

## Se cycling in the critical zone in a seleniferous area in Punjab, India.

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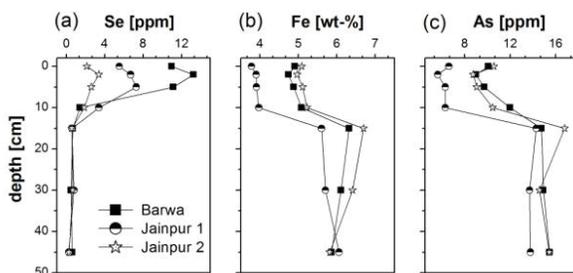
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Elevated selenium concentrations of up to 12 mg/kg occur in top soils from agricultural sites of Jainpur and Barwa in the state of Punjab, North-West India. Selenium concentrations of corresponding groundwaters are highly variable showing maximum concentrations up to 340 µg/L and, therefore, clearly exceeding current guideline values of 40 µg/L [1].

The depth distribution of Se in the soil with highest contents in the top 15 cm (Fig. 1a) suggests that this element is mainly introduced by irrigation with Se rich groundwater. Recent studies indicate that the enrichment of Se in soils and, consequently, in plants has been increasing over the years. This could be explained either by a general increase of Se in the irrigation water and/or by a recent change in agricultural land use practice from wheat-maize to wheat-rice rotation out of which the second is more water intensive.

Considerable percentages of Se in soils seem to be bioavailable as indicated by sequential extraction studies and X-ray absorption measurements. However, the change in agricultural practice probably has an influence on the mobility of Se. Temporary occurrence of stagnant and reducing conditions during rice cultivation may lead to immobilization of parts of Se in soils. This assumption is supported by the detection of Se(0) in the top soil. Furthermore, the Fe, As and Mn content in soils below 15 cm is considerably higher compared to the top soils (Fig 1b/c) indicating a redox-influenced downward translocation of these elements. Volatilization and/or uptake of Se by plants also seem to be important processes which determine Se cycling in the critical zone as lowest Se concentrations in topsoils occur in the upper 2 cm (Fig. 1a).



**Figure 1:** Depth distribution of Se (a), Fe (b) and As (c) in soil profiles from Barwa and Jainpur, Punjab, India.

[1] WHO, 2011. Guidelines for drinking-water quality, 4<sup>th</sup> edition.

## Origin and evolution of reactive and noble gases dissolved in porewater of low-permeable crystalline rocks

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Reactive and noble gases dissolved in matrix porewater of low permeable crystalline bedrock were successfully extracted and characterized for the first time based on drillcore samples from the Olkiluoto investigation site (SW Finland).

In crystalline bedrock systems, gases occur dissolved in fracture groundwater, matrix porewater and in fluid inclusions of rock forming minerals such as quartz and feldspars. Fracture groundwater and porewater, the latter being present in the inter- and intragranular connected pore space of the rock matrix, interact with each other predominately via diffusion. In contrast, mineral fluid inclusions represent isolated reservoirs without exchange for most gases under ambient conditions.

Reactive and noble gases dissolved in porewater and their isotope signatures carry valuable information about the evolution of a hydrogeological system. Information about origin and fluxes of dissolved gases is also important within the context of the safety assessment of a nuclear waste repository. For example, owing to their ability to buffer surface-derived dissolved oxygen, the occurrence of small amounts of hydrocarbons in fracture groundwater might be beneficial to safety assessment. In contrast, large amounts of hydrocarbons (mainly CH<sub>4</sub>) in fracture groundwaters combined with dissolved sulphate may affect safety assessment adversely.

Changes in the chemical and isotopic composition of gases dissolved in fracture groundwater are transmitted and preserved in the porewater, which forms an archive for hydrogeochemical changes in the past. At Olkiluoto, core samples were collected along a continuous profile from a horizontal borehole that intersects with a major water-conducting fracture zone. Porewater and present-day fracture groundwater are in transient state with respect to dissolved CH<sub>4</sub> and He concentration as well as the hydrocarbon mass ratio. Concentrations of CH<sub>4</sub> and He are higher in the porewater and approach those of the fracture groundwater towards the water-conducting zone. For the encountered fracture system this indicates that the circulation of present-day low CH<sub>4</sub> and low He fracture groundwater has been too short to achieve equilibrium between the two reservoirs and CH<sub>4</sub> as well as He is now transferred along chemical gradients from the porewater into the fracture groundwater. Hydrocarbon mass ratios and δ<sup>13</sup>C-CH<sub>4</sub> values suggest the preservation of a small component of bacterially formed hydrocarbons in some parts of the pore water profile, whereas in fracture groundwater and porewater furthest away from the water-conducting zone only evidences for thermogenic formed hydrocarbons could be detected.