## Smell from the Well: Indigenous VOCs in Deep Bedrock Groundwater at Outokumpu, Finland

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Volatile organic compounds (VOCs) comprise a group of carbon-containing, easily volatilized compounds, many of which have a strong odor. In groundwater, VOCs are usually recognized as contaminants. Even though many biological and chemical processes can be responsible for the natural production of VOCs, indigenous occurrence of VOCs in bedrock groundwater remains obscure.

During the fluid sampling campaign in the Outokumpu Deep Drill Hole, Finland, a distinctive smell was detected in the samples. To investigate the source of the smell, samples were taken for thermal-desorption-gas-chromatography-massspectrometric (TD-GC-MS) analysis to identify VOCs. Five fracture zones from 500 to 2300 m depth were targeted. In total, 41 different VOCs were found, and belong to alkanes, alcohols, aldehydes, aromatics, ketones, siloxanes, and organosulfides. The highest concentrations were measured for butane, dimethylsulfide, and benzene.

Several lines of evidence support the indigenous origin of VOCs at Outokumpu. Isolated fracture systems, as underpinned by the previous studies on fluid flow, geochemistry, and residence time [1], protect groundwater at  $\geq$  500 m depth from surface sourced contamination. To minimize possible contaminants from the drilling, several cubic meters of fluid were flushed out from the drill hole before the sampling. Furthermore, co-occurrence of high amounts of methane emphasizes the high intrinsic potential for organic gas accumulation.

The main sources suggested for the VOCs in bedrock groundwater at Outokumpu include black schist, necromass, and microbial metabolites. The widest variety of different VOCs was found at 1820 m depth, coinciding with the thickest black schist layer, in which ketones, aldehydes and other organics are found [2]. Reducing conditions and salinity may support the preservation of VOCs and explain the relative increase in sulfurcontaining compounds and aromatics with depth.

As toxic, flammable, carcinogenic, and potentially corrosive compounds, naturally occurring VOCs may need more attention in drilling and underground construction. They also provide opportunity for identification of microbial metabolic routes and may serve as analogues for exploration of extraterrestrial life, and prebiotic organic synthesis on Earth.

References:

[1] Kietäväinen (2017), Geological Survey of Finland Special Publication 97, 150 p.

[2] Taran, Onoshko & Mikhailov (2011), Geological Survey