release of silicon combined with iron manganese oxide or with organic matter and sulfide. The salinity exerts an influence on release of bio-effective silicon in sediments. The release degree of silicon is different in various salinity ranges, which may have relation to the ionic exchange action and complex action.

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B33A-02 1330h POSTER

Long-term Variability of Landfast Ice along the Beaufort Coast

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Landfast ice thickness computed from a model and fast ice extent derived from ice charts show a large interannual variability along the Beaufort coast between 1976 and 2003. The largest change occurs in spring maximum ice extent, which shows a considerable reduction between the periods 1974-1988 and 1989-2003. This reduction is accompanied by a gradually shortened ice growth season; the maximum fast ice extent appears to contribute the most to the long-term trend. Compared with the Alaska coast, the Mackenzie shelf shows a larger decrease in fast ice cover at the peak of growth season in spring. The interannual variability of surface air temperature in winter and spring, as well as the mean atmospheric circulation patterns represented by the PDO and the AO are thought to be responsible for the observed long-term changes in fast ice cover. Since landfast ice can store a considerable amount of freshwater along the arctic coasts, the decrease in maximum fast ice cover, as well as its shortened growth season and reduced freshwater storage, could have a significant hydrological, biological, and biogeochemical consequences in the coastal regions.

B33A-03 1330h POSTER

Spatial and Temporal Variability of Sedimentary Environments in the Hudson River Estuary

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Sitting at the interface between marine and terrestrial systems, estuaries are sensitive to natural climatic, sea-level and tectonic changes as well as to anthropogenic impacts. Research on estuarine systems has led to improved understanding of estuarine processes, but relation of those processes to the long-term evolution of estuaries is still uncertain. A geophysical survey funded by the New York State Department of Environmental Conservation resolves details of spatial and temporal variability of sedimentary processes in the Hudson River Estuary. Here we present interpreted sedimentary environments and evidence of past environments for a 30-km stretch of the Lower Hudson River Estuary, between Piermont and Haverstraw Bay. Integration of high-resolution seismic surveys, side-scan sonar imagery and multibeam bathymetry with sediment samples allows differentiation of three distinct sedimentary environments in the estuary: depositional, erosional and dynamic. Modern deposition occurs mainly in Haverstraw Bay on shallow marginal flats bounding the river channel as well