Selenium isotope ratios of volatile organoselenium species as an indicator of the conditions of biomethylation

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Selenium is a trace element which is widely distributed in the environment. The concentrations of selenium in soils range from 0.1-2 mg/kg. The anthropogenic input of selenium originating mainly from coal mines and pyrometallurgical industry cause an increase of selenium concentration in the environment.

The effect of selenium compounds range from being essential for microorganisms, plants, and humans to being highly toxic with a relatively low tolerance range. The toxicity of selenium depends on its chemical form. The inorganic selenium forms are considered to be 500 times more toxic than organoselenium compounds. Selenium is cycled by different biological pathways like reduction, oxidation and methylation which occur in soil systems. Therefore biomethylation is a natural process which offers a potential remediation strategy in Se-contaminated areas. It is well known that different kinds of organisms (fungi, bacteria and plants) can produce volatile organoselenium species, mainly dimethylselenide (DMSe) and dimethyldiselenide (DMDSe) from inorganic selenium compounds (selenate and selenite). Selenium isotope ratios ($\delta^{76}Se/^{82}Se$) could serve as indicator of biogeochemical transformations of selenium in soils. We therefore test the hypothesis that the natural abundance of Se isotopes in organoselenium compounds is indicative of the conditions of DMSe and DMDSe formation.

For our experiments we used the fungi *Alternaria alternata* which is widespread in the environment, especially in soils. The organism was cultivated under pH 4 and 7 at a temperature of 30°C and incubated with 5 mg Se kg^{-1} as $NaSeO_4$ or as $NaSeO_3$ for 11-15 days. The volatile selenium compounds released by the fungi culture were collected in three alkaline-peroxide gas traps. Furthermore, nutrient medium and fungi were digested with concentrated nitric acid. A higher methylation was observed by the incubation with selenite than with selenate. By the incubation with selenate only 2-10% of the supplied compounds were converted to organoselenium whereas a methylation of 20-43% was detected if selenite was supplied. The assimilation of selenium in the organism accounted for 12-25% of Se(VI) and 61% Se(IV) of total selenium. Fractionation factors of the methylation were ε = -0.18‰ to 0.30‰ (±0.20‰) for Se(IV) incubation. A greater isotopic fractionation (ε = -3.07‰) was observed for organoselenium compounds if Se(VI) was the substrate. Variations in pH did not influence ε.