

Biogeochemical cycle of chlorine, particularly formation of organically bound chlorine (Clorg), is still known only in outlines. In continental ecosystems chloride acts as stress factor, and also as source of chlorine; it originates from precipitation, which comes from marine cloud masses. Clorg are formed naturally by biotical and abiotical way. The biological factors are microorganisms, soil enzymes, plants and even animals. Halogenation processes undergo in marine environment as well, the main difference is the presence of bromine besides chlorine, therefore the reaction and formation of brominated compounds. One group of Clorg represents volatile chlorinated hydrocarbons (VOCl). Several VOCl can react with atmospheric ozone, consequently causing its depletion. The best known sources of VOCl are soil, the microorganisms living in it, and their exoenzymes released into it.

The heme peroxidases in the group EC 1.11.1.X can perform halogenation of organic compounds. Hydrogen peroxide or organic peroxides are the substrates of this reaction in which hypochlorous acid is generated. The halogen in reactive form then carries chlorine onto the organic compound.

To study enzymatic mediation of chlorination processes, we chose commercially available enzymes (chloroperoxidase from *Caldariomyces fumago* and horseradish peroxidase). To concentrate the formed analytes, we used solid-phase microextraction (SPME) method or cryofocusing method, followed by GC-ECD or GC-MS analysis.

The formation of VOCl was confirmed in experiments, where enzyme, citric acid buffer, halogen ions (KBr, NaCl) and substrates (acetic acid, acetone) were present. Contrary to the literature, both enzymes formed chlorinated and brominated volatile compounds. The main volatile organic halogenated compounds were chloroform, bromoform, trichloroethylene, tetrachloroethylene, halogenated methane derivatives and aliphatic compounds. The formation was dependent on the length of the enzyme reaction.