Biogeochemical Tracers in Arctic Rivers: Linking the Pan-Arctic Watershed to the Arctic Ocean

Project Summary

The Arctic is undergoing unusual and apparently progressive changes in the land, ocean, and atmospheric components of the hydrologic cycle that could have long-term consequences for both local and global climate. The prime motivation of the SEARCH/CHAMP/ASOF initiative (Solicitation NSF-02-071) is to better understand these changes and their consequences, including identification of natural modes of variability and responses to anthropogenic forcing. To achieve this goal, the combined efforts of empiricists and modelers of the linked atmosphere-land-ocean system are needed.

This proposal is submitted as part of a number of independent but highly complementary research efforts and is focused on measuring the biogeochemical characteristics of river waters as they flow from land into the Arctic Ocean. **The overall objective is to use river water chemistry as a means to study the origins and fates of continental runoff**. Tracers in addition to temperature and salinity are needed to identify river contributions to surface waters of the Arctic Ocean because melting of sea ice confounds interpretation of temperature-salinity mixing models. Furthermore, tracers provide a means to distinguish contributions from different rivers regionally. A 5-year project is proposed in which selected parameters focusing on tracers of river water will be measured in the largest 6 rivers that drain the watershed of the Arctic Ocean: the Yenisey, Lena, Ob', Mackenzie, Yukon, and Kolyma. Tracers to be measured include $H_2{}^{18}O$, barium, organic matter, alkalinity, and nutrients. Sampling will be conducted during the high flow season in Years 1 and 4 and during all seasons in Years 2 and 3. Synthesis and modeling will occur throughout the 5-year project. Samples will be collected near the mouths of the rivers (but above tidal influence) in order to get fully integrated watershed signals and the most relevant freshwater endmember values for oceanographic tracking. **To investigate transport pathways of river waters through the Arctic Ocean, newly defined endmember values will be examined in the context of existing and growing oceanographic tracer databases. To study watershed sources, tracers will examined in the context of geomorphology, land cover, and hydrology models. The proposed work will also generate a synoptic pan-arctic database on river biogeochemistry for comparison with past and future data in trend analyses.**

Understanding sources and fates of river discharge is important because rivers make an enormous contribution to the freshwater budget of the Arctic Ocean, presently accounting for 50 to 60 percent of all freshwater inputs. General Circulation Models (GCMs) predict increased moisture transport to high latitudes and melting of ice stores with continued global warming. Should this occur, the resulting freshening of waters exported from the Arctic Ocean may significantly impact North Atlantic Deep Water (NADW) formation. This in turn has consequences for global ocean circulation and climate. Already large-scale changes in the arctic hydrologic cycle are evident, including indications of increasing discharge in major Eurasian arctic rivers. Our proposed work will provide insight into circulation of freshwater through the Arctic Ocean and help elucidate mechanisms responsible for arctic-wide changes in the hydrologic cycle.

PROLOGUE

The proposal described here responds to calls made by NSF for synthesis studies of the Arctic water cycle, as articulated through CHAMP, ASOF and SEARCH steering documents. The complexities of the Arctic water system, however, mean that no proposal will be able to rise to this challenge alone. Linked process studies, observational data development efforts, and modeling studies will be required. This proposal contributes to a broader set of projects discussed during a series of conference calls during Spring 2002. These projects cluster into 3 thematic groups. Each submission stands on its own, though its place in this larger research setting should also be recognized. The accompanying table helps to define the role of the individual contributions. Details of specific linkages across projects will be offered in the body of the text. Many of the individual proposals are collaborative efforts between multiple institutions. The lead institution for each proposal is listed first, followed by the collaborators.

In addition to the linkages shown in the diagram, this proposed study of biogeochemical tracers in river water will be coupled to other ongoing and proposed research including the ship-based efforts of SBI (Western Arctic Shelf-Basin Interactions), SIRRO (German/Russian, Siberian River Runoff) and ASOF. Coordination between our project and these efforts will be facilitated by joint participation of senior personnel. Lee Cooper, who leads the effort on $H_2{}^{18}O$ on the newly funded SBI Phase II project, will participate in the work proposed here to link river tracer fluxes to oceanographic measurements. Similarly, Rainer Amon at the Alfred Wegener Institute (AWI) is involved in both the SIRRO project and the research proposed here. Amon's contribution to the SIRRO project has focused on the transport and processing of riverine organic matter through the Yenisey and Ob' estuaries. Finally, our work will help to refine the basin-scale budget of freshwater and oceanographic tracers in the Arctic Ocean including riverine contributions to exports of freshwater through the Canadian Arctic Archipelago and Fram Strait that are major foci of ASOF.

Observation-based Tracking of Freshwater	**Integrated Modeling**	**Process-based Studies**
Water in the Arctic Land-Ocean-Atmosphere System: Retrospective and Contemporary Analysis U. New Hampshire (Vörösmarty), U. Wash. (Steele), U. Colorado (Serreze)	*Regional Model Synthesis of the Pan-Arctic Land-Atmosphere Water Cycle and its Variability* Iowa State U. (Gutowski) U. Colorado (Cassano)	*Detection and Attribution of Changes in the Hydrologic Regimes of the Mackenzie, the Kuparuk and the Lena River Basins* UAF (Hinzman, Kane, Nolan, Yoshikawa) U. Colorado (Cassano, Lynch) Iowa State University (Gutowski)
Biogeochemical Tracers in Arctic Rivers: Linking the Pan-Arctic Watershed to the Arctic Ocean MBL (Peterson, Holmes), CPPI (Zhulidov), LBNL (Guay), AWI (Amon), USGS (Hooper), WHOI (Raymond), WRD (Milburn)	*Improved Land Surface Schemes* U. Colorado (Serreze) U. Wisconsin (Key) U. Washington (Lettenmaier)	*Arctic Hydrology in Time and Space: A Field and Modeling Study Coupled with Related Earth Sciences* UAF (Kane, Hinzman, McNamara, Jones, Nolan)
Error Analysis on Observational Water Cycle Data Sets U. Delaware (Nelson, Shiklomanov, Willmott, Legates)	*The Role of Land Cover Change and Permafrost Dynamics in the Delivery of Fresh Water to the Arctic Ocean* UAF (McGuire, Rupp, Hinzman, Romanovsky), Lamont Doherty (Stieglitz), UNH (Lammers), MBL (Melillo)	*Effects of Climate Change and Permafrost Dynamics on East Siberian River Discharge: Permafrost Hydrogeology* UAF (Romanovsky and Yang)
	The Influence of the Arctic Freshwater Cycle on the Global Thermohaline Circulation in the 20th and 21st Centuries U. Colorado (Wu, Lynch, Serreze) NCAR (Holland)	*Processes of Transfer and Incorporation of Terrestrial Organic Carbon and Nutrients into Kuparuk-Simpson Lagoon Nearshore System of Arctic Alaska* U. Texas Austin (Brandes, Dunton, Pease)
		Winter Precipitation, Sublimation, and Snow-Depth in the Pan-Arctic: Critical Processes and a Half Century of Change CSU (Liston, Pielke, Mahrt) CRREL (Sturm)

RESULTS FROM PRIOR NSF RESEARCH

"Water and Constituent Fluxes Across the Eurasian Arctic: Evolving Land-Ocean Connections over the Past 20,000 Years" NSF-OPP-RAISE 9818199 (1998-2002; $978,628). Senior personnel: Peterson, Holmes, Vörösmarty, Lammers, Wilmott, Forman, Shiklomanov, Gordeev, and Meybeck.

The goal of this synthesis project ("Pan-Arctic Project") has been to compile databases and develop tools to support the analysis of freshwater and constituent fluxes to the Arctic Ocean from the pan-Arctic watershed. In contrast to the present proposal, this project relied largely on existing data and did not have a major field component. The project has supported more than 40 publications thus far (denoted by an "*" in the References section) and more than 50 conference presentations. These products describe our progress on discharge database development, hydrologic modeling, evaluation of existing constituent flux data sets, biogeochemical sampling on the Ob' and Yenisey rivers, and synthesis of pan-arctic climatologic data. In addition to published papers, we have two manuscripts presently in review that are relevant to the SEARCH/CHAMP/ASOF initiative. "Increasing Arctic River Discharge: Responses and Feedbacks to Global Climate Change" (Peterson et al. 2002) evaluates the robustness of trends in Eurasian river discharge within the past century, their possible links to major climatic variations, and the potential importance of increasing river discharge to NADW formation and Atlantic thermohaline circulation (see Fig. 1). The second manuscript "A Circumpolar Perspective on Fluvial Sediment Flux to the Arctic Ocean" (Holmes et al. 2002) explores reasons for variations in past sediment flux estimates for major arctic rivers, presents previously unpublished long-term data, and provides best estimates of contemporary fluxes.

We have assembled coherent hydrologic and climatologic data sets for calibration and validation of our hydrological models and those of the broader arctic research community. The data have been geographically co-registered to our simulated river network, which allows testing of macroscale hydrology models that simulate runoff formation, river routing, and discharge to the Arctic Ocean. We are providing unrestricted access by the scientific community to the data sets we have assembled. The river discharge database (R-ArcticNET v.2.) contains more than 3700 stations over the pan-arctic region (Lammers et al. 2001). It is available on our project website (www.R-arcticnet.sr.unh.edu) and on CD from the National Snow and Ice Data Center.

We now have the hydrological data sets and models required to perform land-to-ocean constituent flux estimates but our synthesis and critical evaluation of the available constituent data for the pan-arctic watershed has shown that the biogeochemical data are either missing or inadequate to estimate many fluxes reliably (Holmes et al. 2000, Zhulidov et al. 2000, Holmes et al. 2001, Zhulidov et al. 2001). One of the major conclusions from this project is that closing this gap in data, including the lack of sufficient pan-Arctic river tracer data, in the immediate future will require an international collaborative partnership among scientists from Russia, Canada, and the United States. In the longer term it is important that governments realize the need for support of continued monitoring of these key land to ocean fluxes.

Our project has benefited greatly from close cooperation with Russian scientists including Igor Shiklomanov, Viacheslav Gordeev, Alexander Zhulidov, and Alexander Shiklomanov. The Pan-Arctic Project has guided a number of graduate students in their research. Jon Holden, M.S. in Earth Sciences at UNH under co-investigator Vörösmarty, has developed the permafrost water balance model (P/WBM). Mike Rawlins, a graduate student at Delaware under co-investigator Cort Willmott, developed improved climate fields for the pan-arctic region. Balazs Fekete, Ph.D. at UNH, has been working on improved database design to optimize the capabilities of processing and analyzing river discharge data over regional to global scales. Hayo Kohler, University of Hamburg, participated in our expedition to the Ob' and Yenisey rivers in June 2000, and characterized organic matter composition and quality as part of his dissertation research (Kohler et al. 2001).

INTRODUCTION

The Arctic is both influenced by and has strong feedbacks to global climate. Three of the most important linkages between the arctic and global climate systems involve trace gas flux from carbon-rich arctic reservoirs, ice/albedo feedbacks, and freshwater forcing on North Atlantic Deepwater formation (IPCC 2001). Greenhouse warming is expected to increase the melting of arctic ice stores and to increase net atmospheric transport of moisture from lower to higher latitudes (Manabe and Stouffer 1994). At the same time, increased export of freshwater from the Arctic Ocean may inhibit North Atlantic Deep Water (NADW) formation and thus reduce meridional overturning circulation (MOC) (Aagaard and Carmack 1989, Rahmstorf 1995, Clark et al. 2002). Should they occur, these changes in circulation would likely be accompanied by a substantial reorganization of climate patterns in the North Atlantic region, and perhaps globally (Broecker 1997).

While modeling efforts have been grappling with this problem for some time now, observational evidence of progressive changes in arctic hydrology has begun to emerge only more recently. Serreze et al. (2000) describe increases in precipitation, declines in snow cover, loss of glacial volume, warming of permafrost, and declines in sea ice in the Arctic Ocean. Now added to this list are apparent increases in freshwater discharge from major arctic rivers (Fig. 1) (Semiletov et al. 2000, Peterson et al. 2002). This is particularly significant because arctic river discharge provides an integrative measure of the continental water balance and because runoff makes an enormous contribution to the Arctic Ocean freshwater budget. River runoff presently accounts for 50 to 60 percent of all freshwater inputs to the Arctic Ocean, with water import through the Bering Strait and precipitation less evaporation directly onto the Arctic Ocean accounting for most of the remainder (Aagaard and Carmack 1989, Carmack 2000). If arctic river discharge and other freshwater sources continue to increase in response to global warming, the quantity of extra fresh water delivered to the Arctic Ocean within the next 100 years could approach that predicted by climate models to significantly impact NADW formation (Rahmstorf et al. 1995, IPCC 2001, Peterson et al. 2002).

Such projections into the future are accompanied by considerable uncertainty. Interactions between atmospheric circulation, precipitation, vegetation, and permafrost in a warming climate will influence trajectories of river discharge in the future (Serreze et al. 2000). Furthermore, the locations of discharge around the arctic basin, circulation patterns within the Arctic Ocean, effect of river discharge on sea-ice formation, and the state (ice or water) in which freshwater is exported from the arctic basin may all influence the timing and magnitude of impact on

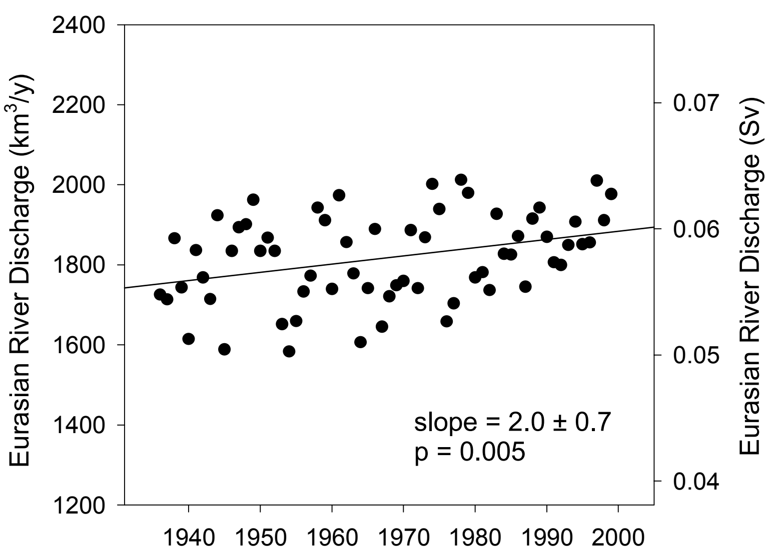

Fig. 1. Combined discharge of the 6 largest Eurasian rivers (Yenisey, Lena, Ob', Kolyma, Pechora, S. Dvina) over the 65 year period of record (from Peterson et al. 2002).

NADW formation (Aagaard and Carmack 1989, Guay et al. 2001, Steele et al. 2001). To predict future impacts of freshwater fluxes on NADW formation with more confidence, an improved understanding of watershed sources and fates of river waters in the Arctic Ocean is needed. The ASOF planning document (http://asof.npolar.no) emphasizes the need to better quantify fresh water exports through Fram Strait and the Canadian Arctic Archipelago. Achievement of this goal would be greatly facilitated by the ability to track river water contributions from different regions. Mixing of freshwater contributions from North American and Eurasian rivers in the Beaufort Gyre and subsequent export pathways from the Arctic Ocean under cyclonic versus anticyclonic circulation regimes are key uncertainties (Guay et al. 1999, Proshutinsky and Bourke 2002).

Fig. 2. Map showing watersheds of rivers included in proposed research, which combined contribute ~50% of total riverine freshwater inputs to the Arctic Ocean. The red dots show our general sampling locations, and the black triangles show proposed ASOF arrays as identified in their Science Plan.

We propose to obtain detailed biogeochemical tracer data for the 6 largest Arctic rivers; the Yenisey, Lena, Ob', Mackenzie, Yukon, and Kolyma (Fig. 2, Table 1). Tracer data are needed in addition to temperature and salinity to identify sources of freshwater once they are in the Arctic Ocean because melting of sea ice provides an alternative source of fresh water (and formation of sea ice generates saltier water) that confounds interpretation of Temperature-Salinity mixing models. $H_2{}^{18}O$ has been used as the primary tracer to separate riverine from sea-ice sources of freshwater because ice (and the meltwater from it) looks isotopically similar to its source (Macdonald et al. 1995, Cooper et al. 1997, Schlosser et al. 2000, Ekwurzel et al. 2001). However, consideration of this tracer alone is insufficient to resolve contributions from different rivers. In general it is possible through use of several mass balance equations to resolve one more water mass component than the number of tracers being used. Barium provides an additional tracer to separate Mackenzie water from Eurasian river contributions (Guay and Falkner 1997, 1998) (Fig. 3). Examination of parameters such as terrestrial biomarkers, organic matter fluorescence, and alkalinity further distinguish different endmembers (Yunker et al. 1995, Guay et al. 1999, Kattner et al. 1999, Opsahl et al. 1999,

Table 1. Discharge and basin areas for the rivers that we propose to sample.

River	Country	Drainage	Discharge (km^3/y)	Basin Area ($10^6 km^2$)
Yenisey	Russia	Kara Sea	620	2.59
Lena	Russia	Laptev Sea	525	2.49
Ob’	Russia	Kara Sea	404	2.99
Mackenzie	Canada	Beaufort Sea	308	1.79
Yukon	USA	Bering Sea	200	0.85
Kolyma	Russia	East Siberian	132	0.66
Sum of above			2189	11.4
Entire pan-Arctic watershed			4115	19.1

Schlosser et al. 2000, Dittmar et al. 2001). These and other potential tracers, however, can behave non-conservatively in different situations/ environments. It is therefore desirable and in many cases feasible to have an over-determined system in which conclusions can be based on a consensus obtained from multiple tracers.

Our overall objective is to use river water chemistry to study the origins and fates of continental runoff in the Arctic Ocean. While riverine endmember values for some tracers in some rivers are fairly well constrained, in no cases are complete sets of tracer data available for any of the 6 largest arctic rivers. In some cases, endmember values have been calculated from estuarine gradients. Furthermore, both calculated values and those measured directly are generally based on relatively few measurements made during spring or summer. It has thus been difficult to examine extended circulation patterns of water from individual rivers using existing tracer data. Instead, it has been necessary to largely treat freshwater contributions from arctic rivers as a single source. Our proposed measurements will constrain the biogeochemical tracer signals of the 6 largest arctic rivers so that further resolution is possible.

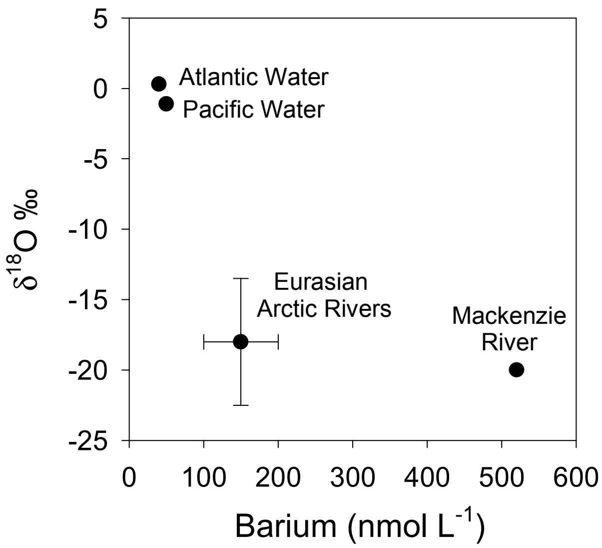

Fig. 3. Plot of barium versus ^{18}O, showing separation of different endmembers that contribute to surface waters in the Arctic Ocean. Bars for Eurasia express the range of Eurasian river endmember values.

We will sample near the mouths of the rivers (but above tidal influence) in order to obtain fully integrated watershed signals and the most relevant freshwater endmember values for oceanographic tracking. Our suite of tracer measurements will include $H_2^{18}O$, barium, various organic matter analyses, alkalinity, as well as other promising constituents. **With these proposed measurements, we will determine 1) the seasonal variations and average values of tracers in each river, and 2) the overall biogeochemical signature of each river.** Data will be examined in the context of hydrology models, geomorphology, and land cover to extract information about watershed sources of freshwater (for example permafrost melt versus precipitation), and in the context of existing and growing oceanographic tracer databases to investigate circulation patterns of river waters in the Arctic Ocean. Together with salinity and temperature, the tracer data are expected to allow resolution of at least 5 endmembers in the ocean. In the central Arctic Ocean this translates into separation of contributions from North American runoff, Eurasian runoff, Pacific water, Atlantic water, and sea ice. In nearshore and shelf regions where either Pacific water or Atlantic water could be eliminated as potential sources, riverine contributions would be further resolved.

While our efforts alone are expected to yield valuable insights about the origins and fates of continental runoff, we recognize that links with other work in the Arctic and North Atlantic will have a strong synergistic effect that will greatly expand our understanding of arctic hydrology and global climate. Several relevant new proposals are listed in the Prologue. Among these proposals, our most direct links are to work planned by Vörösmarty et al., McGuire et al., Hinzman et al., and Romanovsky and Yang. Our proposed work also forms a natural link with oceanographic efforts of SBI, SIRRO, and ASOF.

In addition to the immediate utility of the tracer data collected during the project, the data will provide the contemporary baseline that is essential for detecting future changes. Future trends in tracer values will provide watershed-integrated information that can help identify changing source

Table 2. Institutions and key personnel involved in this proposal.

INSTITUTION	PRIMARY PERSONNEL	EXPERTISE
Marine Biological Laboratory Woods Hole	Peterson, Holmes, McClelland	Arctic river biogeochemistry
CPPI-S Rostov-on-Don, Russia	Zhulidov	Water and constituent fluxes, Russian rivers
U.S. Geological Survey	Hooper, Brabets	Water and constituent fluxes, Yukon River
Water Resources Division Yellowknife, Canada	Milburn	Water and constituent fluxes, Mackenzie River
University of Tennessee	Cooper	Oceanographic tracers
Lawrence Berkeley National Laboratory, Berkeley	Guay	Oceanographic tracers- inorganic
Alfred Wegener Institute Bremerhaven, Germany	Amon	Oceanographic tracers- organic
Woods Hole Oceanographic Inst.	Raymond	Origins and transport of carbon
Shirshov Inst. of Oceanology, Moscow, Russia	Gordeev	Arctic river/ocean biogeochemistry
State Hydrological Institute, St. Petersburg, Russia	Shiklomanov	Arctic river discharge

contributions in a warming climate. For example, melting permafrost and shifts in summer versus winter precipitation may impact river discharge and biogeochemical tracers. To be most useful for detecting long-term change, of course, the tracers would need to be measured on a continuing basis. Some constituents already are monitored by U.S., Canadian, and Russian government agencies. The list of tracers, however, is not consistent among rivers. As a critical part of our effort, we propose to work with local scientists to make at least a subset of tracer measurements standard at these major arctic rivers. In the Russian rivers in particular, this will involve capital investment in sampling devices and analytical equipment upgrades. We will also work to standardize sampling and analytical methods of the tracers as much as possible among rivers.

We have in place the collaborative network (Table 2) and expertise to successfully sample the 6 largest arctic rivers. Scientists from 4 nations are involved, including representatives of agencies responsible for water quality monitoring in the Russian, Canadian, and US Arctic. Working in the Russian Arctic is perhaps most challenging, but our previous collaborations (see Results of Prior Research section) have forged the connections necessary to conduct successful field campaigns in this region. Our research group is also in a strong position to analyze and synthesize information on river tracer fluxes into and through the Arctic Ocean at the pan-Arctic scale because of the diverse expertise brought to the project by hydrologists, biogeochemists, and oceanographers.

The critical need to refine our understanding of freshwater sources and fates in the Arctic Ocean is recognized in the “Arctic Freshwater Cycle: Land/Upper-Ocean Linkages” Announcement of Opportunity, which emphasizes interaction between ASOF, CHAMP, and SEARCH efforts. The Science Plan for ASOF focuses on the linkage between freshwater export from the Arctic Ocean and MOC, while CHAMP emphasizes freshwater cycling within the Arctic System. The overarching goal of SEARCH is to identify long-term change. The three main foci of the Solicitation are 1) Implementation of internationally coordinated observation systems that can serve as prototypes for sustained, long-term efforts, 2) Synthesis and integration of available data and modeling studies, and 3) Documentation and assessment on the decade-to-century timescale of the variability of the Arctic hydrologic freshwater cycle. Our proposed work directly addresses the first two of these foci, and contributes to the third by establishing a pan-arctic baseline of tracer data for detecting future change in the Arctic.

TRACERS TO BE MEASURED

Table 3. Core Measurements.

Fundamental Parameters	Water temperature, salinity, pH, dissolved oxygen
Key Oceanographic Tracers	$H_2{}^{18}O$, barium, organic matter (concentration, fluorescence, compound-specific analyses)
Additional Tracers	Nutrients, major ions, alkalinity, ^{14}C (POC, DOC, DIC), ^{13}C (POC, DOC, DIC)

Our focus is on key biogeochemical tracers of river water in the Arctic Ocean (Table 3). Constituents such as $H_2{}^{18}O$, barium, and specific organic compounds have been successfully used to identify riverine freshwater in the Arctic Ocean, but riverine endmember values are not well constrained at the pan-arctic scale. Thus, our proposed research will generate the data that are needed to better exploit the use of riverine biogeochemical tracers in studies of Arctic Ocean circulation. We also will analyze a number of other constituents that may be useful as oceanographic tracers or that provide insights about watershed sources and processes. Further discussion of specific tracers is found below.

***$H_2{}^{18}O$*.** Measurements of $H_2{}^{18}O$ have been widely used in the Arctic Ocean to separate freshwater contributed by sea ice melt from direct runoff (Bauch et al. 1995, Cooper et al. 1997, Cooper et al. 1999, Munchow et al. 1999). $H_2{}^{18}O$ is useful as a tracer because fractionation during ice formation is small relative to differences in endmember values: water from ice-melt looks much like its original source (a correction factor accounting for a 2.6‰ increase in $\delta^{18}O$ from source to ice is applied in mixing models). Large data sets documenting $\delta^{18}O$ values in Arctic Ocean waters are becoming available as a result of collections in the 1990's (Biggs and Rohling 2000), but the current estimates of river endmembers are dependent on only a small number of ^{18}O measurements from most Arctic rivers. Within this limited data set on riverine endmembers, there is a general west-to-east pattern of decreasing river $\delta^{18}O$ values observed in the Eurasian Arctic (Ekwurzel 1998). However, the $\delta^{18}O$ values in individual Arctic rivers can vary significantly over seasonal and annual scales (Cooper et al. 1993). Lacking better constraints on values from individual rivers, use of the west-to-east gradient for better resolution of rivers has been impossible. Instead, an average pan-arctic value has been used to separate runoff from other sources (Schlosser et al. 2000, Ekwurzel et al. 2001). Collection of higher resolution data for stable oxygen isotopes in river water, including analyses of seasonal, geographical, and interannual variability, will help us to better constrain the average pan-arctic value, and explore the utility of the geographic gradient in $\delta^{18}O$ of runoff when tracking the fate of fluvial water.

Barium. Dissolved Ba has been used successfully as a tracer of river discharge in the upper waters of the Arctic Ocean. Despite temporal variability and complex modification in the mixing zones between fluvial and marine waters, dissolved Ba signals of Arctic rivers clearly persist beyond their estuaries, extending over the shelves and into the interior basins of the Arctic Ocean (Guay and Falkner 1997, Guay et al. 1999, Guay et al. 2001). Of particular interest is the ability of Ba to distinguish between contributions from different arctic rivers. Dissolved Ba is highly elevated in the Mackenzie and Yukon rivers relative to the major Eurasian arctic rivers (Guay and Falkner 1998). This difference, which largely results from the different chemical compositions and weathering characteristics of rocks in their drainage basins, provides a basis for differentiating North American and Eurasian components of fluvial discharge to the Arctic Ocean (Fig. 3). The proposed multi-year measurements of Ba over widely varying seasonal conditions will better define the individual riverine endmembers, which are currently based on a limited amount of data and are therefore associated with a considerable degree of uncertainty. Combining Ba with additional physical and chemical tracers will provide new information concerning the fluvial component of circulation in the Arctic Ocean.

Organic Matter. Plant organic biomarkers (Meyers-Schulte and Hedges 1986, Opsahl and Benner 1997), including the radioactive and stable isotopes of carbon (^{14}C and ^{13}C, respectively), serve as powerful tools for identifying sources of organic matter in aquatic systems. A dual isotopic approach using both ^{13}C and ^{14}C of particulate and dissolved organic matter has been used successfully in carbon studies of rivers, estuaries, continental margins, and the open oceans (Williams and Druffel 1987, Bauer et al. 1992, Druffel et al. 1992, Bauer and Druffel 1998, Raymond and Bauer 2001a, Raymond and Bauer 2001b). Combined with molecular level characterization of DOM, these data identify unique terrestrial organic matter signatures and thus will be useful as tracers of riverine freshwater in the Arctic Ocean (Dittmar et al. 2001).

Dissolved organic matter (DOM) dominates organic matter inputs to the Arctic Ocean (Lobbes et al. 2000). Within the DOM, hydrolysable amino acids (TDAA) and lignin have been identified as recalcitrant pools that behave essentially conservatively when mixing with seawater (Opsahl et al. 1999, Dittmar et al. 2001). At face value, conservative behavior of amino acids seems counterintuitive. As it turns out, however, the labile fraction of TDAAs cycles rapidly and is maintained at a very low concentration leaving the recalcitrant fraction to dominate the standing stock of TDAAs in arctic waters (Dittmar et al. 2001). This is the case for both the river and ocean endmembers, though the concentration of TDAAs is much lower in the ocean. In addition, the composition of amino acids differs between the river and ocean endmembers. As a structural component of vascular plants, lignin also provides a terrestrial-specific marker. Much higher lignin content in Arctic Ocean water as compared to Pacific and Atlantic Ocean waters highlights the extraordinarily strong influence of riverine inputs on the Arctic Ocean (Opsahl et al. 1999).

DOM fluorescence also shows promise as a tracer of terrigenous carbon and river water through the Arctic Ocean (Guay et al. 1999, Kohler et al. 2001), maintaining an identifiable signal as far as the Denmark Strait (Amon and Budeus 2002). With seasonal samples from the 6 largest arctic rivers, we will be able to determine the most characteristic fluorescence signals for arctic river DOM. This information will be used to optimize the settings of optical instruments for the detection of land-derived DOM. These specially adjusted fluorescence probes can be mounted onto CTD units during oceanographic cruises enabling oceanographers to track riverine DOM on a real time basis in the Arctic Ocean.

Alkalinity/DI^{14}C. Alkalinity and DI^{14}C have also been identified as useful oceanographic tracers. DI^{14}C has been used to distinguish coastal/continental sources from ocean endmembers that have been isolated from the atmosphere for different lengths of time (Kashgarian and Tanaka 1991, Schlosser et al. 1995), while alkalinity has been used particularly to identify contributions from river water (Anderson and Dyrssen 1981, Anderson et al. 1994, Anderson 1995, Schlosser et al. 2000). Specific alkalinity (total alkalinity normalized by chloride concentration) is higher in arctic rivers than ocean waters, and elevated values in surface waters of the Arctic Ocean have been linked to the influence of riverine inputs. The net effect of biogenic production and dissolution of calcium carbonate on specific alkalinity appears to be negligible in the Arctic Ocean (Anderson and Dyrssen 1981). Calcium carbonate that precipitates on the walls of brine channels during sea ice formation may contribute to high specific alkalinity in surface waters during ice melting (Jones et al. 1983). However, use of alkalinity in combination with $H_2{}^{18}O$ measurements eliminates this problem. Measurements of alkalinity and DI^{14}C in the 6 largest arctic rivers over the seasonal cycle will help define a pan-arctic value for river inputs. Furthermore, variations in these parameters among drainage basins may help separate individual river endmembers. Variations among river endmembers are expected because of differences in watershed characteristics that influence alkalinity and DI^{14}C such as mineral composition and weathering, permafrost melt, net ecosystem production, and gas exchange.

Nutrients and Major Ions. The non-conservative behavior of many nutrients as they pass through estuaries makes them difficult to use as tracers of freshwater from rivers. As tracers of oceanic water masses, on the other hand, they have been widely applied. In particular, the combined use of silicate, nitrate, and phosphate as tracers has been used to separate Pacific and Atlantic water masses (Bauch et al. 1995, Jones et al. 1998, Cooper et al. 1999). Overall influence of riverine inputs on mixing calculations using nutrients is considered small. However, injection of riverine nutrients into oceanic waters may in fact be significant during some times of year (e.g. before and during ice-out in the spring). Our proposed measurement of nutrients, including nitrate, phosphate, and silicate, will help to constrain the river endmember values, a necessary prerequisite for addressing this issue. Improved nutrient flux estimates will also benefit scientists interested in the productivity of the arctic nearshore zone.

Nutrient and major ion chemistry of river waters also contains information about watershed sources and processes (Gordeev et al. 1996, Holmes et al. 2000). When compared to catchment lithology, major ion chemistry provides information about supply regions and weathering patterns in the watershed (Huh et al. 1998a, Huh et al. 1998b). Nutrient chemistry provides information about biogeochemical processing and production (Peterson et al. 1992, Peterson et al. 2001). Focused sampling near each river's mouth clearly limits the amount of detailed watershed information that we can derive from nutrient and major ion data. Nonetheless, our proposed measurements over the annual cycle will help identify variations in water source regions and biogeochemistry throughout the year. Our data will also provide a contemporary baseline for detecting future changes in the watersheds that may accompany global warming or other anthropogenic forcing.

RESEARCH PLAN

We have developed the strong collaborative team (Table 2) necessary to quantify and interpret fluxes of riverine biogeochemical tracers in the 6 largest arctic rivers. We will build on existing collaborations between Russian and U.S. scientists and will initiate new collaborations with Canadian scientists experienced on the Mackenzie River, USGS scientists working on the Yukon River, and German scientists from AWI with experience on the Ob' and Yenisey estuaries as well as Arctic Ocean and coastal cruises. This interaction between scientists from 4 countries, including employees of all 3 agencies that have responsibility for water quantity and quality monitoring of arctic rivers in Russia, Canada, and the U.S., will provide opportunities for synthesis and intercalibration that have previously been unavailable.

From our prior experiences, we are well prepared to handle the logistical challenges that accompany large, multinational research projects in the Arctic. Many of the challenges are bureaucratic, particularly with respect to sampling Russian rivers. Fortunately, our expedition to the Ob' and Yenisey rivers during summer 2000 (Holmes et al. 2001) demonstrated the ability of our Russian colleagues to secure all necessary permits for sampling these rivers and for traveling with Americans to the study sites (Peterson and Holmes were the US participants, Zhulidov and Gordeev were leaders of the Russian team). Sampling the Canadian and Alaskan rivers also presents significant challenges, but our USGS and Canadian collaborators have extensive experience on these rivers. Moreover, we will work closely with VECO, the NSF-ARCSS polar logistics contractor, to support sample collection and transport at all six rivers (see letter of support in "Supplementary Documentation" section). Thus, our team is in a unique position to accomplish coordinated river sampling at the circumpolar scale.

Work Plan and Project Management

Bruce Peterson (MBL) is responsible for the overall direction of the project and will oversee coordination of the US, Russian, and Canadian collaborations. Max Holmes (MBL) will coordinate day-to-day activities of the project and will annually visit collaborators in all participating countries to assure consistency and standardization in sampling. Management responsibilities at individual field sites are described below.

All 6 rivers will be sampled for 4 years. Sampling during Year 1 and Year 4 will focus on the high flow period (2 sampling trips per river per year), whereas sampling during Year 2 and Year 3 will occur throughout the year (7 sampling trips per river per year). In all years sampling will be skewed to the high discharge period, which typically occurs in June in these rivers, but at least one sampling trip will occur in each season in Year 2 and Year 3 (including winter samples collected through the ice). Year 5 of the project will emphasize synthesis and modeling.

A minimum of 3 depth-integrated samples will be collected across the river channel during each sampling period, with more samples being collected if significant lateral heterogeneity in constituent concentrations is identified. To collect depth-integrated samples, we will use USGS sampler US-D-96 (see http://fisp.wes.army.mil for more information on these samplers). All collaborators will use standard protocols for sample collection and preservation. A workshop involving all project participants will be convened before sampling begins to, among other things, facilitate standardization in sample collection and preservation protocols.

In general, all collaborating laboratories will perform routine biogeochemical analyses such as nutrients, major ions, and alkalinity. Duplicate analyses of these routine measurements will be made at the Marine Biological Laboratory in Woods Hole. Some of the more specialized analyses will only be done at a single laboratory most-experienced and best-equipped to do the analysis (Fig. 4). For example, measurements of $\delta^{18}O$ will be undertaken at the Stable Isotope Laboratory of the Marine Biological Laboratory in Woods Hole, using a CO_2 equilibration/ headspace sampling system mated to a Finnigan MAT stable isotope mass spectrometer. $PO^{13}C$ will also be measured at the Marine Biological Laboratory. $DO^{14}C$, $DO^{13}C$, $DI^{14}C$, $DI^{13}C$, and $PO^{14}C$ will be analyzed by Pete Raymond (currently at the Woods Hole Oceanographic Institution -WHOI - but moving to Yale in autumn 2002) using methods described in Raymond and Bauer (2001b). Selected water samples will also be subjected to ultrafiltration, solid phase extraction or rotoevaporation in order to obtain enough concentrated dissolved organic matter to allow a number of additional chemical analyses to be conducted on identical sample material. These analyses will include elemental, isotopic (C, N), molecular level (amino acids, lignin phenols), and NMR analysis by Rainer Amon and colleagues at the Alfred Wegener Institute in Bremerhaven, Germany. Finally, barium will be measured by Chris Guay at the Lawrence Berkeley National Laboratory in Berkeley, California. Details of sampling at specific sites are presented below.

Yenisey, Lena, and Ob' Rivers. Sampling will be done at Dudinka (Yenisey), Kyusyur (Lena), and Salekhard (Ob'). Sample collection and analysis for these rivers will be under the direction of Zhulidov from CPPI-S,

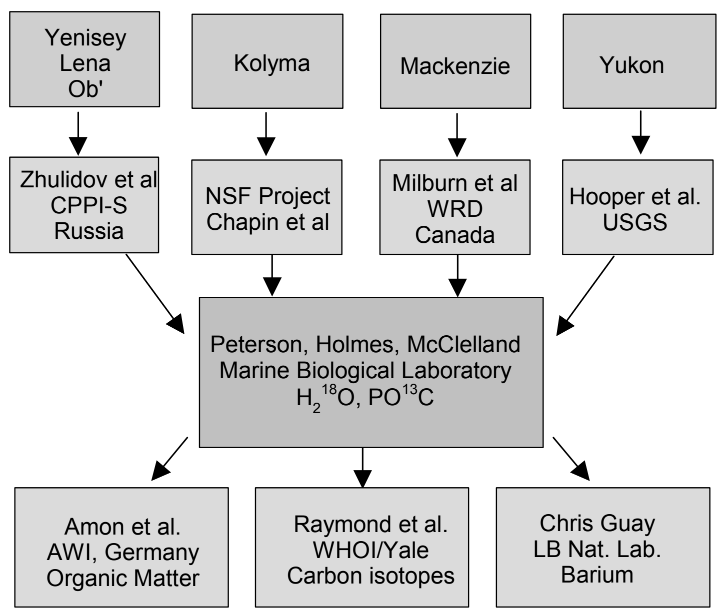

Fig. 4. Chart showing sample movement from rivers to analytical laboratories. Routine analyses (such as nutrients, major ions, and alkalinity) will be done at CPPI, WRD, and USGS laboratories, with replicate analyses done at MBL. Specialty analyses done at only a single laboratory are noted.

Rostov-on-Don, Russia. Scientists from CPPI-S and the Hydrochemical Institute (Federal Service of Russia on Hydrometeorology and Environmental Monitoring "Roshydromet") in Rostov-on-Don will travel to the rivers for sample collection, and will work closely with personnel from the local Roshydromet laboratories that are responsible for the regular water quality monitoring of the rivers. Samples will be flown back to Rostov for chemical analysis at CPPI-S/Hydrochemical Institute, and subsamples will be provided to the local Roshydromet laboratories for analysis. Replicate samples will be sent to MBL for repeat analyses, measurement of additional parameters, and archiving.

Although our primary objective is to obtain high-quality samples for analysis at established laboratories in the United States and in Rostov-on-Don, Russia, an additional goal is to assist the local Roshydromet laboratories to upgrade their analytical capabilities. Although laboratory facilities, equipment, and supplies are often substandard at local Roshydromet water quality laboratories (Zhulidov et al. 2000, Zhulidov et al. 2001), during our expedition to the Yenisey and Ob' rivers in summer 2000 we were favorably impressed by the personnel running these laboratories and performing the chemical analyses. We therefore propose to assist the local Roshydromet laboratories to upgrade their analytical facilities and training, with the longer-term goal of being able to rely on them to produce the range and quality of data needed by the global change research community. Some funding for this effort is included in this proposal, and additional funding for improvement of Roshydromet laboratories on the Yenisey, Lena, and Ob' rivers will be sought from other sources.

Kolyma River. We will obtain samples from the Kolyma River in far-eastern Siberia through collaboration with the NSF-ARCSS project of Terry Chapin et al. on carbon dynamics in the Siberian tundra. Sampling will be done near the mouth of the Kolyma River at Cherskiy, using the facilities of the Northeast Science Station where Chapin et al. work. Chapin et al. have generously agreed to collect samples using our standard protocols and provide these samples and supporting data to our project (see attached letter from Chapin). Additional support for Kolyma River sampling will be provided by VECO.

Mackenzie River. Mackenzie samples will be collected by Francis Jackson and others from the Water Resources Division (WRD) in Yellowknife, NWT. Samples from the Mackenzie River and from a major tributary (the Arctic Red River) will be collected near the village of Arctic Red. Following collection, samples will be taken to Kathleen Racher at the WRD analytical laboratory in Yellowknife, which has state-of-the-art water quality laboratories and analytical capabilities. Duplicate samples will be sent to MBL for further analysis and archiving.

The WRD, under the direction of David Milburn (Table 2), is responsible for managing water resources in the Northwest Territories, Canada, including developing and maintaining long-term networks for water quality and quantity. Due to budget constraints, however, the WRD is not currently assessing biogeochemical fluxes from the Mackenzie River to the Arctic Ocean. Several intensive studies of the Mackenzie River, Mackenzie estuary, and Beaufort shelf (Yunker et al. 1995, Macdonald et al. 1998, Macdonald et al. 1999a, Macdonald et al. 1999b, Goni et al. 2000, Naidu et al. 2000) will provide useful context for our results.

Yukon River. The USGS NASQAN program has recently initiated a five-year project on the Yukon River. As part of this effort, the USGS is collecting samples at Pilot Station, near the mouth of the Yukon River, approximately seven times per year. A wide range of constituents is being analyzed, and the USGS will provide sub-samples to our project for additional analyses.

In collaboration with the USGS, we will use funding from our project to collect high-resolution samples from the Yukon River. We will contract a local resident of Pilot Station to collect daily samples during the high-discharge spring and summer period and approximately weekly samples throughout the rest of the year. These samples will help us better interpret flux calculations made using our normal sampling protocol of approximately seven sampling periods per year. Samples will be periodically taken to Anchorage by USGS personnel working on the Yukon River, and then shipped to MBL and the USGS National Water Quality Laboratory in Denver for Analysis. USGS personnel have already identified a potential candidate (Nikki Meyers) for the position at Pilot Station.

Data Quality and Management

QA/QC. One of the greatest challenges in arctic research is the acquisition of high quality data. Field sites are often remote, sampling equipment rudimentary, sample preservation difficult, and analytical facilities primitive. Existing data sets for Russian arctic rivers typically contain no QA/QC information, and limited QA/QC information is available for many arctic rivers in North America. Our experiences with analyzing long-term nutrient and suspended sediment datasets for rivers in the Russian Arctic have clearly demonstrated the negative consequences of inadequate QA/QC (Holmes et al. 2000, Zhulidov et al. 2000, Zhulidov et al. 2001, Holmes et al. 2002), so we are keenly aware of the necessity of a rigorous quality control program.

In Year 1 of the project, we will hold a workshop in Woods Hole. Project participants from Russia, Canada, and the United States will attend the workshop, and during this time we will agree on standard protocols for sample collection and preservation. In general, we will follow protocols used by the USGS, although we will also consider alternative approaches.

Routine analyses such as nutrients, major ions, and bulk organic matter concentrations will be done in duplicate by CPPI-S (Russian rivers), WRD (Mackenzie River), and USGS (Yukon River). In addition, splits of all samples will be sent to the MBL for independent determinations. Significant discrepancies in values between laboratories will be immediately investigated and samples will be reanalyzed as necessary. Samples will then be archived (for at least 2 years after the end of the project) at MBL for further QA/QC where necessary or for later analysis of additional parameters. In addition to routine analysis of field blanks and double-blind standards, blind evaluations will be performed with ambient and spiked samples distributed to all labs.

Databases. Our data management procedures will serve the dual purpose of furthering QA/QC and of promoting exchange of data with the wider scientific community. Initially, the CPPI-S, WRD, and USGS laboratories will compile analytical results after each sampling period. The data will then be sent electronically to the MBL and entered into the project database along with results of analyses done at MBL, and then posted on the access-restricted project web page. After all laboratories have reviewed data on the restricted web page for accuracy and consistency, data will be moved to the public domain project web page and provided to the ARCSS program database at the National Snow and Ice Data Center.

SYNTHESIS

Variations in individual tracer values, as well as the mix of tracers, will be evaluated within and among years for each of the arctic rivers under study. Seasonal and annual values for individual tracers will be identified along with estimates of their variability, and the overall biogeochemical signature of each river will be identified. These data will then be considered in the context of watershed sources and fates of river water in the Arctic Ocean.

Tracer fluxes to the Arctic Ocean will be calculated using river discharge data routinely collected by Roshydromet (Russian rivers), WRD (Mackenzie River), and USGS (Yukon River). Over the past several years, data from these different agencies have been compiled into a single database by the "Pan-Arctic Project" of Peterson et al. and more recently by the "ARCTIC-RIMS" project of Vörösmarty et al. As part of a new effort (see Prologue), Vörösmarty et al. propose to continue maintaining this database. Should their proposal be funded, the ability of Vörösmarty et al. to acquire arctic river discharge data in near-real time would greatly facilitate our calculations of tracer fluxes. If necessary, however, we will work directly with the various government agencies to acquire timely discharge data for the rivers in our study.

The tracer fluxes that we calculate will provide a contemporary baseline for each river, a benchmark for detecting future changes. Detection of these changes will, of course, require long-term monitoring of at least some key tracers. Involvement in our proposed research of personnel from the Russian, Canadian, and U.S. agencies responsible for water quality monitoring of arctic rivers will encourage routine measurement of the most important tracers in the future.

Tracer fluxes for the Yenisey and Ob' rivers will be used in combination with data collected by the SIRRO project (Rainer Amon and others; www.awi-bremerhaven.de/GEO/SIRRO) to explore estuarine and nearshore circulation patterns of freshwater from these rivers. The SIRRO project is a bilateral Russian-German investigation of organic matter dynamics in the estuaries of the Ob' and Yenisey rivers and in the Kara Sea. Comparison of river endmembers to estuarine and nearshore tracer values will help identify the most conservative constituents; those which are most useful for tracking river water in the Arctic Ocean. At the same time, non-conservative behavior of other constituents will provide insights to biogeochemical processes occurring in the estuaries.

We will also compare the flux data to existing oceanographic data on freshwater tracers. Our work will be coordinated as closely as possible with the Shelf-Basin Interactions project (SBI; see http://utk-biogw.bio.utk.edu/SBI.nsf). Lee Cooper, a participant in this proposal, is funded through the SBI project to analyze samples and interpret $H_2^{18}O$ data from all process cruises, which are operating at the shelf-basin boundary of the Chukchi and Beaufort Seas. Additional chemistry and tracer work on the SBI project, including radium isotopes (David Kadko, University of Miami), nutrient analyses (SBI Service Measurements Team), salinity (SBI Service Measurements Team), and sea ice structure studies (Hajo Eicken and Rolf Gradinger, University of Alaska Fairbanks) are also potentially of value for addressing the transfer of shelf waters into the deep basin. We will also coordinate with modeling approaches being employed in SBI (Wieslaw Maslowski, Naval Postgraduate School), and with data collection efforts associated with moored instrument arrays in Bering Strait and along the Chukchi and Beaufort shelves (Knut Aagaard, Rebecca Woodgate, University of Washington, Bob Pickard, Woods Hole Oceanographic Institution).

Cooper's funded work through SBI includes water column analyses of nutrient, salinity, and $H_2^{18}O$ fields to separate components of sea ice melt, brine injection, river runoff, and Bering Strait inflows within various arctic water masses. Linkage with the work proposed here will include coordination of runoff samples that are analyzed with the larger tracer data sets associated with SBI and other arctic projects including the environmental observatory in Bering Strait (Lee Cooper is lead PI). The environmental observatory project is centered on developing a year-round on-shore water pumping and analysis capability on Little Diomede Island for monitoring the Bering Strait inflow into the Arctic Ocean, and could also potentially be a key point of linkage for evaluating the transfer of shelf waters across the Arctic basin. This on-going and proposed work on modeling organic carbon transformations, assessing tracer distributions, and modeling biological and physical processes over the continental shelves and slopes, while geographically distinct from our proposed work, is important for assessing physical transport, mixing, and biogeochemical transformations in the Arctic Ocean. Our project will be of direct relevance to these efforts by providing input functions for organic matter and tracers, thus forming a natural linkage with SBI investigators.

To investigate the relationship between major watershed characteristics and the mix of tracers exiting the watersheds, we will use a GIS-based approach. Large-scale differences in land cover, land use, soil type, bedrock composition, permafrost extent, etc. among the watersheds of the 6 rivers are expected to correlate with biogeochemical signatures in the river water. Some catchment characteristics are relatively static (e.g., parent lithology), whereas others are sensitive to anthropogenic change. Modeling efforts and process-based studies of the hydrologic cycle in the watersheds of major North American and Siberian rivers (see Prologue) would facilitate data interpretation.

Charlie Vörösmarty and colleagues at the University of New Hampshire have developed pan-Arctic hydrology models that move water from catchment sources to the Arctic Ocean. We have included funds to work closely with the Vörösmarty et al. program to compare our tracer/GIS-based analysis of watershed sources to their model output. This comparison will help calibrate and validate model output, and thus facilitate accurate scaling-up of biogeochemical tracer fluxes to the entire pan-arctic watershed. Charlie Vörösmarty, Mark Serreze, and Mike Steele are also submitting a new proposal (see Prologue) that includes circulation of river waters through the Arctic Ocean. A tracer component is being built into this model. We plan to work together to incorporate our comprehensive tracer data from the 6 largest arctic rivers into their ocean circulation model.

OUTREACH AND EDUCATION

A primary outreach activity of this project will be to assist local Roshydromet laboratories in Noril'sk (Yenisey River), Kyusyur (Lena River), and Salekhard (Ob' River) to upgrade their sampling and analytical capabilities. While we are not relying on these laboratories for our study (samples will be shipped to CPPI-S and MBL for analysis), they are nonetheless responsible for long-term monitoring of water quality. Given the very large contribution that the Yenisey, Lena, and Ob' rivers make to the Arctic Ocean it is of both local and global interest that this monitoring be done well. Some infrastructure for water quality analyses exists at the Noril'sk, Kyusyur, and Salekhard stations, but insufficient funding of laboratories, inadequate equipment and reagents, and insufficient understanding of data requirements of the scientific community have hindered data quality in the past (Zhulidov et al. 2000, Holmes et al. 2001, Zhulidov et al. 2001). We believe that these deficiencies can be corrected, but that change will be slow without assistance. Therefore, we propose to work closely with the local Roshydromet laboratories with the goal of helping them produce the best possible data in the future. Our project, with logistical coordination from VECO, is requesting funding for laboratory upgrades (10K each for labs in Noril'sk, Kyusyur, and Salekhard) and for improving collection capabilities from their sampling boats (4k each, for depth integrating samplers and winches for raising and lowering samplers). This level of funding will be a good start, but we expect that additional funding will be necessary. We will therefore seek additional funding from other sources such as U.S. Civilian Research and Development Foundation (www.crdf.org).

Outreach will also involve participation of high school-aged students living in villages near our study sites. Under the supervision of local teachers or researchers, these students will collect periodic surface water samples from "their" rivers. We have already established contacts with several potential student supervisors and have identified some prospective students. They will perform basic analyses such as temperature, pH, and conductivity, after which the samples will be frozen for later constituent analysis at their regional labs and at Woods Hole. Participating students will also be active in exchange of data via the web where available. Scientists from our research group will visit the students and discuss the project, present lectures to their classes, and involve the students in as many aspects of the project as possible. We will also learn from the students about their experiences living near the rivers. Students will have the opportunity to experience scientific research first-hand and will contribute to the overall project by providing more frequent sampling (for some constituents) than would be possible during our major sampling trips alone.

Our project will contribute to undergraduate and graduate student education via several channels. The MBL has a semester-long undergraduate education program ("Semester in Environmental Science", http://courses.mbl.edu/SES/menu.html) that draws students from over 40 small liberal arts colleges throughout the United States. These students will be exposed to our research during course lectures by Peterson. Our project will also take advantage of the NSF-REU program (Research Experience for Undergraduates) and involve undergraduate students in both field and laboratory components of our research. Graduate students will participate in our research at Yale (w/Raymond) and AWI (w/Amon) as well as during visits to Woods Hole.

BROAD SIGNIFICANCE OF PROPOSED RESEARCH

The goal of the SEARCH/CHAMP/ASOF initiative is to measure, understand and ultimately predict the impacts of climate change on the arctic freshwater cycle as it affects ocean circulation. While the overall effort is widespread, we propose to measure the biogeochemical tracers in the major rivers of the Arctic. These data are needed for 3 specific tasks. The first is to use the river chemistry as a means of understanding watershed dynamics such as water sources, storage and weathering. As permafrost melts to greater depths stored water is released and chemical weathering increases. The second is to establish a baseline data archive that will be used to quantify progressive change in the chemistry of rivers in the future. The third is to obtain chemical fingerprints of freshwater entering the coastal oceans. Several studies have shown that watershed-derived isotopes, ions and organic matter can be quantified in waters throughout the surface layers of the Arctic Ocean. What we now lack is a systematic and comprehensive data set covering several annual cycles for multiple tracers. Our proposed research will provide this. The scientific benefit will be the ability to more accurately identify freshwater source contributions to oceans waters as they circulate throughout the Arctic and into the North Atlantic Ocean. Thus the tracers give a more complete picture of ocean circulation, including freshwater storage and transport, and ultimately help identify the sources of freshwater reaching the GIN and Labrador Seas.

The societal relevance of the proposed research is high because the links between CO_2 emissions, climatic warming, hydrological changes and ocean circulation create a feedback loop that can be disruptive to human society and especially agriculture. Widespread warming at high latitudes is presently underway. The temperature increases are consistent with the predictions of several Global Climate Models in response to greenhouse gas emissions. The hydrological cycle is expected to change as greenhouse warming accelerates the poleward transport of water vapor through the atmosphere leading to increased precipitation on northern land and ocean. One predicted result is increased discharge of rivers, the dominant source of freshwater to the Arctic Ocean. As arctic temperatures and moisture convergence increase, the overall result is a freshening of the surface layers of northern oceans. This freshening is predicted by several GCMs to reduce North Atlantic Deepwater formation. The end result could be a variability or cessation of northern transport of warm ocean waters into the North Atlantic leading to climatic swings or regional cooling unprecedented in the past 8000 years.

Society must judge the benefits of cheap fossil fuel use against the possible negative factors such as climate instability. Our research can narrow the uncertainty through improved understanding of the arctic hydrologic cycle as it affects ocean circulation. That is the goal of our proposal and the overall initiative. There is a significant risk of disruption of North Atlantic Deepwater formation within a 50 to 150 year time frame. Given the several decade lag required for conversion to alternative energy sources, societal decisions about energy policy will need to be made within the next several decades to be effective.

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