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Chemical weathering of silicate rocks in Karelia region and Kola peninsula, NW Russia: Assessing the effect of rock composition, wetlands and vegetation

E.A. Zakharova [a], O.S. Pokrovsky [a,*], B. Dupré [a], J. Gaillardet [b], L.E. Efimova [c]

[a] Laboratoire de Mécanismes et Transfert en Géologie, CNRS, IRD (UMR 5563)-Observatoire Midi-Pyrenées, Université Paul-Sabatier, 14, Avenue Edouard Belin 31400, Toulouse, France

[b] Laboratoire de Géochimie et Cosmochimie, Institut de Physique du Globe de Paris, Universite Paris 7, UMR CNRS 7154, 4 Place Jussieu, 75252 Paris Cedex 05, France

[c] Department of Hydrology, Faculty of Geography, Moscow State University, Vorobievy Gory 1, 119899, Moscow, Russia

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Abstract

This study is aimed at assessing the effect of factors including lithology, forest/peatland coverage, dissolved organic carbon, and vegetation on chemical fluxes and concentrations of major elements in rivers. The mean annual element concentrations and dissolved fluxes of acid and basic rock dominated watersheds of the Karelia region and Kola peninsula, NW Russia, have been estimated from the chemical composition of river water samples collected in the summers of 1996–2000 and from annual discharge and chemical composition data of 16 watersheds collected from 1961 to 1975. The mean annual flux corrected for atmospheric input varies from 0.5 to 5.6 t/km^2/y and is dominated by alkali metals for the Kola alkaline rocks and by calcium for the Karelian granito-gneisses. The pure "granitic" and pure "basaltic" river chemical denudation rates in the Baltic shield are 0.33 and 2.3 t/km^2/y, respectively. The cationic and silica fluxes of both granitic and basaltic watersheds are comparable with those of other boreal regions having similar runoff, compositions, and climate. The cationic flux of the rivers is positively correlated with the basic rock fraction of the watershed, whereas the dissolved organic carbon flux increases with the increasing peatland fraction. The chemical composition of the river water is controlled by bedrock dissolution during dry periods, and by plant litter degradation and washout of organic debris from the topsoil horizon during wet periods. Taking account the chemical composition of the plant litter and the biological turnover intensity, it was estimated that the plant litter degradation in Kola and Karelia regions provides 10–40% of total annual dissolved riverine element flux.

Keywords: Chemical weathering; River water; Granite; Vegetation

1. Introduction

Chemical weathering of crystalline silicate rocks is considered to be the main factor controlling the atmospheric CO_2 cycle on long timescales (Berner, 1992). Assessing the river water composition and fluxes is a major tool to quantitatively model CO_2 uptake during chemical weathering. Characterizing the factors that control the chemical erosion of silicate rocks in various climate zones is, therefore, crucially important for predicting continental chemical weathering rates both in the past and

* Corresponding author.
E-mail address: oleg@lmtg.obs-mip.fr (O.S. Pokrovsky).

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in the future. A large number of studies have been devoted to rock weathering in tropical and temperate climate (Sarin et al., 1989; Yuretich et al., 1993; Benedetti et al., 1994; Edmond et al., 1995; Dupré et al., 1996; Das et al., 2005), and within the boreal cold or glacial watersheds (Miller and Drever, 1977; Drever and Zobrist, 1992; Gislason et al., 1996; Berner and Rao, 1997; Anderson et al., 1997; Huh et al., 1998; Huh and Edmond 1999; Anderson et al., 2000; Ingri et al., 2000; Stefansson and Gislason, 2001; Nezat et al., 2001; Millot et al., 2002, 2003; Anderson et al., 2003; Gaillardet et al., 2003; Oelkers and Gislason, 2004; Ingri et al., 2005; Gislason et al., 2006). Many important issues, however, such as relative role of lithology, peatland, and vegetation coverage, remain unresolved. Moreover in most previous studies, only short-time sampling series were considered and long-term systematic observations of rivers draining silicate terrains in boreal environments are still lacking.

This paper is aimed at characterizing the rock weathering rates and rivers hydrochemistry in cold high-latitude environments. Large boreal regions such as NW Russia are likely to play an important role in the terrestrial CO_2 cycle because they are both extensive and overlaid by organic-rich soils and wetlands that constitute a major carbon sink (Botch et al., 1995). The behavior of the elements during organic carbon and cation mobilization induced by global warming is a key environmental issue related to these regions (Guo et al., 2004; Smedberg et al., 2006). Increase of river discharge and the unfrozen layer thickness in the Russian Arctic over past several decades (Peterson et al., 2002; Serreze et al., 2002; Oelke et al., 2003) are likely to increase elemental fluxes to the ocean as well as change their aqueous speciation and bioavailability. The high fragility of the Arctic landscapes to environmental change makes this region very sensitive to human pollution (i.e., Roederer, 1991). The long-term monitoring of the river water compositions is, therefore, crucially important in this region. Most of the Russian Arctic coast is constituted of silicate rocks and sediments. The Karelian and Kola granito-gneisses provinces are an ideal laboratory for studying silicate weathering on a large scale under contrasting landscapes; moreover, as these provinces are sparsely populated they are subject only to moderate anthropogenic influence. Recent investigations in the Northern part of this region were performed by the Geological Surveys of Finland and Norway and by the Russian Central Kola Expedition and were aimed at monitoring the anthropogenic impact of Kola smelters on this region (de Caritat et al., 1996; Reimann et al., 1997a,b; de Caritat et al., 1998). In contrast, this study is concentrated on the least polluted watersheds of this region. Moreover, much of the data used in this study was collected before 1976, when anthropogenic impacts were much lower.

Weathering rates determined in this study are based on two data sources. The first source is samples collected and analyzed by the Russian Hydrological Survey from 1961 to 1975. The second data source is water samples collected during the summers of 1996–2000 from rivers draining monolithological granitic or mixed granitic/basaltic terrains. These data sets allow 1) the rigorous estimation of mean annual dissolved element fluxes for silicate watersheds of various sizes and establishing the relative mobility of elements during weathering, 2) the resolution of how various factors effect weathering rates, and 3) how these effects depend on the season. Unlike many regions of the world, the Arctic and subractic zone exhibit extreme variations in the discharge and chemical elements concentration (c.f. Gislason et al., 2006). The quantitative description of these systems, therefore, requires an understanding of how weathering rates vary seasonally. An additional goal of this study is to assess the relative role of mineral versus plant litter dissolution in chemical weathering. Although several recent studies used isotopic techniques in an attempt to resolve the sources of elements in Hawaiian and Siberian rivers (Derry et al., 2005; Reynolds et al., 2006), the contribution of mineral versus plant litter remains poorly constrained particularly for boreal watersheds. Precise knowledge of these sources is essential for predicting the response of Arctic ecosystems to the global warming as the plant litter production and degradation responds more rapidly to environmental change than inorganic mineral dissolution.

2. Study area and methods

2.1. Lithology, soils, vegetation, climate and hydrology

The study area (~150,000 km^2 from 31°W, 64.2°N and 39°W, 69.3°N, Fig. 1) is located in NW Russia and it is a part of the Eastern Fennoscandian Shield. It is situated within three large geological structures: the Kola and Karelia Provinces, and the Belomorian belt. The Karelian Province, aged 3.2–2.8 Ga, consists mainly of granito-gneisses and schists whereas the Kola craton, aged 3.0–2.7 Ga, consists of granulito-gneisses (Lobach-Zhuchenko et al., 1998). The narrow Pechenga-Varzuga Belt is located in the middle of the Kola Province. It consists of Proterozoic volcanogenic high-Mg and alkali basalts aged 2.45–1.9 Ga (Sharkov and Smolkin, 1997). The bedrock composition of the 2.8–2.7 Ga Belomorian Belt is dominated by Archean amphibole and biotite-

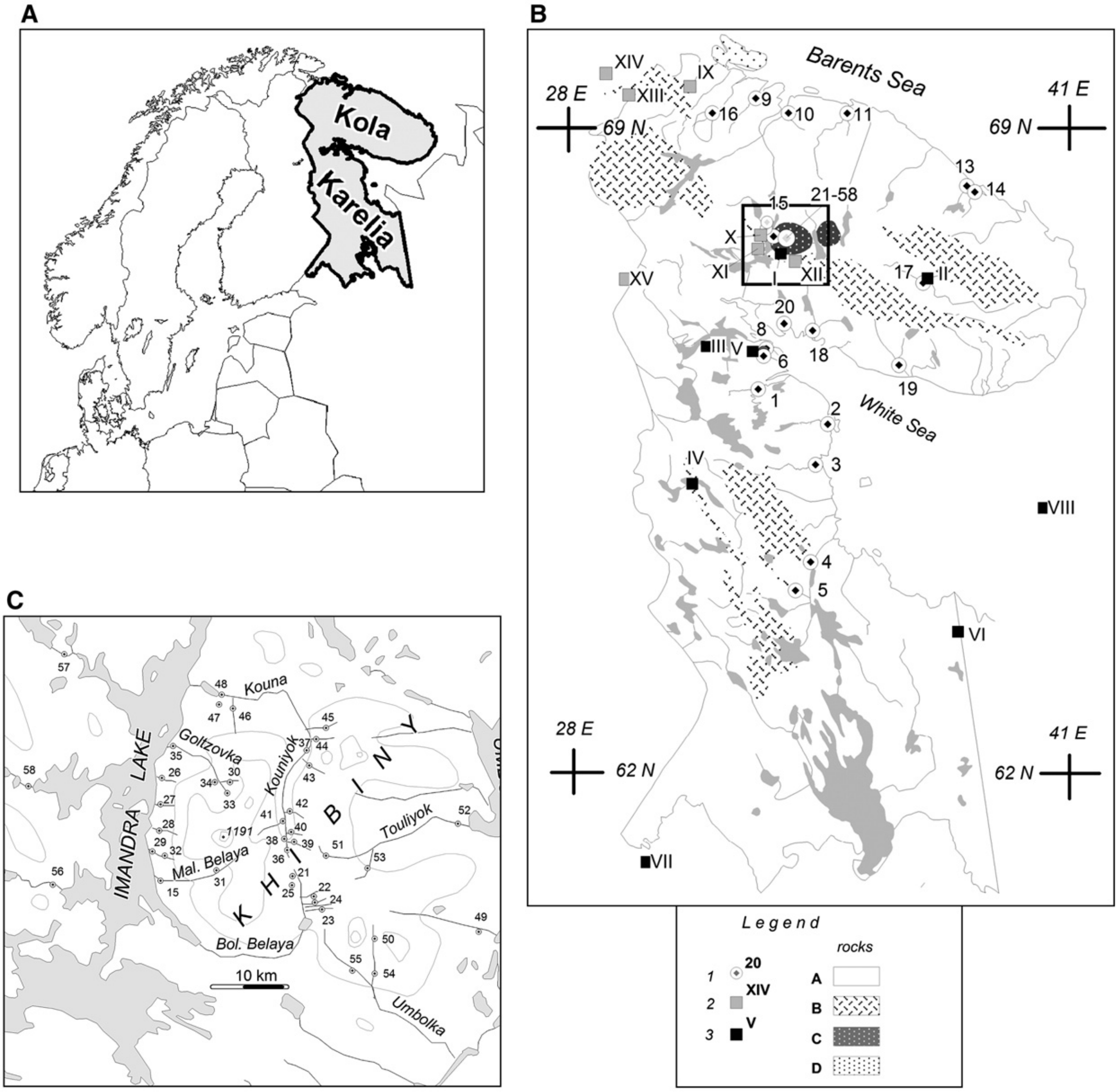

Fig. 1. A — Study area, B — location of sampling points: 1 — sampling points listed in the Table 1; 2 — sites of atmospheric precipitation and soil sampling (Table A2 of the electronic supplementary information, from Reiman et al., 1997a,b), 3 — meteorological stations; C — location of sampling points within alkali intrusion of Khibiny massif listed in the Table 1A). Rocks: A — granites and gneisses of Archaean age, B — basalts and volcanic rocks (2.5–2.0 Ga), C — alkaline rocks of Khibiny massif: nephelin or K-feldspar syenites (371–365 Ma); D — sedimentary rocks: neoproterozoic sandstones and conglomerates (900–1050 Ma).

amphibole gneisses and middle and low-proterozoic granites. On the seacoast, this complex consists of biotite and amphibole-biotite gneiss, trondhjemite, and tonalite. Small intrusions of late Lopian complex consisting of primarily olivinite, harzburgite, pyroxenite and serpentinite are located in the central part of the metamorphites. In the central and western part of the Belomorian Belt, middle and low-proterozoic granites are ubiquitous, whereas in the southern part sandstones, quartzites, siltstones, limestones, carbonate-sericite-chlorite schists associated with dykes and sills of diabase and gabbro-diabase are abundant (Lobach-Zhuchenko et al., 1998; Bibikova et al., 2001).

The area was affected by glaciation at least 3 times during the Pleistocene (Reimann and Melezhik, 2001). The region has been slowly rising since the disappearance of the last glacier 25,000–10,000 years ago. Because this region was in the center of the glaciation, and due to the dominance of erosion over the accumulation, the thickness of the Kola and Karelia quaternary deposits are lower than that of the southern and central part of the Russian Plane, and it rarely exceeds 10 m (State Geological Map, 2001). The late quaternary deposits are represented by a complex pattern of glacial products. The moraine consists mainly of sand and loamy sand with gravel and boulder inclusions. The glaciolacustrine and lacustrine as well as fluvio-glacial deposits in the form of lenses are also wide spread. They have a layered structure and are formed by fine and loam sands, rarely by a loam. Along the White Sea coast, marine sands and clays of Weichselian age are ubiquitous. The palustrine deposits have formed since the Early Holocene. At present, they occupy 25–30% of the surface and their thickness ranges from 0.3 to 3 m in the Kola peninsula to 7 to 9 m in Karelia.

Podzol is the main type of soil. In most areas, the soil depth varies from 15 to 50 cm; a soil depth of 15 to 20 cm is typical of areas >200 m above sea level (Evdokimova, 1957). A brown tundra soil is typical for the north of Kola peninsula where it exhibits a shallow profile of 10 to 20 cm with high proportion of organic detritus. The Gley peat soil occurs in valleys, wide plains, gentle slopes and local depressions.

There are two contrasting vegetation zones in this region. The tundra zone extends over 20–30 km along the Barents Sea coast; in the central part of the Kola Peninsula it can be found at the altitude above 350–400 m. The main part of the territory is occupied by boreal taiga forest consisting of pine (*P. silvestrus*), spruce (*P. abies* on the south and *P. obovata* on the north), and birch (*B. pubescence*). *Vaccinum myrtillus* and green moss *Plurozium shreberi* dominate the forest-floor coverage. Large amount of peatlands, located in glacial depressions, provide high concentrations of dissolved organic carbon (DOC) in surface waters. Another major source for DOC to the river water is the riparian zone along all the small streams and rivers. The importance of near-stream riparian zone in determining the flowpath dynamics in boreal cathments and its impact on the interaction between shallow groundwater–peatland complexes for boreal regions are widely known (McGlynn et al., 1999; Ferone and Devito, 2004).

The climate of the study region is milder than the Eastern part of the Russian Arctic. The mean annual air temperature ranges from 0 °C at the Barents Sea coast to − 4 °C in the central part of the Kola Peninsula. Further southward the average temperature is 3 °C. The snow-free period lasts for 4–5 months. The amount of precipitation decreases from 700 mm on the Barents Sea coast to 550 mm in the west of the Kandalaksha Bay (White Sea). The seasonal variations of precipitation and temperature are depicted in Fig. 2A.

The morphometrical characteristics of the rivers sampled by the Hydrometeorological Service were taken from Koupriyanov (1971) and are given in Table 1. Annual river runoff varies from 700 mm in the North to 300 mm in the South of Karelia and in the central part of the Kola Peninsula. The annual discharge pattern of rivers exhibits a strong dependence on season and rain events (Fig. 2B and C). From November to April the rivers carry between 10 and 30% of the annual discharge. The spring flood occurs each spring, lasting from 40–50

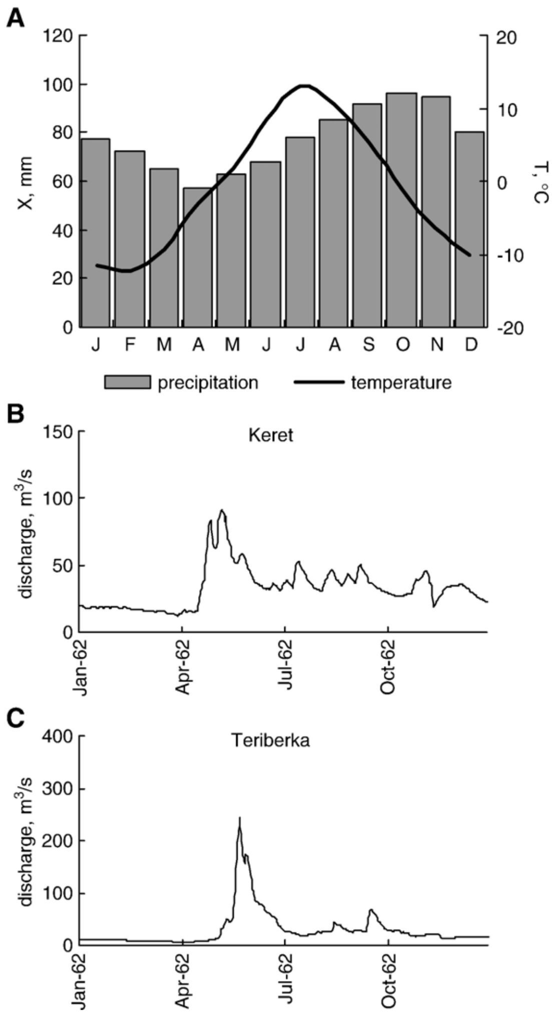

Fig. 2. Typical seasonal distribution of atmospheric precipitation and temperature (A) in Kirovsk station (67°38′N 33°49′E) and water discharge in the eastern part of the Baltic shield: (B)— Keret (No. 1), 18% of lakes, (C) — Teriberka (No. 11), 7% of lakes. Significant difference in hydrographs of rivers is due to the effect of lakes on water regime regulation.

Table 1
Morphometrical and hydrological characteristics of watersheds sampled by the Russian Hydrological Survey

No.	River	Area, km^2	River slope, m/km	Watershed mean elevation, m	Watershed mean slope, m/km	Lakes, %	Peatland, %	Forest, %	Tundra, %	Annual runoff, mm	Basic rocks, %
Karelian rivers											
1	Keret	2660	0.31	113	n/d	18	2	80	0	278	12
2	Gridina	468	1.3	79	20.4	15	9	76	0	320	0
3	Pongoma	1190	1.1	91	n/d	11	35	54	0	245	0
4	Letnyaya	505	1.1	108	23.8	7	13	80	0	352	86
5	Onigma	349	0.87	132	25.7	6	31	63	0	336	34
Kola rivers											
9	Ura	1020	3.3	180	n/d	10	15	40	n/d	487	0
10	Bolshaya Tuva	351	5.6	180	n/d	10	5	20	65	795	0
11	Teriberka	2020	2.1	220	66	7	10	5	75	535	0
12	Muchka	176	8	180	81	5	0	0	95	686	0
13	Varzina	1090	3.6	240	n/d	21	10	0	65	514	2
14	Drozdovka	408	4.7	220	57	20	5	5	70	618	0
15	Malaya Belaya	79.9	45	650	307	1	0	10	n/d	1381	0
16	West Litsa	720	1.8	200	55	6	20	70	0	466	0
17	Ponoy	3810	1	220	n/d	1	30	25	40	348	22
18	Umba	6470	1.4	210	n/d	13	30	50	7	435	13
19	Varzuga	7940	0.7	160	n/d	3	50	45	2	321	49

n/d – no data.

to 80–90 days. This flood contributes 60 to 80% of the annual water flux decreasing from the north to the south-west and increasing with basin size. The remaining part of the warm season, from July to October, accounts for 10–30% of the annual water flux. Deep groundwater from the crystalline basement contributes 15% of the annual water flux (Resources, 1970, 1972). Two typical hydrographs of rivers having different proportion of lake coverage are depicted in Fig. 2B and C. It can be seen that the presence of lakes leads to "smoother" discharge-time dependence; the winter low-water period and the spring flood are less pronounced for the watershed with higher proportion of lakes.

All rivers of the White Sea basin exhibit low suspended particulate matter (SPM) concentration; typical SPM values for the largest Karelian rivers (Kem and Keret) vary from 1 to 7 mg/L (Dolotov et al., 2002; Shevchenko et al., 2005) and for Kola rivers, similar values of SPM were reported by the Hydrological Survey: Varzuga No. 19, 5 mg/L; Umba No. 18, 1 mg/L; Ponoi No. 17, 4 mg/L (Resources, 1970).

2.2. Data and methods

2.2.1. Sources of information

This study is based on data obtained from systematic surveys by the Hydrometeorological State Committee of the former USSR Goskomgidromet and Roskomgidromet. These data are published in the annual issues of the State Water Cadastre (Hydrological Yearbooks of two studied regions: Karelia and Kola peninsula) and generalized in the "Resources of surface waters of the USSR, 1970 and 1972". Sixteen rivers draining Precambrian granitoid terrain were selected for detailed investigation; the location of these rivers is shown in Fig. 1. The watersheds vary in size from 5 to 7940 km^2 and the length of sampled rivers ranges from several kilometers to hundred kilometers The data from the Hydrological Survey include the water daily discharge and from 4 to 11 measurements per year of major cations, anions, silica and iron concentrations for each of 16 hydrological stations. In addition, measurements of dissolved element concentrations were performed on samples collected during our field expeditions in this region from 1996 to 2000.

2.2.2. Sampling and analysis

Two different sets of samples were used in this study; the first were collected and analyzed by the Russian Hydrological Survey in the 1960s and 70s and the second collected after 1996. Water sampling and analysis methods applied to the more recent field samples are similar to those used by the Russian Hydrological Survey (RHS, Semenov, 1977). Analyses of solutes performed by the Hydrological Survey are described elsewhere (Semenov, 1977; Gordeev and Sidorov, 1993; Zakharova et al., 2005; Pokrovsky et al., 2005). Water samples of the post 1996 period were filtered through 0.45 μm ash-free acetate cellulose, in contrast to the 0.8 μm paper filters used by the RHS, and stored in acid-cleaned 500 mL plastic bottles. Major dissolved components were analyzed in the laboratory within several days after sampling as described by Pokrovsky and Schott, 2002; Pokrovsky et al., 2005; Zakharova et al., 2005. Calcium and magnesium were measured by volumetric titration with EDTA and have an uncertainty of ±2% and a detection limit of 0.4 and 0.3 mg/L for Ca and Mg, respectively. Sodium and potassium were analyzed using flame atomic absorption with an uncertainty of ±10% and a detection limit of 0.05 mg/L, or calculated from the ionic charge balance according to the method of RHS. Si, Fe, and SO_4 were determined by spectrophotometry with molybdenum blue with detection limit of 3 µg/L, oxiquinoline with a detection limit is 5 µg/L, and $BaCl_2$ with a detection limit of 100 µg/L, respectively. The uncertainty in these Si, Fe, and SO_4 measurements are ±5%. Dissolved organic matter concentration was determined via permanganate oxidation (PO) in an acidic medium (Semenov, 1977) and expressed as gram of oxygen per liter. An average conversion coefficient of 1.05±0.05 was used to relate PO and Total Organic Carbon in the river water of the boreal tundra and taiga zone (Maltzeva et al., 1977).

The data of the Russian Hydrological Survey were supplemented with more recent samples and chemical analyses. The sampling was carried out on small rivers (No. 21–58, Fig. 1C and Table A1) of the central Kola Peninsula draining the Khibiny mountains in 1996 and 2000. Samples of the river Poria (No. 20) located in the southern Kola peninsula were collected in 2000. Three Karelian rivers (Chernaya (No. 6) and Upper and Low Ershov Creeks (No. 7 and 8)) were sampled in 1990. Additional data collected in 2000 and reported by Pokrovsky and Schott (2002) were also considered in this study. All samples were collected during the summer corresponding to baseflow conditions.

2.2.3. Flux estimation

The morphometrical characteristics of the rivers sampled by the Hydrometeorological Service were reported by (Koupriyanov, 1971). Proportion of different bedrocks and the lake coverage for each watershed were numerically estimated via MapInfo software using the geological maps of 1:500,000 for Karelia region and 1:1,000,000 for Kola region. The characteristic features of the rivers considered in this study are given in Table 1.

Daily discharge of all studied rivers were obtained from the stage-discharge rating curve established by the Hydrological Survey for each gauging station according to the International Standards (ISO, 1983) and published in the Hydrological Yearbooks (1961–1975).

The annual fluxes of i-th chemical element (R_i) were calculated for rivers sampled by the RHS using daily concentrations, daily discharges and the catchment area:

$$R_i = \Sigma(C_i \times Q)/A \quad (1)$$

where R_i is element flux, C_i is daily concentration of i-th element, Q is daily water discharge, and A represents the surface area of the catchment. These fluxes are normalized to the total watershed surface area. Lakes and peatlands, however, can occupy up to 50% of the watershed area. Therefore, the chemical weathering fluxes were also normalized both to non-lake, non-peatland surface area of the catchment.

For rivers with highly variable hydrology, such as those considered in this study, Eq. (1) is more accurate than other methods commonly used for estimating the mean annual discharges and element fluxes in Siberian Rivers (Gordeev and Sidorov, 1993; Gordeev et al., 1996; Pokrovsky et al., 2005; Zakharova et al., 2005). The daily discharge and the watershed areas were taken from the annual issues of the State Water Cadastre, whereas the daily element concentrations were available only during main hydrological events. The first method of daily C_i estimation was linear interpolation between the measured concentrations available several times per year. Such an interpolation works well for dry periods, when both the discharge and the element concentration are quasi-constant (Zaslavskaya and Tikhotskaya, 1978). The second method of C_i estimation for each day of the year implies a correlation between the daily measured element concentrations and the daily discharge (Q) recorded over the full period of observation. For this, all data of chemical analysis from 1961 to 1975 were used to generate the coefficients k and n in the Equation

$$C_i = k \times Q^n \quad (2)$$

where C_i is the measured concentration of the i-th element for a given day of the year, k and n are the empirical constants for each river. The typical difference of the annual flux estimates obtained using linear interpolation and those obtained using Eq. (2) for C_i estimation is commonly 5 to 11%, but it reaches 20% for some years.

3. Results

3.1. Atmospheric input

Due to the proximity of the study area to the sea, atmospheric inputs to riverine fluxes are significant. Original data on atmospheric precipitation composition and atmospheric fluxes of elements were provided by Savenko et al. (unpublished) and taken from Reimann et al. (1997a,b). These data are compiled in Table A2 of the electronic supplement. They stem from annual and year-round observations from 8 meteorological stations and 8 catchments (nos. I–VIII and IX–XVI, on the map, Fig. 1). The atmospheric precipitation have [Na+K]/[Cl] and [Mg]/[Cl] ratios close to those in seawater. This precipitation is also enriched in Ca compared to the seawater suggesting some influence of terrestrial aerosols (Savenko, 1990, see Fig. 3A–C). Sea salt is the main source of alkalis (Na and K) for most rivers near the coastal zone. Despite high dispersion, the [Na+K]/[Cl] ratio in the river water is often close to that in the seawater as illustrated in Fig. 3D–F.

The composition of the rivers Bolshaya Tuva (No. 10), West Litsa (No. 16), Ura (No. 9) exhibit some anthropogenic influence as they are located within 50 km of Nickel and Zapolyarniy smelters and Murmansk city. Therefore, atmospheric correction was made on samples from these rivers by subtracting element atmospheric fluxes measured at meteorological stations located in the industrial zone (Apatity station and Zapolyarniy catchment). For rivers Muchka (No. 12), Drozdovka (No. 14), Teriberka (No. 11) and Varzina (No. 13) located in the pristine region and strongly affected by the sea salt input, the atmospheric correction was made by normalizing chlorine concentration according to methods reported by Négrel et al. (1993) and Oliva et al. (2003). For rivers Ponoy (No. 17), Varzuga (No. 19), Umba (No. 18), Keret (No. 1), Pongoma (No. 3), Gridina (No. 2), Onigma (No. 5) and Letnyaya (No. 4), the atmospheric input of elements was estimated from the attenuation gradient calculated as a function of the distance from the seashore.

3.2. Chemical composition of the river water

Concentrations of major elements vary by a factor of 2 to 15 over the annual cycle. Examples of discharge and element concentration variations during several years are shown in Fig. A1 and A2 of the electronic supplement. For most rivers, the total dissolved solids (TDS = Ca + Mg + Na + K + SiO_2 + Fe) range from 13 to 33 mg/L. Note that this definition of TDS is different from that commonly used as it does not include anions. Mean arithmetic concentrations of solutes in rivers studied in this work are given in Table 2. These concentrations are comparable with independent measurements for this region (Maksimova, 1967; Pokrovsky and Schott, 2002) and similar to those reported for organic-rich tropical (Dupré et al.,

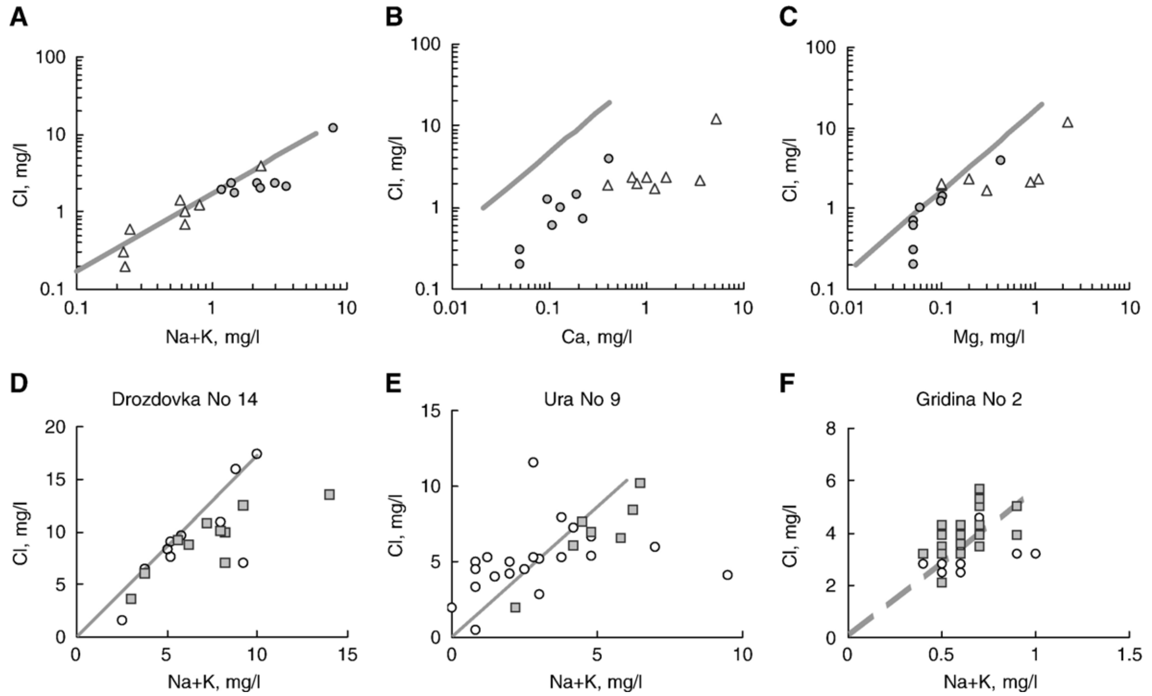

Fig. 3. (A–C) Chloride concentration in the atmospheric precipitates as a function of Na+K (A), Ca (B) and Mg (C) concentrations. Circles represent the snow data from de Caritat et al. (1998); triangles represent total precipitates from Savenko et al. (in preparation, unpublished), grey line corresponds to seawater dilution assuming conservative behaviour. (D–F) Chloride concentration in selected rivers as a function of Na+K concentrations. Circles represent high water periods, squares represent low-water periods and the grey line corresponds to seawater relationship.

Table 2
Mean average and standard deviation of annual concentrations of major elements in river waters

No.	River	Years of the sampling	No. of analysis	Ca, mg/L	Mg, mg/L	Na+K, mg/L	Si, mg/L	Fe, mg/L	TDSc, mg/L	TDS, mg/L	HCO_3, mg/L	SO_4, mg/L	Cl, mg/L	PO, mg/L	Miner, mg/L
1	Keret	1961–1963, 1972–1975	49	2.19±0.31	0.85±0.23	1.52±0.77	1.73±0.61	0.24±0.20	4.57±0.85	8.37±1.66	8.5±1.81	2.45±0.52	1.82±0.39	11.0±4.24	17.3±2.90
2	Gridina	1961–1963, 1972–1975	53	1.55±0.28	0.61±0.14	2.02±0.84	2.15±0.78	0.24±0.16	4.19±0.96	9.10±1.94	3.29±1.91	2.61±0.83	3.60±0.71	16.4±4.56	13.7±3.22
3	Pongoma	1961–1963, 1972–1975	46	1.6±0.50	0.57±0.24	2.06±1.03	2.06±1.06	0.43±0.21	4.22±1.43	9.05±2.75	4.15±3.50	2.63±1.01	3.07±0.79	22.2±7.64	13.9±5.12
4	Letnyaya	1961–1963, 1972–1975	38	5.38±1.95	1.34±0.50	1.96±1.01	2.11±0.72	0.22±0.22	8.69±3.10	13.5±3.73	19.9±8.80	2.80±0.86	2.51±0.84	10.3±5.23	34.0±12.4
5	Onigma	1961–1963, 1972–1975	43	2.88±1.00	0.95±0.37	1.51±1.00	2.54±1.06	0.49±0.28	5.36±1.98	11.2±3.43	10.3±6.01	2.88±1.21	1.90±0.93	20.2±5.67	20.4±7.88
9	Ura	1965–1968	28	2.07±0.54	1.01±0.44	3.32±2.22	1.55±0.84	0.22±0.21	6.41±2.36	9.95±3.11	6.84±3.71	3.06±1.01	5.38±2.38	6.94±2.53	21.7±6.98
10	Bolshaya Tuva	1965	8	2.27±0.76	1.18±0.48	3.33±2.18	0.78±0.70	0.14±0.08	6.8±2.55	8.62±3.55	6.17±4.66	2.83±0.56	7.02±2.07	5.38±0.50	22.8±8.46
11	Teriberka	1961–1968	52	1.69±0.58	1.14±0.76	5.35±3.80	1.31±0.81	0.15±0.17	8.19±4.29	11.1±4.90	7.11±4.71	2.99±2.08	7.35±3.07	6.42±3.02	25.5±10.4
12	Mouchka	1961–1964	22	1.69±0.65	1.17±0.40	8.66±5.23	1.51±0.55	0.12±0.11	11.5±5.28	14.9±5.28	11.4±8.42	2.55±0.93	9.43±3.39	5.65±2.60	34.4±13.9
13	Varzina	1962–1965	21	1.23±0.34	0.94±0.18	6.69±4.91	0.81±0.36	0.10±0.06	8.87±4.80	10.4±4.55	10.2±8.23	1.91±0.55	6.56±1.96	4.95±1.47	26.9±11.4
14	Drozdovka	1962–1964; 1967–1968	20	1.6±0.43	0.86±0.30	6.84±2.77	1.03±0.45	0.12±0.09	9.31±2.98	11.4±2.93	6.93±3.81	2.64±0.98	9.28±3.76	4.7±1.37	28.1±8.39
15	Malaya Belaya	1961–1964	27	0.62±0.27	0.37±0.20	5.31±2.12	3.23±1.69	0.10±0.10	6.29±2.22	13.2±4.32	10.4±3.87	2.05±1.81	2.15±1.29	3.98±3.22	20.6±7.05
16	West Litza	1962–1964	20	1.9±0.65	0.96±0.32	1.76±0.70	2.25±0.60	0.27±0.10	4.62±1.13	9.71±2.15	6.84±3.37	1.92±0.55	3.64±0.71	7.42±1.38	17.0±4.64
17	Ponoy	1961–1962, 1964–1968	44	2.41±1.13	0.78±0.40	2.62±1.57	2.55±1.42	0.66±0.35	5.70±2.62	11.8±5.01	10.3±6.71	1.84±1.66	2.92±1.02	8.26±3.03	20.8±9.64
18	Umba	1961–1968	68	2.65±0.55	0.98±0.50	5.22±3.60	1.76±0.98	0.16±0.10	8.83±3.72	12.7±3.68	17.1±8.17	2.71±1.56	3.33±1.96	7.68±3.61	31.7±12.4
19	Varzuga	1961–1963, 1965	26	4.34±3.20	1.50±0.80	3.8±3.74	2.70±1.74	0.69±0.33	9.19±7.22	15.4±10.0	18.1±17.5	2.32±1.14	4.81±2.85	12.4±4.69	33.6±27.4

1996; Viers et al., 1997) and boreal (Millot et al., 2002) rivers draining igneous silicate rocks.

On a seasonal scale, chemical composition variations are linked to the hydrology. The highest salt concentration occurs during the winter period, when the rivers are fed exclusively by deep ground waters of the crystalline basement. The lowest winter salt concentrations of 25–30 mg/L are typical for rivers draining the western coast of White Sea where the wetlands are abundant and the contact between the groundwater and the rocks is very restricted due to the shallow depth of the river valley. The highest winter TDS concentration (~100 mg/L) is found at the northern coast of the White Sea. Sodium and calcium are the main cations in most studied rivers. Their concentrations range from 4 mg/L for Karelian rivers to 10 mg/L for Kola Peninsula rivers. Chloride and bicarbonate dominate the anionic composition, especially in the coastal rivers of the western Kola region (West Litza No. 16, Ura No. 9, Bolshaya Tuva No. 10) and for the Gridina river (No. 2) in Karelia.

The lowest TDS (4–20 mg/L or 125–500 μmol/L) are observed during the spring flood, when the rivers are fed by thawed snow. During this period, the coastal rivers of the Barents Sea (West Litza No. 16, Ura No. 9, Bolshaya Tuva No. 10, Mouchka No. 12, Teriberka No. 11, Varzina No. 13, Drozdovka No. 14) are NaCl-rich, with 3 to 9 mg/L of Cl, whereas in rivers of the inner part of the Kola peninsula (Malaya Belaya No. 15 and Ponoy No. 17) and in some rivers of the White Sea (Onigma No. 5, Letnyaya No. 4, Umba No. 18), bicarbonate becomes important with concentrations ranging from 5 to 15 mg/L, compared with that of chloride (1–3.5 mg/L). In all Kola and Karelia rivers (except Onigma No. 5 and Letnyaya No. 4), sodium and potassium dominate the cationic charge during the flood period with [Na+K] ranging from 4 mg/L to 1 mg/L, respectively.

The chemical composition of the river water in summer is controlled by the precipitation regime and results from the mixing of rain, subsurface (soil) waters, and groundwaters. Moreover, as many rivers flow through the lakes and swamps, they are fed by the waters accumulated in these reservoirs during the preceding spring flood. The summer dry period waters are several times more diluted than the winter low-level waters, with total salts concentration of around 15–20 mg/L.

3.3. Dissolved element fluxes of rivers

The average annual total dissolved solid cation flux (TDSc = Ca + Mg + Na + K) normalized to the lake and peatland free surface area and corrected for atmospheric precipitation ranges from 0.5–2.9 t/km^2/y for the Karelian rivers to 2.1–5.6 t/km^2/y for the Kola peninsula rivers (see Table 3). The total dissolved solid flux (TDS = Ca^+ + Mg^+ + Na^+ + K^+ + SiO_2+Fe) ranges from 2.1–5.0 t/km^2/y for the Karelia rivers to 4.0–8.8 t/km^2/y for the Kola peninsula rivers. Sodium and potassium dominate the cationic flux in the Kola rivers, accounting for ~55%

Table 3
River, atmospheric, and groundwater fluxes (t/km^2/y) of elements in studied region

No.	River	River fluxes corrected for atmospheric input							Atmospheric fluxes			Ground water fluxes			
		Ca	Mg	Na+K	TDSc	TDS	SiO_2	PO	Ca	Mg	Na+K	Ca	Mg	Na+K	SiO_2
1	Keret	0.49/0.40	0.18/0.14	0.08/0.06	0.75/0.60	2.14/1.71	1.38/1.11	3.6/2.86	0.23	0.10	0.39	0.13	0.05	0.05	0.21
2	Gridina	0.26/0.20	0.09/0.07	0.16/0.12	0.51/0.39	2.5/1.90	1.99/1.51	N.D./ N.D.	0.29	0.13	0.48	0.05	0.02	0.07	0.12
3	Pongoma	0.34/0.18	0.07/0.04	0.15/0.08	0.56/0.30	2.78/1.50	2.22/1.20	10.4/5.63	0.24	0.10	0.41	0.06	0.02	0.10	0.17
4	Letnyaya	1.93/1.54	0.44/0.35	0.53/0.42	2.89/2.31	4.96/3.97	2.07/1.65	4.3/3.45	0.08	0.04	0.11	0.11	0.03	0.04	0.09
5	Onigma	0.97/0.61	0.31/0.19	0.41/0.26	1.69/1.06	4.07/2.56	2.38/1.50	8.9/5.59	0.08	0.04	0.11	0.20	0.08	0.11	0.31
9	Ura	1.17/0.67	0.62/0.35	1.53/1.14	1.85/2.16	4.06/3.81	2.21/1.66	5.00/3.74	0.32	0.15	0.53	0.22	0.10	0.48	0.38
10	Bolshaya Tuva	1.79/1.52	0.95/0.81	2.09/1.78	4.84/4.11	5.87/4.99	1.03/0.88	4.9/4.17	0.12	0.03	0.52	0.34	0.16	0.48	0.47
11	Teriberka	0.92/0.76	0.4/0.33	0.81/0.67	2.13/1.77	3.92/3.25	1.79/1.49	4.1/3.38	0.07	0.22	2.08	0.13	0.07	0.24	0.24
12	Mouchka	0.92/0.87	0.38/0.36	2.4/2.28	3.7/3.52	5.98/5.68	2.28/2.16	4.1/3.90	0.13	0.38	3.64	0.09	0.06	0.29	0.14
13	Varzina	0.91/0.62	0.38/0.26	2.82/1.95	4.11/2.84	5.38/3.71	1.27/0.87	4.00/2.73	0.07	0.21	1.95	0.12	0.08	0.37	0.12
14	Drozdovka	1.05/0.79	0.29/0.22	1.15/0.86	2.48/1.86	4.35/3.26	1.86/1.40	3.8/2.85	0.10	0.29	2.73	0.16	0.08	0.65	0.21
15	Malaya Belaya	0.56/0.56	0.39/0.39	3.01/2.98	3.96/3.93	7.00/6.93	3.04/3.00	4.6/4.53	0.12	0.03	0.52	0.22	0.14	2.09	1.63
16	West Litsa	1.09/0.80	0.53/0.39	0.81/0.60	2.43/1.80	5.32/3.93	2.89/2.14	4.8/3.53	0.08	0.06	0.24	0.27	0.13	0.15	0.48
17	Ponoy	0.88/0.61	0.33/0.23	1.07/0.74	2.28/1.58	5.01/3.45	2.72/1.88	4.4/3.03	0.15	0.03	0.24	0.17	0.05	0.14	0.38
18	Umba	1.74/0.99	0.64/0.37	3.24/1.85	5.62/3.21	8.82/5.03	5.83/3.32	13.5/7.69	0.15	0.03	0.24	0.27	0.10	0.36	0.32
19	Varzuga	2.3/1.08	0.9/0.42	1.42/0.67	4.61/2.17	8.34/3.92	3.72/1.75	10.1/4.75	0.15	0.03	0.24	0.38	0.10	0.32	0.40

The fluxes normalized to the "solid" (lake-free) part of the catchment and to the total area of the watershed are presented in the numerator, and in the denominator, respectively. Atmospheric and groundwater fluxes are normalized to the total area.

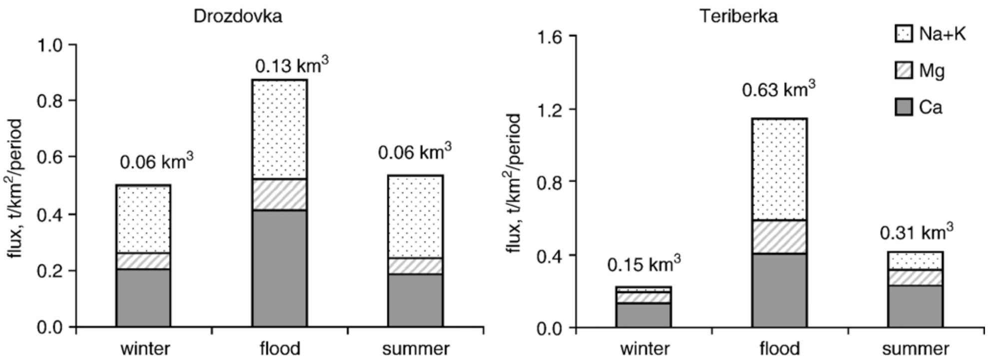

Fig. 4. Seasonal distribution of cation fluxes and water flow (in km^3) for Drozdovka river (20% of lakes) and Teriberka (7% of lakes). All fluxes are corrected for the atmospheric precipitation. The values represent mean over 1962–1968 years estimation for each hydrological period. Three major periods are defined by the hydrograph stage: "winter" is the ice period, "flood" is the spring time of dominating thawed snow in the river channel, and "summer" is the period of summer and autumn low-water that also comprises rain storms.

of TDSc. Ca provides 55 % of the cationic flux in the Karelian rivers. In both regions, almost a half of the total annual cation flux is released during the spring flood in May–June while the low-water summer and winter periods account for 25–30% of this flux (see Fig. 4). The presence of lakes decreases the relative contribution of the spring flood to the annual fluxes as it is seen by comparing the data for the Drozdovka (No. 14) and Teriberka (No. 11) rivers given in Fig. 4.

In accord with previous studies of granitic weathering rates (White and Blum, 1995; Gaillardet et al., 2003; Oliva et al., 2003; Zakharova et al., 2005), the rivers of Karelia and the Kola peninsula, which drains mostly granites and gneisses, exhibit a positive correlation between chemical denudation rate and water runoff (see Fig. 5A). The mean annual total dissolved cations concentration (TDSc) also exhibits a strong positive linear relationship with water runoff (see Fig. 5B).

3.4. Underground fluxes

To distinguish between cation fluxes derived from surface and soil waters and that derived from ground waters for Kola and Karelian rivers, we postulated that the input of deep groundwater originating from the crystalline basement is constant throughout the year. Furthermore, we accepted that (1) the minimal winter discharge corresponds to the deep groundwater discharge, and (2) the deep groundwater chemical composition can be approximated by the river water composition measured during the baseflow winter period. Deep groundwater fluxes listed in Table 3 represent the minimum estimates of element input to the river waters from underground rock weathering. A stack diagram showing the relative

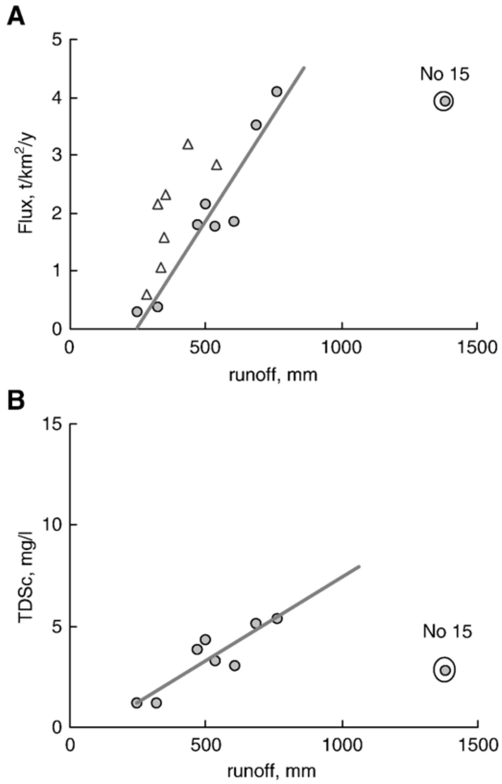

Fig. 5. Dependence of TDSc flux on mean annual runoff for granitic (circles) and basaltic (triangles) rivers (A) and the relationship between the mean weighted concentration of cations and water runoff for pure granitic rivers of Kola and Karelia (B). The line represents the best fit for granitic watersheds, excluding mountain river Malaya Belaya (No. 15, encircled). This river is excluded because it is the only mountainous river having high slope watershed and thus very low-water residence time in soil. Due to its overall elevation, important weathering-controlling factors – the vegetation coverage, mean annual temperature and the duration of unfrozen period – for this river are much lower than those for other "granitic" rivers used to construct this diagram.

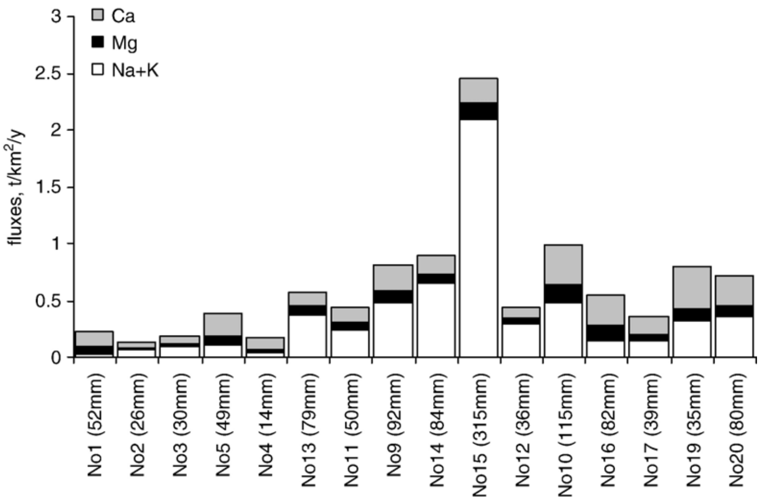

Fig. 6. Groundwater fluxes of cations for different rivers. The groundwater runoff is given in the parentheses.

contribution of each cation to deep groundwater fluxes is depicted in Fig. 6. A high deep groundwater cationic flux is observed in the Malaya Belaya River (No. 15). It is caused by elevated groundwater runoff, which stems from high atmospheric precipitation. This river is located in mountainous terrain on the western windward side of the Khibiny massif. In addition to the climatic effects, the high fissuring of the local alkaline intrusive rocks may be also responsible for the high deep groundwater flux.

In rivers draining mainly granitic terrains, Na+K dominate among the cations fluxes. In basalt-bearing watersheds (rivers Letnyaya No. 4, Onigma No. 5, Varzuga No. 19), proportion of Ca in the groundwater flux is the highest. The overall average contribution of the deep groundwater input is the total, atmospheric-corrected riverine fluxes to 26, 29, 44 and 20% for Ca, Mg, Na+K, and SiO_2, respectively. This is somewhat higher than estimates of deep groundwater discharge into Northern Sweden rivers (Land et al., 2000).

4. Discussion

4.1. Sources of dissolved elements in river waters: atmosphere, rocks, underground waters, soils and plant litter

The chemical composition of the river water is controlled by the hydrological regime and most likely results from the mixing of rain, snow melting, and groundwater inputs. This implies insignificant contributions to river water chemistry of i) SPM and the bed sediments, ii) precipitation of carbonate or silicate minerals in the river channel, and iii) biological uptake of petrogenic elements in the river channel by peryphyton, phytoplankton or macrophytes.

4.1.1. Influence of bedrock on river compositions during base flow periods

The composition of groundwater is directly linked to that of the bedrock and thus it can be used to trace inorganic water/rock interaction. Groundwaters from the Kola peninsula exhibit relative cation concentrations that depend on the major lithology of the watershed; ultra-mafic, basic rocks, and nypheline syenites exhibit the following relative cation concentrations: Mg>Ca>Na>K, Ca>Mg>Na>K and Na>K>Ca>Mg, respectively, (Antonov, 1964). River water samples collected during the lowest discharge periods (ice-covered period and, sometimes, the middle of the summer) provide the best characterization of rock-related solute sources because the rivers are fed primarily by groundwater during these periods. This is illustrated in cationic ternary and binary diagrams of rock and the river water compositions during the winter and summer low-water level periods shown in Fig. 7. It can be seen that waters of “basaltic” rivers are shifted towards the Na+K apex because they are enriched in Ca vs. Mg compared to the bedrock. This confirms relative mobility of different cations during chemical weathering (Na, K>Ca>Mg) similar to that deduced in earlier studies (c.f. Polynov, 1944). Indeed, mineralogical studies in similar region (Northern Sweden) indicate that all dissolved Na is derived from plagioclase which is altered to Ca-beidellite, and two third of the dissolved K is derived from biotite which is altered to vermiculate and one third is derived from K-feldspar which is altered to kaolinite, and that plagioclase, biotite and amphibole are the most important minerals with respect to weathering of till (Land et al., 1999). The river water composition during the winter period reflects the watershed bedrock composition: 1) Na, K, Ca-rich granites for Teriberka No. 11, Mouchka No. 12, Bolshaya Tuva No. 10, Ura No. 9, Drozdovka No. 14, Varzina No. 13, Gridina No. 2, Pongoma No. 3; 2) Na, Ca, Mg-rich granites + basalts (Ponoy No. 17,

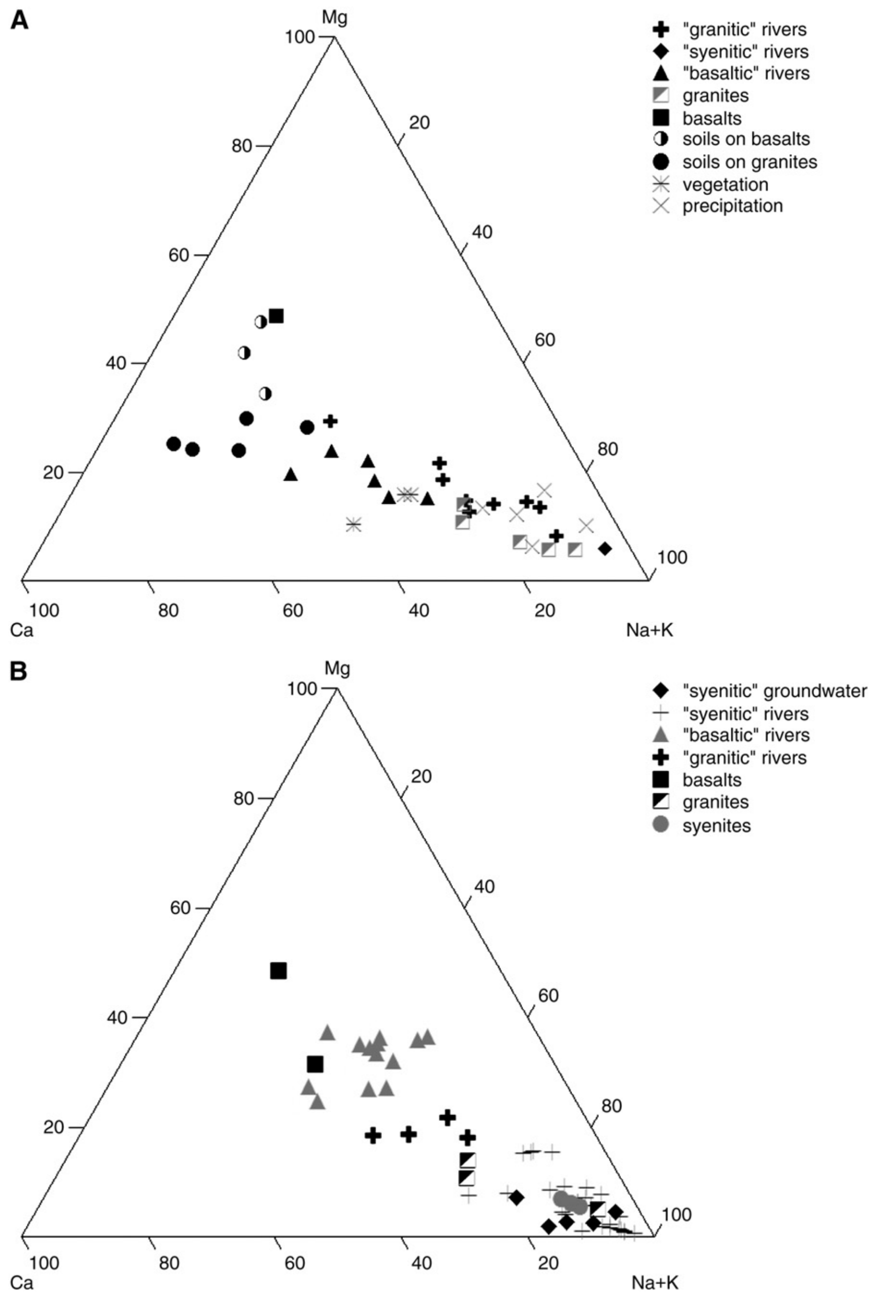

Fig. 7. Cation molar ternary diagram of low-discharge-period river water, rocks, vegetation and upper soil horizon of basalts and granite composition. (A) data of Hydrometeorological Service collected in winter period, (B) measurements of this study pertinent to the low-water summer period (rivers are listed in Table 1). The rock composition is taken from Mintz et al., 1996; the soil composition is from Reimann et al. (1997a), the atmospheric precipitation is from Reimann et al. (1997b), and the vegetation data are from Reimann and Melezhik (2001). Molar ratio of Ca/Na + K vs. Mg/Na + K concentrations. (C) data of Hydromoteorological Service collected in winter period. (D) Data of this study collected during the low-water summer period.

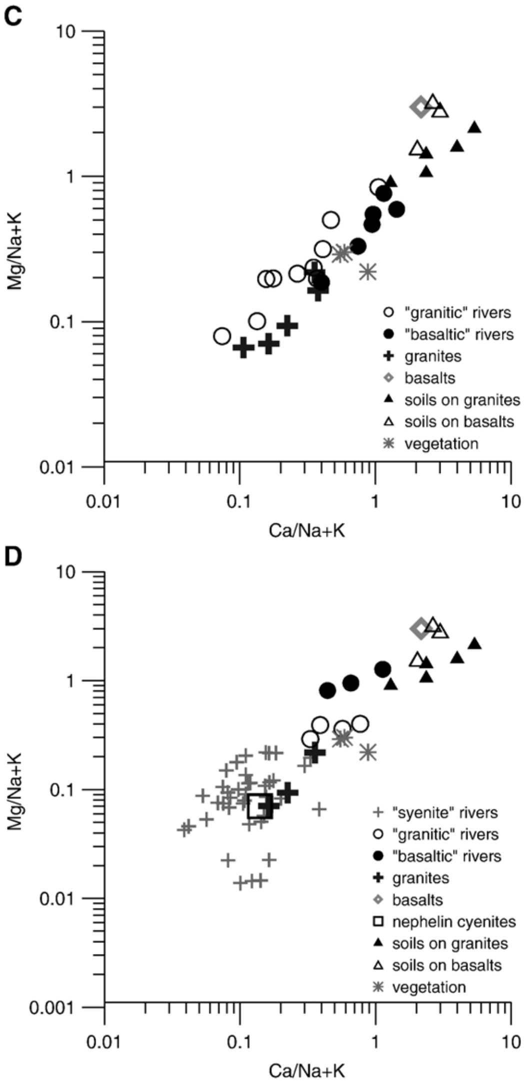

Fig. 7 (*continued*).

Varzuga No. 19, Onigma No. 5, Letnyaya No. 4, Keret No. 1, Umba No. 18, Poria No. 20 and rivers of Monchetundra (Vite No. 58, Moncha No. 57) and 3) Na, K-rich syenite for Malaya Belaya (No. 15) and other rivers of Khibiny massif (Nos. 21–55). The relative proportion of Ca+Mg vs. Na+K in rivers during low-discharge periods decreases in the order “basaltic”–“granitic”–“syenitic” rivers (see Fig. 7B), reflecting the chemical composition of rocks they drain.

Normally, the higher the basic rock fraction of the watershed, the higher the relative content of Ca and Mg in the river water during the winter. However, there are several exceptions. Although the Umba river (No. 15) watershed is composed of only 13% basic rocks, sodium and potassium constitute over 50% of the dissolved components during the winter. This river originates from the Umba Lake situated between two intrusive nypheline syenite massifs, strongly enriched in alkalis. The combined effect of alkaline and basic rocks gives this river an intermediate composition. Another example is the West Litza river (No. 13). According to the geological map, this river drains gneisses and passes through several potassium granites intrusives. The ternary diagram of this river, however, shows its composition to be closer to basalts than to granites (see Fig. 7A). A possible reason for this observation is the proximity of the upper reaches of this river to the volcanogenic Pechenga-Varzuga basaltic belt (Sharkov and Smolkin, 1997). The apparent “basaltic” chemical signature of this river becomes more pronounced during the winter, when the river is fed by the groundwaters from deeper aquifers probably connected to the adjacent basaltic territory.

4.1.2. The influence of upper soil horizons and plant litter during high discharge periods

The soil pore and river water compositions during the highest discharge periods, corresponding to the snowmelt and summer rainfalls, are similar to that of the upper soil horizons (podzol and peat soil) and plant litter. The shift towards soil horizon and plant litter compositions from winter to spring is evident in the ternary diagram shown in Fig. 8 for the Ura (No. 9) and Gridina (No. 2) rivers, which have the highest proportion of forest in their watersheds. This probably reflects a significant contribution of Ca and Mg release from degrading vegetation litter and subsurface organic-rich soil horizons to river waters. Note that the rivers become rich in dissolved organic carbon during high discharge (wet) periods (see Fig. 9). This is likely due to DOC washing out from plant debris and litter degradation products in the upper soil horizons. A similar process was reported for other European (Land and Ohlander, 2000; Ingri et al., 2005) and Siberian (Pokrovsky et al., 2005) watersheds. The concentration of dissolved organic carbon in streams draining forested catchments have been found to rise significantly during snowmelt and heavy rainstorms, consistent with dissolved organic matter flushing from the forest floor (Easthouse et al., 1992; Kaiser and Guggenberger, 2005). Results of the present study imply that in addition to DOC, the major dissolved cations in rivers originate partially from plant litter. Bearing in mind that a high proportion of the water discharge and TDS transport occurs during the spring flood, the contribution of the litter to the river water composition on the annual scale becomes significant (see Section 4.3).

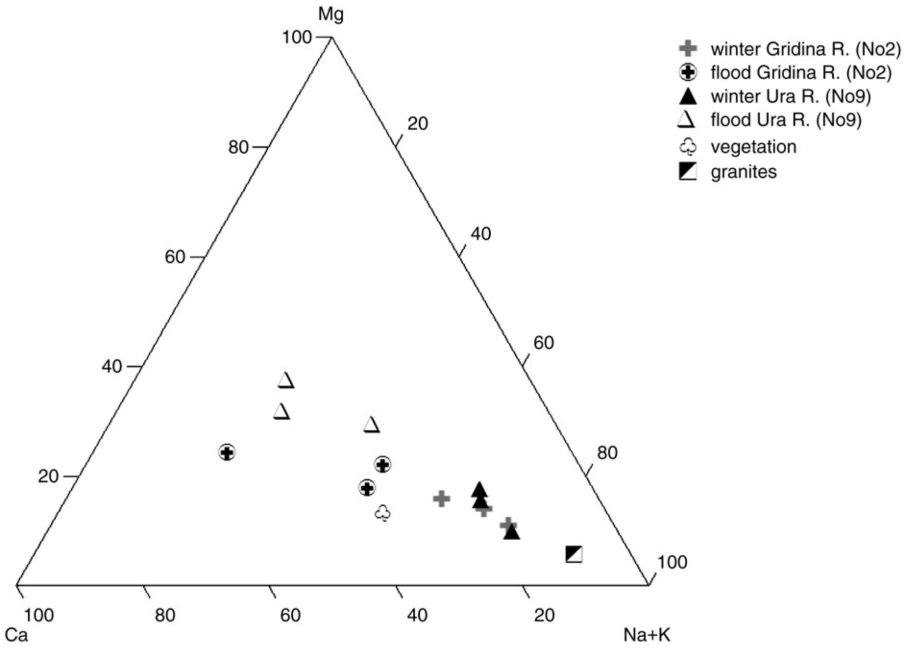

Fig. 8. Ternary molar cation diagram for selected rivers of Kola and Karelia during the low-discharge winter and the spring flood for different years.

4.2. Factors controlling the chemical erosion intensity

4.2.1. Influence of bedrock composition on chemical fluxes

The bedrock composition is one of the major factors controlling chemical denudation rate. The presence of trace quantities of highly soluble reactive minerals can strongly influence the intensity of chemical weathering and the fluxes of major ions (i.e., carbonates, Anderson et al., 1997; White et al., 1999, 2005; Ca-plagioclases, Oliva et al., 2004; apatite, Godderis et al., 2006). The presence of trace calcite in granites can be significant (White et al., 1999, 2005). However, we have not observed significant enrichment of Ca compared to Mg of rivers during base flow winter periods (Fig. 7C), compared to summer periods (Fig. 7D), although both the rock/water ratio and calcite solubility are higher in winter. As a result, if trace calcite affects river water chemistry, the slope of Mg(Na+K) vs. Ca/(Na+K) plots would be lower in winter compared to summer. This is not seen in Fig. 7A–B.

The presence of basic rocks in the watershed increases the total cationic flux. This is evident for Karelian rivers that drain granito-gneisses and basic intrusions of the Belomorian belt. These rivers (Keret No. 1, Gridina No. 2, Pongoma No. 3, Onigma No. 5 and Letnyaya No. 6) have similar water runoff, watershed vegetation coverage and soil composition, and they exhibit a good correlation between the proportion of basic rocks and the chemical

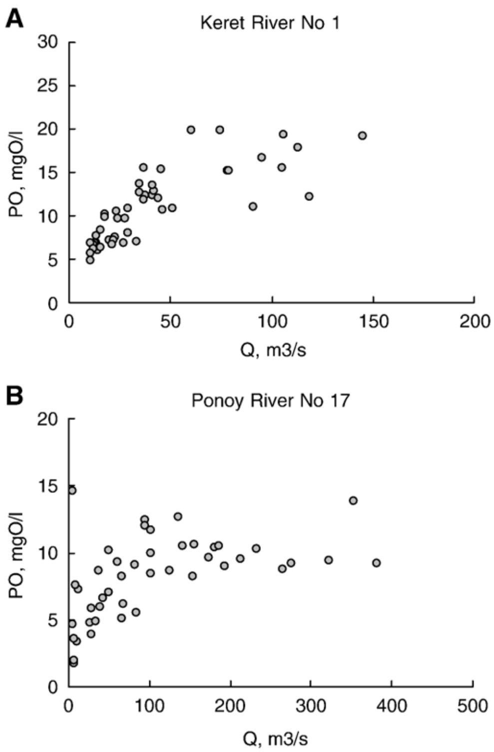

Fig. 9. Relation between water discharge and organic matter content expressed as permanganate oxidation for Keret river, No. 1 (A) and Ponoy river, No. 17 (B).

denudation rate (TDS and TDSc) as can be seen in Fig. 10. This correlation allows estimation of pure "granitic" and pure "basaltic" rivers chemical denudation rates in the Baltic shield: TDS = 1.6 t/km^2/y, TDSc = 0.33 t/km^2/y and TDS = 3.6 t/km^2/y, TDSc = 2.3 t/km^2/y, respectively. These granite weathering rates are in agreement with those proposed for other boreal regions with similar runoff. For example, Millot et al. (2002) reported that the chemical denudation rate (TDSc) of Canadan granites are 1 t/km^2/y; Zakharova et al., 2005 reported that the TDSc of Aldan Craton granites are 2–2.5 t/km^2/y. Oliva et al. (2003) estimated TDSc and TDS of 1.4 ± 0.6 and 3.3 ± 1.1 t/km^2/y for "granitic" regions with mean annual temperature less than 5 °C and runoff of 200–400 mm/y. Karelian TDSc flux is somewhat higher than that of the Canadian shield and lower than that of the Aldan Craton for similar values of river runoff (Fig. 11). The silica fluxes in these boreal regions are similar for runoff values up to 500 mm/y. The basalt weathering rate in the boreal zone at 200–400 mm/y runoff was reported to be TDSc = 4.5–5.5 t/km^2/y for large monolithological watersheds of Central Siberian basalts (Pokrovsky et al., 2005) which is twice higher than the values for the Karelia basalts determined in this study. Note, however, that abundant deciduous larch trees of Central Siberia are likely to enhance cation flux due to the contribution of plant litter degradation (see Section 4.3). The dominant coniferous vegetation of Karelia region is likely to contribute less to element mobilization from degrading plant litter. Overall, our estimates demonstrate much higher weathering rates of basalts compared to granites in boreal zone in accord with previous studies of other world regions and comparative experimental studies (Wolff-Boenisch et al., 2006).

4.2.2. Influence of dissolved organic matter (DOM)

Over the past decade, dissolved organic carbon has been widely reported as a potentially important catalyst of silicate rocks weathering (Drever, 1994; Viers et al., 1997; Oliva et al., 1999; Millot et al., 2002, 2003; Zakharova et al., 2005). Experimentally, a strong effect of organic ligands on feldspar and natural glass dissolution rates has been also reported (Drever and Stillings, 1997; Oelkers and Schott, 1998; Oelkers and Gislason, 2001). In contrast, there appears to be little effect of dissolved organic matter on Ca- and Mg-bearing silicate and basic rocks dissolution rates at conditions similar to those of natural rhizosphere environments (Pokrovsky et al., 2004; Golubev et al., 2006; Golubev and Pokrovsky, 2006). For this reason, and also due to the low abundance of basalt-dominated aquifers in Karelia and Kola peninsula, the rivers having basalts in their watersheds (i.e., Letnyaya No. 4, Onigma No. 5, Keret No. 1, Umba No. 18, Varzuga No. 19, Ponoy No. 17) were excluded from this discussion of the effect of organic matter on weathering rates.

Most of Karelian "granitic" rivers, flowing through northern taiga zone, exhibit higher organic matter content than the Kola rivers, whose watersheds are covered essentially by tundra and forest-tundra vegetation. Widely distributed peatlands, especially in the riparian zone, are the main source of organic matter in the river water which contains 15–25 mg/L of dissolved organic carbon (Pokrovsky and Schott, 2002). Indeed, as can be seen in Fig. 12, the higher the proportion of peatlands and the forest coverage in the watershed, the higher the flux and the concentration of dissolved organic matter. Karelian watersheds with >50% of forest coverage have organic matter fluxes twice higher than that of the low biomass tundra landscapes of Kola peninsula. Similar observations were reported by Smedberg et al. (2006) in their study of two small watersheds in Northern Sweden. In addition, particulate organic carbon (POC) concentration in White Sea basin rivers is ten times lower than that of the DOC (Shevchenko et al., 2005; Lukashin et al., 2003).

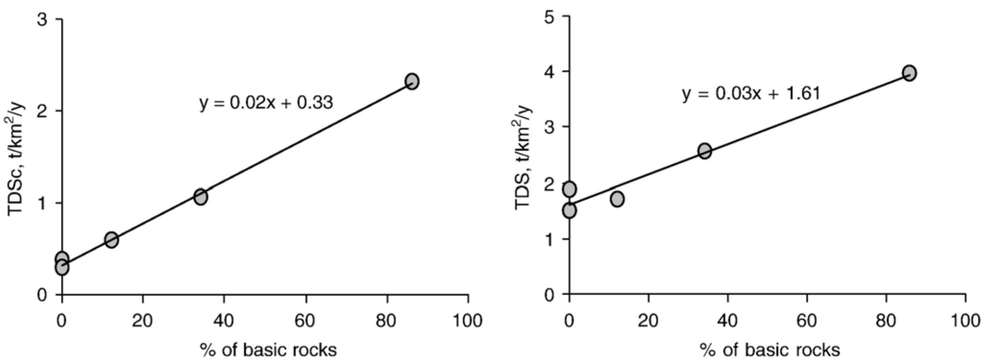

Fig. 10. Dependence of TDSc and TDS fluxes on the proportion of basic rocks in the watershed for Karelian rivers (runoff = 380 ± 60 mm/y).

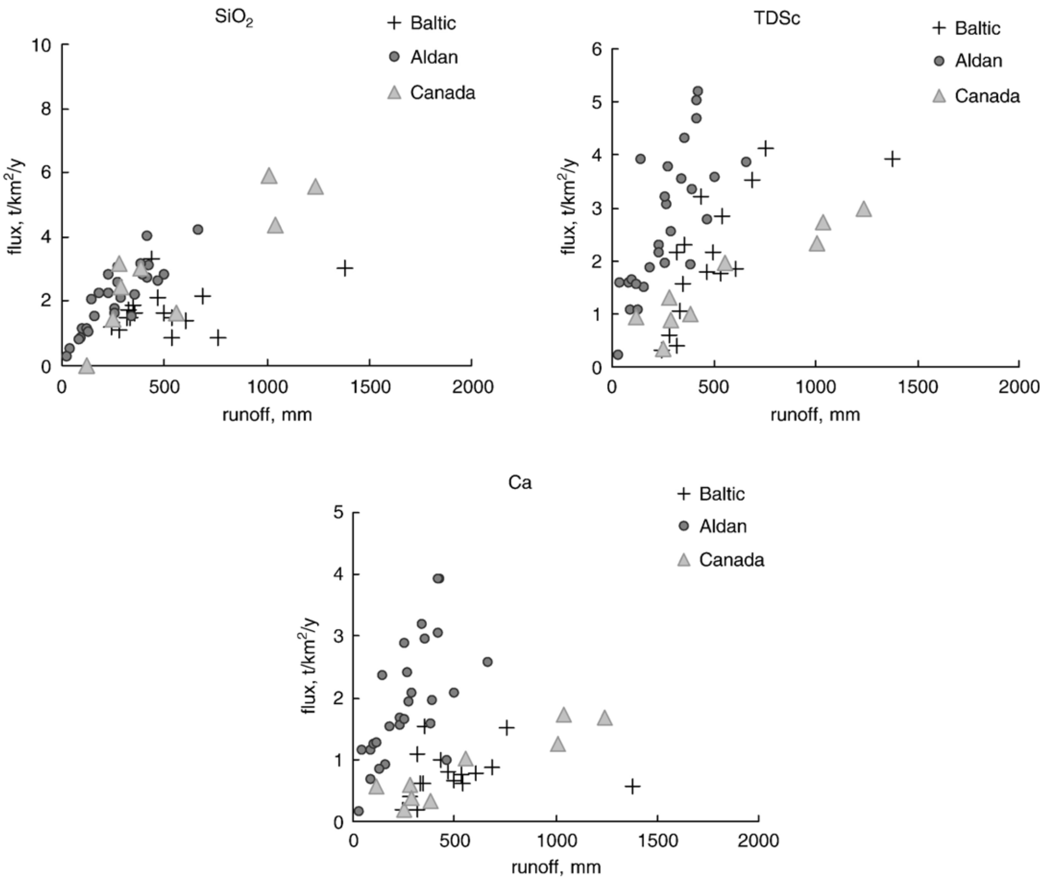

Fig. 11. Silica, cationic and Ca fluxes for three boreal granitic regions vs. river runoff. The data for Canadian shield are from the database of Oliva et al. (2003) and the data for Aldan shield are from Zakharova et al. (2005).

The influence of DOM on chemical denudation rate is well pronounced for rivers of the eastern part of Fennoscandian shield. Similar to Swedish (Humborg et al., 2004) and Canadian (Millot et al., 2002) watersheds, Kola and Karelian rivers exhibit a strong positive correlation between the mean flow weighted annual SiO_2 concentration and organic matter concentration (see Fig. 13A). Note that the previous studies of Arctic rivers focused on rivers having far lower organic matter concentrations (i.e., 1–7 mg/L of TOC and 0.3–3 mg/L of Si for Swedish rivers, Humborg et al., 2004). The atmosphere-corrected Ca and Mg concentrations of Kola rivers are also correlated with that of the organic matter (see Fig. 13B and C). The positive correlation between [PO] and [SiO_2] may reflect the impact of plant phytolithes on the terrestrial Si cycle (Alexandre et al., 1997; Derry et al., 2005; Fraysse et al., 2006). It is known that phytolith-producing plants (e.g. horsetail, spruce and larch trees) are typical for boreal wetlands and they may contribute to the isotopic signatures of silicon in the river water (i.e., Reynolds et al., 2006). As a result, both DOC and biogenic silica may be derived from plant litter in the wetlands, especially in the riparian zone. Note that on the annual scale the biological uptake of Si due to diatom activity in the lakes is compensated, to a great extent, by its return to the water

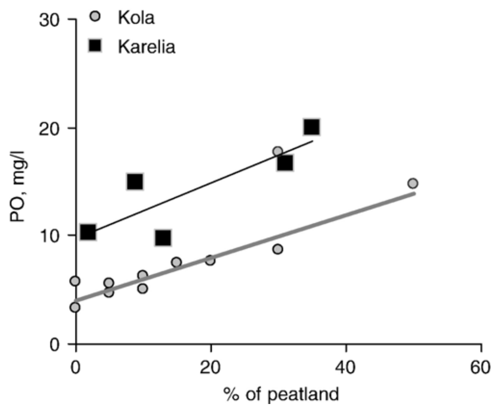

Fig. 12. Relation between mean weighted permanganate oxidation and the proportion of peatlands in the watersheds of Karelian and Kola rivers.

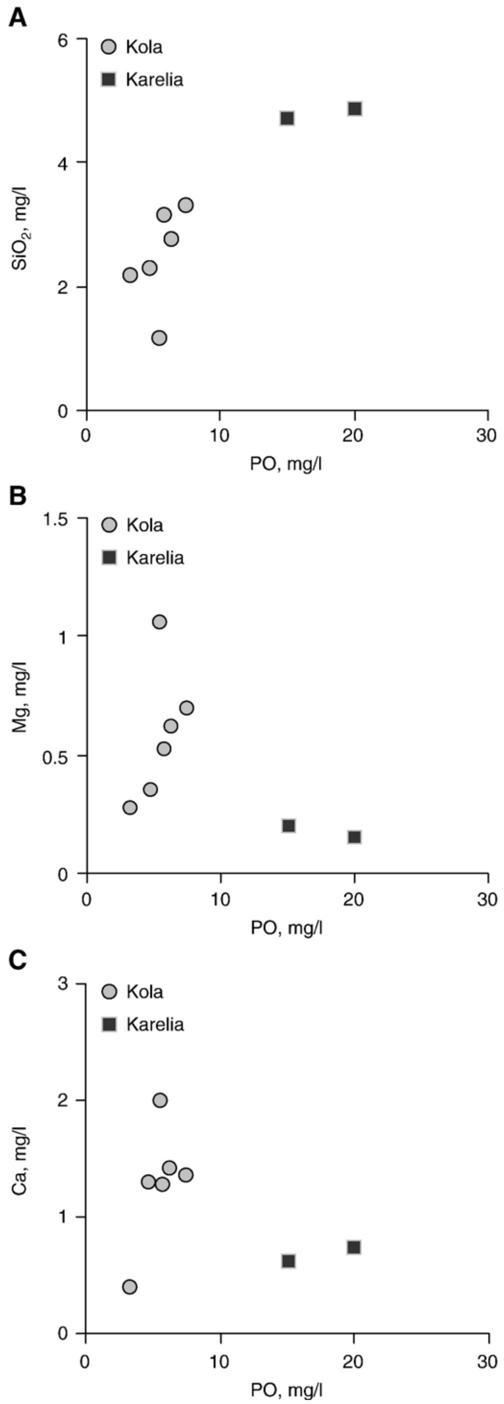

Fig. 13. Relationship between mean dissolved discharge-weighted concentrations of SiO_2 (A), Ca (B), Mg (C) and organic matter content expressed as permanganate oxidation. Only the rivers having predominance of granites in their watersheds were selected for these graphs.

column. Therefore, the mean annual discharge-weighted silica concentration and fluxes discussed in this work present a reasonable estimate of chemical erosion rates.

Two mechanisms of DOC-associated weathering can be suggested. First, DOC — driven silicate rock dissolution: the low depth of soil profile provides relatively easy access of mobile small-size fulvic and humic acids typical for humid boreal region (i.e., Targulian, 1971) to the bedrocks and unaltered minerals of soil C horizon. This effect is likely to be more pronounced in Kola's watersheds having soils of lesser thickness and lower proportion of peatlands. Thin soils facilitate transport of aggressive fulvic acids originated in the litter horizon to the deep parts of soil profile and, consequently, mobilization of cations from primary minerals. Indeed, the concentration of both Ca and Mg exhibits good correlation with that of the organic matter in the Kola peninsula (Fig. 13B and C). The second mechanism is related to plant litter degradation: cold climate slows organic matter humification while sufficient soil moisture and abundant precipitation lead to rapid leaching of major inorganic components (Ca, Mg, Si) and organic carbon from the degrading plant litter. We will attempt to distinguish between the contribution of chemical weathering and litter degradation in the next section.

4.3. Quantitative contribution of different sources

It has been widely argued that degrading plant litter is an important source of the dissolved major and trace elements found in river water (Polynov, 1944; Glazovskaya, 1956; Kovda, 1956; Pokrovsky et al., 2005, 2006). Indeed, recent studies of granite (Millot et al., 2002) and basalt environments (Moulton and Berner, 1998; Moulton et al., 2000) demonstrated that the chemical denudation rate can be several times higher in vegetated areas compared to that of bare rocks. It is known that the majority of the nutrients taken up by trees on an annual basis is recycled. Two major sinks for nutrients are storage in plants and secondary mineral precipitation in soil. There is also an annual net loss of nutrients from ecosystems due to superficial flow (i.e., Berner et al., 2003).

The contribution of plant litter degradation to river water concentrations can be assessed from the analysis of the litter composition and the annual Net Primary Productivity (NPP) for the region. For Fennoscandian watersheds we accept the following values of NPP estimated on the basis of SPOT VGT S10 images processed by VITO (Flemish Institute for Technological Research, Geosuccess, 2005): 120 g C/m^2/y for watersheds of the Barents Sea basin having $\geq$50% tundra coverage (Teriberka No. 11, Drozdovka No. 14, Varzina No. 13, Bolshaya Tuva No. 10, Mouchka No. 12, Malaya Belaya No. 15), 200 g C/m^2/y for watersheds of the

Barents Sea basin with dominating forest vegetation (West Litza No. 16 and Ura No. 9), 250 g $C/m^2/y$ for rivers Umba No. 18, Varzuga No. 19 and Ponoy No. 17, and 320 g $C/m^2/y$ for Karelian rivers of the White Sea basin (Keret No. 1, Pongoma No. 3, Gridina No. 2, Onigma No. 5, Letnyaya No. 4). These values are compatible with the estimates of litter fall in 150-years old Karelian spruce forest: 400–500 $t/km^2/y$ or 180–250 g $C/m^2/y$ and the measurements of litter fall in the Karelian and Kola taiga: 530 and 200–300 $t/km^2/y$, respectively (Rodin and Bazilevich, 1965).

A key parameter for estimating the impact of litter degradation on dissolved element transport is the ratio of the export flux (J), or the annual loss of elements from degrading litter in soil horizon towards the river to the net primary production (NPP). The J/NPP ratio is extremely low for biogenic elements such as N, C, and P but reaches 0.88 for mineral components including Ca, Mg, Na, K, Fe, Al, and Si in the boreal taiga region as estimated by Bazilevich, (1976) based on the results of Remezov et al. (1959) and Rodin and Bazilevich (1965). Assuming steady-state forest biomass and soil organic layer thickness and converting J/NPP to element content in the dry biomass using the data from the literature (Table 4), yields annual Ca, Mg, Na and SiO_2 fluxes (F_{litter}) equal to 0.40, 0.12, 0.03 and 0.42 $t/km^2/y$, respectively. These values correspond to J/NPP = 0.88 and the litter fall equals to 450 $t/km^2/y$. The actual values of F_{litter} may differ from these estimates by a factor of 3 considering the large variation of element content in the plant biomass. Indeed, Evdokimova et al. (1976), based on detailed work of Manakov (1972), reported that typical element removal rates from degrading plant litter via surface runoff are 1.5–2.9 $t/km^2/y$ for Ca and ~0.7 $t/km^2/y$ for Mg in tundra and forest regions. These values actually exceed the overall dissolved fluxes in rivers assessed in the present study. Marchenko and Karlov (1962) reported that the elemental concentrations of spruce needles and green moss of the Arkhangelsk region are 5 to 10 times higher than those accepted in this work. Pokrovsky et al. (2005) reported even higher concentrations in mosses and larch trees (see Table 4). However, in the present work we used the lowest element concentration range in the plant litter to assess the minimal possible value of $F_{litter.}$

We used the annual fluxes of river dissolved components, together with atmospheric and underground inputs listed in Table 3 to estimate the relative proportion of various sources to the annual average river water cationic composition. The overall flux is given as

$$F = F_{atmosphere} + F_{groundwater} + F_{litter} + F_{RW} \quad (3)$$

where F_{RW} is direct bedrock and soil mineral chemical weathering via rock–water interaction with soil porewater fluids. In this equation, we distinguish between the riverborne elements originated from "inorganic" sources comprised of initial and secondary minerals in soil and rock and from "organic" sources including plant litter although in both cases the primary source of elements is

Table 4
Elemental composition of plant litter in boreal regions based on literature data (mg/g dry biomass)

Object	Ca	Mg	Na	Si	Reference
Kola and Karelia regions					
Pine, needles	0.34	0.09	N.D.	0.07	Remezov et al. (1959)
Spruce, needles	0.15–1.5	0.07–0.8	0.02–0.1	0.1–0.7	Rodin and Bazilevich (1965)
	0.49	0.10	N.D.	0.49	Remezov et al. (1959)
Birch, leafs	1.44	0.23	N.D.	0.056	Remezov et al. (1959)
B. nana leafs	0.3–0.7	0.05–0.2	0.01–0.05	0.02–0.05	Manakov (1972)
Green mosses	0.2–0.4	0.1–0.2	0.05–0.1	0.1–0.3	Manakov (1972)
Pine, needles (60 y)	0.30	0.14	N.D.	0.10	Evdokimova (1957)
Birch, leafs	0.72	0.37	N.D.	0.11	Evdokimova (1957)
Spruce, needles	0.91	0.10	N.D.	0.62	Smirnova (1951)
Moss	0.39	0.11	N.D.	0.17	Smirnova (1951)
Average vegetation	1.0	0.3	0.1	0.5	Accepted in this work
Other regions (Arkhangelsk, Siberia)					
Spruce, needles	3–18	1.3–1.9	N.D.	1.1–5.9	Marchenko and Karlov (1962)
Birch, leafs	3.6	4.0	N.D.	0.6	Marchenko and Karlov (1962)
Green moss	3.4–4.1	1.7	N.D.	1.5–2.6	Marchenko and Karlov (1962)
	2.7	0.9	0.2	N.D.	Pokrovsky et al. (2005)
Larch, needles	9.4	3.4	0.9	20	Pokrovsky et al. (2005)

Average numbers and the range of reported values are based on 50 measurements performed on different sites of Karelia and the Kola peninsula.

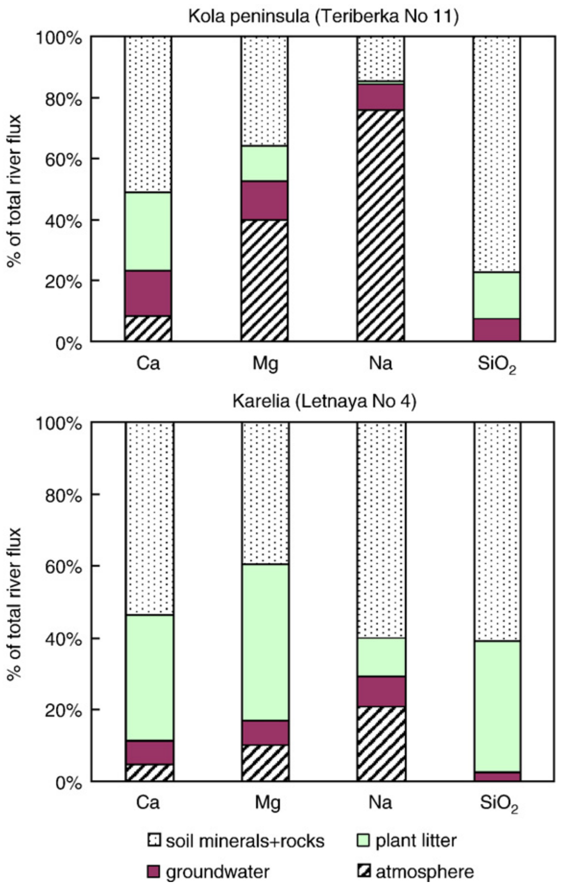

Fig. 14. Contribution of different sources to annual fluxes of dissolved silica and cations in typical river of the Kola Peninsula (Barents sea basin, Teriberka, No. 11, A) and Karelia region (White Sea basin, Letnyaya No. 4). The values of annual plant litter production used are 240 and 640 t/km^2/y for Kola and Karelia, respectively, corresponding to NPP = 120 and 320 t C/km^2/y; J/NPP = 0.88 and the element content in dry biomass are 1, 0.3, 0.1 and 1.07 g/kg for Ca, Mg, Na, and SiO_2.

the bedrock. The contribution of the “inorganic” source to the total dissolved river cationic and silica fluxes equals to 60, 50, and 60–80% for Ca, Mg, and SiO_2. The contribution of plant litter degradation to overall river fluxes ranges from 10–20% in the Kola peninsula to 30–40% in Karelia region, depending mostly on primary production (Fig. 14). Note that these estimates are subjected to large uncertainties that stem from the poor knowledge of the *J*/NPP ratio of each individual element and the element concentration in the litter fall.

5. Conclusions

The present study allows the quantification of the chemical erosion of silicate rocks in boreal regions of NW Russia. The chemical erosion rate is correlated to the fraction of basaltic rocks present in the watersheds; this correlation allows the estimation of the erosion rates of the pure end-member granite and basaltic rocks in the region. Cationic weathering fluxes estimated from river water chemical compositions are among the lowest in the world: TDSc = 0.33 and 1.61 t/km^2/y for pure granitic and pure basaltic watersheds, respectively. For granite-dominating watersheds, the flux and concentration of dissolved cations is similar to that previously reported for Canadian and Siberian watersheds.

The composition of the river waters during the wet spring periods, when more than half of the annual element flux occurs, approaches that of the plant litter and upper soil horizons rather than of the bedrocks suggesting intensive surface leaching of cations from soil organic layers. During the dry winter and summer periods, the dissolution of parent rocks is responsible for river water enrichment in most labile elements like alkalis and Ca. However, this source contributes less than 20% to the annual element fluxes.

The mean annual discharge-weighted concentrations of TDSc, Ca, and Si are positively correlated with that of DOC. Two major sources of river water compositions are: 1) an “inorganic” source consisting of the primary and secondary minerals in soil and rock and 2) an “organic” source consisting of plant litter and phytoliths. On average, the contribution of inorganic source to the annual flux is 60, 50, and 60–80% for Ca, Mg, and SiO_2. The release of cations from degrading plant litter during wet periods exerts an important control on the annual element flux, contributing from 10 to 40% of the flux depending on the primary production, intensity of biological turnover and the element concentration in the biomass. The increase of both temperature and pCO_2 in the Arctic region will increase the NPP production by 25–40% (i.e., Bergh et al., 2003). It follows that the impact of global warming on element transport from the land to the ocean will be more pronounced than it can be expected from temperature–weathering flux relationship implying solely the activation energy of mineral dissolution.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemgeo.2007.03.018.

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