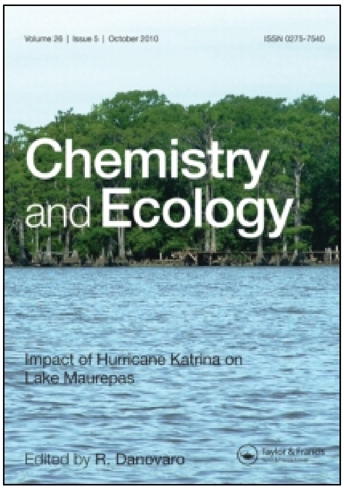

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Surface water chemistry: the key to partitioning dissolved matter sources and assessing carbon cycle parameters

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Surface water chemistry: the key to partitioning dissolved matter sources and assessing carbon cycle parameters

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For the first time, the contributions of surface water base cation sources, such as atmospheric deposition, weathering and organic matter mineralisation were estimated using only water chemistry data. Estimations were based on a comparison of acid neutralising capacity (ANC) and dissolved organic carbon (DOC) export ratios measured for the ice-covered and the ice-free periods. The highest export of cations from both atmospheric and organic origin was observed during mid-summer, when the maximum precipitation coincides with maximum temperature, which favours organic decomposition. Organic matter contribution decreases from spring to autumn, contrary to the increase in weathering contribution. In the first half of the ice-free period, this is conditioned by the optimisation of soil conditions favourable to weathering, and in the second half it is mostly due to the decrease in precipitation and, consequently, in lateral flow. Since the ANC represents cations released due to carbonic and carboxylic acid reactions and organic mineralisation, it can also be considered a parameter of the carbon cycle. The export value of mineralisation-derived cations can serve as the basis for evaluating the CO_2 emission from soil.

Keywords: surface water; weathering; atmospheric deposition; organic matter mineralisation; contribution, carbon cycle parameter

1. Introduction

Partitioning the sources of dissolved matter and, consequently, separating the hydrograph has been a great concern for the last two decades. Since the only signature for a water source is its chemical composition, all common approaches use the concentration of water solutes as tracers. Some studies deal with major solutes, such as SiO_2, Ca^{2+}, Mg^{2+}, K^+, Na^+, SO_4^{2-}, NO_3^-, Cl^-, and Al^{n+} [1–3]. In other studies, solution micro-components like Sr, Rb [4], element ratios Ca/Sr, Ba/Sr [5], Ge/Si [6] or stable isotope ratios $^{87}Sr/^{86}Sr$ [7], $\delta^{18}O$ [8] are used. The distinction of source contributions is based on considering stream water as the mixture of two or more end-member sources. The soil percolate [9,10] or exchangeable fraction [11] from different horizons and the base flow were used more frequently as end-members. To visualise the source proportion, the mixture parameter values can be plotted against those of end-members on simple X–Y [12] or triangle [11] mixing diagrams, or even in three-dimensional space [13]. Source

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contributions can be obtained by solving the mixing equations. The main problem with these studies is representativeness of collected samples by the corresponding mixture component (mineral and organic soil matter, exchangeable fraction, rocks, deposition, vegetation, etc.). The only solution to the problem is to carry out comprehensive field and laboratory work which would sufficiently reveal spatial variability of component properties by collecting and analysing a large number of samples. To make the hydrograph/source separation easier in the field and laboratory, it is necessary to apply a universal chemical characteristic which is based on water-only chemistry and reflects quantitative changes in source combination. The ratio between organic and inorganic solute export values can be such a characteristic.

The surface water chemistry in any season is controlled by two factors: (i) the chemical composition of dissolved matter sources such as atmospheric deposition (Dep), weathering (W), and organic matter (OM) mineralisation; and (ii) predominant water flowpath. In soil unsaturated with water, the dissolved matter is transported by vertical flow and the most organic matter is absorbed by soil on the way down, while base cations (BC) and bicarbonate ions are easily leached out from the soil profile. This explains why the minimum dissolved organic carbon (DOC) concentration is always observed in groundwater. Due to the higher thickness of mineral horizons with respect to organic ones, and due to the uptake of ‘organic’ cations by roots on the way down, base cations exported by vertical flow are mostly of mineral origin. After soil saturation the lateral flow predominates and more organics from the upper soil horizons come to the river. Base cations in such a flow originate from organic matter mineralisation. Thus, the ratio between the amounts of organic (DOC) and inorganic (BC) solutes exported from the watershed reflects the flow pathways ratio (lateral/vertical) and dissolved matter sources ratio (organic/mineral) at the same time. Our estimates of the dissolved matter source contributions to surface water chemistry are based on comparing the ratio from the studied period with the ratio from the period (ice-covered) when the predominant flowpath is known.

The aim of our study was to develop and validate the easiest and cheapest method of distinguishing the dissolved matter sources which is not dependent on spatial variability of ecosystem component chemistry. To achieve this aim we performed several tasks: (i) elaborating the criteria for distinguishing between the mineral and organics-originated fractions of dissolved matter using only water chemistry; (ii) collecting the historical and contemporary data for running the calculations; and (iii) interpreting calculated data in the light of existing knowledge on water chemistry dynamics drivers and terrestrial ecosystem functioning patterns to support the validity of the method proposed.

2. Materials and methods

2.1. *Sampling strategy and analytical procedures*

For our estimates we used chemical data taken from the literature [14]. The new dataset (2002–2004) was collected by the authors. New samples were taken four times a year – in June, July, September and December. Water was sampled in 1 litre polyethylene bottles after washing with riverine water. Bottles were closed below water level to force out air. Duplicate samples were taken at each location. Samples were transported to the laboratory in cooler boxes filled with freezer packs. For analyses of ionic composition, water was filtered through 1 μm pore size Whatman filters. Alkalinity was measured in unfiltered samples. Chemical analyses were performed according to international guidelines [15,16]. Cations were determined by flame spectrophotometry (Karl Zeiss, Jena AAS-30 spectrophotometer). Sulphate, chloride, and nitrate concentrations were measured by high-performance liquid chromatography. Bicarbonate was measured using potentiometric titration and the DOC was measured by means of catalytic oxidation. Overall data quality was controlled by calculating the charge balance. The maximum possible charge balance error for the both sets of data was 5%. The error of DOC measurement was 5% in recent years and 10% for earlier data. This suggests that results calculated from these two data sets are quite comparable.

2.2. *Sampling areas*

Climatic conditions of the Lake Baikal watershed, as well as its surface geology and relief are characterised by great diversity that makes it unique for testing different environmental hypotheses. The combination of these three abiotic conditions causes a variety of biome types. On this small territory (588,000 km^2) there are biomes characterised by differing intensity of biogeochemical turnover: from steppes and mountain tundra with annual precipitation of about 200 mm, the southern taiga and middle taiga (including their mountain vegetation belt analogs) with precipitation of 400–600 mm, to relic mixed forests of foothills and mountain taiga with precipitation of up to 2000 mm.

The territory characterised by a temperate moisture regime (400–600 mm) is the mountainous surroundings of the lake, except for the Khamar-Daban Ridge located on the southeastern coast (Figure 1). Most of the precipitation (up to 85%) falls during the summer, causing higher riverine water discharge in the ice-free period compared with the ice-covered period (Figure 2). The annual average temperature at the ground level (450 m above sea level) is about -3°C, with a winter minimum of -50°C and a summer maximum of 40°C. Soils are frozen from November until May and rivers are covered with ice from December until April. The western and the eastern coasts of the lake have different reliefs, soils, geology and vegetation.

Soils of the eastern shore are acidic (excluding part of Barguzin river basin), since they are developed mostly on acid intrusive (granites) and metamorphic (gneisses) rocks. The mountains on the eastern shore reach 2500 m [17]. Predominant species are *Abies sibirica*, *Pinus sibirica* and *Picea sibirica*. Tributaries of the eastern shore, namely Verkhnaya Angara (V. Angara hereafter), Barguzin, and Selenga contribute up to 90% of the annual Baikal water budget. The chemical composition of these rivers is quite similar. According to long term average data, summer concentrations of predominant ions such as bicarbonate and calcium vary, respectively, between 0.83 meq l^{-1} and 0.70 meq l^{-1} in V. Angara to 1.11 meq l^{-1} and 1.34 meq l^{-1} in Barguzin (Table 1).

The Khamar-Daban Ridge is a peculiar place on the eastern coast of Lake Baikal. Due to the prevailing northwestern air mass transfer, the spatial orientation of the ridge causes high amounts of atmospheric precipitation on its windward slopes. Air masses travel along the Angara River, the only Baikal outflow, towards Baikal. When they reach Baikal, they become saturated with water above the lake surface, and pass as a narrow front along the southeastern shore. The amount of precipitation in the mountains is above 1700 mm yr^{-1}. High precipitation volume causes extremely low water mineralisation (sum of ions is 0.7–1.5 meq l^{-1}) of the Khamar-Daban Ridge rivers – Khara-Murin, Utulik, and Snegnaya. For example, the highest concentrations of HCO_3^- and Ca^{2+} typical for Utulik in winter are just 1.01 meq l^{-1} and 0.83 meq l^{-1} respectively, and the lowest concentrations typical for Khara-Murin in summer are four times lower: 0.27 meq l^{-1} and 0.21 meq l^{-1}, respectively.

Soils of the western coast are developed mostly on sedimentary material, including carbonates. The vegetation cover is composed of predominantly light coniferous species like *Pinus silvestris* and *Larix sibirica*. The height of the mountains does not exceed 1600 m. The biggest rivers on the western shore are Buguldeika and Goloustnaya. These rivers have mineralisation several times higher than the other lake tributaries: in particular, magnesium and sulfate concentrations.

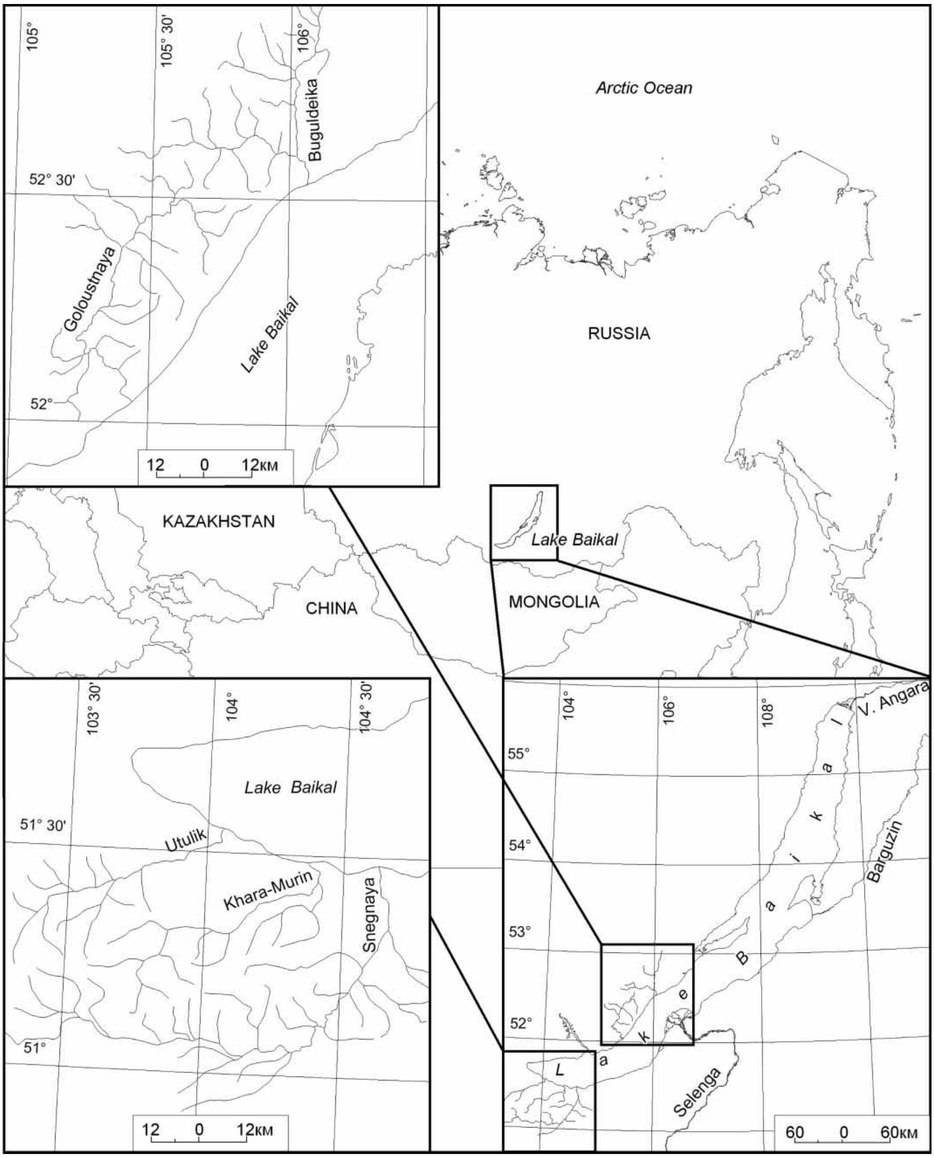

Figure 1. The study area.

Concentrations of magnesium in Buguldeika reach values of 1.39 meq l^{-1} in the ice-free period and 2.30 meq l^{-1} in the ice-covered period, and concentrations of sulfate are 0.39 meq l^{-1} and 0.62 meq l^{-1}, respectively.

2.3. *Partitioning the dissolved matter sources*

Dissolved organic carbon export from the watershed (DOC_{ex}) was quantified using DOC concentrations and water volume discharged from the watershed. The sum of BC released from weathering and from organic matter decomposition can be obtained by subtracting the atmospheric BC fraction (assuming that atmospheric acidity deposition in unpolluted areas is neutralised by

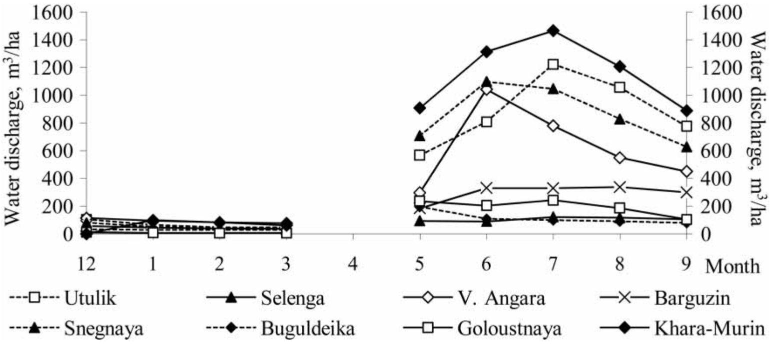

Figure 2. The hydrograph of studied rivers in ice-free (VI–IX) and ice-covered (XII–III) periods.

dust deposition) from the total BC export. This value is called the acid neutralising capacity (ANC) and is calculated as the difference between the sum of BC and the sum of anions of strong mineral acids (SO_4^{2-}, NO_3^-, Cl^-):

$$\mathrm{ANC_{ex}},\ \mathrm{keq\,ha^{-1}} = ([\mathrm{Ca^{2+}}] + [\mathrm{Mg^{2+}}] + [\mathrm{K^+}] + [\mathrm{Na^+}] - [\mathrm{SO_4^{2-}}] - [\mathrm{NO_3^-}] - [\mathrm{Cl^-}]) \cdot \mathrm{Q},$$

where $\mathrm{ANC_{ex}}$ is the ANC export value and Q is a runoff volume.

The volume-weighted ANC values were already used by Robson and Neal [9] as a tracer for distinguishing the contributions of soil percolate and the base flow to surface water. In this work, we used only riverine water concentrations but, for soils containing mineral acid anions such as SO_4^{2-} and Cl^-, ANC should be calculated using rainwater or throughfall concentration of corresponding anions multiplied by precipitation/runoff ratio. This procedure imitates the soil solution concentration increase due to evaporation and transpiration (the internal ecosystem nutrient uptake/return balance is assumed to be zero) and also can be applied to ‘compensate’ for nitrate uptake by vegetation. To check whether the soil contains these anions it is necessary to compare the calculated concentration with the measured one. The higher measured value should indicate the presence of easily soluble minerals (gypsum, halite etc.). Thus, in watersheds containing these minerals, the $\mathrm{ANC_{ex}}$ evaluated from calculated anion concentrations equals the total soil BC release, while the $\mathrm{ANC_{ex}}$ evaluated from riverine water anion concentrations is the contribution of non-sulfate (non-chloride) material. The difference between these two ANCs gives us the contribution of sulfate (chloride) material. Atmospheric deposition of base cations ($\mathrm{BC_{Dep}}$) was calculated from the difference between total BC export ($\mathrm{BC_{ex}}$) and $\mathrm{ANC_{ex}}$:

$$\mathrm{BC_{Dep}},\quad \mathrm{keq\,ha^{-1}} = \mathrm{BC_{ex}} - \mathrm{ANC_{ex}}.$$

Since the groundwater contains mostly weathering products, weathering contribution to ANC export (W_f) in any period was assumed to be proportional to the measure of similarity of surface water chemistry in this period to groundwater/base flow chemistry. The winter base flow (the water sampled in winter from under the ice) was used as the groundwater. Winter export is characterised by the maximum-possible $\mathrm{ANC_{ex}/DOC_{ex}}$ value or, conversely, the minimum-possible $\mathrm{DOC_{ex}/ANC_{ex}}$ value among the other flow exports, thus the measure of riverine water and groundwater chemistry similarity can be expressed as follows:

$$\frac{(\mathrm{DOC_{ex}/ANC_{ex}})_{\mathrm{winter}}}{(\mathrm{DOC_{ex}/ANC_{ex}})_{\mathrm{studied}}} = \mathrm{W}_f = \frac{(\mathrm{ANC_{ex}/DOC_{ex}})_{\mathrm{studied}}}{(\mathrm{ANC_{ex}/DOC_{ex}})_{\mathrm{winter}}},$$

where $(\mathrm{DOC_{ex}/ANC_{ex}})_{\mathrm{winter}}$ and $(\mathrm{ANC_{ex}/DOC_{ex}})_{\mathrm{winter}}$ are winter average values.

Table 1. Chemical and hydrological characteristics of the rivers studied (the numerator indicates the average value and the denominator indicates the minimum and maximum values).

Period, month	DOC, mg l^{-1}	HCO_3^- (meq l^{-1})	SO_4^{2-} (meq l^{-1})	Cl^- (meq l^{-1})	NO_3^- (meq l^{-1})	Ca^{2+} (meq l^{-1})	Mg^{2+} (meq l^{-1})	Na^+ (meq l^{-1})	K^+ (meq l^{-1})	Runoff, $m^3\ ha^{-1}$	Watershed square, km^2
1	2	3	4	5	6	7	8	9	10	11	12
Long-term average data Selenga											
VI-IX	2.90 2.06–3.36	1.41 1.09–1.63	0.13 0.10–0.16	0.031 0.025–0.045	0.014 0.004–0.017	1.02 0.87–1.09	0.35 0.30–0.42	0.09 0.06–0.11	0.06 0.04–0.07	107 89–121	440,000
XII-III	0.99 0.79–1.22	2.03 1.83–2.26	0.16 0.13–0.18	0.039 0.031–0.045	0.013 0.010–0.015	1.36 1.28–1.46	0.57 0.50–0.73	0.17 0.14–0.20	0.08 0.06–0.09	7 5–11	
V. Angara											
VI-IX	1.33 1.05–1.58	0.83 0.63–0.98	0.08 0.01–0.12	0.012 0.003–0.014	< 0.001	0.70 0.51–0.97	0.13 0.08–0.18	0.04 0.01–0.06	0.03 0.02–0.04	705 450–1041	20,600
XII-III	0.90 0.71–1.11	1.43 1.16–1.63	0.12 0.07–0.16	0.024 0.006–0.029	0.011 0.004–0.013	1.02 0.90–1.12	0.40 0.25–0.49	0.08 0.04–0.11	0.04 0.03–0.05	92 76–114	
Barguzin											
VI-IX	2.36 2.05–2.58	1.34 0.98–1.47	0.15 0.10–0.17	0.031 0.022–0.038	< 0.001	1.11 1.00–1.25	0.21 0.15–0.32	0.09 0.05–0.14	0.07 0.05–0.08	323 298–330	19,800
XII-III	0.78 0.67–0.95	1.95 1.68–2.34	0.19 0.15–0.23	0.043 0.030–0.050	0.019 0.009–0.026	1.60 1.34–1.72	0.23 0.08–0.31	0.18 0.12–0.24	0.10 0.07–0.12	44 35–56	
Buguldeika											
VI-IX	2.13 1.40–5.92	3.25 2.21–3.88	0.39 0.31–0.47	0.014 0.007–0.025	< 0.001	2.19 1.51–2.42	1.39 0.71–1.65	0.05 0.03–0.07	0.02 0.01–0.03	94 78–109	1,700
XII-III	0.68 0.53–0.84	4.78 3.45–5.38	0.62 0.49–0.77	0.023 0.017–0.031	0.021 0.015–0.029	3.00 2.61–3.28	2.30 1.94–2.73	0.08 0.05–0.10	0.05 0.03–0.07	29 28–32	
Goloustnaya											
VI-IX	2.55 2.14–6.50	1.38 1.02–1.62	0.28 0.21–0.37	0.012 0.006–0.031	< 0.001	1.00 0.69–1.21	0.55 0.39–0.78	0.07 0.04–0.09	0.03 0.02–0.04	184 104–243	2,260
XII-III	0.77 0.63–0.88	2.54 1.87–2.94	0.51 0.38–0.58	0.021 0.014–0.027	0.020 0.015–0.028	1.79 1.47–2.02	1.04 0.87–1.24	0.15 0.09–0.18	0.06 0.04–0.07	8 5–12	

Khara-Murin											
VI-IX	1.47 0.95–5.20	0.27 0.14–0.32	0.08 0.05–0.09	< 0.001	0.009 0.007–0.042	0.21 0.18–0.24	0.06 0.05–0.08	0.04 0.01–0.06	0.03 0.02–0.05	1218 880–1465	
I-III	0.36 0.30–0.47	0.46 0.30–0.52	0.12 0.10–0.13	0.014 0.003–0.026	0.018 0.015–0.019	0.39 0.34–0.41	0.14 0.11–0.19	0.04 0.02–0.07	0.02 0.01–0.04	80 61–98	1,130
Utulik											
VI-IX	1.44 1.02–2.08	0.67 0.42–0.71	0.15 0.08–0.19	< 0.001	0.031 0.016–0.050	0.57 0.49–0.64	0.16 0.11–0.18	0.06 0.02–0.07	0.04 0.03–0.06	965 775–1223	
XII-III	0.52 0.41–0.62	1.01 0.82–1.31	0.21 0.18–0.22	< 0.001	0.021 0.019–0.024	0.83 0.75–0.89	0.30 0.28–0.34	0.05 0.02–0.06	0.03 0.02–0.04	66 47–104	959
Snegnaya											
VI-IX	1.73 1.38–2.64	0.51 0.44–0.65	0.08 0.07–0.09	< 0.001	0.012 0.006–0.013	0.43 0.30–0.54	0.06 0.05–0.08	0.06 0.03–0.08	0.02 0.01–0.03	900 627–1098	
XII-III	0.51 0.45–0.65	0.80 0.64–0.91	0.13 0.11–0.15	< 0.001	0.022 0.012–0.025	0.73 0.68–0.85	0.11 0.09–0.13	0.05 0.03–0.07	0.03 0.02–0.04	50 32–80	3,000
2002 – 2004 average data Khara-Murin											
VI-IX	1.83 1.23–6.15	0.21 0.10–0.18	0.14 0.08–0.23	< 0.001	0.010 0.007–0.051	0.17 0.14–0.20	0.10 0.08–0.13	0.07 0.03–0.09	0.02 0.01–0.04	1120 889–1312	
XII-III	0.50 0.41–0.67	0.33 0.27–0.45	0.20 0.14–0.29	< 0.001	0.020 0.016–0.023	0.29 0.22–0.37	0.13 0.10–0.19	0.09 0.03–0.11	0.03 0.01–0.05	72 58–87	1,130
Utulik											
VI-IX	1.93 1.21–2.43	0.80 0.49–0.87	0.34 0.17–0.42	0.011 0.006–0.017	0.015 0.009–0.019	0.62 0.50–0.71	0.31 0.17–0.40	0.09 0.05–0.12	0.05 0.02–0.07	1057 790–1121	
XII-III	0.72 0.52–0.88	0.92 0.82–1.19	0.48 0.31–0.58	0.013 0.005–0.017	0.029 0.020–0.035	0.83 0.70–0.92	0.37 0.29–0.42	0.11 0.04–0.14	0.07 0.04–0.09	81 72–90	959
Snegnaya											
VI-IX	1.84 1.42–3.01	0.44 0.40–0.53	0.15 0.10–0.21	0.013 0.007–0.016	0.014 0.006–0.016	0.45 0.29–0.60	0.12 0.06–0.16	0.05 0.03–0.07	0.02 0.01–0.03	837 599–940	
XII-III	0.53 0.42–0.66	0.80 0.59–1.01	0.19 0.13–0.29	< 0.001	0.021 0.009–0.027	0.73 0.59–0.90	0.13 0.08–0.16	0.07 0.03–0.10	0.03 0.02–0.05	44 31–52	3,000

Since the W_f value represents the ratio of two ratios – we can ignore the fact that DOC and ANC are expressed in different units – even if we divide DOC by its equivalent weight to convert it into an equivalent, these denominators (/3) will be cancelled reciprocally.

We realise that the chemical composition of riverine water changes during the winter due to the reduction in depth of the soil profile and, consequently, to the increasing contribution of lower horizons. This is seen from the DOC_{ex}/ANC_{ex} ratio: lowering the ratio denotes lowering the water table. Thus, establishing the groundwater component of BC is limited by the rate of DOC_{ex}/ANC_{ex} ratio decrease: the faster and sharper the changes, the lower the similarity of winter average water chemistry to that of vertical flow in the ice-free period. The error value is proportional to the magnitude of ratio change. To minimise this discrepancy, the winter DOC_{ex}/ANC_{ex} ratio that stands until its first substantial shift can be used. The weathering value (BC_W) was calculated as a product of weathering contribution and ANC_{ex}:

$$BC_W, \quad \mathrm{keq\,ha^{-1}} = W_f \cdot ANC_{ex}$$

Base cation release due to organic matter decomposition (BC_{OM}) was calculated from the difference between ANC_{ex} and BC_W:

$$BC_{OM}, \quad \mathrm{keq\,ha^{-1}} = ANC_{ex} - BC_W$$

The Dep, W and OM contributions were calculated from BC_{Dep}, BC_W and BC_{OM} values. It should be noted that the high OM contribution that exceeds the sum of deposition and weathering contributions does not mean progressive losses of organic matter and exhaustion of the pool of nutrients incorporated into organics. In a mature ecosystem, nutrient losses at OM mineralisation (nutrients exported from washed) should be compensated by uptake of an equivalent fraction of weathering and deposition, just as uptake by vegetation should be equal to nutrient return with litterfall (the balance is zero). In other words, BC_{ex} should theoretically be equal to the sum of BC_{Dep} and BC_W, but in fact, it consists of residues of BC_{OM}, BC_{Dep} and BC_W which were not taken up by vegetation.

3. Results and discussion

As aforementioned, rivers from different parts of the Lake Baikal watershed have different concentrations of main ions and water discharges and, consequently, different export values. Nevertheless, the chemical composition of studied rivers changes during the year in a similar way. Concentrations of dissolved organic carbon as well as DOC_{ex} values decrease from May to April. In most tributaries, winter DOC concentrations are 3–5 times lower than in the summer, so the small water discharge during the ice-covered period makes the winter DOC export values almost a hundred times lower than summer values. In contrast to DOC, cation concentrations increase from spring to winter and the winter ANC_{ex} values are 3–10 times lower than those of summer.

The DOC_{ex}/ANC_{ex} ratio values decrease from spring to autumn, being much higher than those in the ice-covered period. This is due to the predominance of lateral flow versus vertical flow: the calculated contributions of organic horizons are 0.7–0.8 in May and 0.5–0.6 in September (Figure 3a), whereas weathering contributions are just 0.03–0.07 and 0.25–0.3, respectively. The contributions of atmospheric deposition in most watersheds vary insignificantly with an average of 0.25. Maximum values are observed in May due to snowmelt. The highest deposition contributions, of up to 0.45, are typical for the rivers of the Khamar-Daban Ridge, since this area has high annual precipitation. These data are in agreement with those obtained earlier [18] using isotopic techniques.

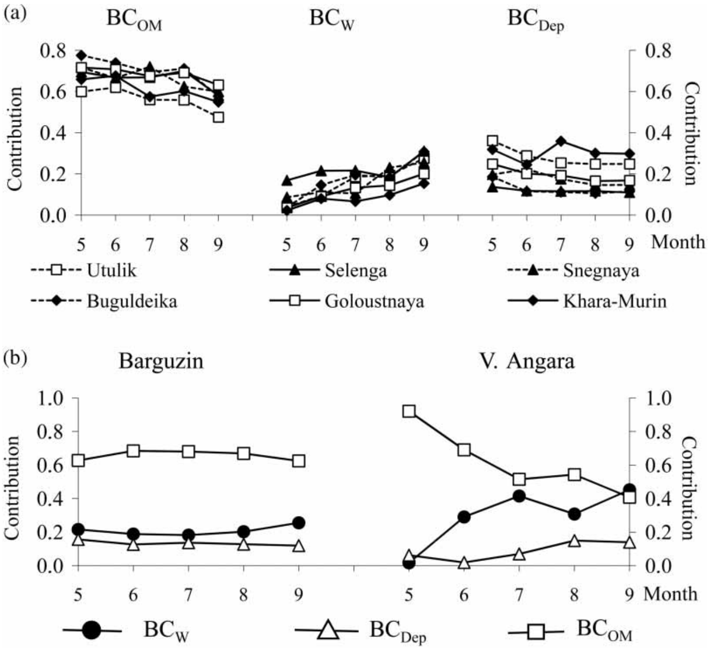

Figure 3. Base cation source contributions.

The description of dissolved matter composition in terms of contributions mostly represents the qualitative estimate: contribution decrease may be accompanied by corresponding quantity increase and vice versa. Thus, the maximum BC$_{Dep}$ and BC$_{OM}$ values were observed in the middle of summer (Figure 4), whereas their contributions were maximal in May (Figure 3a). This discrepancy is due to the fact that cation export in July is three times higher than in May, while contributions of deposition and organic mineralisation are 1.25 and 1.50 times less, respectively. Maximum BC$_{Dep}$ values are due to maximal precipitation and maximum BC$_{OM}$ values are due to both the maximum precipitation providing maximum lateral flow and maximum temperature favouring organics decomposition. The changes of BC$_W$ values during the ice-free period follow the weathering contributions, i.e. the increase from spring to autumn. In the first half of the period this increase is connected with an improvement in hydrothermic conditions and in the second half with the reduction of lateral flow.

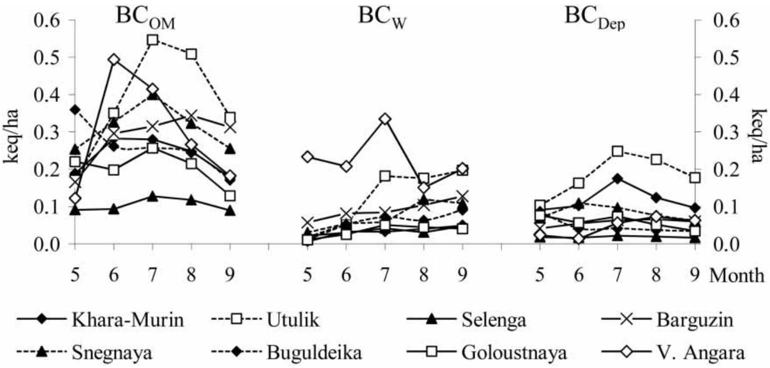

Figure 4. Base cation fluxes from different sources.

The patterns described above are not, to various degrees, observed for the V. Angara and Barguzin Rivers. The V. Angara was not included in the contribution diagrams because of its high weathering contribution and low contribution of organic matter, which are different from those observed for the other rivers (Figure 3b). Besides this, V. Angara is also characterised by the highest BC_{OM} (except Utulik) and BC_W values. High BC_W and BC_{OM} values are probably caused by thawing of alluvial permafrost soils occupying the largest part of the watershed and containing a large amount of dissolved matter released due to freezing-thawing cycles. That is why the highest BC_{OM} values are observed in June, when the upper layers start to melt, whereas the highest BC_W values coincide with highest temperatures in July. The highest BC_{Dep} values coincide with the maximum precipitation, in August.

The main peculiarity of the Barguzin River is the quite low (within the range of 10%) variation of contributions of corresponding sources (Figure 3b). Uniform contributions are probably caused by uniform distribution of precipitation, which is clearly seen from the hydrograph in Figure 2 and, consequently, by the constancy of the water flowpath. So, the simultaneous rise of BC_W and BC_{OM} values (Figure 4) simply follows the temperature that is highest in August.

The comparison of results calculated from the 2002–2004 and earlier data (Table 2) shows the difference in atmospheric deposition and organic matter contributions. This is probably due to the anthropogenic loading increase in the last decade, which is also evident from comparing the water chemistry from the two datasets (Table 1).

Table 2. Average (numerator), minimum and maximum (denominator) BC fluxes in the ice-free period.

	BC_{Dep}		BC_W		BC_{OM}	
River	keq ha^{-1}	Contribution	keq ha^{-1}	Contribution	keq ha^{-1}	Contribution
Average long-term data (May–September)						
Khara-Murin	0.12	0.30	0.03	0.08	0.23	0.62
	0.09–0.17	0.24–0.36	0.01–0.05	0.02–0.15	0.18–0.28	0.55–0.68
Utulik	0.18	0.28	0.12	0.16	0.38	0.56
	0.10–0.25	0.25–0.36	0.01–0.20	0.04–0.28	0.17–0.55	0.48–0.62
Snegnaya	0.08	0.18	0.07	0.16	0.31	0.66
	0.06–0.11	0.15–0.22	0.03–0.12	0.09–0.24	0.25–0.40	0.59–0.71
Selenga	0.02	0.12	0.03	0.22	0.10	0.66
	0.017–0.022	0.11–0.14	0.02–0.05	0.17–0.31	0.09–0.13	0.57–0.70
V.Angara	0.05	0.09	0.23	0.30	0.30	0.61
	0.01–0.07	0.03–0.16	0.15–0.33	0.03–0.43	0.12–0.49	0.42–0.93
Barguzin	0.06	0.13	0.09	0.21	0.29	0.66
	0.04–0.07	0.12–0.16	0.06–0.13	0.18–0.25	0.17–0.33	0.62–0.67
Buguldeika	0.05	0.13	0.06	0.17	0.26	0.70
	0.03–0.09	0.11–0.19	0.02–0.09	0.04–0.31	0.17–0.36	0.58–0.77
Goloustnaya	0.06	0.20	0.03	0.12	0.20	0.68
	0.03–0.08	0.17–0.25	0.01–0.05	0.04–0.20	0.13–0.26	0.62–0.72
Average long-term data (June, July, September)						
Khara-Murin	0.12	0.30	0.04	0.10	0.25	0.60
	0.10–0.17	0.23–0.35	0.03–0.05	0.07–0.14	0.18–0.28	0.54–0.67
Utulik	0.20	0.26	0.14	0.19	0.41	0.55
	0.16–0.25	0.25–0.29	0.05–0.20	0.09–0.28	0.34–0.55	0.48–0.62
Snegnaya	0.09	0.18	0.07	0.16	0.33	0.66
	0.06–0.11	0.14–0.21	0.05–0.11	0.11–0.24	0.26–0.40	0.59–0.71
Years 2000–2004 (June, July, September)						
Khara-Murin	0.18	0.43	0.05	0.12	0.19	0.45
	0.15–0.21	0.41–0.45	0.03–0.09	0.07–0.19	0.15–0.25	0.35–0.53
Utulik	0.34	0.34	0.20	0.21	0.44	0.45
	0.27–0.41	0.33–0.37	0.14–0.26	0.12–0.27	0.36–0.58	0.40–0.51
Snegnaya	0.16	0.27	0.08	0.15	0.34	0.58
	0.10–0.24	0.22–0.37	0.05–0.12	0.09–0.18	0.28–0.43	0.46–0.68

The obtained values of base cations released due to weathering and organic matter mineralisation can be considered as parameters of the carbon cycle. The carbon cycle is tightly coupled with the base cation cycle. For example, in areas unpolluted with mineral acids, the amount of cations released due to weathering is equivalent to the amount of hydrogen atoms incorporated into acidic groups of carbonic and carboxylic acids and, consequently, to the amount of carbon in these groups. The same is true for organic matter mineralisation: the amount of cations released in this process is equivalent to a certain amount of carbon that can be obtained from the C/BC ratio in plant tissues. The latter could give us the possibility of evaluating the approximate CO_2 emission from soil on the basis of BC_{OM} values, without direct CO_2 measurements. The main problem would be to take into account the cation uptake by vegetation from organic horizons.

4. Conclusions

The validity of the proposed approach was confirmed by the correspondence between calculated sources combinations and existing knowledge of ecosystem functioning and within-year surface water chemistry dynamics. It is the most cost-effective and the least laborious way to evaluate the magnitudes of three main ecosystem nutrient sources such as organics mineralisation, weathering and atmospheric deposition. Its reliability is conditioned by the use of only surface water chemistry and hydrology data, without data on terrestrial ecosystem components like soil, characterised by great spatial variability. Results obtained using this approach can be used to assess some carbon cycle parameters, such as CO_2 emission from the soil and the amount of carbon incorporated into acid functional groups putting together the total rate of organic matter oxidation. The restriction of the approach is its application only in areas with precipitation excess.

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