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Chemical transformation of water at small catchments in extratropical monsoon zone (a case of Sikhote Alin Mountains, Pacific Russia)

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Abstract : In the paper, the results of field observations of water chemical composition obtained during warm periods of 2011-2012 at a representative small catchment are presented. Seven basic landscape types of water were distinguished and investigated, namely, cyclonic and air-mass rainfall, 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 100 l/s·km^2). A result of the interaction between the rainfall and landscape components is that all natural water types examined differ to the maximum extent in the anionic composition. A chemical pattern of the stream water is found to depend definitely on many-days prehistory in hydrological conditions; it is predominantly formed in the soil-ground cover and does change with increase in discharge ambiguously and nonlinearly.

Keywords : Water chemical composition; Stream water; Rainfall; Throughfall; Soil flow; Flood; Small catchment; Sikhote alin mountains; Pacific Russia.

The hydrochemical regime of a river is a result of cumulative effect of processes in the near-surface hydrological cycle. That is why it reflects an influence of the landscape-geochemical environment. 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, in soil, in rain, in aquifer may reflect the landscape-geochemical and runoff formation processes and, therefore, serve as an indicator of the runoff sources[2, 6, 16]. The relevant research methodology was detailed in our publication[17].

Rainfall, subsurface soil flow and groundwater flow are considered as principal environmental water types – the flow 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 their contributions into the streamflow chemistry 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 located within the Pravaya Sokolovka River watershed – a IV-order tributary of the Upper Ussuri River, Pacific Russia (Figure 1).

This basin is composed by a number of the medium-altitude highlands with slight saddles and dividing crests of slightly-curvy type[24]. 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

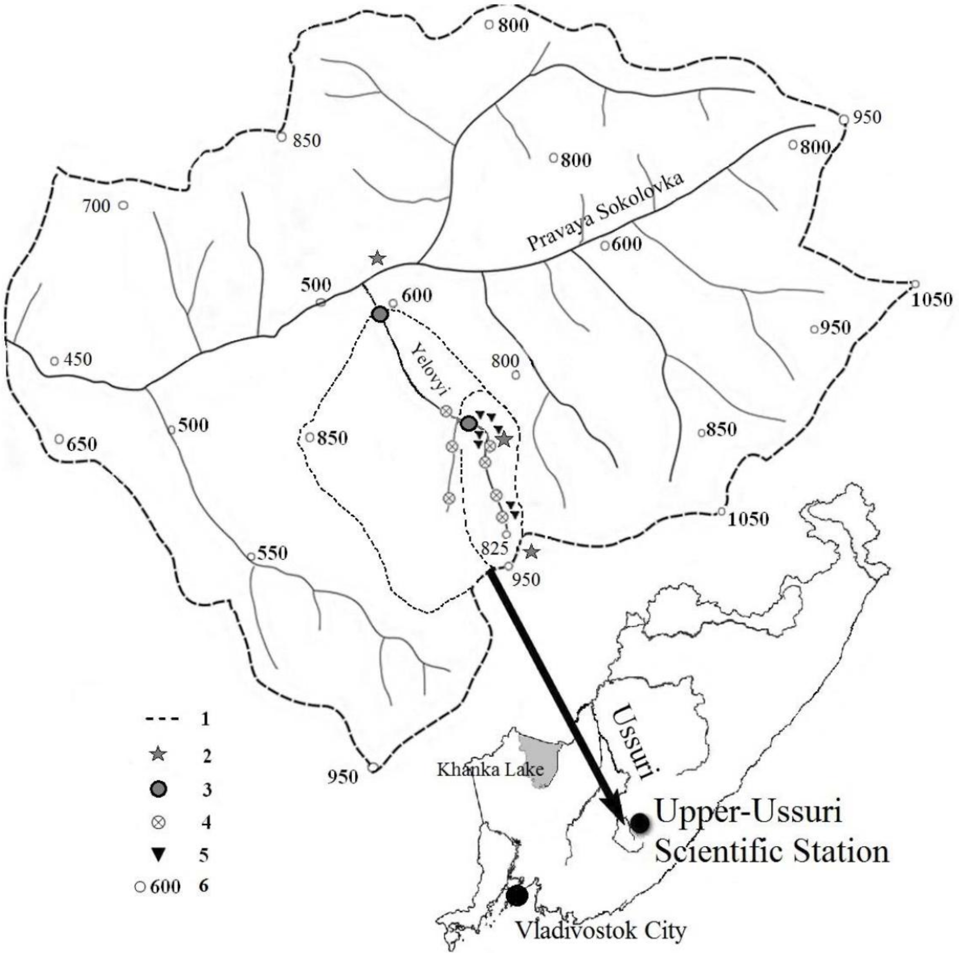

Figure 1 : Schematic map of the Yelovyi Creek representative catchment in the Pravaya Sokolovka River watershed. Legend: 1) boundaries of experimental basins; 2) locations of rain recorders and weather station; 3) locations of stream-gauging stations; 4) sites of one-time taking of river water samples;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

within the Sergeevsky terrain (its north-eastern part) nearby tectonic contacts with the Samarkinsky and Zhuravlevsky terrains of the Sikhote Alin accretionary system[9]. 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 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[8]. 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[24]. 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[24]. 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[11]. The average annual precipitation total 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 (Figure 1) used for detailed hydrogeochemical investigation has an area of 0.82 km^2. It is located in the Yelovyi Creek headwaters the total area of which is 3.53 km^2. 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 streamflow 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 rain gauges HD2013 Delta-OHM and the weather station WS-GP1 Delta-T. The rain gauges were installed at a height of 2 m above earth surface, one of them was mounted in the Yelovyi Creek watershed at elevation about 900 m above sea a.s.l. while the other – nearby the Yelovyi Creek mouth, at elevation about 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 height of about 650 m above sea level.

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 No. 4 (a small concrete dam[24]) 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 relation $Q=f(H)$. The latter was 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 hydrological 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 (talus, soil) and river water were being sampled systematically. Then concentrations of a number of dissolved components in samples were determined.

The precipitation samples were collected into polyethylene funnel suspended outdoor at a distance of no less than 5 m from neighboring trees. The throughfall was taken into the similar polyethylene funnel suspended under a leaf canopy at a height of 0.5-1.0 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 (linden, maple and elder) deciduous, as well as coniferous (fir, spruce, Korean pine) species.

For slope (soil) water sampling, the tension-lysimeters of 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 every 1-3 days). Tl-1, Tl-2 and Tl-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 (Tl-5, Tl-8 and Tl-9) were installed into the mountain brown soil under the Korean pine – broad-leaved forest partially felled more than 40 years ago.

When taking the stream samples, the water temperature and specific electrical conductivity () 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". 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). 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-V_{CPN} (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 TABLE 1–3 (see the Appendix below).

A verification of analysis was made, i.e. the difference in percent between the anions total and the cations total was determined by formula $R1=100*(C-A)/(C+A)$ where C is the cations total, μEq/L; À is the anions total, μEq/L[21]. Eventually, for all stream water samples, R1 is less than ±3% provided that Cà$^{2+}$, Ìg^{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 $A^{n-}=TOC*CD$, where $CD=4.7-6.87*\exp(-0.332*TOC)$[13], balance is also satisfactory: $R1< \pm10\%$. 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 $< \pm30\%$ because ammonium was not determined and was not taken into the balance estimated.

RESULTS AND DISCUSSION

Rainfall and throughfall

Atmospheric precipitation is considered a major source of water on the earth surface. Our results concerning the chemistry of rainfall supplement 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, often with predominance of hydrocarbonate, but chloride or sulfate can prevail while sodium and calcium dominate against other cations[3, 5, 10].

According to our observations, the occasional rainstorms occurring predominantly in the first half of summer (June-July) are different from cyclonic ones related to the large-scale atmospheric processes in August-September.

Cyclonic rainfalls are ultra-fresh (mineralization is 2–4 mg/l), acidic, hydrocarbonate-sulfate, mainly calcic ones (hereinafter, waters are 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[10]. All macrocomponents 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 M.G. Kurlov[14] (ratio of principal ions in %-equivalents, the secondary ions which is less than 20%-eq. are within square brackets) is as follows:

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

The cyclonic atmospheric precipitations do not practically contain microelements in dissolved forms (TABLE 2). The limits of occurrence in μg/l for the majority of elements are comparable 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 subjected to the local landscape factors effect, are ultra-fresh (mineralization is 4–31 mg/l), acidic, sulfate or chloride-sulfate, potassium-calcic (Figure 2).

The sub-saline (brackish) rains are of weak buffering, therefore, any change of landscape-geochemical factors affects the chemical composition of this rain water. As already mentioned, the sulfate composition of rain water can result from global transport

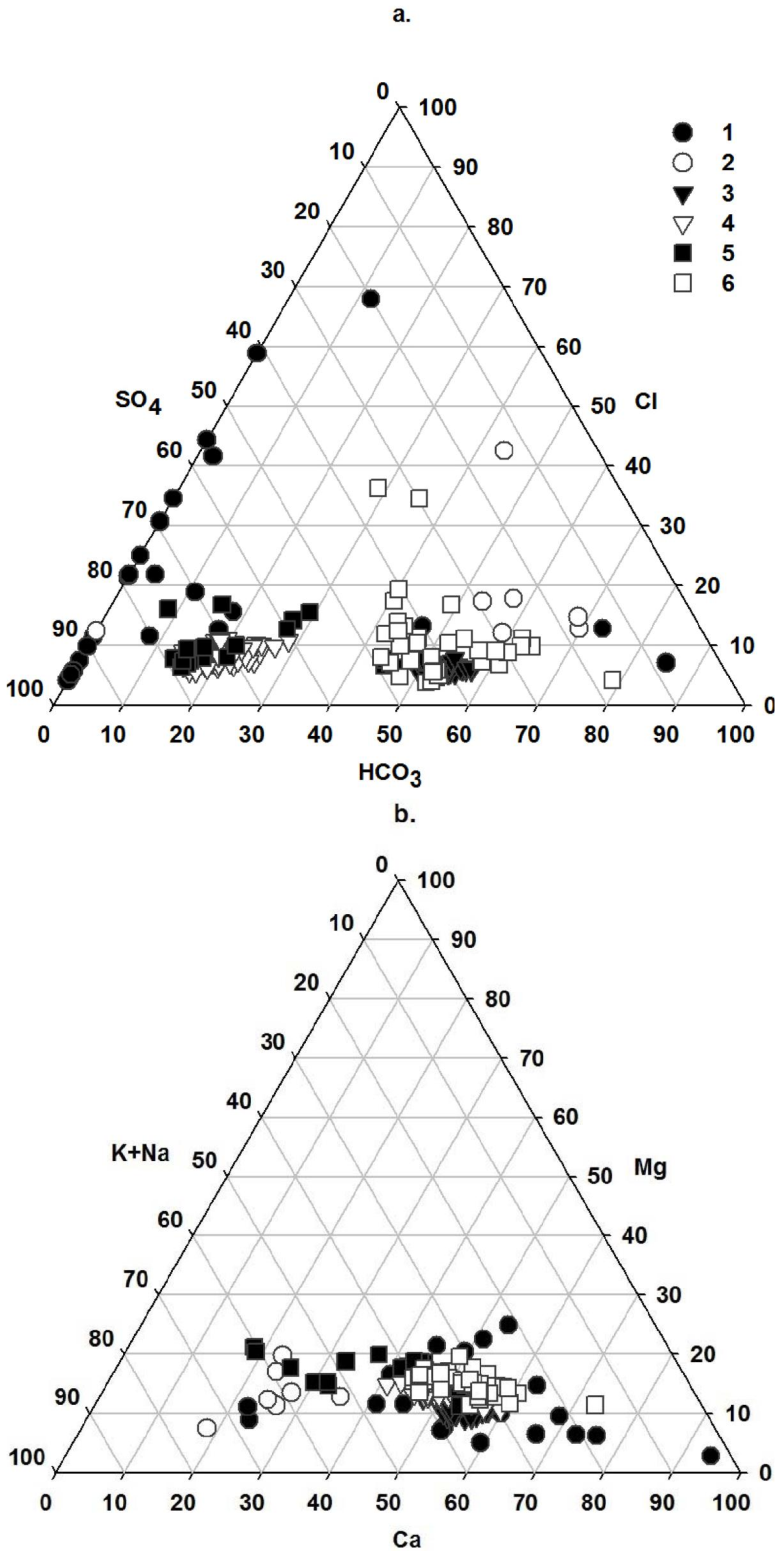

Figure 2 . Proportion of basic ions (a. – anions, b. – cations) in the examined genetic types of waters, %-equiv.: 1-rainfall; 2 – throughfall; 3 – Yelovyi Creek, mouth; 4 – Yelovyi Creek, weir No. 4; 5 – tension-lysimeters 1, 2 and 10; 6 – tension-lysimeters 5, 8 and 9

of technogenious substances, the same can also explain a high concentration of nitrate[10]. 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, 12].

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:

$$M_{0,01}\frac{SO_4^{2-}51\ NO_3^{-}31[Cl^{-}15HCO_3^{-}3]}{H^{+}46Ca^{2+}25\ K^{+}\ 20\ [Mg^{2+}5\ Na^{+}3]}pH3.8-5.4$$

The microelements in rainstorm water are shown in the TABLE 2. 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 observed.

The continuous canopy is an environment where the rain water undergoes the intense biochemical transformation[1, 12, 15, 23]. Our observations confirm an essential difference of gross composition of throughfall from that of rainfall water collected.

Low-rate rainstorms are mostly entrapped by the forest canopy. The cyclonic rain water percolating through 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

TABLE 1 : Microelements (μg/l) in rainfall and throughfall.

Element	Type of precipitation		
	Rainfall (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, in brackets – arithmetic average)

and acidic (pH 4.3–5.6), and, simultaneously, total dissolved substance in throughfall increases (6–14 mg/l), but a share of hydrocarbonate grows. So, throughfall becomes sulfate-hydrocarbonate calcic-potassium. We found the enrichment of throughfall with potassium and calcium. Water formula in this case is:

$$\mathbf{M_{0,01}\frac{HCO_3^{-}49SO_4^{2-}30[Cl^{-}13NO_3^{-}8]}{K^{+}47Ca^{2+}25\left[Mg^{2+}13Na^{+}8H^{+}6\right]}pH4.3-5.6}$$

Microelement composition in throughfall changes against rainfall water. Lead, cadmium and arsenic prevail in the acidic air-mass atmospheric precipitations and throughfall with respect to other examined genetic types of waters. 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.

Therefore, the variations in microelements in atmospheric water are significant, especially in rainstorms. 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 microelements as earlier noted for other regions[12]. Predominance of aluminum in rainfall and throughfall 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 P.V. Yelpatyevsky results, 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 the landscape factors (rocks, soils, vegetation and climate) effect the chemical composition of slope flow. As a result, the considerable differences in the chemistry of water under the different environments were found out. According to a ratio of principal anions, the slope water in the upper part of the Yelovyi Creek (Tl-1 and Tl-10), where the spruce-fir forest and humic-illuvial soil predominate, differ from the slope water formed under Korean pine-broad-leaved forest with brown mountain-taiga soils (Tl-5, Tl-8, Tl-9) (Figure 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 (Figure 2). The water from Tl-1 could be described by the following formula:

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

The nitrate follows next to sulfate as in rainfall water. After interaction with soil, the water acquires the sodium-calcium composition, i.e. potassium which is abundant in the throughfall, is confined in the soil profile or, obviously, absorbed by vegetation. 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.

The microelements, 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 elements – aluminum and iron – prevail, and, then, boron, zinc and manganese follow (TABLE 2).

The water from other tension-lysimeters (Tl-5, Tl-8 and Tl-9) are found to be slightly acidic or neutral and to have the sulfate-hydrocarbonate, sodium-calcium composition. The water in the mouth of the Yelovyi Creek is identical, in its composition, to the examined slope flow (Figure 2). Water formula for the water from Tl-8 is:

$$\mathbf{M_{0.03}\frac{HCO_3^{-}50SO_4^{2-}40\ [Cl^{-}9NO_3^{-}1]}{Ca^{2+}57\ Na^{+}23\ [Mg^{2+}14\ K^{+}6]}pH6.1-7.2}$$

The microelements (µmol/l) in water from Tl-5, Tl-8 and Tl-9, in a whole, are lower than that in the

TABLE 2 : Microelements (μg/l) in the soil water (slope flow).

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, in brackets – arithmetic average)

previous group but features of their distribution is 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, 18]. At the same time, the stream water at the experimental catchment outlet (the weir No.4) has some essential features. A number of main ions in the river are determined 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·km^2), 2) lower floods (from 2.5 до 16 l/s·km^2) and 3) medium floods (from 16 to 100 l/s·km^2). Rather seldom cases of high rain floods were not observed in 2011-2012.

During rainless periods, the Yelovyi Creek water at the experimental catchment outlet is found to be ultra-fresh, slightly acidic, sulfated and sodium-calcic one (Figure 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 Tl-10).

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

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

A low water mineralization during the rainless periods when the ground component prevails in the river flow allows to suggest the atmospheric genesis of soil (slope) water, a predominance of magmatic rocks there and a slight degree of their chemical denudation in the watershed. A short time of water interaction with rocks due to quick water exchange contributes also to low mineralization of the water examined. A predominance of sulfate in the river water and a 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[19].

The microelements in the waters during rainless period is subjected to landscape-geochemical fac-

TABLE 3 : Trace elements (μg/l) in the Yelovyi Creek at different water conditions

Element	Yelovyi Creek, weir No.4			Yelovyi Creek, mouth		
	Hydrological conditions					
	Low water period (discharges up to 2.5 l/s·km^2) (n = 18)*	Low flood (2.5-16 l/s·km^2) (n = 42)	Medium flood (16 -70 l/s·km^2) (n = 11)	Low water period (discharges up to 2.5 l/s·km^2) (n = 17)	Low flood (2.5-16 l/s·km^2) (n = 17)	Medium flood (16 -70 l/s·km^2) (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, in brackets – arithmetic average)

tors, primarily, biota which results 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) ≥ T l(<0.0001). In the stream water during rainless period, the barium is determined higher than that in the rainfall and even in lysimetric water which can be related to additional influent of this element with deeper ground flow.

During low floods, the water composition varies only slightly. A weak increase in mineralization and acidity, growth in nitrates, magnesium, sodium and potassium as well as reduction of sulfates, hydrocarbonates and calcium are observed. The higher floods caused by abundant rainfalls are characterized by reduction in mineralization and pH, at the same 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 comparatively enriched in aluminum while iron, manganese and zinc in average decrease (TABLE 3). An increase in discharge leads to a sharp increase in metals during the flood rise and at its peak and slow lowering during the flood recession (Figure 3, E and F).

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 found to be 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 (Figure 2). In summer low-water periods, the water is ultra-fresh (total dissolved substances is 28–33 mg/l), neutral (pH is 6.6–7.1), sulfate-hydrocarbonate and sodium-calcic one. Water formula is as follows:

$$\mathrm{M}_{0.03}\frac{\mathrm{HCO_3^{-}\,51\,SO_4^{2-}\,39\,[NO_3^{-}\,5\,Cl^{-}\,5]}}{\mathrm{Ca^{2+}\,53\,Na^{+}\,29\,[Mg^{2+}\,11\,K^{+}\,7]}}\mathrm{pH}6.6-7.1$$

Total suspended substances are maximal on the flood rise (up to 30 mg/l) whereas in other periods, it is insignificant (1.6–13.0 mg/l). The water-soluble organic substance is minimal during rainless period – 1.8–2.5 mg/l and increases to 7.5 mg/l in the course of heavy rainfalls. Silicon, in the contrary, is maximal during the rainless period and lowers, as water discharge increases, which confirms its delivery to the river with ground flow. In cases of slight increase in discharge, the mineralization increases while pH and water chemical type is found 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 concentration sequence of microelements is similar to that for the Yelovyi Creek outlet 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 compared with those in the Yelovyi Creek at the outlet of the experimental catchment.

The major components in the river water were investigated in terms of streamflow discharge. As a result, the components were separated into four categories: 1) the components to increase clearly with water discharge rising – dissolved organic carbon and nitrates (Figure 3, À); 2) the components to decrease against the flow growth – pH, silicon, calcium and sulfates (Figure 3, B); 3) the components to have a complicated indistinct relation to the flow rate – total dissolved substances, hydrocarbonates, sodium and suspended matter (Figure 3, C); 4) the components to be factually not related to the river regime – potassium, magnesium and chlorides (Figure 3, D).

It seems the upper soil horizons where the processes of humification and nitrification take place are a source of riverine organic matter and nitrates. An increase in organic matter and nitrates with rising discharge is considered typical for many riv-

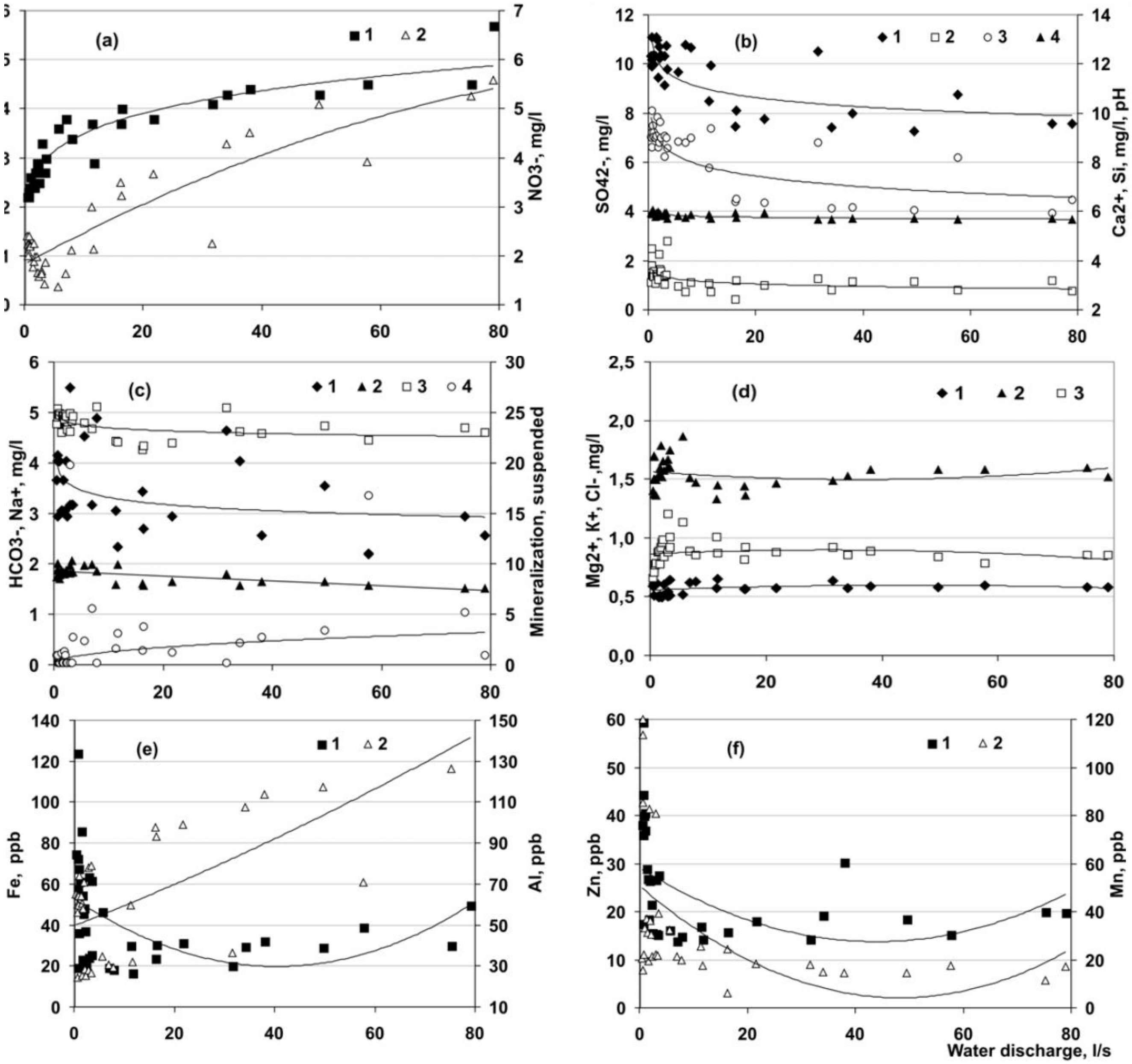

Figure 3 : Relation of some chemical parameters in the Yelovyi Creek at weir No.4 to water discharge: A (1 – C_{org}, $R^2 = 0.92$; 2 – NO_3^-, $R^2 = 0.82$); B (1 – SO_4^{2-}, $R^2 = 0.57$; 2 – $Ca^{2+,}$ $R^2 = 0.29$, 3 – Si, $R^2 = 0.62$, 4 – pH, $R^2 = 0.60$); C (1 – HCO^{3-} $R^2 = 0.17$, 2 – Na^+, $R^2 = 0.49$; 3 – mineralization, $R^2 = 0.31$; 4 – suspended substances, $R^2 = 0.25$); D (1 – Ma^{2+}, $R^2 = 0.076$; 2 – K^+, $R^2 = 0.040$; 3 – Cl^-, $R^2 = 0.024$); E (1 – Fe, $R^2 = 0.21$; 2 – Al, $R^2 = 0.52$); F (1 – Zn, $R^2 = 0.37$, 2 – Mn, $R^2 = 0.39$)

ers[20, 22]. Silicon, calcium and sulfates are supplied with deep ground water; therefore, rising of stream discharge should result in lowering of their concentrations in the river.

Most likely, the obtained evidence of chemical similarity of 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. 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 warrants additional investigation.

The content of trace elements in the Yelovyi Creek is rather typical for clean rivers of Primorye[4, 18] but peculiar features exist also. Aluminum, being slow-moving lithophile aquatic migrant, characterizes most clearly types of water: its minimum content is observed in rainfall 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 alkali-acidic 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). Barium is found to migrate weakly, its maximum concentrations are observed in the Yelovyi Creek and in slope flow. Concentration of arsenic is tenths of μg/l in river and soil water, and in atmospheric water, it drops to 1 μg/l; maximum concentration is found in shallow soil water.

CONCLUSION

In the course of moving to small rivers, the atmospheric water is subjected to significant chemical transformation. As a result, all examined natural water types differ, to the fullest extent, in anionic composition, but at the same time, its cationic pattern also changes. The rainfall is found extremely low-mineralized, and sulfate, nitrate and hydrocarbonate as well as hydrogen and calcium predominate there. The rainstorm to occur usually in a small temporal-spatial scale contains also significant amount of sulfate and nitrate while a share of potassium in cationic pattern increases, perhaps, due to its income to the atmosphere within transpiration fluxes.

The soil is considered a major source of hydrocarbonate, sulfate, calcium, magnesium, sodium as well as dissolved forms of silicon. The slope (lysimetric) water samples can be separated into two basic groups: 1) sulfated ones mainly from the areas where the illuvial-humic processes in soil dominate and 2) sulfate-hydrocarbonate water genetically related to the brown mountain-forest soils. The chemical type of river water is quite stable and does not change with increase in water discharges. The river water composition looks rather identical to the slope (soil) water since the former is formed within shallow slope deposits. The sufficiently stable relation was established between a streamflow rate and such components as nitrate, dissolved organic carbon, sulfate and silicon. At recorded low mineralization of natural waters, the mentioned components could serve indicators of genetic water types (tracers). In all water types, aluminum, zinc, iron, manganese and boron prevail among microelements. The river water is characterized by higher barium while the atmospheric precipitations – by higher copper, nickel, lead, cadmium and arsenic.

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