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Halogen-Derived (I, Br, Cl, F) Species Recorded in Alpine Ice-Cores

Content

Anthropogenic emissions of HCl and HF degrade air quality, whereas reactive iodine, bromine and chlorine species – through interaction with tropospheric ozone – potentially improve air quality. Uncertainties exist, however, in understanding tropospheric halogen budgets and their changes since pre-industrial times. In polar regions, studies suggest that iodine and bromine ice-core records are heavily influenced by sea-ice processes. Here we review 20th-century records of HCl, HF, total iodine and total bromine developed from ice cores extracted in the French and Swiss Alps, and discuss to what extent they reflect past mid- and low-latitude halogen emissions not related to sea-ice processes.

The observed three-fold iodine increase in Alpine ice since 1950 is particularly interesting since iodine is a major public health issue in the Alps and it is the most reactive halogen with respect to tropospheric ozone. Model studies suggest that the primary iodine source is HOI emitted from the ocean through the reaction of ozone with iodide. A confirmation of this source is difficult, since atmospheric HOI measurements are very limited. The location close to the Mediterranean Sea and industrialized regions characterized by high emissions of both, anthropogenic ozone and iodine, means that Alpine ice records are particularly useful for testing model simulations of past iodine emissions, transport, and deposition. Bromine also plays an important role in the tropospheric ozone budget. However, Alpine ice-core records contain significant bromine from PbBrCl aerosol emitted by leaded-gasoline combustion. These aerosols are not reactive with tropospheric ozone.

The Alpine ice-core records suggest that the fluoride budget in Western Europe is driven by emissions from aluminum smelters in France, Switzerland, Italy, and Germany, with coal burning emissions being less significant. The post-1975 reduction of fluoride emissions related to the setup of aluminum oxide filters is well recorded in Alpine ice.

Finally, we show that HCl, the main free tropospheric component of reactive chlorine, is also useful to reconstruct the tropospheric budget but the evaluation of the HCl fraction from total chloride present in continental ice is a challenge. Nevertheless, we were able to identify waste incineration, coal burning, acid-displacement of sea-salt, and biomass burning as processes modulating past HCl content in alpine ice.

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