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Multielement composition of an extremely acidic (pH 1-3) river - lake system in Patagonia (Argentina) influenced by volcanic fluids.

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The Redfield's ratio (C:N:P=106:16:1) is a central paradigm in limnology and oceanography, and is used as a first approach to the study of nutrient limitation for planktonic primary production. Considering the phytoplankton´ species diversity, it is expected that the assemblage is not limited by a single factor, and that their nutritional needs require a variety of macro and micro-nutrients.

The River Agrio - Lake Caviahue system is located at North-East Patagonian Andes (37˚53'S; 71˚02'W), and it is fed by acid fluids from Copahue Volcano. Multielement ratios of different compartments of the acidic ecosystem were calculated (Redfield expanded) in order to explain the chemical composition along the pH gradient, its relationship with algal limitation and the evolution of eutrophication process due to waste-water that the lake receives from a small village. Samples were taken during March-April 2000 and March 2003. Stream samples directly from the flowline; lake samples with a Van Dorn Bottle. Sediment cores (80 m depth) by a Uwitec gravity corer. Porewater by centrifugation and filtration 0.2 μ; seston: suspended material retained on fiber-glass filters. Water samples, and seston and sediment samples (after digestion) were analyzed as: Sulfate by IC; alkali and earthalkali elements as well as Al, Fe, Mn, and a selection of heavy metals and trace elements using methods of atomic spectroscopy (AAS, ICP-OES, ICP-MS, TXRF) at UFZ Labs, Magdeburg,Germany. Si, N and P (colorimetry) at Bariloche lab. We obtained the following relationships (Molar):

Upper River Agrio (pH: 0.8 – 1.8) (at inflow to the lake)

Water $N_{0.1}$ P_1 S_{4800} Mg_{2500} $(Al,Fe,Na)_{1000-1300}Ca_{700}$ $Si_{300}K_{125}Mn_{50}(Zn,Sr)_3As_1Ba_{0.1}$ **1**

Seston $N_{0.1}P_1$ Si_{25} $(Fe,Al)_{10-20}$ $(K,Ca)_5$ $Mg_{0.2}$ $Ba_{0.15}$ $(As,Sr)_{0.1}$**2**

Lake Caviahue (pH: 1.8 – 3.0)

Water $N_{0.5}P_1S_{440}$ $(Al,Mg)_{80}$ (Na,Ca, Si, Fe)$_{40-50}$ $K_{14}Mn_2$ $Sr_{0.2}$ $(Ba,Zn)_{0.05}$ $As_{0.01}$**3**

Seston N_2 P_1(Si, Na)$_5$$Fe_3(Al,Mg, K)_2$$Ca_{1.5}(Zn,As)_{0.1}$ **4**

Pore water $N_{0.1}P_1S_{2280}Al_{770}(Mg,Ca,Fe,Na)_{320-410}K_{98}Mg_9As_{2,2}Sr_{1.5}Zn_{0.9}(Cr,Cu,Pb)_{0.12-0.17}Cd_{0.02}$**5**

Sediments $N_{0.02}P_1Al_{30}(Fe,Na,Ca)_5(S,K,Mg)_{23}Ba_{0.09}(As,Sr)_{0.05}Mn_{0.04}(Cu,Cr)_{0.03}(Ni,Zn,Pb)_{0.02}Cd_{0.0002}$**6**

Lower River Agrio (pH: 7.6) (downstream Lake Caviahue)

Water N_2P_1 S_{343} Si_{265} $(Ca,Mg)_{200}$ Na_{140} K_{40} $(Al,Fe,Mn)_{0.9}$ $Sr_{0.7}Ba_{0.2}$ **7**

Seston N_2P_1 Al_{69} $Fe_{50}Si_{33}$ $Ca_{13}K_{1.3}$ **8**

Under conditions of low pH it is expected the dissolution of some metals and the precipitation of others. The net result expected for acidic environments of low productivity is the accumulation. Our results agree with the accumulation of Organic Matter on the sediments and with the deposition of strengite, but a high proportion of elements remains in solution, both in the water column (**3**) and in sediment pore water (**5**). This is evident of ratios (e.g. Fe and Al) from sediments (**6**), to pore water (**5**), to water (**3**) and seston (**4**). Multielement relationships **1**-**2** (Upper) to **7**-**8** (Lower) and **3**-**4** (L. Caviahue), are representative of the pH gradient. In the upper river and the lake, where pH is lower than 3.0, the elements are mostly in solution, and with a very low N:P ratio (N:P = 0.1-2.0). With increasing pH, the relationships show a successive replacement of S by the Fe system and finally by the Al, and the consequent precipitation of salts and formation of new substrate. The contribution of urban waste-water of alkaline pH and rich in ammonium, slowly lead to the eutrophication process, with increase of N:P ratio and the pH, which will change the system due to the precipitation of Fe and Al.