



## **Biogeochemistry of sulfur in the Vienna Woods: Study of sulfur stable isotope ratios by MC-ICP-MS as indicator of biogeochemical S cycling**

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Sulfur entering forest ecosystems originates mainly from combustion of fossil fuels. This source of sulfur has been strongly (by more than 95 %) reduced in last decades and recently, higher sulfur output (in soil solution or stream water) than sulfur input (in rain water) in an ecosystem was registered in many monitored forest ecosystems. This unbalance may be caused by weathering of sulfur-bearing rocks, desorption of sulfur adsorbed in soil in the past or (re)mineralization of organic sulfur compounds. This 'negative' balance leads to mobilization of base cations along with  $\text{SO}_4^{2-}$  and as such to an acidification of soils. As hypothesis,  $\delta^{34}\text{S}/^{32}\text{S}$  depletion in stream water will be observed if a considerable proportion of atmospherically deposited sulfate is cycled through the organic S pool.

Rain water and soil solutions samples were collected for this study at 3 sites (beech stands) in the Vienna Woods, Austria twice a month from May 2010 to April 2012. Due to the expected sulfate concentration gradient with respect to the distance from a tree, sampling was carried out at 5 intervals from a stem. The sulfur concentration in the samples was determined by ion chromatography. Sulfur isotope ratios ( $\delta^{34}\text{S}/^{32}\text{S}_{VCDT}$ ) were analyzed by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) in edge-resolution mode. The method was validated using IAEA-S-1 and IAEA-S-2 isotopic certified reference materials. The combined standard uncertainty of the measurement ( $u_c = 0.10 \text{ ‰}$ ,  $k = 1$ ) proves the suitability of the developed method.

The concentration of sulfur in rain water showed expected behavior, with a seasonal maximum in winter months, in contrast to the corresponding  $\delta^{34}\text{S}/^{32}\text{S}_{VCDT}$  isotope ratios, where no or low seasonal trends were observed. The sulfur isotope ratios in soil solution samples show a dependence on the distance from a tree stem and the sampling depth with lower  $\delta^{34}\text{S}/^{32}\text{S}_{VCDT}$  ratios as compared to the precipitation. The measured isotopic fractionation in soil solution samples might be ascribed to aforementioned biogeochemical redistribution of organic sulfur.