

Identification and assessment of relative importance of natural processes regulating stream water chemistry in a subalpine area

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When we study the geochemistry of an aquatic system, we record both the characteristics of natural processes and those due to human activities, and it is difficult to discriminate the share of each one in the water global signature. Therefore, we require an aquatic system where the part due to human activities is small enough to be neglected as a reference site. The *reference site* will allow us to identify and quantify the natural background in order to subtract it (in an appropriate manner) to the global signature of similar (in geology, geomorphology, climate) aquatic systems where human activities cannot be neglected.

Alpine zone, with steep slopes and torrential runoff (short water-rock and water-soil contacts), thin soils (weak buffering capacity) and temporary biological activity, are very sensitive in any modification of weathering conditions and in biochemical inputs due to human activities. This is even more true for crystalline zones because of their low reactive rock. For the same reasons crystalline alpine and subalpine areas are also highly sensitive to any change in atmospheric input.

We work on a middle mountain, the Rila massif, Bulgaria, underlain by a highly fractured Hercynian granitic pluton. The massif is rich in rivers and lakes and supplies Sofia city via the Iskar river. This area has been partly prohibited for 50 years to preserve water quality. It offers a rare possibility to study the weathering and biological activity impacts in a medium size basin, the upper Iskar watershed ($\approx 400 \text{ km}^2$ from the top, 2925 m high, to 1000 m high), where local anthropogenic activities seem negligible (Gassama and Violette 1997).

As a first step, our aim was to identify the processes regulating the stream water chemistry and to assess their relative importance. From the snowmelt to the first snows, the weathering conditions and the biological activity are significantly different. For these purposes, we recorded the evolution of stream water chemistry from early

April to late October.

We sampled stream waters and rainfalls or snows in July 94, April and October 96, dissolved and total fractions. Here we present results on dissolved fractions for some major and minor ions.

Results on major ions

Major element trends with elevation evolves in the same way between each other and along the year (Table 1). For a given period, linear regression slopes are in the same magnitude. Spring linear regression slopes are greater than autumn ones which are greater than summer ones. Also in spring major element concentration increase with elevation is greater than during the other periods, concentration increase due to the balance between atmospheric inputs, soil/rock extraction, soil adsorption, and biological uptake and input.

Chloride trends are different for the three studied periods. Cl^- concentrations remain constant between 2900 and 1300-1500m elevation and then increase downward. It is likely there is no extraction-uptake-adsorption process in the high part of the watershed.

Rain waters composition presents characteristics of continental ones with chloride contents lower than detection limit when they are of convective origin.

The next step is to define the relative importance of export and consumption (i.e. soil adsorption and biological uptake) for a given element during each period. For this calculation we need a tracer of atmospheric inputs to estimate their share in the global budget and to subtract it.

Trends seem to point out that chloride concentration is mainly due to atmospheric inputs. If this hypothesis is correct and if we assume that the X/Cl^- precipitation ratio is constant for a given period, we can calculate the X share from atmosphere for each sample i : $[\text{X}]_{i,\text{atm}} = ([\text{X}]/[\text{Cl}^-])_{\text{atm}} \text{ average} \times [\text{Cl}^-]_i$. Then we can define a ΔX_i as: $\Delta\text{X}_i = [\text{X}]_i - [\text{X}]_{i,\text{atm}}$. If $\Delta\text{X}_i > 0$, we have an export of X to the output, if

TABLE 1. Evolution of major compound concentrations according to elevation in stream samples of the upper Iskar watershed. Concentrations (C) are expressed in mol/l and altitude (A) is in m

	Summer 94 best fit equation	R	Spring 96 best fit equation	R	Autumn 96 best fit equation	R
Na	$\log C = -4.4E-4 A-3.6$	0.83	$\log C = -0.9E-3 A-2.8$	0.75	$\log C = -4.7E-4 A-3.5$	0.81
K	$\log C = -4.6E-4 A-4.5$	0.64	$\log C = -1.3E-3 A-3.2$	0.83	$\log C = -8.3E-4 A-3.8$	0.82
Ca	$\log C = -3.4E-4 A-3.6$	0.83	$\log C = -0.9E-3 A-2.7$	0.81	$\log C = -6.2E-4 A-3.2$	0.89
Mg	$\log C = -6.2E-4 A-4.1$	0.77	$\log C = -1.4E-3 A-2.8$	0.85	$\log C = -9.1E-4 A-3.5$	0.83
Cl	$\log C = -1.9E-4 A-4.4$	0.62	$\log C = -1.7E-3 A-2.5$	0.74	$\log C = -8.7E-4 A-3.6$	0.79
SO ₄	$\log C = -2.6E-4 A-3.9$	0.80	$\log C = -0.9E-3 A-2.8$	0.88	$\log C = -5.1E-4 A-3.6$	0.85

$\Delta X_i < 0$, we have a consumption or a storage of X in the watershed, if $\Delta X_i = 0$, processes are in equilibrium or there is no reaction.

Results show on major elements:

- in summer time, ΔX_i is around 0 with a little export tendency for Na and Ca;
- in autumn, all cations show export trends instead anions showing consumption or storage ones;
- during spring time, Na, Ca and Mg are exported, K, SO₄²⁻ and NO₃⁻ are uptaken or stored.

Short discussion and Results on Si, Fe and Mn

Na, Ca and Mg are mainly exported out of the watershed instead of K which is uptake by plant during the main growth phase. The ecosystem is

quite in equilibrium in summer. ΔK results show there is no more plant growth in autumn. Negative ΔSO_4^{2-} and ΔNO_3^- in autumn can be related to organic matter degradation or to soil adsorption.

Si is exported with an increase in lower altitude excepted in spring when its concentration is limited by biological activity.

Fe and Mn are also exported but less in spring time and more in autumn, this behaviour has to be related to biological activity but perhaps above all to redox potential and pH conditions.

References

- Gassama, N. and Violette, S. (1997) *Wat. Res.*, **31**, 767-76.