WATER QUALITY AND PROTECTION: ENVIRONMENTAL ASPECTS

Chemical Composition of Geographical Types of the Small River Basin Waters (Central Sikhote-Alin Mountains, Pacific Asia)[1]

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Abstract—In the article, the results of field observations of the chemical composition of the small river basin waters obtained during warm periods in 2011–2012 are presented. Seven basic geographical types of water were investigated, namely, cyclonic rainfall, rainstorm, throughfall, subsurface soil flow, low water flow (specific discharges of waters do not exceed 2.5 L/s km^2), low floods (peak specific discharges are from 2.5 to 16 L/s km^2) and medium floods (peak specific discharges are from 16 to about 100 L/s km^2). A result of the interaction between the rain water and landscape constituents is that all examined natural waters differ to the maximum extent in the anionic composition. A chemical type of stream waters is sufficiently stable; it is formed predominantly within the soil-ground cover and does not change with increase in flow rate.

Keywords: chemical composition of natural waters, geographical types of waters, small river basin, Sikhote-Alin Mountains, Pacific Asia

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INTRODUCTION

The chemical composition of river waters is a result of cumulative effect of the near-surface hydrological cycle processes reflecting an influence of all land-scape-geochemical factors. Conventional quality monitoring and episodic hydrochemical surveys of water bodies being generally the most valuable water storage, not always provide insight into a mechanism of runoff formation and its chemical composition. This gap can be essentially compensated by the experimental joint hydrological-geochemical surveys to be made in small representative river basins. Within framework of such surveys, the content and dynamics of one or another solute in a stream, soil, rain, and aquifer may reflect the landscape-geochemical and runoff formation processes and, therefore, serve as an indicator of the runoff sources [2, 6, 17]. The relevant research methodology was detailed in our recent publications [8, 18].

Rainfall, slope (soil) flow and groundwater flow are considered the principal geographical types of waters—or the streamflow substitutes. A representativeness of the obtained water samples with respect to the defined flow substitutes is provided with drawing and analysis of a great number of samples to account for spatial variability of the chemical composition.

The aim of this work is to study the chemical composition of principal flow substitutes and, then, to assess the transformation of the water composition in a course from atmosphere into a river as deduced from a representative catchment case.

OBJECTS

The observations were carried out in 2011–2012 at the Upper–Ussuri scientific station of the Institute of Biology and Soil Science, Far-Eastern Branch Russian Academy of Sciences (FEB RAS), located within the catchment of the Pravaya Sokolovka River–a IV–order tributary the Upper Ussuri River (Fig. 1). This basin is formed by a number of the medium-altitude highlands with slight saddles and dividing crests of slightly-curvy type [25]. A mean drainage density is 0.6–0.8 km/km^2, and the valleys of watercourses are deep-entrenched, often V–shaped, with slope steepness up to 35°.

The Pravaya Sokolovka River basin is located within the Sergeevsky terrain (its north-eastern part) nearby tectonic contacts with the Samarkinsky and Zhuravlevsky terrains of the Sikhote Alin accretionary system [10]. The right slope of the basin is formed by ancient metamorphic basic rocks (gabbroids, etc.) while the left one by predominantly small fields of volcanites (tuffs) and sub-volcanic acid and intermediate

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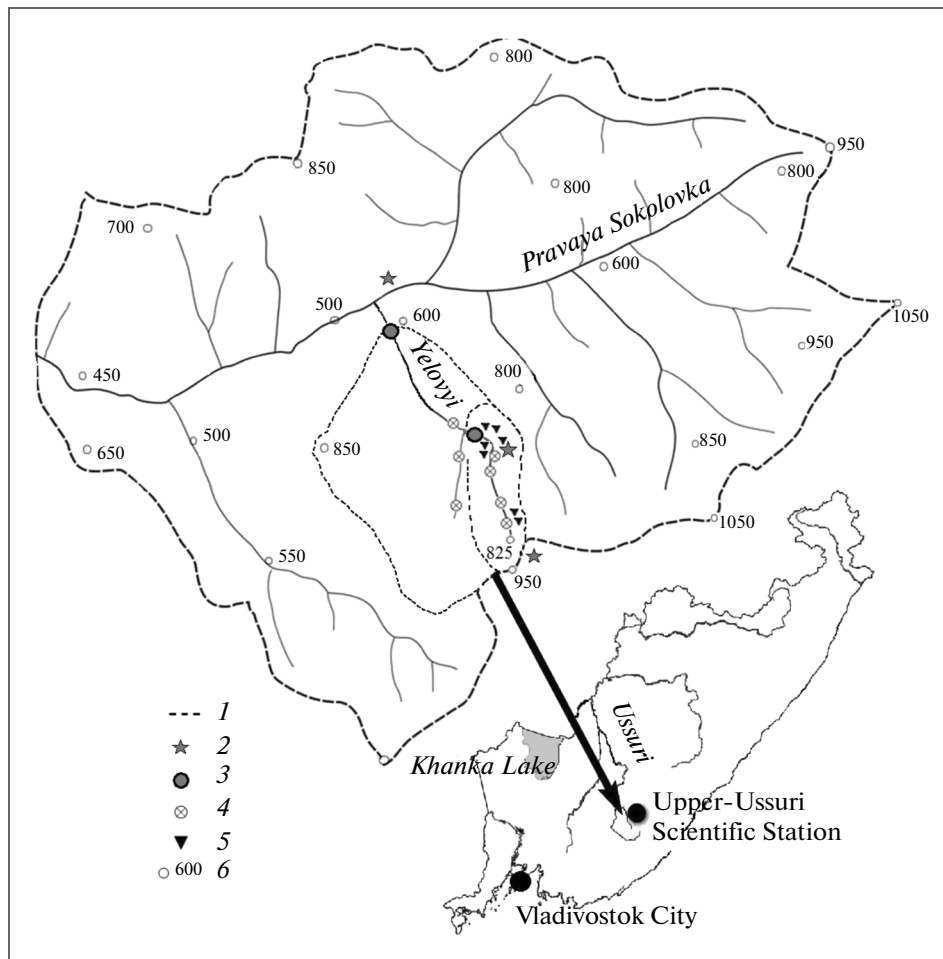[1] The article is published in the original.

Fig. 1. Schematic map of the Yelovyi Creek representative catchment in the Pravaya Sokolovka River basin. Legend: *1*—boundaries of experimental basins; *2*—locations of rain recorders and weather station; *3*—locations of stream-gauging stations; *4*—sites of one-time taking of river water samples; *5*—locations of soil water sampling using tension-lysimeters; *6*—relief elevation points according to the Baltic system of heights.

rocks (granites, diorites and syenites). The soil-forming rocks of the left border are predominantly liparite porphyries, porphyrites, dacites and syenites.

This territory belongs to the Sikhote-Alin hydrogeological folded region. In valleys of rivers, the water-bearing stratum of recent alluvial deposits is well-developed. Here, fracture and fracture-vein waters are limited to compact strongly dislocated terrigenous-siliceous and terrigenous-volcanogenic rock formations of predominantly Mesozoic and Upper Paleozoic age [9]. The groundwater with mineralization of 0.05–0.20 g/L are hydrocarbonate and calcic-magnesium while, within zones of sulfide mineralization, the sulfate or sulfate-hydrocarbonate waters with combined cationic composition occur.

As for the natural characteristics, the territory is typical of mid-mountain belt of the South Sikhote Alin Mountains and serve as a unique reference of the southern taiga with predominance of broad-leaved-Korean pine and fir-spruce forests. At elevations of

500 to 800–900 m above sea level, on alluvial deposits under the mixed coniferous-broad leaved forests, the mountain-valley soils prevail while the mountain-forest brown soils with slightly differentiated profile were defined [25]. Of these landscapes, the highest calcium content in the forest floor and litterfall prevents the illuviation of substances along the soil profile [1].

Within the belt of 800 to 1100 m a.s.l., under the fir-spruce forests, on eluvial and eluvial-deluvial deposits of watershed heads and slopes, the brown-taiga humic-illuvial soils were identified where the processes of Al-Fe−humic migration result in the decolorized eluvial horizon development [25]. Here, a few ash and calcium in litterfall was found that is inadequate to compensate the aggressive fulvic component. This determines high active soil acidity, higher water-soluble organic substance and typomorphic elements and their deep illuviation [1]. In the middle part of the Yelovyi Creek catchment, the contact belt of the fir-spruce and broad-leaved-Korean pine forests results

in development of different transitional soils. The high gritty consistency of the soils described, their loose structure and steep slopes provide speed water infiltration and the dense network of subsurface watercourses.

The humid and boreal climate of the area considered is formed under the influence of the East Asian temperate monsoon. The average annual air temperature is 0.7°C. The absolute air temperature maximum of 37−38°C is observed in July−August, while the absolute minimum of minus 43−45°C in January [12]. The average annual precipitation is 780 mm and more than 80% of it occurs in warm period−from April through October. The precipitation varies essentially from year to year and, in the summer-fall period, the deviations can reach 40−170% of the average rainfall total. Maximum daily rainfall rate often reaches 100−200 mm due to tropical cyclones in August−September. The seasonal snow cover as usual appears in November. The maximum snow cover accumulates late in March−early in April, and snow cover depth is 52−102 cm, at water storage in snow of 96−205 mm. A seasonal frost in soil is found, usually, as long as 206 days. The average maximum depth of freezing is 53−125 cm.

The experimental catchment (Fig. 1) used for detailed hydrogeochemical investigation has an area of 0.82 km². It is located in the Yelovyi Creek headwaters the total area of which is 3.53 km². The total watercourse length is 1670 m, and its total average slope is 148‰. The slopes of the Yelovyi Creek watershed have a convex form, their steepness reaches 25°; closing the stream mouth, slopes are slightly flattened and become of a concave form. In the stream valley, the flooded areas occur, limited as a rule to the groundwater egresses. The depth of impervious material is 3 m. The stream flow is perennial there.

METHODS

The general goal of observations within the experimental catchment was to elucidate in detail the processes of hydrological cycle based on advanced technical observation facilities. Rainfall events were registered by the digital raingauges HD2013 Delta−OHM and the weather station WS−GP1 Delta−T. The raingauges were installed at a height of 2 m above earth surface, one of them was mounted within the Yelovyi Creek watershed at the elevation of 900 m above sea a.s.l. while the other−nearby the Yelovyi Creek mouth, at the elevation of 500 m a.s.l. The weather station was installed on the right-bank slope of the experimental catchment, not far from its mouth, at the elevation of 650 m a. s. l.

The water level and temperature records were performed at two seasonal stations equipped with the hydrostatic water level recorders LT Levelogger Junior Solinst. In the mouth of the experimental catchment, at one station, a broad-crested weir (a small concrete dam No. 4 [25]) built in 1970s was used. The seasonal station in the mouth of the Yelovyi Creek has no special facilities. The data obtained from LT Leveloggers were used for the discharge calculations by curve $Q = f(H)$. This curve was constructed based on 87 discharges measured with a high-accuracy electromagnetic flow meter FlowSens SEBA and, in low water period, by a bucket (at the weir No. 4).

The variation range in moisture conditions during two seasonal observation cycles in 2011 and 2012 proved to be quite wide. The amplitude of water level fluctuation registered at the weir No. 4 was 17.1 cm. The discharge was varying from 0.32 to 90.7 L/s (0.001 to 0.40 mm/h). For the mouth station, the level fluctuation amplitude and discharges were 43.4 cm and from 0.09 to 234 L/s (0.00 and 0.24 mm/h), respectively.

In order to study chemical composition of runoff substitutes the precipitation, throughfall, slope (soil) and river water were being sampled systematically. The concentrations of a number of dissolved components in samples were determined.

The precipitation samples were collected into polyethylene funnels suspended at a distance of no less than 5 m from trees. The throughfall was taken into the similar funnels suspended under a leaf canopy at a height of 1.0−1.5 m above earth surface. A leaf canopy at the throughfall collection sites presents a logging area of 40 years ago overgrown mainly with small-leaved (white and yellow birch, aspen and poplar) and broad-leaved deciduous (linden, maple and elder), as well as coniferous species (fir, spruce, Korean pine).

For the slope (ground) water sampling, the tension-lysimeters with ceramic tips and of the 0.5 and 1.0 m lengths installed in undisturbed soil were used [7]. The tension-lysimeters (Tl) were arranged at the sites of gravitational moisture accumulation at different depths which allowed us to take samples quite often and in sufficient volumes (200−500 mL per 1−3 days). The Tls 1, 2 and 10 were installed at the upper part of the Yelovyi Creek watershed where the fir-spruce forests and mountain-taiga humic-illuvial soil prevails. Other lysimeters (Tls 5, 8 and 9) were installed into the mountain brown soil under the Korean pine−broad-leaved forest partially affected by cuts more than 40 years ago.

When taking the stream samples, the water temperature and specific electrical conductivity (χ) were measured using a portable thermo-conductometer Ciba Corning M90 and a portable water analyzer YSI Professional Plus while measurements of pH were carried out by pH meter "Expert 001" at the same day.

The hydrocarbonate ions were determined by potentiometric titration in the unfiltered samples on the sampling date by the standard procedure. Other dissolved components were determined after filtration using 0.45 μm filter (Durapore Millipore).

Table 1. Microelements (μg/L) in the rain and throughfall water

Element	Type of precipitation		
	Cyclonic rainfalls ($n = 9$)*	Rainstorm ($n = 13$)	Throughfall ($n = 6$)
Zn	0.9−30.7 (13.5) **	20.4−287.4 (74.3)	13.1−61.3 (40.2)
Fe	<0.1−29.0 (10.3)	10.4−118.4 (45.8)	5.2−74.3 (45.3)
Al	<0.1−16.3 (7.2)	12.1−206.8 (45.7)	4.3−108.2 (52.9)
Mn	0.1−12.1 (4.5)	6.3−116.3 (30.9)	78.5−164.9 (107.1)
B	0.07−3.53 (1.60)	<0.01−21.24 (5.03)	2.60−34.35 (17.39)
Ba	0.20−3.60 (1.50)	2.30−27.60 (8.20)	4.50−11.40 (7.60)
Pb	0.05−3.28 (1.17)	0.85−22.57 (5.87)	1.00−173.4 (31.64)
Cu	0.02−1.99 (0.66)	1.03−8.58 (3.79)	1.32−8.74 (3.04)
Ni	0.20−1.09 (0.51)	0.68−7.02 (2.78)	0.71−8.33 (3.24)
Se	<0.01−1.33 (0.44)	0.12−4.86 (1.63)	0.07−2.28 (0.76)
As	0.01−0.72 (0.30)	0.44−6.94 (2.10)	0.25−6.49 (1.89)
Ti	0.03−0.41 (0.21)	0.25−3.74 (1.29)	0.13−1.50 (0.74)
V	0.02−0.25 (0.15)	0.19−2.32 (0.75)	0.09−0.89 (0.36)
Cr	0.04−0.40 (0.12)	0.07−4.56 (1.03)	0.06−0.67 (0.36)
Cd	0.01−0.13 (0.07)	0.10−1.24 (0.36)	0.06−1.07 (0.29)
Mo	<0.01−0.04 (0.02)	0.05−0.49 (0,17)	0.01−0.42 (0.09)
Co	0.01−0.03 (0.01)	0.02−0.49 (0.15)	0.02−0.19 (0.09)
Be	<0.01−0.02 (0.01)	<0.01−0.09 (0.02)	<0.01−0.04 (0.02)
Tl	<0.01−0.02 (<0.01)	<0.01−0.40 (0.08)	<0.01−0.05 (0.02)

 * Number of samples.
** Variation limits, within the brackets—arithmetic average.

For analyses by the AAS, AES and ICP−MS methods, the samples after filtration were acidified with the nitric acid to pH of 1−2. The anions (Cl⁻, NO_3^-, SO_4^{2-}) were determined using the liquid chromatograph Shimadzu LC 10Avp (lower detection limit is 0.1 mg/L for Cl, 0.25 mg/L for NO_3^-, SO_4^{2-}) while the cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) using spectrophotometer Shimadzu AA 6800 (lower detection limit is 0.01 mg/L for Mg^{2+}, K^+, Na^+ and 0.05 mg/L for Ca^{2+}). A determination of dissolved organic carbon (DOC) was carried out using TOC−analyzer Shimadzu TOC−VCPN (lower detection limit is 0.5 mg/L). The above mentioned analyses were performed at the Laboratory for Geochemistry in PGI, FEB RAS. Silicon and microelements (Al, Zn, Fe, Mn, B, Cu, Ba, Ni, Ti, As, Pb, Se, Cr, V, Cd, Co, Mo, Be and Tl) were determined using the ICP-MS method (Agilent 7500 cx Series) in the Marine Biology Institute, FEB RAS (lower detection limit is 0.1 μg/L for Al, Zn, Fe, Mn and 0.01 μg/L for remaining microelements). In total, 300 water samples were taken and analyzed. The summary report is presented in Tables 1−3.

A verification of analysis was made, i.e., the difference in percent between the anions total and the cations total was determined by formula $R1 = 100 \times (C − A)/(C + A)$ where C is the cations total, μEq/L; A is the anions total, μEq/L [22]. Eventually, for all stream water samples, $R1$ is less than ±3% provided that Ca^{2+}, Mg^{2+}, K^+, Na^+, HCO_3^-, SO_4^{2-}, Cl⁻ and NO_3^- are considered principal ions. As for soil water, a presence of water-soluble organic substance can exert a considerable impact on ion balance. Allowing for C_{org} by formula $A^{n-} = TOC \times CD$, where $CD = 4.7−6.87\exp(−0.332 \times TOC)$ [14], balance is also satisfactory: $R1 < ±10\%$. In case of samples with pH < 5 and mineralization of less than 100 μEq/L which is characteristic for precipitation samples, ions of hydrogen, aluminum and ammonium sound essential components in ion balance, therefore, $R1$ for precipitation is <±30% because ammonium was not determined and not taken into the balance estimated.

RESULTS AND DISCUSSION

Rainfall Water and Throughfall Water

Atmospheric precipitation is considered a major source of water on the earth surface. Our results on the

Table 2. Microelements (µg/L) in the soil (slope flow) water

Element	Tension-lysimeter No., depth, cm					
	Tl 1, 50 cm (n = 11)*	Tl 2, 35–40 cm (n = 3)	Tl 10, 50 cm (n = 4)	Tl 5, 35–40 cm (n = 12)	Tl 8, 50 cm (n = 19)	Tl 9, 50 cm (n = 9)
	Spruce–fir forest, mountain–taiga humic–illuvial soils			Korean pine– broad-leaved forest, brown mountain–forest soils		
Al	22.7–92.2 (58.7)**	104.7–132.0 (121.0)	15.7–204.1 (89.3)	11.5–96.6 (42.3)	18.8–132.5 (74.5)	1.3–55.3 (28.0)
Fe	9.2–110.5 (30.2)	62.2–200.9 (110.7)	7.0–45.8 (23.4)	1.4–118.7 (28.4)	3.0–123.0 (34.6)	0.6–45.0 (13.3)
Zn	12.1–106.6 (28.7)	13.6–55.2 (28.0)	12.1–28.8 (21.9)	2.6–82.7 (17.7)	0.65–104.5 (18.6)	2.7–7.6 (4.4)
Mn	2.9–117.9 (19.1)	21.8–171.8 (73.0)	20.8–39.2 (27.2)	1.5–88.3 (14.6)	1.1–82.3 (9.0)	23.1–237.9 (73.8)
Ba	10.1–31.3 (17.9)	8.2–23.0 (13.2)	11.7–20.0 (16.5)	5.8–18.5 (9.9)	3.4–15.9 (6.7)	4.4–6.9 (5.7)
B	2.9–10.6 (6.0)	2.4–3.7 (2.9)	3.7–11.5 (8.1)	1.6–12.7 (4.5)	0.9–20.9 (5.4)	0.9–16.0 (6.2)
Cu	0.31–24.07 (3.10)	1.48–5.91 (3.12)	0.50–1.19 (0.76)	0.41–7.45 (1.60)	0.47–6.95 (1.71)	0.47–0.96 (0.70)
Ti	1.18–3.01 (1.56)	1.58–2.74 (1.97)	0.97–1.57 (1.15)	1.05–3.10 (1.44)	1.29–4.60 (1.94)	1.16–1.66 (1.39)
Cr	<0.01–4.13 (0.51)	0.17–0.62 (0.36)	0.24–0.45 (0.36)	0.02–1.26 (0.25)	0.14–1.42 (0.42)	0.05–0.16 (0.13)
Pb	0.01–2.45 (0.33)	0.16–0.41 (0.30)	0.01–0.39 (0.15)	<0.01–0.96 (0.23)	<0.01–0.82 (0.19)	<0.01–0.09 (0.02)
V	0.09–0.95 (0.27)	0.11–0.15 (0.13)	0.06–0.64 (0.31)	0.12–2.53 (0.54)	0.08–5.99 (0.53)	0.10–0.35 (0.18)
Co	0.10–1.08 (0.25)	0.16–2.26 (0.87)	0.24–0.44 (0.36)	0.02–0.78 (0.12)	0.02–0.67 (0.10)	0.05–1.09 (0.32)
Se	<0.01–0.68 (0.21)	0.15–0.83 (0.42)	0.12–0.49 (0.26)	<0.01–0.66 (0.15)	<0.01–1.37 (0.42)	<0.01–0.35 (0.15)
As	0.08–0.37 (0.20)	0.36–0.73 (0.49)	0.17–0.56 (0.35)	0.13–0.61 (0.23)	0.09–0.42 (0.21)	0.08–0.46 (0.16)
Mo	0.02–1.04 (0.17)	0.09–0.65 (0.28)	0.04–0.09 (0.06)	0.02–0.47 (0.10)	0.02–0.82 (0.12)	0.03–0.07 (0.04)
Cd	0.04–0.18 (0.07)	0.07–0.12 (0.10)	0.03–0.06 (0.05)	0.01–0.09 (0.03)	<0.01–0.31 (0.04)	0.02–0.05 (0.03)
Be	0.03–0.11 (0.06)	0.07–0.10 (0.08)	0.03–0.08 (0.05)	0.02–0.08 (0.06)	0.04–0.10 (0.07)	0.01–0.08 (0.06)
Tl	<0.01–0.02 (0.01)	0.01–0.02 (0.01)	0.01–0.03 (0.02)	<0.01–0.02 (<0.01)	<0.01–0.02 (<0.01)	<0.01

* Number of samples.
** Variation limits, within the brackets–arithmetic average.

Table 3. Microelements (μg/L) in the Yelovyi Creek at different water conditions

Element	Yelovyi Creek, weir No. 4			Yelovyi Creek, mouth		
	Phase of water regime					
	low water period (discharges up to 2.5 L/s km²) (n = 18)*	low flood (2.5–16 L/s km²) (n = 42)	medium flood (16–70 L/s km²) (n = 11)	low water period (discharges up to 2.5 L/s km²) (n = 17)	low flood (2.5–16 L/s km²) (n = 17)	medium flood (16–70 L/s km²) (n = 12)
Al	24.4–74.1 (54.6)**	25.2–101.7 (64.3)	36.6–162.5 (98.6)	6.9–31.8 (21.9)	7.5–45.7 (25.8)	22.3–115.9 (64.6)
Fe	16.6–124.0 (54.6)	12.6–168.1 (48.5)	20.2–49.6 (31.3)	8.3–126.4 (34.6)	9.7–126.6 (39.4)	22.4–90.4 (48.7)
Mn	15.4–121.7 (52.6)	9.0–80.6 (22.1)	6.3–25.6 (16.5)	0.61–3.52 (2.03)	1.24–8.55 (2.37)	0.37–9.68 (5.32)
Zn	12.7–59.4 (28.2)	10.9–40.0 (25.2)	14.4–30.3 (18.6)	0.14–16.14 (7.03)	0.76–42.93 (9.54)	3.93–16.87 (7.84)
Ba	15.1–27.2 (23.1)	13.6–25.3 (19.7)	13.9–17.6 (15.1)	4.99–9.42 (7.33)	4.73–8.22 (6.73)	5.32–7.77 (6.22)
B	1.81–5.37 (4.17)	0.28–7.61 (3.34)	3.05–7.14 (3.82)	1.86–5.88 (4.37)	1.99–7.65 (5.68)	2.64–6.54 (3.50)
Ti	1.18–3.00 (1.65)	1.19–4.88 (2.16)	1.15–1.91 (1.33)	1.40–2.24 (1.87)	1.27–3.21 (1.99)	1.48–2.43 (1.81)
Ni	0.61–3.96 (1.25)	0.52–3.60 (1.45)	0.59–0.94 (0.73)	0.14–1.37 (0.62)	0.16–1.36 (0.51)	0.27–1.21 (0.59)
Cu	0.11–2.53 (0.85)	0.13–4.64 (1.37)	0.28–0.49 (0.38)	0.09–2.39 (0.78)	0.04–1.96 (0.47)	0.24–0.50 (0.34)
As	0.33–0.90 (0.60)	0.26–0.86 (0.56)	0.30–0.47 (0.40)	0.18–0.46 (0.33)	0.23–0.54 (0.36)	0.32–0.50 (0.38)
Se	<0.01–1.29 (0.47)	<0.01–1.28 (0.41)	<0.01–0.38 (0.22)	<0.01–1.23 (0.47)	<0.01–1.35 (0.30)	<0.01–0.39 (0.24)
Cr	<0.01–1.30 (0.31)	<0.01–3.47 (0.45)	0.13–0.26 (0.17)	<0.01–1.06 (0.27)	<0.01–2.26 (0.26)	0.09–0.23 (0.14)
Pb	0.03–0.75 (0.28)	0.03–3.98 (0.49)	0.03–0.22 (0.08)	<0.01–0.58 (0.20)	<0.01–1.37 (0.19)	<0.01–0.31 (0.09)
Be	0.08–0.23 (0.17)	0.10–0.29 (0.17)	0.10–0.17 (0.12)	0.02–0.07 (0.06)	0.04–0.16 (0.10)	0.06–0.19 (0.09)
Co	0.04–0.19 (0.10)	0.03–0.15 (0.08)	0.03–0.06 (0.04)	0.01–0.06 (0.03)	0.01–0.09 (0.04)	0.01–0.05 (0.03)
Cd	0.02–0.13 (0.07)	0.02–0.11 (0.05)	0.03–0.06 (0.04)	<0.01–0.07 (0.02)	<0.01–0.04 (0.01)	<0.01–0.04 (0.01)
V	0.03–0.11 (0.06)	0.03–0.29 (0.08)	0.03–0.07 (0.05)	0.03–0.08 (0.05)	0.03–0.08 (0.06)	0.05–0.10 (0.07)
Mo	<0.01–0.04 (0.01)	<0.01–0.54 (0.08)	<0.01–0.01 (0.01)	0.02–0.09 (0.04)	0.01–0.24 (0.06)	0.02–0.05 (0.03)
Tl	<0.01–0.01 (0.01)	<0.01–0.02 (0.01)	<0.01–0.01 (0.01)	<0.01	<0.01	<0.01

* Number of samples.
** Variation limits, within the brackets–arithmetic average.

chemistry of rainfall water supplement the data obtained earlier in the Primorye territory (Pacific continental Russia) [3, 5]. Atmospheric precipitation composition depends there, first of all, on the direction of air-masses transport in different seasons of year. During summer months, the principal directions are northerly (northern Far East and Siberia) and south-westerly (Central China), and the transport out of the Sea of Japan is the rarest [10]. According to literature data, the atmospheric precipitation in the southern Far East of Russia is of complicated composition. Antecedently, it was detected the predominance of hydrocarbonate, but chloride or sulfate could prevail sometimes while sodium and calcium dominated against other cations [3, 5, 11].

According to our observations, the occasional short-term air mass precipitations—rainstorms—occurring predominantly in the first half of summer (June—July) are different from much longer cyclonic rainfalls related to the large-scale atmospheric processes in August—September.

Water of cyclonic rainfalls are ultra-fresh (mineralization is 2—4 mg/L), acidic, hydrocarbonate-sulfate, mainly calcic one (hereinafter, water is named according to predominant ions). The acidic composition of cyclonic rainfalls can be explained by effect of prevailing south-westerly atmospheric transfer of pollutants—sulfur and nitrogen oxides [11]. All macro-components are found at their levels of detection limits. In acidic atmospheric rainfalls, a significant role in ionic balance belongs to hydrogen and nitrate which, as a rule, are not principle ones in the river waters. Taking these ions into account, formula for atmospheric waters according to [15] (ratio of principal ions in %-equivalents, the secondary ions which is less than 20%-eq. are within square brackets) is as follows:

$$M_{\leq 0.01} \frac{SO_4^{2-}41NO_3^-27HCO_3^-21[Cl^-11]}{H^+64Ca^{2+}26\left[Mg^{2+}4K^+4Na^+3\right]} pH4.6-5.2.$$

The cyclonic rainfalls do not practically contain trace elements in dissolved forms (Table 1). The limits of occurrence in µg/L for the majority of elements are consistent with data by V.A. Chudaeva [5]. Based on arithmetic mean concentrations expressed in equivalent quantities (µmol/L), the determined microelements can be placed in the following sequence: Al (0.3) > Zn, Fe (0.2) > B (0.15) > Mn (0.08) > Ba, Cu (0.01) > Ni (0.009) > Pb (0.006) while contents of remaining elements in the solution are less than 0.005 µmol/L.

Rainstorms water affected by the local landscape factors, are ultra-fresh (mineralization is 4—31 mg/L), acidic, sulfate or chloride-sulfate, potassium-calcic one (Fig. 2). The sub-saline (brackish) rainfalls are of weak buffering, therefore, any change of landscape-geochemical factors affects the chemical composition of this rainfall water. As already mentioned above, the sulfate prevalence in the rainfall water can result from

global transport of technogenious substances, the same can also cause high concentrations of nitrate [11]. During warm period, the composition of rainstorms, obviously, depends on all landscape-geochemical processes, especially, biogenic ones. The potassium preponderance compared to sodium can be caused by the forest vegetation influence and significant distance of the study area from the seashore. As to the forested territories, the transpiration secretions from vegetation are of great importance for the element composition of rainstorm water even on deforested area. In transpiration moisture, biophile elements (potassium, phosphorus, magnesium etc.) are found to increase [1, 13].

The average content of nitrate ions was found out at the level of the regional background (2—3 mg/L) but some rains are characterized by concentrations of up to 11 mg/L. Amount of total dissolved organic carbon depends on seasonality, rainfall amount, "origin" of rainfall and varies within quite broad limits, from 2 to 14 mg/L. The silicon in solution is at the level of its detection limit (0.01—0.15 mg/L). The suspended matter is up to 123 mg/L but its considerable part is found as organic particles. Formula for the rainstorm water is as follows:

$$M_{0.01} \frac{SO_4^{2-}51NO_3^-31[Cl^-15HCO_3^-3]}{H^+46Ca^{2+}25K^+20[Mg^{2+}5Na^+3]} pH3.8-5.4.$$

The trace elements in rainstorm water are shown in Table 1. Eventually, the microelement series (in µmol/L) is identical to cyclonic rainfalls, but concentrations are significantly higher: Al (1.69) > Zn (1.14) > Fe (0.82) > Mn (0.56) > B (0.47) > Cu, Ba (0.06) > Ni (0.05) > Ti, As, Pb (0.03) > Se, Cr (0.02) > V (0.015) > Cd, Co (0.003) > Mo, Be (0.002) > Tl (0.0004). The predominance of such elements as aluminum and iron in rainstorm water is typical, and essential concentrations of zinc, manganese and boron there were also detected.

The continuous forest canopy is the environment where the rain water undergoes the intense biochemical transformation [1, 13, 16, 24]. That is why the water percolated through the canopy—the throughfall water—gets specific chemical features. Our observations confirm an essential difference of gross composition of the throughfall water from that of the rainfall water collected.

Low-rate rainstorms are mostly entrapped by the forest canopy. The cyclonic rain water percolating through the leaf canopy of mixed forest (white birch, yellow birch, aspen, maple species, white-bark fir, Ajan spruce, Korean pine, lime-tree et al.) is discussed below. The throughfall remains ultra-fresh and acidic (pH 4.3—5.6), and, simultaneously, the total dissolved substance in throughfall increases (6—14 mg/L), but a share of hydrocarbonate grows. So, throughfall water becomes sulfate-hydrocarbonate calcic-potassium one. We found enrichment of throughfall water with potassium and calcium. Water formula in this case is:
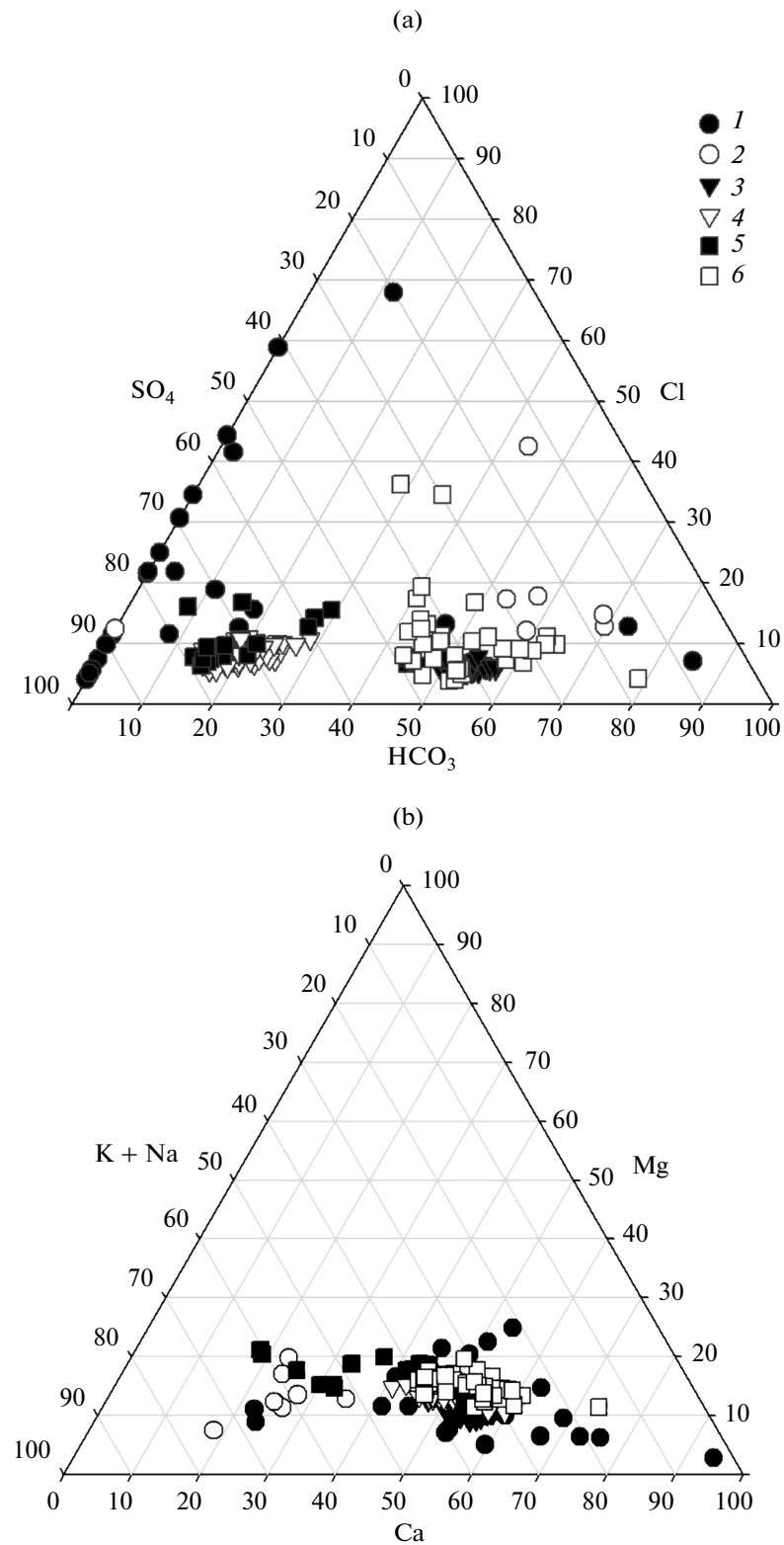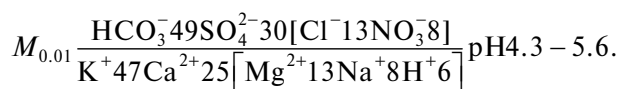
(a)

(b)

Fig. 2. Proportion of main ions (a—anions, b—cations) in the examined geographical types of waters, %-equiv.: *1*—cyclonic rainfall and rainstorm; *2*—throughfall; *3*—Yelovyi Creek, mouth; *4*—Yelovyi Creek, weir No. 4; *5*—tension-lysimeters 1, 2 and 10; *6*—tension-lysimeters 5, 8 and 9.

$$M_{0.01} \frac{HCO_3^- 49 SO_4^{2-} 30 [Cl^- 13 NO_3^- 8]}{K^+ 47 Ca^{2+} 25 [Mg^{2+} 13 Na^+ 8 H^+ 6]} pH4.3 - 5.6.$$

Microelement composition in throughfall changes prominently against rainfall water. Lead, cadmium and arsenic prevail in the acidic air-mass rainstorms and in throughfall with respect to other examined geographical types of water. The content of nickel in the atmospheric precipitations is measured by first micrograms (Table 1). The concentration series in an equivalent form is as follows: Al (1.96) > Mn (1.95) > B (1.61) > Fe (0.81) > Zn (0.62) > Pb (0.15) > Ba = Ni (0.055) > Cu (0.048) > As (0.025) > Ti (0.015) > Se (0.10) > Cr = V (0.007) > Cd (0.003) > Be = Co (0.002) > Mo (0.001) ≥ Tl (0.0001). In the throughfall, aluminum is first and manganese ranks next to aluminum as the biogenic element needed for plant growth. The atmospheric water is enriched by silicon when percolates through the leaf canopy, so, silicon increases from 0.05 up to 0.25 mg/L averagely.
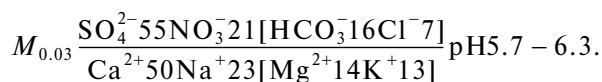
Therefore, the variations in trace elements in atmospheric water are significant, especially in rainstorms due to the dusted and vegetation-influenced local air masses. The chemical composition of atmospheric water within forested areas is impacted by the transpiration products. This could explain high content of zinc and manganese against other trace elements as earlier noted for other regions [13]. Predominance of aluminum in rainfall and throughfall water seems as a result from acidic reaction of environment and a dissolution of terrigenous suspended matter where aluminum predominates as well [5].

Slope Flow (Lysimetric Water)

Along a soil profile, all of major factors of the river water chemical composition are concentrated. According to the results of P.V. Yelpatyevsky, the spring (shallow ground) water concentrates the slope flow and, in relation to the total dissolved substances, is close to water of lower soil horizons [1].

All constituents of the landscape (rocks, soils, vegetation and climate) effect the chemical composition of the slope flow. As a result, considerable chemical differences in the water in different environments were found out. According to a ratio of principal anions, the slope water in the upper part of the Yelovyi Creek (Tls 1 and 10), where the spruce-fir forest coupled with humic-illuvial soil predominate, differ from the slope water formed under Korean pine-broad-leaved forest with brown mountain-taiga soil (Tls 5, 8 and 9) (Fig. 2). The water from Tl 2 was found to fall in between.

The slope flow in the catchment headwaters are acidic or subacidic sulfate sodium-calcic (Fig. 2). The water from Tl 1 could be described by the following formula:

$$M_{0.03} \frac{SO_4^{2-} 55 NO_3^- 21 [HCO_3^- 16 Cl^- 7]}{Ca^{2+} 50 Na^+ 23 [Mg^{2+} 14 K^+ 13]} pH5.7 - 6.3.$$

The nitrate follows next to sulfate as in rainfall water. After interaction with soil, the water fallen on the slope surface acquires the sodium-calcium composition. Potassium which is abundant in the throughfall is confined in the soil profile or, obviously, absorbed by the vegetation roots. So, sodium takes the second position there. In general, the sodium-calcium cation composition is typical for all the examined slope water and, subsequently, the river water. Penetrating from the forest canopy into the soil, water is enriched by silicon tremendously: from 0.25 up to 7.2−7.8 mg/L. Thereat, DOC is depleted from 21.0 to 3.4−5.2 mg/L owing to the intensive binding by soil particles.

The trace elements, in order of diminishing (µmol/l) for water from Tl1, form the following sequence: Al (2.18) > B (0.56) > Fe (0.54) > Zn (0.43) > Mn (0.35) > Ba (0.13) > Cu (0.05) > Ti (0.03) > Cr (0.01) > Be (0.007) > V (0.005) > Co (0.004) > Se, As (0.003) > Mo, Pb (0.002) > Cd (0.001) > Tl (<0.0001). Among microelements, the typomorphic metals—aluminium and iron—prevail, and, then, boron, zinc and manganese follow (Table 2).

The water from the lower part of the catchment (Tls 5, 8 and 9) are defined slightly acidic or neutral, and its composition becomes sulfate-hydrocarbonate and sodium-calcium one. The remarkable fact is that the sampled slope water composition is identical to that in the Yelovyi Creek mouth (Fig. 2). Water formula for the water from Tl 8 is:

$$M_{0.03} \frac{HCO_3^- 50 SO_4^{2-} 40 [Cl^- 9 NO_3^- 1]}{Ca^{2+} 57 Na^+ 23 [Mg^{2+} 14 K^+ 6]} pH6.1 - 7.2.$$
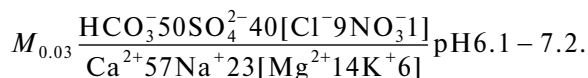
The content of silicon in this type of water is detected higher than in the slope water from the coniferous-forested headwaters as 8.5 mg/L averagely. Simultaneously, DOC increases slightly to about the averaged 5 mg/L.

The trace elements (µmol/L) in water from the brown mountain-taiga soil, in a whole, are lower than that in the previous group but pattern of their distribution is quite similar: Al (2.76) > Fe (0.62) > B (0.49) > Zn (0.28) > Mn (0.16) > Ba (0.05) > Ti (0.04) > Cu (0.03) > V (0.01) > Cr, Be (0.008) > Se (0.005) > As (0.003) > Co (0.002) > Mo, Pb (0.001) > Cd (0.0004) > Tl (<0.0001).

River Water

The composition of water in the mouth of Yelovyi Creek is close to the composition of the adjacent rivers being no subject to anthropogenic pollution [4, 19]. At the same time, the stream water at the experimental catchment outlet (the dam No. 4) has some essential features. A number of main ions in the river are deter-

mined by hydrological regime while a character of this relation reflects a specificity of geochemical processes within the drained soil layers and underlying rocks. In this regard, the whole number of the river water samples was divided into three groups according to three phases of river regime: (1) low-water flows (specific discharge is less than 2.5 L/s km²), (2) lower floods (from 2.5 to 16 L/s km²) and (3) medium floods (from 16 to 100 L/s km²). Rather seldom cases of high floods were not observed in 2011−2012.

During the rainless periods when the ground component prevails in the river flow, the Yelovyi Creek water at the experimental catchment outlet is defined ultra-fresh, slightly acidic, sulfated and sodium-calcic one (Fig. 2). In general, the macro-element composition of the Yelovyi Stream water is similar to the composition of soil water in the upper part of the basin (Tl 1 and 10). Silicon in the river water rises from the headwaters to the mouth as 8.20 to 9.74 mg/L, while DOC is revealed to be substantially stable − 2.1−2.5 mg/L.

The Kurlov formula as applied to this type of water is as follows:

$$M_{0.02} \frac{SO_4^{2-}65[HCO_3^-18NO_3^-10Cl^-7]}{Ca^{2+}52Na^+23[Mg^{2+}13K^+12]} pH5.8-6.1.$$

A low water mineralization during the rainless periods allows to suggest the atmospheric genesis of soil (slope) water, a prevalence of magmatic rocks there and their weak chemical denudation in the watershed. A short time of water interaction with rocks due to quick water migration through the slope deposits, contributes also to low mineralization of the water studied. A predominance of sulfate in the river water and low hydrocarbonate reflect both specific processes of organic matter decomposition in the humic-illuvial soils with sulfates and possible sulfide mineralization impregnation within the river basin. The lysimetric water from podzolic soils, within the temperate forest area, contains the considerable amount of water-soluble organic substance, sulfates and potassium as compared with sodium which is, obviously, due to an important role of organic matter in the water composition [20].

The trace elements in the water during low water period are subjected to the landscape-geochemical factors, primarily, to biota resulting in considerable variability of values (Table 3). The concentration sequence of microelements (μmol/L) is as follows: Al (2.02) > Fe (0.98) > Mn (0.96) > Zn (0.43) > B (0.39) > Ba (0.17) > Ti (0.03) > Ni (0.02) ≥ Be (0.02) > Cu (0.013) > As (0.008) > Se = Cr (0.006) > Co (0.002) > Pb (0.001) > V (0.001) > Cd (0.0006) > Mo (0.0001) ≥ Tl (<0.0001). In the stream water in rainless periods, the barium is determined higher than that in the rainfall and even in lysimetric water which could point on additional contribution of this element with deeper flow from the underlying rocks.

During low floods caused by rainstorms, the water composition changes slightly. A weak increase in mineralization and acidity, growth in nitrate, magnesium, sodium and potassium as well as reduction of sulfate, hydrocarbonate and calcium against the low water are observed. At that time, Fe, Ba, B and above all Mn go down in water because of dilution, but Al, Ti, Ni, Cu, Cr, Pb, V and Mo rise due to their migration capacity increased (Table 3).

The higher floods generated by relatively abundant cyclonic rainfalls are characterized by reduction in mineralization and pH, at that time, the sulfates continue to decrease while the nitrates increase further and ratio of other ions varies slightly. At the time of floods, the microelements concentration sequence remains factually unchanged: aluminum and iron remain predominant in the solution whereas manganese and zinc become lower and boron takes the third position. The flood water is quite enriched in aluminum while iron, manganese and zinc averagely decrease (Table 3). An increase in water flow leads to a sharp increase in metals along the flood rise and slow lowering at the flood recession (Figs. 3e, 3f).

The chemical composition of the first-order watercourses is foremost addicted to change in the landscape-geochemical environment while, with increase in watershed area and watercourse order, a local effect of geochemical factors is leveled and the chemical composition becomes more stable. The water in the Yelovyi Creek mouth significantly differs in anionic composition from that at the experimental catchment outlet (Fig. 2). In summer low-water periods, the water is ultra-fresh (total dissolved substances is 28−33 mg/L), neutral (pH 6.6−7.1), sulfate-hydrocarbonate and sodium-calcic one. Water formula is as follows:

$$M_{0.03} \frac{HCO_3^-51SO_4^{2-}39[NO_3^-5Cl^-5]}{Ca^{2+}53Na^+29[Mg^{2+}11K^+7]} pH6.6-7.1.$$

Total suspended substances reach their maximum (up to 30 mg/L) in the course of the rising of the flood whereas in other periods, it is not significant (1.6−13.0 mg/L).

The water-soluble organic substance is minimal during rainless period—1.8−2.5 mg/L and increases up to 7.5 mg/L in the course of heavy rainfalls. Silicon, in the contrary, is maximal during the rainless period and goes down as water discharge increases, which confirms its migration to the river with ground flow. In cases of slight increase in discharge, the mineralization increases while pH and water chemical type is detected to not change. The higher floods result in a slight decline in mineralization and pH, water remain sulfate-hydrocarbonate and sodium-potassium, and a share of nitrates increases slightly at the expense of reduction of sulfates and hydrocarbonates.

The higher floods result in a weak decline in mineralization and pH, the water remains sulfate-hydrocarbonate and sodium-potassium, and a share of nitrates
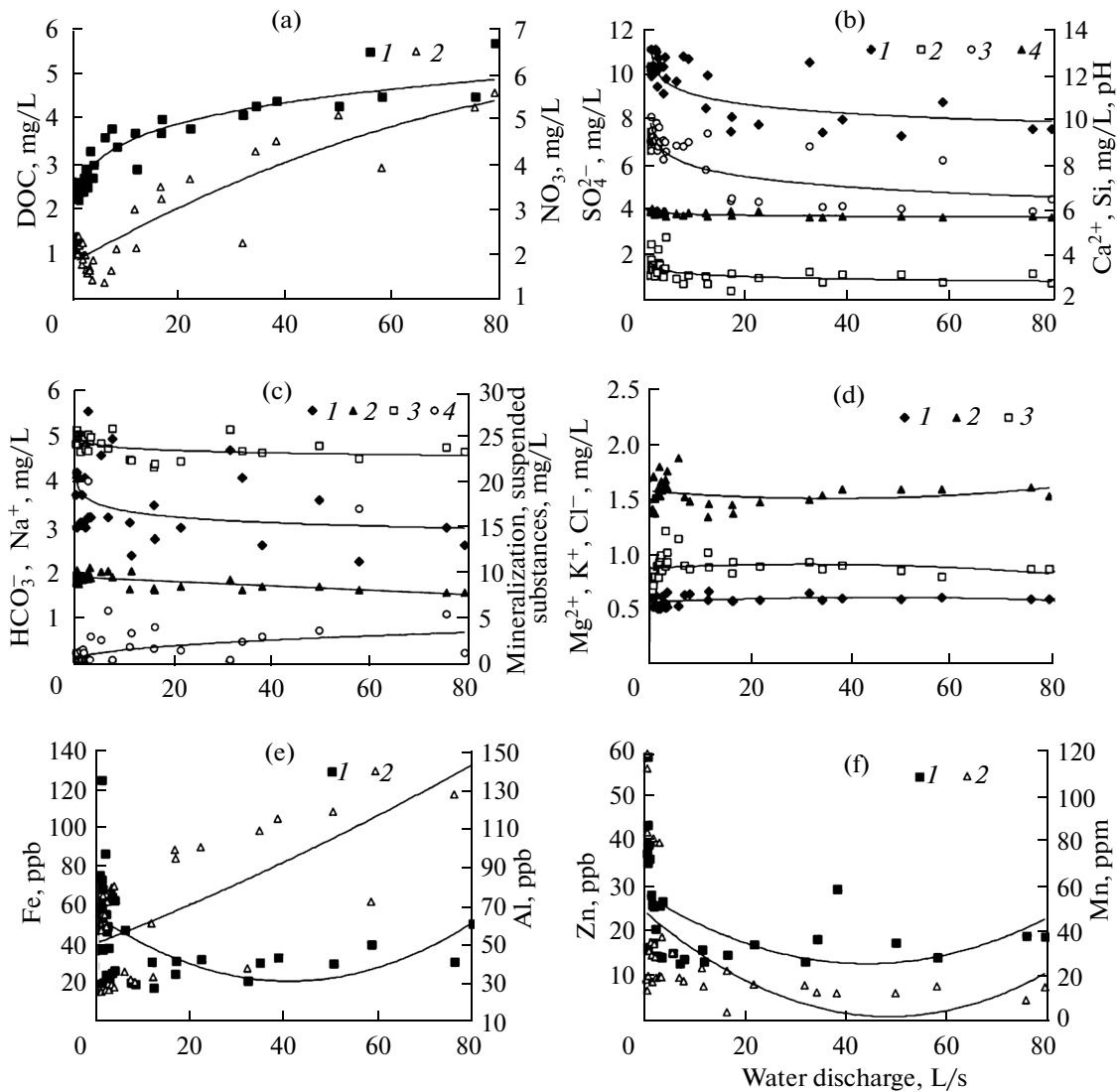
Fig. 3. Relation of macrocomponents and microelements in the Yelovyi Creek, at weir No. 4, to water discharge: *1*—C_{org}, $R^2 = 0.92$; *2*—NO_3^-, $R^2 = 0.82$ (a); *1*—SO_4^{2-}, $R^2 = 0.57$; *2*—Ca^{2+}, $R^2 = 0.29$; *3*—Si, $R^2 = 0.62$; *4*—pH, $R^2 = 0.60$ (b); *1*—HCO_3^-, $R^2 = 0.17$; *2*—Na^+, $R^2 = 0.49$; *3*—mineralization, $R^2 = 0.31$; *4*—suspended substances, $R^2 = 0.25$ (c); *1*—Ma^{2+}, $R^2 = 0.076$; *2*—K^+, $R^2 = 0.040$; *3*—Cl^-, $R^2 = 0.024$ (d); *1*—Fe, $R^2 = 0.21$; *2*—Al, $R^2 = 0.52$ (e); *1*—Zn, $R^2 = 0.37$, *2*—Mn, $R^2 = 0.39$ (f).

increases slightly owing to the reduction of sulfates and hydrocarbonates. The concentration sequence of trace elements is similar to that for the Yelovyi Creek at the mouth but the absolute values (μmol/L) are much lower: Al (0.81) > Fe (0.62) > B (0.40) > Zn (0.11) > Ba (0.053) > Ti (0.039) > Mn (0.037) > Cu (0.012) > Ni (0.011) > Be (0.007) > Se (0.006) > Cr (0.005) > As (0.004) > V = Co = Pb (0.001) > Mo (0.0004) > Cd (0.0002) > Tl (<0.0001). The distinctive feature is low concentration of zinc and manganese as similar to the Yelovyi Creek headwaters.

Some components in the river water were investigated in connection to a streamflow discharge. As a result, the components were separated into four categories: (1) the components which increase evidently with water discharge rising—dissolved organic carbon and nitrates (Fig. 3a); (2) the components which decrease with the flow rising—pH, silicon, calcium and sulfates (Fig. 3b); (3) the components which have a complicated indistinct relation to the flow rate—total dissolved substances, hydrocarbonates, sodium and suspended matter (Fig. 3c); (4) the components which are practically not related to the river regime—potassium, magnesium and chlorides (Fig. 3d).

It seems the upper soil horizons where the processes of humification and nitrification take place are

a principal source of riverine organic matter and nitrates. An increase in organic matter and nitrates with rising discharge is considered typical for many rivers [21, 23]. Silicon, calcium and sulfates are supplied with deep ground water; therefore, rising of the rainfall flood discharges should result in lowering of their concentrations in the river.

Most likely, the obtained evidence of chemical similarity of the soil and streamflow water is to reflect the fact that the first and second Shreve orders watercourses, due to their weakly-shaped valleys, drain only comparatively shallow slope deposits of Cretaceous rocks. Considerable fluctuations in dissolved substances could say that chemical composition of the slope flow depends on precipitation volume (moisture content over a whole basin). But it needs to be confirmed by additional investigation.

The content of trace elements in the Yelovyi Creek is rather typical for clean rivers of Primorye [4, 19] but peculiar features exist also. Aluminum, being a slow-migrating lithophile aquatic migrant, characterizes most evidently the environmental types of water: its minimum content is observed in cyclonic rains while maximum one is confined to soil solutions, that is why it's concentration in river fluctuates (Table 3). Iron, zinc and manganese are cationic biophile elements. They are sensitive to changes in acid-alkaline and reductive-oxidative conditions; this is to explain sufficiently great dispersion of their concentrations, especially in slope and river water in the rainless periods. Copper is easily extracted from water by clay and organic colloids, so, its minimum concentrations are detected in soil solutions within the upper soil horizons (litter and humus-accumulative ones). Barium migrates weakly, its maximum was observed in the Yelovyi Creek in low water period and in deep slope flow. Concentration of arsenic is tenths of μg/L in river and soil water, and it is detected as up to $1-2$ μg/L in some types of precipitation water with maximum in the rainstorm water.

CONCLUSIONS

In the course of moving to small rivers, the atmospheric water is subjected to significant chemical transformation.

As a result, all examined environmentally related types of natural water differ, to the fullest extent, in anionic composition, but at the same time, its cationic composition changes too. The cyclonic rainfall water is determined as extremely low-mineralized, and sulfate, nitrate and hydrocarbonate as well as hydrogen and calcium predominate among cations there.

Water of air mass rainstorms that occur in a local temporal-spatial scale contains $4-5$ times more significant amount of sulfate, chloride, nitrate as well as Fe, Al, B, Ba, Pb, Se, V, Cd compared to cyclonic rainfall water, while a share of potassium and magnesium (perhaps, owing to its coming into the atmosphere with transpiration fluxes from the plant canopy) and Zn, Mn, Cu, Ni, As, Ti, Cr, Mo, Co and Tl increase 6 times and even more. The total dissolved substances and DOC rise up about 4 times against the cyclonic rainfall water.

The throughfall water contains dissolved calcium, sulfate, chloride, Zn, Se, Ti, V, Cr, Mo, Tl and suspended substances $2-3$ times, and nitrate 5 times less, while potassium, Si, DOC, Mn, B, and Pb $3-5$ times more, and hydrocarbonate up to around 12 times more than the rainstorm water. The total dissolved substances, Na, Mg and some trace elements as Fe, As, Ca, Cd, Ni and Be in the atmospheric water are found quite stable on the course of its percolation through the canopy.

The soil is a major source of hydrocarbonate, sulfate, Ca, Mg, Na, Al, somewhere Fe, Ba, Ti, Mo and Be as well as dissolved forms of Si, but soil also serves a sink of Zn, Mn, Pb, Se, Cu, As, V, Cd, B and Co. The slope (soil) water can be separated into two basic groups: (1) sulfated one extracted mainly from the soil where the illuvial-humic processes dominate, and (2) sulfate-hydrocarbonate water related originally to the brown mountain-forest soil.

The chemical type of river water is quite stable and does not change with increase in water discharges. The river water composition looks rather similar to the slope (soil) water since the former is formed within the shallow slope deposits. The streams draining the coniferous-forested headwaters concentrate more Al higher flow rate, but lower part of the catchment contributes more Al, Fe and Mn at the same conditions. Medium floods enhance a migration capacity for some components as total ions, suspended substances, DOC, nitrate, Ti, Ni, Cu, Cr, Be and Pb. Extreme floods cause obvious dilution of total ions, suspended substances, Si, hydrocarbonate, sulfate, Ca, Fe, Ti, Ni, Cu, Cr, Pb and Mo.

The sufficiently stable relation was established between a streamflow rate and such components as nitrate, DOC, sulfate, hydrocarbonate and silicon. At recorded low mineralization of natural waters, the mentioned components could serve indicators of the studied environmental water types (tracers). In all water types, Al, Zn, Fe, Mn and B prevail among trace elements. The river water is characterized by higher Ba while the atmospheric water—by higher Cu, Ni, Pb, Ca, and As.

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