



Characterization of hot spots for natural chloroform formation: Relevance for groundwater quality

Ole S. Jacobsen, Christian N. Albers, and Troels Laier
Geological Survey of Denmark and Greenland, Copenhagen, Denmark (osj@geus.dk)

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O. S. Jacobsen, C. N. Albers, T. Laier
Department of Geochemistry
Geological Survey of Denmark and Greenland,
Øster Voldgade 10, DK-1350 Copenhagen K, Denmark
E-mail: osj@geus.dk

Chloroform soil hot spot may deteriorate groundwater quality and may even result in chloroform concentration exceeding the Danish maximum limit of 1 $\mu\text{g/L}$ in groundwater for potable use. In order to characterize the soil properties important for the chloroform production, various ecosystems were examined with respect to soil air chloroform and soil organic matter type and content. Coniferous forest areas, responsible for highest chloroform concentrations, were examined on widely different scales from km to cm scale. Furthermore, regular soil gas measurements including chloroform were performed during 4 seasons at various depths, together with various meteorological measurements and soil temperature recordings. Laboratory incubation experiments were also performed on undisturbed soil samples in order to examine the role of various microbiota, fungi and bacteria. To identify hot spots responsible for the natural contamination we have measured the production of chloroform in the upper soil from different terrestrial systems. Field measurements of chloroform in top soil air were used as production indicators. The production was however not evenly distributed at any scale. The ecosystems seem to have quite different net-productions of chloroform from very low in grassland to very high in some coniferous forests. Within the forest ecosystem we found large variation in chloroform concentrations depending on vegetation. In beech forest we found the lowest values, somewhat higher in an open pine forest, but the highest concentrations were detected in spruce forest without any vegetation beneath. Within this ecotype, it appeared that the variation was also large; hot spots with 2-4 decades higher production than the surrounding area. These hot spots were not in any way visually different from the surroundings and were of variable size from 3 to 20 meters in diameter. Besides this, measurements within a seemingly homogenous hot spot showed that there was still high variability at 10 cm level. We suggest that the mechanism behind the formation of chloroform is an unspecific chlorination of organic matter, caused by microbial activity in the soil forming trichloroacetyl compounds. Laboratory measurements on intact soil cores have identified that the F and H horizons in the forest soil are the main producers of chloroform. Despite various attempts to identify the mechanisms responsible for the variability within a visually and chemically homogeneous area we have not yet succeeded. Parameters like soil respiration, inorganic and total organic chlorine, organic matter and soil structure were studied without any significant difference in favour of hot spots. By the use of ^{13}C -isotopes we could identify the natural origin of the chloroform, and over a three years period we could conclude that the hot spots were permanent on the sites. At the same time a significant seasonal variation were measured depending on temperature and soil moisture.