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Chloroform formation in Arctic and Subarctic soils – mechanism and emissions to the atmosphere

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It is well established that halogenated organic compounds are formed naturally in the terrestrial environment. These compounds include volatiles such as trihalomethanes that may escape to the atmosphere. In deed most of the atmospheric chloroform (and other trihalomethane species) is regarded to have a natural origin. This origin may be both marine and terrestrial. Chloroform formation in soil has been reported in a number of studies, mostly conducted in temperate and (sub-) tropical environments.

We hereby report that also colder soils emit chloroform naturally. We measured in situ the fluxes of chloroform from soil to atmosphere in 6 Subarctic and 5 Arctic areas covering different dwarf heath, wetland and forest biotopes in Greenland and Northern Sweden. Emissions were largest from the forested areas, but all areas emitted measurable amounts of chloroform. Also the brominated analog bromodichloromethane was formed in Arctic and Subarctic soils but the fluxes to the atmosphere were much lower than the corresponding chloroform emissions. No other volatile poly-halogenated organic compounds were found to be emitted from the study areas.

It has previously been proposed that chloroform is formed in temperate forest soils through trichloroacetyl intermediates formed by unspecific enzymatic chlorination of soil organic matter. We found positive relationships between chloroform emissions and the concentration of trichloroacetyl groups in soil within the various biotopes. The hydrolysis of trichloroacetyl compounds is, however, very pH dependent, excluding a simple relationship between trichloroacetyl concentration and chloroform emission in any given soil. However, our results show that at low pH, turnover time of soil trichloroacetyl compounds may be counted in decades while at pH above 6, turnover time may be just a few months. We found no relationship between trichloroacetyl concentration and total organic chlorine concentration in the soils indicating that more than one chlorination mechanisms occurs. The competition for free halides may be high in Arctic and Subarctic soils, as more than 90% of soil chlorine and 99% of soil bromine and iodine was organically bound.