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Nutrient chemistry of the Ob' and Yenisey Rivers, Siberia: results from June 2000 expedition and evaluation of long-term data sets

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Abstract

Although containing only ~1% of global ocean volume, the arctic Ocean receives almost 10% of global river discharge. Nutrients carried by arctic rivers influence the productivity of their estuaries and coastal seas and may serve as important indicators of changing conditions in their watersheds. The three largest arctic rivers (Yenisey, Ob', and Lena) enter the arctic Ocean from Siberia and together account for nearly 35% of river-water inputs to the arctic Ocean. Although several nutrient flux estimates have been published for Eurasian arctic rivers, recent publications have highlighted uncertainties in these estimates and have cautioned against their uncritical use, particularly with respect to ammonium data. In order to help clarify the situation and evaluate the validity of existing long-term data sets, we went to Siberia during June 2000 to collect and analyze new nutrient samples from the downstream reaches of the Yenisey and Ob' rivers. Samples were independently analyzed by as many as four groups/laboratories in order to maximize confidence in analytical results. Whereas long-term data sets report average ammonium concentrations of 710 and 360 μg N/l in the Ob' and Yenisey rivers, respectively, we measured concentrations of only 10–15 μg N/l in both rivers in June 2000. We conclude that existing long-term data sets for these two rivers are grossly in error with respect to ammonium concentrations, and by extension that other surprisingly high values of ammonium reported for Russian arctic rivers (for example Pur, Taz, Nadym, and Pechora rivers) must be considered extremely doubtful. The situation is better for nitrate and phosphate, but our one-time sampling is insufficient to fully evaluate the reliability of existing data sets for these nutrients. Because a substantial percentage of the total freshwater input to the arctic Ocean comes from Russian rivers, the large revisions in ammonium concentrations needed for the Ob', Yenisey, and probably other Eurasian arctic rivers will significantly reduce estimates of dissolved inorganic nitrogen (DIN) fluxes to the arctic Ocean as a whole. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Nutrient chemistry; arctic Ocean; Dissolved inorganic nitrogen; Ammonium; Siberia; Ob' River; Yenisey River

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1. Introduction

Nutrients carried by rivers to oceans are important indicators of changing conditions in watersheds as well as important controls on biotic activities in estuaries and coastal seas (Meybeck, 1982; Howarth et al., 1996). In the arctic, these fluxes assume increased importance due to the large volume of riverine inputs relative to the volume of the shelf seas and the small area of the arctic Ocean compared to its drainage area (Opsahl et al., 1999; Lobbes et al., 2000; Lammers et al., 2001). These riverine

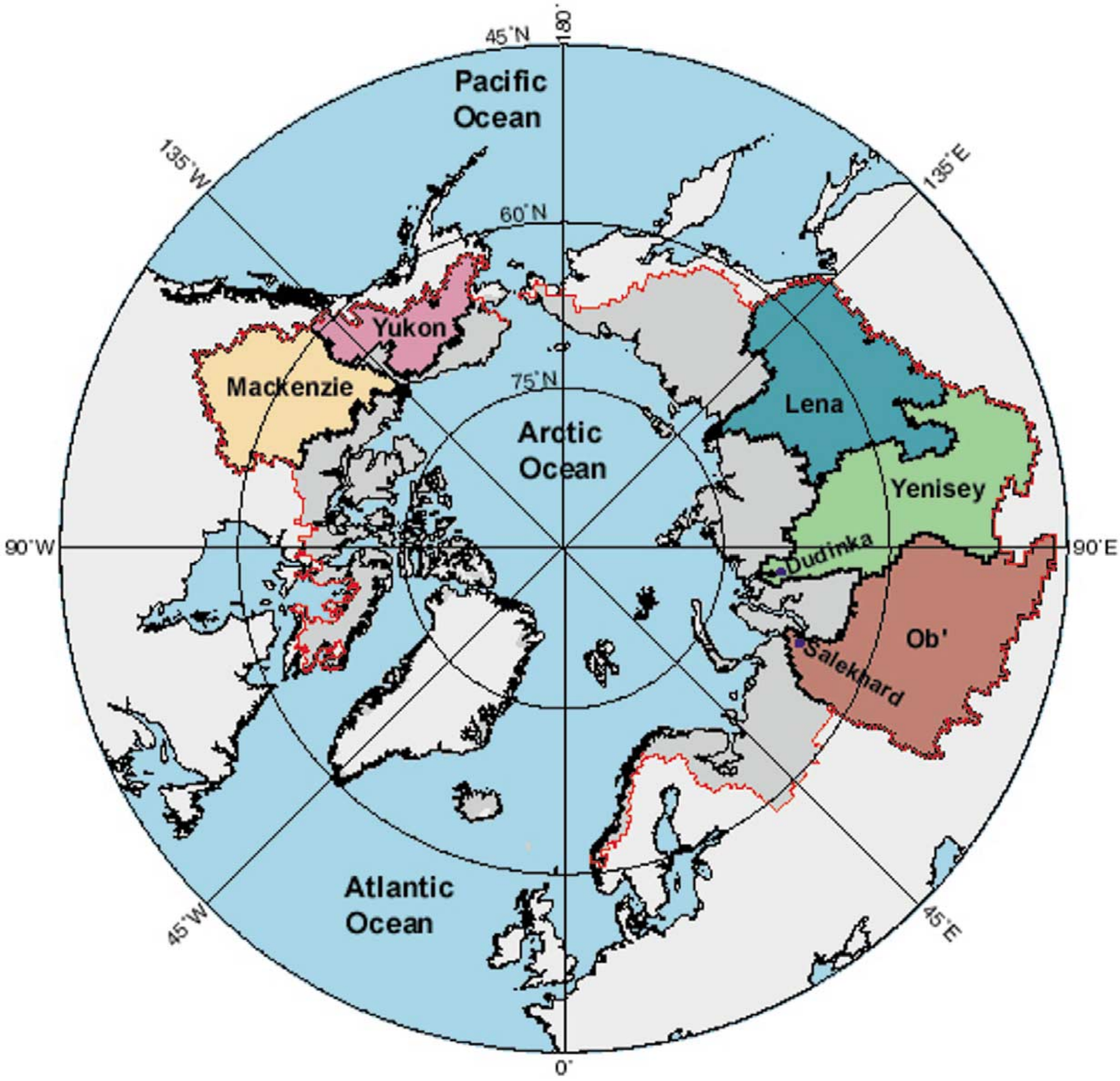

Fig. 1. Polar view of arctic showing watersheds of the largest arctic rivers. The red line shows the watershed of the arctic Ocean, including the Yukon River which enters the Bering Sea and is then transported to the arctic Ocean by prevailing currents. The Yenisey and Ob' rivers, sampled during this expedition, are the first and third largest arctic rivers (by discharge). Samples were collected near the towns of Salekhard (Ob' River) and Dudinka (Yenisey River), at the exact transects which have been sampled long-term by the Soviet/Russian water quality monitoring network (OGSNK pre-1992, GSN afterwards).

inputs significantly impact the salinity distribution and circulation of the arctic Ocean (Aagaard and Carmack, 1989) and help support productive commercial and subsistence fisheries. A major unresolved question in arctic research is how freshwater and nutrient inputs to the arctic Ocean will change with future climate or land-use changes (Kassens et al., 1998).

The watersheds of the three largest arctic rivers (Yenisey, Lena, Ob') cover much of Siberia and together account for about 35% of all river-water inputs to the arctic Ocean (Fig. 1). All three rank within the top 10 rivers globally in terms of catchment areas and are among the largest 13 when ranked by discharge (Shiklomanov, 1993; Vörösmarty et al., 2000). Thus, to adequately estimate freshwater and material flux to the arctic Ocean, it is critical to accurately account for the fluxes of these large Siberian rivers.

During the Soviet era, the Russian water quality monitoring network was one of the most extensive on Earth. For many Russian arctic rivers, records of nutrient concentrations span periods of 10–20 years of approximately monthly sampling. Although these data have been used to calculate nutrient flux estimates for rivers in the circumpolar arctic (Alekin and Brazhnikova, 1964; Tarasov et al., 1988; Smirnov, 1994; Gordeev et al., 1996; Tsirkunov et al., 1998; Gordeev, 2000), a recent paper highlighted uncertainties in the long-term data sets for Eurasian arctic river nitrate, ammonium, and phosphate concentrations (Holmes et al., 2000). In particular, reported ammonium concentrations averaged ~1 mg/l NH_4–N in several Russian arctic rivers, much higher than what would be expected in relatively pristine river systems (Holmes et al., 2000). The majority of the water quality data available for rivers of the Former Soviet Union and current Russian Federation come from the State Service of Observation and Control of Environmental Pollution (OGSNK prior to 1992 and GSN from 1992 onward; hereafter referred to as OGSNK/GSN), and a recent critique identified numerous problems that could compromise data quality (Zhulidov et al., 2000). Given these uncertainties and the unavailability of independent data sets against which to compare the OGSNK/GSN data, we concluded that the reliability of existing data sets could only be evaluated through comparisons with newly collected samples (Holmes et al., 2000).

Therefore, in order to evaluate the quality of the existing data sets and move toward establishing a contemporary baseline of riverine nutrient flux to the arctic Ocean, we went to the downstream-most established nutrient monitoring stations on the Ob' and Yenisey Rivers during June 2000 to collect and analyze new samples. Samples were independently analyzed for nitrate, ammonium, and phosphate by as many as four groups/laboratories in order to maximize confidence in measured nutrient concentrations. Here we report the results of the expedition and consider the current state of affairs with respect to quantifying nutrient flux to the arctic Ocean.

2. Methods

We sampled the Ob' River at Salekhard (66.6°N, 66.6°E) and the Yenisey River at Dudinka (69.2°N, 86.1°E) on 17 June 2000 and 26 June 2000, respectively. June is typically the high discharge period for these rivers, and discharge on our sampling dates was likewise high (Fig. 2). The Salekhard and Dudinka sites correspond to the downstream-most stations sampled for nutrient concentrations by the OGSNK/GSN monitoring network. Salekhard (Ob' River) is also the downstream-most site where discharge is monitored routinely by Federal Russian Service of Hydrometeorology and Environmental Monitoring (Roshydromet), whereas the downstream-most discharge station on the Yenisey is well upstream of Dudinka at Igarka (Holmes et al., 2000).

Ob' River surface water and near-bottom water samples were collected at three points across the river, and a mid-water sample was also collected at the mid-channel site. Thus, a total of seven samples were collected. Ten samples were collected on the Yenisey River; seven approximately evenly distributed surface water samples across the width of the river, with near-bottom water samples being collected below the third, fifth, and seventh surface samples. Surface water samples were collected using a dip-bucket and deep water samples were collected using a 2-l stainless steel Kimmerer bottle on the Yenisey River and a plastic sampler on the Ob' River.

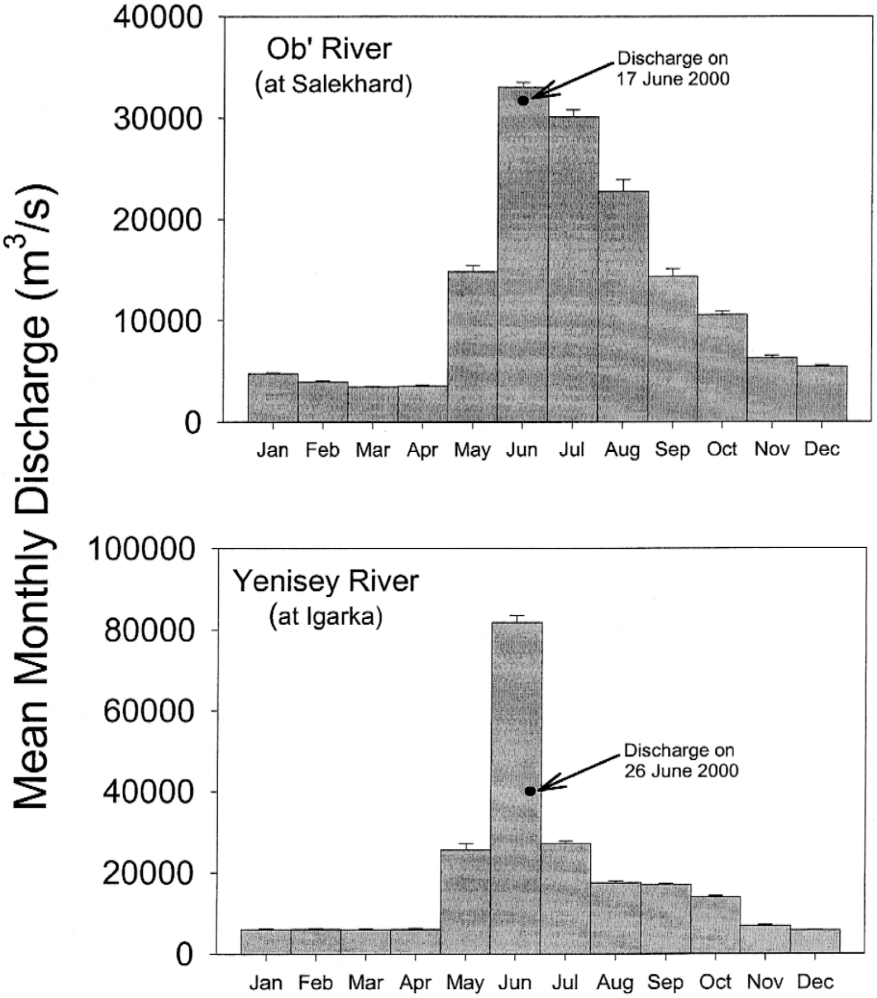

Fig. 2. Mean monthly discharge (± S.E.) of the Ob' River (upper panel) and Yenisey River (lower panel) for the periods 1936–1994 and 1936–1995, respectively, compared to discharge on dates which we sampled these rivers for nutrient concentrations. Long-term discharge data are from the r-arcticNet database (http:\\www.R-arcticnet.sr.unh.edu) (Lammers et al., 2001).

All samples were independently analyzed by scientists/technicians from several laboratories (Marine Biological Laboratory "MBL" — Woods Hole, USA; Shirshov Institute of Oceanology "SHIRSHOV" — Moscow, Russia; Centre for the Preparation and Implementation of International Projects on Technical Assistance "CPPI" — Rostov-on-Don, Russia; Roshydromet laboratories "ROSH" — Salekhard and Norilsk, Russia). Ammonium was analyzed by all groups but due to logistical constraints, Yenisey River samples were not analyzed for nitrate and phosphate by CPPI, and Ob' River samples were not analyzed by MBL for nitrate or phosphate. Prior to analysis, all samples were filtered through Whatman GFF filters, except ammonium samples analyzed by MBL which were not filtered.

As reported by Holmes et al. (2000), the greatest uncertainty with respect to nutrient concentrations previously reported for Eurasian arctic rivers involved ammonium values. Thus, a variety of methods were used to analyze ammonium in Ob' and Yenisey river samples during the June 2000 expedition. The common indophenol blue method (Solorzano, 1969; Hydrochemical Institute Report, 1987, 1995a) was used by analysts from SHIRSHOV and CPPI, an OPA/fluorometric method (Kérouel and Aminot, 1997; Holmes et al., 1999) was followed by MBL, and the Nesslerization protocol without distillation (Hydrochemical Institute Report, 1995b) was used by the Roshydromet laboratories in Salekhard and Dudinka. All groups used variations of the cadmium reduction method for nitrate and molybdenum blue method for phosphate (Clesceri et al., 1998).

3. Results and discussion

A central objective of our expedition to the Ob' and Yenisey rivers during June 2000 was to determine the cause of puzzlingly high ammonium concentrations previously reported from Eurasian arctic rivers (Smirnov, 1994; Gordeev and Tsirkunov, 1998; Tsirkunov et al., 1998; Gordeev, 2000; Holmes et al., 2000). Although we had no explanation as to why ammonium should be so high, neither could we understand how long-term data sets for multiple rivers could be grossly in error.

During our expedition, mean ammonium concentrations of 10–15 μg N/l were measured in both the Ob' and Yenisey rivers by analysts from MBL, SHIRSHOV, and CPPI, whereas analysts at the Roshydromet laboratories reported values greater than 1000 μg N/l for the Ob' River and nearly 260 μg N/l for the Yenisey River (Fig. 3, Table 1). Both indophenol blue and OPA/fluorometric methods gave similar and low values, whereas the Nesslerization method without distillation used by the Roshydromet laboratories yielded far higher concentrations. The values determined by the Roshydromet laboratories were similar to what they had previously measured, as reported in the long-term OGSNK/GSN data set (mean values of long-term data set shown by horizontal dashed lines in Fig. 3).

Interestingly, internal directives within the OGSNK/GSN (as far back as 1978) recommended switching from the Nesslerization method to the indophenol method for measuring ammonium

Table 1
Summary of nutrient concentration data for downstream stations on the Ob' and Yenisey rivers.
Values are reported as microgram N or P per liter, with standard errors shown parenthetically.

Sampling period	Data source	Ob' River at Salekhard			Yenisey River at Dudinka		
		NH_4–N	NO_3–N	PO_4–P	NH_4–N	NO_3–N	PO_4–P
Long-term data[a]	GEMS-Water Database[b]	890	160	–	140	80	–
	GEMS-Glori Database[c]	600	60	65	280	20	8
	Holmes et al. (2000)[d]	710	90	58	360	30	11
June 2000 expedition[e]	Roshydromet Laboratory (Salekhard or Norilsk)	1074 (16.2)	66 (3.8)	42 (1.6)	259 (2.3)	15 (2.2)	12 (0.7)
	Shirshov Institute of Oceanology (Moscow)	15 (2.8)	117 (9.9)	35 (3.4)	14 (0.6)	10 (0.4)	16 (1.3)
	CPPI (Rostov-on-Don)	12 (3.8)	55	33	10 (1.2)	–	–
	Marine Biological Laboratory (Woods Hole)	11 (3.6)	–	–	10 (0.6)	8[f] (0.3)	–

[a]These three databases all use data originally collected by the Roshydromet laboratories in Salekhard and Norilsk. These same laboratories also analyzed samples collected during the June 2000 expedition.

[b]1991–1993 averages from the GEMS-Water Database, http://www.cciw.ca/gems/.

[c]Values reported in Meybeck and Ragu, GEMS-Glori database (book draft), originally from Kimstach et al. (1998). A Water Quality Assessment of the Former Soviet Union.

[d]Calculated using OGSNK/GSN nutrient monitoring data from 1985 to 1995 for the Yenisey River and 1986–1995 for the Ob' River.

[e]Samples were collected 17 June 2000 (Ob' River at Salekhard) and 26 June 2000 (Yenisey River at Dudinka), and divided among the various laboratories/groups for independent analyses. Values shown are means (standard errors shown parenthetically) of several samples collected across the river channels and at different depths, except for nitrate and phosphate values from CPPI which are from a single sample collected in the center of the Ob' River.

[f]This value is the sum of nitrate and nitrite concentrations, whereas other "NO_3" values in this table represent nitrate alone. However, nitrite concentrations are generally insignificant compared to nitrate values.

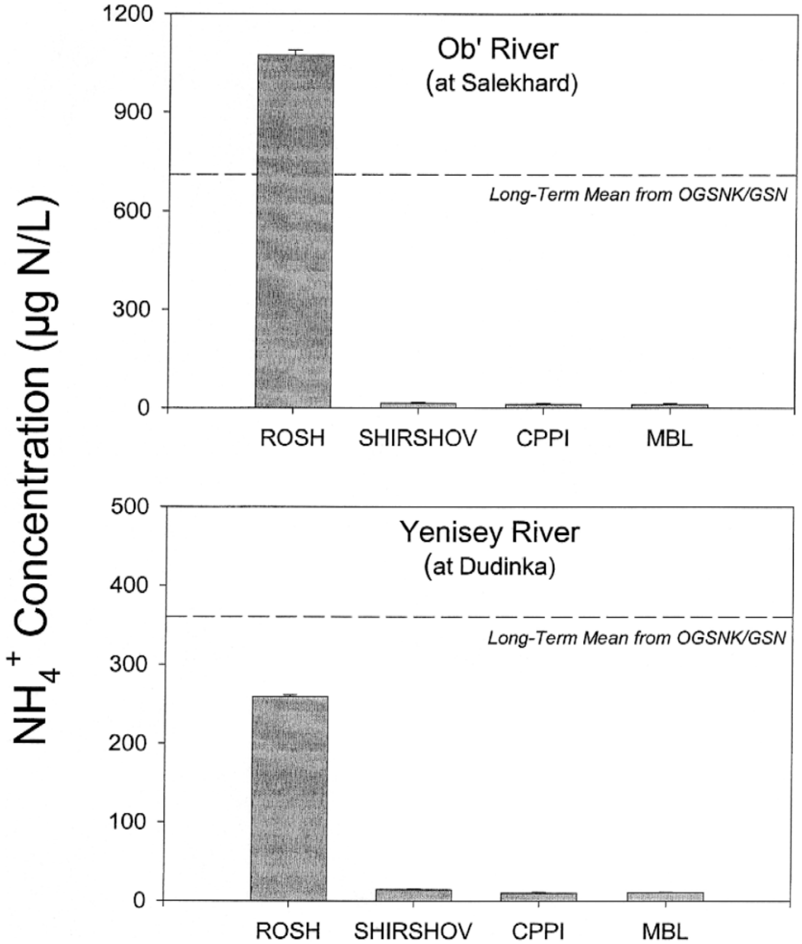

Fig. 3. Summary of ammonium measurements (means ± S.E.) for the Ob' River (upper panel) and Yenisey River (lower panel) made by analysts from the local Roshydromet laboratories in Salekhard and Norilsk (ROSH), the Shirshov Institute of Oceanology in Moscow (SHIRSHOV), the Centre for the Preparation and Implementation of International Projects on Technical Assistance (CPPI), and the Marine Biological Laboratory in Woods Hole (MBL). The long-term mean concentrations derived from the OGSNK/GSN data set (Holmes et al., 2000) are shown by the horizontal dashed lines.

(Boeva, Hydrochemical Institute, personal communication). Reasons cited for this change included interferences leading to false high values in waters with high dissolved organic carbon (DOC) concentrations, as well as interferences caused by turbidity, high iron content, and sulfides. A number of these characteristics, especially high DOC concentrations, are found in rivers of the Eurasian arctic (Telang et al., 1991; Kattner et al., 1999; Lobbes et al., 2000), thus indicating the inappropriateness of the Nesslerization method for these samples. The simple and unavoidable conclusion is that the existing long-term data set for ammonium in the Ob' and Yenisey rivers is erroneous, in large part due to inappropriate analytical methods. No systematic offset in values is apparent, thus correcting of past OGSNK/GSN ammonium data for the Ob' and Yenisey rivers is not feasible. By extension, other surprisingly high values of ammonium reported in the OGSNK/GSN data set, for example in the Pur, Taz, Nadym, and Pechora rivers (Holmes et al., 2000), must be considered highly doubtful. Unfortunately, the use of the Nesslerization method without distillation continues to this day in some Roshydromet laboratories, in large part due to financial constraints which limit the acquisition of upgraded analytical instruments and more expensive reagents.

Although the long-term data set for ammonium in the Ob' and Yenisey rivers is erroneous and uncorrectable, the situation appears to be better for nitrate and phosphate data (Table 1). For example, nitrate and phosphate concentrations measured by all groups during our June 2000 expedition were generally within the range of values reported in the long-term data sets (Table 1). However, more samples will be required in order to fully evaluate the reliability of the long-term data set with respect to nitrate and phosphate concentrations since our one-time sampling is unable to unambiguously validate the long-term OGSNK/GSN data set. Although there is reason for some optimism, numerous potential problems for these analyses have been previously noted (Zhulidov et al., 2000), so further validation is needed.

The impact of these findings on estimated nutrient fluxes to the arctic Ocean are profound. Based on existing long-term data sets, the Ob' River apparently transported more ammonium than any other river on Earth, nearly 300×10^3 t N/year (Smirnov, 1994; Gordeev, 2000; Holmes et al., 2000). If we assume that our June 2000 samples are representative of the annual average (and thus use 13 μg NH_4–N/l in our calculations), estimated annual ammonium flux in the Ob' River drops almost 18% to 5×10^3 t N/year. Similarly, long-term data sets for the Yenisey River indicate that 208×10^3 t N/year were transported as ammonium (Gordeev, 2000; Holmes et al., 2000), whereas if our June 2000 samples are representative of the annual average, only about 7×10^3 t N/year are actually being transported to the arctic Ocean. Since a large percentage of river-water entering the arctic Ocean comes from Russia, these revisions will greatly reduce estimates of DIN input to the arctic Ocean as a whole. Moreover, since dissolved organic nitrogen (DON) is calculated as the difference between total dissolved nitrogen (TDN) and dissolved inorganic nitrogen (DIN; nitrate, nitrite, and ammonium), overestimates of ammonium concentration will lead to underestimates of DON concentration.

In addition to the inorganic nutrients measured as part of this expedition, there is a great deal of interest in organic matter (dissolved and particulate) and suspended sediment flux to the arctic Ocean (Anderson et al., 1998; Lobbes et al., 2000; Meade et al., 2000; Rachold et al., 2000). This information is vital to an understanding of large-scale terrestrial biogeochemistry and land–ocean linkages in the arctic, and is used by oceanographers to study water movement and the transport and processing of terrigenous materials in the arctic Ocean (Olsson and Anderson, 1997; Wheeler et al., 1997; Fahl and Stein, 1999; Kattner et al., 1999; Bussmann and Kattner, 2000). Limited long-term organic matter and suspended sediment data are available for Eurasian arctic rivers, and their reliability is largely unknown (Zhulidov et al., 2000), except for DON data which will be erroneous when ammonium results are faulty. A few recent studies have made one-time measurements of organic matter quality and quantity in Eurasian arctic rivers (Opsahl et al., 1999; Lobbes et al., 2000), but none have systematically evaluated seasonal and annual fluxes. Thus, there is a need to either improve existing monitoring programs or initiate new projects that will simultaneously and relatively frequently measure a variety of inorganic and organic river-water constituents. One-time sampling programs have yielded considerable insight, but further advancement in our understanding of land–ocean linkages in the arctic, the impact of climate and land-use changes on these linkages, and the circulation of river inputs through the arctic Ocean will require a coordinated pan-arctic measurement and assessment program. Although a multinational project to assess contemporary river constituent flux to the arctic Ocean is a challenging objective, it may be feasible given the dominance of a relatively small number of very large rivers to whole-arctic material budgets.

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Erratum

Erratum to "Nutrient chemistry of the Ob' and Yenisey Rivers, Siberia: results from June 2000 expedition and evaluation of long-term data sets" [Mar. Chem. 75 (3) (2001) 219–227][☆]

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The publisher regrets the error that appeared in the above article. The corrected version is published below.

Page 225, line 26–31: If we assume that our June 2000 samples are representative of the annual average (and thus use 13 μg NH_4–N/l in our calculations), estimated annual ammonium flux in the Ob' River drops almost 98% to 5×10^3 t N/year.

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