

mature site were 5^o/100 greater than in recently exposed sites. We conclude that 1) the primary nitrogen source to this ecosystem must be atmospheric deposition, 2) low plant ¹⁵N content generally corresponds with greater influence of mycorrhizal fungi on plant N supply, and 3) ¹⁵N content of mycorrhizal fungi may be a marker of proteolytic capabilities, and may therefore indicate the importance of organic nitrogen cycling to plant nitrogen supply.

B43A CC: 220 C-E Thursday 1330h

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

Presiding: T Moore, McGill University; K Bishop, Swedish University of Agricultural Sciences

B43A-01 1330h POSTER

Dissolved organic carbon and C cycling in Canadian forests

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Although the export of DOC from temperate - boreal forested catchments ranging from 1 to 10 g C m⁻² yr⁻¹ is small compared to the overall flux of C, the internal transfers of DOC are larger, with leaching from the forest floor and organic soil horizons ranging from 10 to 85 g C m⁻² yr⁻¹ with subsurface fluxes ranging from 1 to 40 g C m⁻² yr⁻¹. This suggests considerable internal cycling of DOC within the forest litter and soil, affecting processes such as CO₂ flux and the availability and transport of nutrients. To address this issue, I am starting a project on fluxes of DOC in Canadian forests, utilizing natural and disturbed sites that are part of the Fluxnet Canada network. In addition to determining fluxes, the project will also examine patterns of DOC bio-availability, production, sorption and mineralization across the sites and provide information to calibrate models. Based on incubations of organic and mineral soil samples from the sites, I present initial results on net DOC production potential, its dependence on temperature and soil properties and the partitioning of C mineralization between DOC and CO₂.

B43A-02 1330h POSTER

Spatial and Temporal Variability of Dissolved Organic Carbon and Nitrogen Fluxes in the Hermine, a Forested Watershed of the Canadian Shield

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Recent studies have established the essential role of carbon (C) and nitrogen (N) in the biogeochemical cycles of elements in forested ecosystems (McDowell and Likens, 1988). Carbon and N are essential nutrients for biological processes and growth (Kalbitz et al. 2000; Buffam et al. 2001), and they play a key role in soil acidification, pedogenesis, trace metal and nutrient transport and mineral weathering (Likens and Bormann, 1995; Williams et al. 2001). However, there is a gap in knowledge regarding the spatial and temporal variability of C and N fluxes in forested ecosystems. Moreover, the factors controlling the fluxes of dissolved C and N at the event scale is poorly understood (Prechtel et al. 2000; McHale et al. 2000; Buffam et al. 2001). In this context, the first objective of this study is to quantify the fluxes of dissolved organic carbon (DOC) and of dissolved N (NO₃, NH₄ and DON) between the biogeochemical compartments of a forested watershed (Hermine) at a range of temporal scales. The second objective is to identify the role of antecedent soil moisture conditions on the hydrochemistry of the stream, at the event scale. The results show that there is a significant difference ($\alpha = 0.05$) in the concentrations of dissolved C and N between the five compartments (precipitation, throughfall, soil solution in the organic and mineral horizons and, stream). The fluxes of dissolved C and N increase as the water flows through the forest canopy to reach a maximum in the

organic horizons. The decrease of dissolved C and N concentrations as the soil solution percolates through the mineral horizons is significant ($\alpha = 0.01$) and is explained by the physico-chemical retention reactions (Guggenberger and Kaiser, 2003) and biological processes (Qualls and Haines, 1992). In all compartments, the speciation of total dissolved nitrogen is dominated by dissolved inorganic nitrogen (DIN). As water flows through the soil profile, the absolute dissolved organic nitrogen (DON) concentration increases, but its proportion remains smaller than that of DIN ($\alpha = 0.05$). The temporal variability of DOC and dissolved N is strongly influenced by climatic factors. For example, significance seasonal variations ($\alpha = 0.01$) are observed for DOC, DON and DIN in organic horizons. This is explained by the biological activity that allows the uptake inorganic nitrogen compounds and the production of organic compounds (Qualls, 2000). The high concentrations of NO₃ in the meltwater in the stream of both years is explained by the reduced microbial activity during winter (Brooks and Williams, 1999). No temporal trends ($\alpha = 0.10$) are observed for dissolved C and N in the mineral horizons notably because the retention reactions there are driven by non-climatic factors (Qualls, 2000). At the annual scale, the relationship between the concentrations of DOC and streamflow is poorly significant ($R^2 = 0.03$; $\alpha = 0.05$; $n = 431$). However, at the event scale, this relationship becomes much more significant ($R^2 = 0.95$ to 0.35 ; $\alpha = 0.05$). The various dissolved N species in the stream present weaker links to discharge at the event scale ($R^2 = 0.010$ to 0.804 (DON); 0.014 to 0.646 (NO₃); 0.016 to 0.197 (NH₄); $\alpha = 0.10$). Moreover, the concentrations of DOC and dissolved N in the stream differ significantly as a function of the antecedent soil moisture conditions ($\alpha = 0.05$).

B43A-03 1330h POSTER

Controls on DOC Export and DOM Character in a Cutover and a Recently Restored Peatland

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Dissolved organic matter (DOM) dynamics were examined at a restored cutover peatland in the context of its changing hydrology before and after restoration and also with respect to variations in DOM character that are related to hydrology and restoration. The study, which covered three growing seasons, compared results from a portion of the peatland that was cutover to another portion that was cutover and later restored. In addition a nearby peatland that was not harvested (natural) was also studied for comparison. DOC concentrations increased post restoration while DOC export decreased because of decreased runoff caused by the blockage of drainage ditches. Compared to the natural peatland both the restored and the cutover sites exhibited a greater humic DOM character. No differences in DOM character were evident in the water released from both the restored and cutover sites. The most active layer for DOM production was the upper 75 cm within the range of seasonal water table fluctuation. Water storage units such as pools and ditches also played an important role in DOM export from the site. The most significant DOC export event is the spring snowmelt when export was significantly larger than those measured during the growing season. Differential solubility of the DOM fractions is a factor that controls their mobility and impacts on the DOM character found at the outflows. Storm events contributed significantly to the summer DOC output. Summer DOC dynamics were affected by antecedent moisture conditions and differences emerged between the restored and cutover site during this period. The results of this study emphasize the importance of managing water table fluctuations and the restoration (re-establishment) of Sphagnum species in order to improve the retention of DOM within cutover peatlands.

B43A-04 1330h POSTER

Factors of influencing dissolved organic carbon stabilization in two cambic forest soils with contrasting soil-forming processes

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Stabilization of Dissolved Organic Carbon (DOC) in forest soil is a major process of soil organic carbon formation. However, the factors influencing DOC stabilization are poorly understood. To clarify the factors that affect the stabilization of DOC in forest soil mantle, we measured DOC concentrations and soil properties which were DOC adsorption efficiency at two adjacent cambic forest soils with contrasting forest management histories in Tanakami Mountains, central Japan. Matsuzawa was devastated about 1,200 years ago by excessive timber use and remained denuded for a long period. Hillside restoration and reforestation work have been carried out over the last 100 years and soil loss has been reduced. Fudoji is covered with undisturbed forest (mixed stands of cypress and oaks) with developed forest soils (more than 2,600 years old). There was no apparent seasonal variation in DOC concentration in the soil solution in either catchment. In addition, there were no significant relationships between the DOC concentration, soil temperature, and new water ratio. These results indicate that temporal variation in biological activity and rainfall-runoff process have little effect on temporal variation in DOC. The vertical variation in the DOC adsorption efficiency and DOC concentration differed between Matsuzawa and Fudoji, and the highest DOC removal rate occurred at the lowest DOC adsorption efficiency in the 0 to 10-cm soil layer at Fudoji. These results suggest that DOC removal rate is independent of DOC adsorption efficiency. Below 60 cm soil depth, DOC fluxes were constant and dissolved organic Al concentrations were little or zero in either catchment. These results suggest that abiotic precipitation of DOC is a major mechanism for stabilization of DOC. Therefore, DOC content which is able to form metal complexes may be the most important factor of influencing DOC stabilization in cambic forest soil.

B43A-05 1330h POSTER

Spatial Flux Variations of Dissolved Organic Carbon (DOC) Along Streams in two Boreal Catchments in Northern Sweden

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To evaluate spatial variability in DOC amount and quality within two Swedish boreal catchments (sub-catchment areas 0.01-78 km²), samples were taken at every junction (103 in total) of the stream network during June 2000 when flows were stable and low. There was a very large variation in DOC-concentrations in the headwaters, and less variation downstream where the different headwater sources have mixed. The standard deviation (s.d.) of DOC in the subcatchments smaller than 15 km² was 7.2 (mean 17.1 mg l⁻¹, n = 78), while the s.d. for larger catchments was 4.1 (mean 14.1 mg l⁻¹, n = 25). Volume-weighted concentrations of DOC were higher in headwaters than downstream. Conservative mixing of downstream inflowing water could explain this DOC-pattern. This does not, of course, rule out in-stream processing. There are, however, only a few hours for in-stream processes to occur, and no consistent change in quality (SUVA = 254 nm / DOC, C/N ratio, and apparent molecular weight) was found that might indicate such in-stream processing. The apparent concentration of DOC in downstream runoff was 18 to 63 percent of the headwater DOC concentrations. Headwaters contribute to 40 percent of total catchment size but could contribute up to 65 percent of total DOC-flux at the outlet, although most water volume enters downstream from the headwaters. A more detailed sampling in 2002, gave results similar to those from the 2000 sampling.

B43A-06 1330h POSTER

Sources and Quantity of Dissolved Organic Matter Released From Flooding Upland Boreal Forests for Reservoir Creation

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Flooding of northern landscapes for the creation of hydroelectric and drinking water reservoirs results in elevated emissions of greenhouse gases and methylmercury in fish. Dissolved organic matter (DOM) is an integral component of both carbon and mercury cycling. At the Experimental Lakes Area in NW Ontario, three reservoirs were created by flooding boreal forests of differing carbon stocks with water from a nearby oligotrophic lake in the FLUDEX experiment. In the reservoirs, DOM concentrations continued to be elevated in all 5 years of flooding. DOM was the dominant form of nitrogen loss and comparable to dissolved inorganic carbon (DIC) release from all reservoirs as a result of flooding. Magnitude of DOM release did not mimic the order of carbon stores and is consistent with laboratory experiments. Changes in the quality of DOM generated throughout the experiment were followed by ¹³C/¹²C, ¹⁵N/¹⁴N and C/N ratios, spectral absorbance, and organic alkalinity. Sources of DOM and processes affecting the fate of DOM were followed in each year of flooding by determining the ¹³C/¹²C, ¹⁵N/¹⁴N and C/N ratios of vegetation, soils and periphyton, leaching experiments of flooded and unflooded soils, and constructing DOC, DON and DIC. ¹³C/¹²C budgets for each reservoir in conjunction with DIC-¹³C/¹²C budgets.

B43A-07 1330h POSTER

Relationship Between Land Use and the Amount and Reactivity of Dissolved Organic Carbon Exported from Coastal Watersheds

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Changes in the amount and biological reactivity of organic C, N, and P were investigated in coastal watersheds along a gradient of land use. Concentrations of inorganic N and P declined from suburbanized and agricultural headwaters to urbanized reaches further downstream. In contrast, concentrations of organic C, N, and P increased along the river network. At the outflow, organic N and organic P comprised 53% and 71% of the total N and P exported to Chesapeake Bay. The biological reactivity of organic C, N, and P varied with land use and season. Across sites and seasons, 0-41% of organic carbon, 0-41% of organic nitrogen, and 0-58% of organic P were biologically available over a time scale of 3 days. The bioavailability of organic carbon typically increased from forested and agricultural headwaters to larger suburban and urban drainages. Activities of esterase and endopeptidase enzymes by stream microbes also followed similar spatial patterns suggesting that both the bioavailability and chemical composition of organic matter were changing en route to the ocean. Measurements of bacterial production and respiration efficiency suggested that growth and metabolism of microbes in urban streams were less limited by organic matter quality and the availability of inorganic nutrients as compared to forested streams. Substantial quantities of bioavailable DOC, DON, and DOP accumulated along flow paths while concentrations of inorganic nutrients declined. The potential role of agricultural, suburban, and urban streams as transformers of inorganic nutrients to reactive organic fractions may need to be considered when predicting changes in oxygen demand and the total export of bioavailable C, N, and P to coastal environments.

B43A-08 1330h POSTER

Dissolved Nitrogen Dynamics and Dissolved Organic Carbon Biogeochemistry in an Ombrotrophic Bog

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As an extension of an ongoing study on carbon cycling and sequestration, Mer Bleue bog near Ottawa, Ontario was studied for dissolved nitrogen dynamics. Since nitrogen is an important nutrient for plant growth, the retention and export by the bog could reflect the impact of nitrogen deposition on bog productivity and carbon sequestration. Dissolved inorganic and organic nitrogen (DIN, DON) and dissolved organic carbon (DOC) inputs, export, and groundwater concentrations were measured over the 2003 field season (from May 21 to November 18, 2003). Nitrogen inputs were found to be entering the bog dissolved in precipitation in very small concentrations, ranging from 0 to 6 mg/L, and were dominated by NH₄⁺. Export DON and DOC concentrations followed similar patterns, increasing with a decrease in outflow discharge with drier bog conditions throughout the season. Rough budget estimates for DOC, DON and DIN for the 2003 field season are roughly 0.034, 0.101, and 2.861 g · m⁻² · t⁻¹, respectively. The bog was also characterized for groundwater concentrations of DIN, DON, and DOC in the saturated and unsaturated zones of the bog. The general patterns of concentrations show dominance of NH₄⁺ deeper in the saturated zone, and DON dominating in the unsaturated, biologically active zone. Although deposited nitrogen is dominated by inorganic forms, the internal processing of nitrogen results in DON export correlated to DOC. The results provide greater insight as to the influence and importance of dissolved nitrogen on carbon retention and sequestration.

B43B CC: 524 A Thursday 1330h

Isotopes in Biogeochemistry: Sediments and Records of Environments

Presiding: S Macko, University of Virginia; M E Uhle, University of Tennessee

B43B-01 1330h

Assessing the Distribution and Sources of Organic Matter in a Coastal Marine Environment Using Compound Specific Carbon Isotopic Analysis of Sedimentary Lipids: Evidence from the Hauraki Gulf, New Zealand

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The Hauraki Gulf, on the northeast coast of the North Island of New Zealand, is highly productive, supporting a large local fishing industry. River runoff to the Gulf is local and limited in volume, whereas the Gulf has prevailing currents and quasi-annual upwelling events that deliver open ocean waters and nutrients to the shelf and are believed to drive the high productivity in the area. Organic matter in coastal and shelf sediments are commonly derived from both allochthonous and autochthonous sources. Bulk chemical characterization of sedimentary organic matter alone cannot conclusively differentiate marine and terrestrial organic matter. Molecular level analysis, however, can yield detailed information on source of organic matter input as chain length and carbon number of marine and terrestrial derived lipids is source specific. The presence of C₂₇, C₂₉ and C₃₂ n-alkanes and C₂₄, C₂₆ and C₂₈ n-alkanoic acids are indicative of input from higher-plant waxes, whereas short chain C₁₂, C₁₄ and C₁₆ n-alkanoic acids are dominant components of algal-derived lipids. Compound specific isotope analysis further pinpoints sources because carbon isotopic values

of marine organic matter are typically enriched in δ¹³C relative to values for C₃ terrestrial plants. We report here on sediment samples recovered from the Hauraki Gulf during the summer of 1999. Samples were collected using a multi-corer from both near-shore and open environments to investigate the sources and distribution of organic matter in the gulf. Results show a mix of sources throughout the gulf and somewhat follow current flows. Nonetheless, the most upcurrent site showed significant terrestrial inputs. Other sites within the gulf, including those located on the shelf, show a mixture of sources. These results indicate that a significant amount of terrestrial organic matter is being transported out onto the narrow shelf of the gulf through small rivers. In contrast, the site most landlocked and furthest down current, showed a strong predominance of marine input. The organic matter at Firth of Thames where relatively high discharges of fresh water enter the gulf, is predominantly derived from algal input and not terrestrial sources as may be expected at the mouth of a river. The dominant n-alkanes are typically short chain (C₁₅, C₁₇, and C₁₉) and the carbon isotope values range between -25 and -30 ‰, typical of marine derived lipids. We interpret the predominance of marine input at this site as due to the influx of nutrients from the surrounding farmland enhancing phytoplankton growth.

B43B-02 1345h

Diagenesis of Organic Matter in a Virginia Salt Marsh: Evaluation Through Compound Specific Isotope Analysis

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Resolving the early diagenetic pathways to preservation of organic matter in a sedimentary sequence is one of the most intriguing challenges in organic geochemistry. What is preserved is usually ascribed to be either the product of retention of refractory materials or "protected" remnants of the destruction of the more labile matter, or more likely, a combination of both processes. A third mechanism, acquisition of newly synthesized material resulting from microbially mediated reactions, is less frequently invoked. In this study, the sources for the preserved organic matter and the sedimentary history of a Spartina marsh sequence on North Hog Island at the Virginia Coast Reserve Long Term Ecological Research (VCR-LTER) site are reported. Through the utilization of both carbon and nitrogen bulk isotopic compositions and compound specific isotopic analyses (CSIA) as well as the distributions of individual fatty acids, the depositional sequences are assessed. The variations in the cores for bulk organic carbon and nitrogen delta 13C and delta 15N typically ranged from -17 to -15 permil and +4 to +10 permil, respectively. The isotopic compositions generally show a trend of increasing in the heavy isotope downcore. These variations can be attributed to microbial utilization of amino acids resulting in bulk isotopic enrichments in deeper layers. Extensive microbial activity was evidenced at depth with increased amounts of odd-chain and branched-chain fatty acids. Overall, there is a decline with increasing depth in the amount of quantifiable fatty acids. Through the CSIA measurements, the original source of the preserved molecular components was observed to be essentially that of the Spartina, with loss of unsaturation deeper in the sequence. At greater depths, newly synthesized, longer-chain, unsaturated fatty acids were observed, possibly resulting from anaerobic pathways. Through mass balance using isotopic compositions of proposed bacterial endmember fatty acids, a significant portion of the preserved material can be shown to be the result of newly synthesized organic matter.

B43B-03 1400h

Formation of Carbonate Minerals in Basaltic sea Caves by Abiotic and Microbial Processes

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A detailed isotopic and geochemical study of carbonate-rich (aragonite, calcite, magnesite) basaltic