

Effect of acidification in water samples before and after filtration: a caution for hydro-geochemical studies

In geochemical studies of water it is a general practice to filter the water samples through a $0.45\ \mu\text{m}$ membrane. Filtered samples are then acidified with a mineral acid (mostly nitric acid) to a $\text{pH} < 2$, to stabilize various cations. It was observed that if this procedure is not followed strictly and if samples are acidified prior to filtration, the elemental concentration of cations changes drastically. To estimate such changes, we had collected 24 water samples from Indus and Beas rivers and one adjoining hot spring. An aliquot of the sample was acidified without filtering and the other was acidified after filtration. Concentrations of Ca, Mg, Na, K, Al, Fe, Mn, Zn, Ba, Ni, Co, Cr, Cu and Sr were measured in both the aliquots. It was observed that most of the elements showed higher concentration in unfiltered acidified samples and probably this is because of the reaction of the acid with the suspended matter present in the sample.

The two fundamental processes of erosion, mechanical and chemical, result in suspended and dissolved loads in the rivers. The quality and quantity of suspended sediments and dissolved load are affected by relief, drainage area, basin geology, type of vegetation cover, rainfall, presence of lakes along the river course and anthropogenic influences. Dissolution of calcite and associated interactions of suspended sediments with aqueous solution were investigated by Fairchild *et al.*¹.

They observed that calcite dissolution is normally directly proportional to exposed surface area of the mineral. Gupta and Ahmed² studied the degradability of limestone, shale and siltstone at different pH solutions and observed that rocks containing calcite or dolomite are more susceptible to degrade at lower pH.

Water of high-altitude lakes, rivers and glaciers are generally clean. Assuming insignificant suspended sediment concentration, water samples of such locations are sometimes acidified without carrying out the filtration process for analysis of dissolved trace metals. This may lead to a different result because the concentration of cations of such samples is enhanced manifold. We carried out acidification of some samples collected from the Indus and Beas rivers, and a hot spring before filtration to observe the differences in concentration of the cations.

A total of 52 samples were collected from Indus and its streams, the Beas and the adjoining hot-water springs, the hot-water springs of Puga, Chumathang and high-altitude Kyung Tso lake³. Among these, 24 samples were divided into two aliquots. One aliquot was acidified to a $\text{pH} < 2$ without carrying any filtration process and the other portion was filtered and acidified with nitric acid. Both the samples were analysed for various cations using ICP-AES and flame photometer. Analytical error ranged between ± 6 and 10%.

Results of the analysis are graphically shown in Figure 1a and b. The unfiltered, acidified samples exhibited an increase in the concentration of almost all the cations. However, increase in Mg, Fe and K concentration was more in comparison to Ca and Na, which indicates the abundance of ferromagnesian minerals in the suspended matter. This is also consistent with the changes expected with different grain sizes⁴. Concentration of Fe, Mn and Zn was found to increase manifold in the portion acidified before filtration. An increase in concentration of Ni, Cr, Cu and Co was also noted in the portion acidified before filtration. These elements were below detection limit in the portion acidified after filtration (detection limit Ni and Co: 50 ppb; Cu and Cr: 5 ppb). It was observed that in most of the samples analysed, the increase in the abundance of cations is consistent with the increase in total suspended matter (TSM) of that sample. However this was not true for all cases. Protons can exchange base cations (like Na, K, Ca and Mg) absorbed in the minerals. The acid treatment would be expected to dissolve carbonates to a great extent and to slightly attack silicates, depending on their reactivity. This can also be related to the surface complexation process. Adsorption of cations can be regarded as a competition between cations and H^+ for surface sites. At low pH, adsorption of cations is minimal⁵.

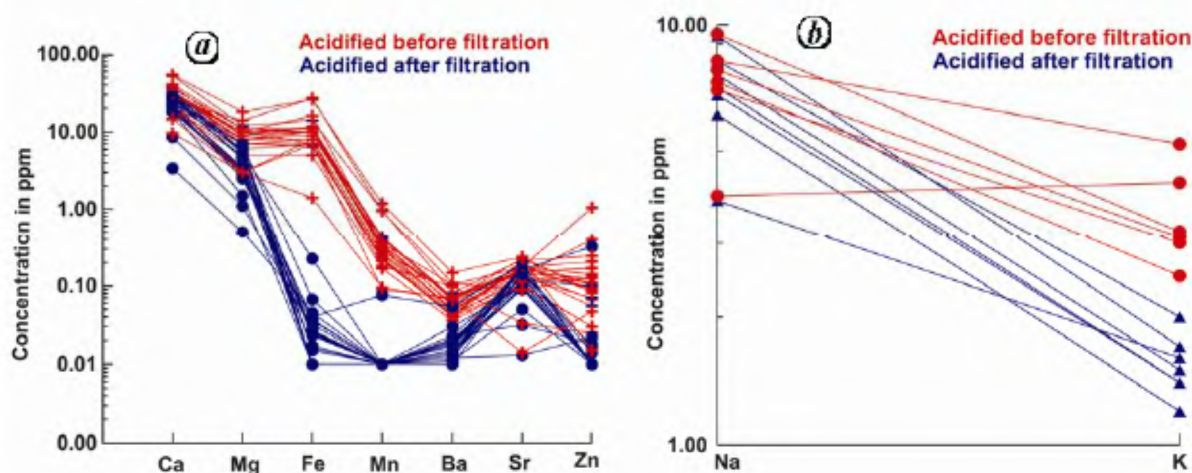


Figure 1. Effect of acidification on concentration of cations before and after filtration.

If a water sample is acidified before filtration, the concentration of various cations is enhanced to a great extent. This increase in concentration depends upon the quantity and composition of the total suspended material present in the sample. Dissolution of different species is not congruent. Grain size plays an important role in the distribution of Fe, Mn, Cu, Zn, Ni and Cr. In general, the concentration of heavy metals tends to increase as the suspended sediments get finer in size. Suspended sediments are an integral part of the rivers and therefore, the water samples should always be filtered before acidification.

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