Sources of Watershed Dissolved Organic Carbon and its Potential Impacts on Wetland and Estuarine Waters of the York River Estuary, Virginia

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Introduction

Although wetlands account for only ~8-10% of the world's land surface[1], their soils contain ~20-30% of global terrestrial carbon[2]. Despite this clear relevance of wetlands to global carbon reservoirs and cycling, an important component of wetland carbon pools, dissolved organic matter (DOM), is poorly understood. Determining the sources and sinks of DOM within wetlands is therefore critical to understanding the biogeochemical changes wetlands are undergoing as a result of human impact and even climate change. Changes in wetland DOM as a result of inputs from land and/or losses to estuaries may further alter carbon dioxide balances with the atmosphere by wetland photosynthesis and respiration, as well as estuarine food webs through altered C, N, and P stoichiometries[3-6].

At present, the key factors controlling the fluxes, compositional characteristics, and reactivity of terrigenous inputs of DOM to wetlands, and their scales of variability are poorly understood [7-9]. Long-term variability in DOM inputs and losses from wetlands is complicated by changes in physical factors such temperature and local hydrology on both upland and wetland soil organic matter (OM). For example, northern hemisphere rivers have been undergoing a dramatic rise in the amount of DOM they export over the past 1-2 decades [10-12], along with increases in river water color[13] and decreases in soil OM content[14]. Long-term factors such as the equilibrium exchange of OM between mineral soils and groundwaters, observed decreases in soil acidity, and increases in soil enzyme activity, have been offered as partial explanations for the observed DOM increases[7-19]. In coastal settings, these organic materials directly impinge downstream aquatic and sedimentary environments in wetlands and estuaries. Short-and long-term variability in DOM export from watersheds to wetlands and estuaries may alter the sources, ages, chemical composition, and reactivity of this DOM in systems such as the York River Estuary[20-22]. Therefore, temporal variability in watershed-derived DOM quantities, character, reactivity and export may directly and indirectly impact the ecological functioning of wetland and other coastal ecosystems. The overarching goal of this project is to assess the factors contributing to variability in the amounts and character of DOM transported from soils, and to examine the reactivity and fate of this DOM in stream, wetland and estuarine waters.

Study Methodology and Goals

In order to evaluate the factors contributing to the scales of variability in the quantities, composition, and reactivity of DOM exported from watersheds to downstream wetland and estuarine systems, soils and waters of a first-order stream in Taskinas Creek, a tributary of the York River Estuary, Virginia, will be examined. Taskinas Creek (Figure 1) is a forested watershed with mixed wetlands that include maple-gum-ash swamps and freshwater marshes. The study will monitor system hydrology within the first-order stream (Figure 2) and will sample stream and wetland waters, catchment vegetation, and soils for a hydrologic year, including disproportionately impactful storm events (Goal 1). These efforts will be complemented by experiments that evaluate

Figure 1: The photo above, taken by April Bahen, CBNER-RVA, shows Taskinas Creek. Taskinas Creek is a mixed wetland with several first- order feeder streams .

Figure 2: The first-order stream study area where hydrologic monitoring will occur.

mineral-DOM associations and microbial and photochemical factors controlling the reactivity and fate of DOM (Goals 2 and 3). Together, the results of achieving Goals 1-3 will allow the assessment of the factors contributing to variability in the amounts and character of DOM transported from soils, and an understanding of the reactivity and fate of this DOM in stream, wetland, and estuarine waters.

Goal 1: Determine the amount, sources and reactivity of terrigenous DOM in Taskinas Creek, and how these vary with changes in hydrologic conditions.

At the study site, ground and surface waters are expected to flow from the topographical ridges of the Taskinas watershed into the valley, through associated wetlands, and then to Taskinas Creek and the estuary. Ten wells will be constructed and installed within the study region. Sampling sites will be prepared by augering, during which time soil samples will be collected at each soil horizon and preserved for future analysis. The water levels in the wells will be measured twice per month. Contours of hydrologic head will be used to determine groundwater flow. Total rainfall and discharge will also be measured for the Taskinas watershed. Peeper lysimeters will be placed adjacent to each well in each soil horizon for monthly sampling of surface and soil pore waters.

The sources of DOM to wetland and estuarine waters downstream will be determined by a combination of $\delta^{13}C$, $\Delta^{14}C$, and $\delta^{15}N$ isotopes. Vegetation, soils, leaf litter, and DOM isolated from surface and soil pore waters will be examined. Terrestrial plants have a range of $\delta^{13}C$ values (-20 to -35‰) and freshwater values range from (-18 to 46‰), making it possible to discern the sources and processes impacting stream water DOC, as long as the sources and sinks are well constrained. $\delta^{15}N$ used in conjunction with $\delta^{13}C$ better constrains the precursor materials[23] when there is overlap in the $\delta^{13}C$ data. Finally, $\Delta^{14}C$ will be used as it has a broader natural range in vegetation and soils [24] than $\delta^{13}C$ and $\delta^{15}N$, although it is a more analytically challenging and expensive analysis. $\Delta^{14}C$ will also be used to trace the relative contributions of surface and groundwaters. This region's surface waters are actually artificially elevated in ^{14}C that is deposited atmospherically from the North Anna nuclear facility in Louisa county, Virginia (J. Bauer, unpublished data). By determining the $\Delta^{14}C$ of DOM end-members (surface and deep groundwaters, soils and vegetation), determining approximately how much stream DOM discharge is derived from these sources is possible. Through this combined isotope approach, we will determine whether significant quantities of DOM are mobilized during storm events compared to low stream flow periods, and the sources of fluxes observed. Laboratory experiments, described later, will be used to determine the reactivity of the DOM released.

Goal 2. Determine the relationship between upland soil composition and grain size and the amount, character and reactivity of soil-derived DOM desorbed and mobilized downstream.

Soil samples taken during well installation will be analyzed for grain size, clay and oxide mineralogy, isotopic and C and N composition. Water-soluble DOM will be extracted from the soils with Milli-Q de-ionized water. A portion will be analyzed for the C, N and P content of DOM, and its isotopic and molecular composition. The remaining water-soluble DOM will be used for microbial and photochemical degradation experiments described in Goal 3. Statistics will be used to examine the relationship between degradation of DOM and mineralogy.

Goal 3. Determine the impact microbial and photochemical degradation has on the reactivity and availability of DOM to wetland and estuarine food webs.

Microbial degradation experiments. Bacterial concentrates isolated from soil porewaters and stream waters (0.1 µm membrane filtration or hollow fiber ultra-filtration) will be re-suspended in UV-oxidized creek water (to remove background DOC) supplemented with DOM extracted from soils (Goal 2) and DOM isolated from surface and pore waters (Goal 1). All incubations will be conducted in clean polycarbonate bottles in the dark at controlled ambient temperatures. DOM concentrations will be monitored over time, and when significant degradation has occurred (minimum of 20% of starting DOM concentrations) the incubations will be terminated, and the isotopic composition of the starting vs. degraded material will be determined.

Photochemical degradation experiments. Parallel experiments to the microbial experiments will be conducted in optically clear quartz flasks exposed to ambient levels of sunlight, with and without bacteria, to evaluate the potential photochemical reactivity of DOM extracted from soils and isolated from pore waters.

Significance to Wetlands Conservation

The results of the proposed research will provide key baseline information about how upland feeder streams within coastal watersheds impact the amounts, reactivity and composition of terrestrial DOM delivered to wetlands and estuaries. In addition, these studies will provide information about the importance of DOM within wetland and estuarine food webs via microbial and photochemical degradation. This research will also provide the Chesapeake National Estuarine Research Reserve (CBNERRS) and the Garden Club of America (GCA) with the field infrastructure required for long-term hydrologic monitoring of this coastal wetland, well after my dissertation is completed. This baseline information for understanding the present biogeochemical functioning of wetland waters, together with the infrastructure required for future, continuous monitoring, will be invaluable for assessing changes in hydrological and biogeochemical conditions as they occur within this wetland. These contributions will allow environmental resource managers such as CBNERRS and the Department of Conservation and Recreation (DCR) of Virginia, and interested organizations such as GCA, to identify potential future changes in watershed-wetland-estuarine linkages and to make decisions that promote the conservation of these systems. Additionally, and more immediately, an understanding of the sources and fates of DOM in wetland and estuarine waters, which is an important component of the global carbon cycle, will improve our ability to make management decisions about managing wetlands and wetland resources. In addition, assessing impacts of long-term change, including climate change, in wetland and estuarine systems, is critical for their future conservation.

Portion of Research to be Funded

As my dissertation field work is just commencing, a scholarship from GCA will be most helpful. This work will fund additional field equipment needed as well as isotope analysis of water samples. These analyses require specialized equipment present only at a few laboratories in the United States. The GCA scholarship therefore will support all three goals presented in this proposal.

Literature Cited

1. Sahagian, D., and J. Melack (eds.) 1998. Global wetland distribution and functional characterization: Trace gases and the hydrologic cycle. IGBP report 46, 92pp.
2. Mitsch, W.J. and J.G. Gosselink (eds).2007. Wetlands. 582 pp.
3. Azam,F, Fenchel, T., Field, J.G., Gray, J.S., Meyer-Reil, L.A., and F. Thingstad. 1983. The Ecological Role of Water-Column Microbes in the Sea. Marine Ecology Progress Series 10:257-263.
4. Pomeroy, L.R. 1974. The ocean's food web, a changing paradigm. Bioscience 24:499-504.
5. Nakagawa, Y., Eguchi, M., and Miyashita, S. 2007. Pacific bluefin tuna, *Thunnus orientalis*, larvae utilize energy nutrients of the microbial loop. Aquaculture 267:83-93.
6. Henchel,T. 2008 (in press). The microbial loop-25 years later. Experimental Marine Biology and Ecology.
7. Eimers, M.C., Buttle, J., Watmaugh, S.A. 2008. Influence of Seasonal Changes in Runoff and Extreme events on dissolved organic carbon trends in wetland and upland draining streams. Canadian Journal of Fisheries and Aquatic Sciences 65:796-808.
8. Bellamy., P.H; Loveland, P.J.; Bradley, R.I.; Lark, R.M., Kirk, G.J.D. 2005. Carbon losses from all soils across England and Wales 1978-2003. Nature, 437 (7956):245-248.
9. Skjelvalke, B.L., Stoddard, J.L., Jeffries, D.S., Torseth, K., Hogasen, T., Bowman, J., Mannio, J., Monteith, D.T., Mosello, R., Rogora, M., Rzychon, D., Vesely, J., Wieting, J., Wilander, A., Worsztynowicz, A. 2005. Regional scale evidence for improvements in surface water chemistry 1990-2001. Environmental Pollution, 137 (1):165-176.
10. Worrall, F., Burt, T., Shedden, R. 2003. Long term records of riverine dissolved organic matter. Biogeochemistry, 64 (2):165-178.
11. Worrall, F., Harriman, R., Evans, C.D., Watts, C.D., Adamanson, J., Neal, C., Tipping, E., Burt, T., Gieve, I., Montheith, D., Naden, P.S., Nisbet, T., Reynolds, B., Stevens, P. 2005. Trends in dissolved organic carbon in rivers and lakes. Biogeochemistry, 70 (3):369-402.
12. Evans, C.D., Montehith, D.T. and Cooper, D.M. 2005. Long-term increases in surface water dissolved organic carbon: observations, possible causes, and environmental impacts. Environmental Pollution 137:55-71.
13. Hongve, D., Rijse, G. and Kristiansen, J.F. 2004. Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water- a result of increased precipitation? Aquatic Sciences 66:231-238.
14. Knorr, W; Prentice, I.C.; House, J.I.; Holland, E.A. 2005. Long term sensitivity of soil carbon turnover to warming. Nature 433:298-300
15. Hejzlar, J., Dubrovsky, M., Buchtele, J., Ruzicka, M. 2003. The apparent and potential effects of climate change on the inferred concentration of dissolved organic matter in a temperate stream (the Malse River, South Bohemia). Science of the Total Environment, 310 (1-3):143-152.
16. Findlay, S.E.G. 2005. Increased carbon transport in the Hudson River: unexpected consequence of nitrogen deposition? Frontiers in Ecology and the Environment, 3(3):133-137.
17. Freeman, C.; Fenner, N; Ostle, N.J.; Kang, H.; Dowrick, D.J.; Reynolds, B; Lock, M.A.; Sleep, D.; Hughes, S.; Hudson, J. 2004. Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels. Nature 430:195-198.
18. Burns,D.A., McHale, M.R., Driscoll, C.T., Roy, K.M. 2006. Response of surface water chemistry to reduced levels of acid precipitation: comparison of trends in two regions of New York, USA. Hydrological Processes, 20(7):1611-1627.
19. Freeman,C., Evans. C.D., Monteith,D.T., Reynolds, B.R., and Fenner, N. 2001. Export of organic carbon from peat soils. Nature 412:785.
20. McCallister ,L. S., J.E. Bauer, and E.A. Canuel. 2006. Bioreactivity of estuarine dissolved organic matter: A combined geochemical and microbiologicalapproach. Limnology and Oceanography 51:94-100.
21. McCallister, L.,S., J.E. Bauer, and E.A. Canuel. 2004. Assessing sources and ages of organic matter supporting river and estuarine bacterial production: A multiple isotope (^{14}C, ^{13}C and ^{15}N) approach. Limnology and Oceanography 49:1687-1702.
22. Raymond, P. A. and J. E. Bauer. 2000. Bacterial consumption of DOC during transport through a temperate estuary. Aquatic Microbial Ecology 22: 1-12.
23. Raymond, P.A, and Bauer, J.E. 2001. Use of 14C and 13C natural abundances for evaluating riverine, estuarine, and coastal DOC and POC sources and cycling: A review and synthesis. Organic Geochemistry, 32:469-485.
24. Raymond, P. A., J. E. Bauer, N. F. Caraco, J. J. Cole, B. Longworth, and S. T. Petsch. 2004. Controls on the variability of organic matter and dissolved inorganic carbon ages in northeast US rivers. Marine Chemistry 92: 353-366.