Geophysical Research Abstracts
Vol. 14, EGU2012-11663, 2012
EGU General Assembly 2012

New method to quantify volatile organic compounds (VOCs) in cloud droplets sampled at the puy de Dôme research station.

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In recent years several studies have focused on the health and environmental effects of atmospheric pollution, and especially on the emissions of volatile organic compounds (VOCs). In cloud droplets, chemical reactions in the liquid phase modify the amount of radicals which drive the oxidizing power of the atmosphere.

The objective of this project was to identify and quantify VOCs in cloud water samples at the puy de Dôme research site using a combination of stir bar sorptive extraction (SBSE)-thermal desorption (TD)-gas chromatography-mass spectrometry (GC-MS).

Experimental studies were carried out at the puy de Dôme (PDD) Station (48°N, 2°E; 1465 m a.s.l.), in the Massif Central Region (France). It is a strategic point from which to observe warm and mixed clouds that are present 30% of the time on an annual basis. Clouds are frequently formed at the top of the site either during advection of frontal systems or by orographic rise of moist air. The station is in the free troposphere a large fraction of the time and air masses are usually exempt from the influence of local pollution. Non-precipitating cloud droplets are sampled using a single-stage cloud collector. Cloud droplets larger than 7 μm (cut-off diameter) are collected by impaction onto a rectangular plate at a flow rate of approximately 86 m3 h^{-1}.

This work has established a functional procedure to allow the quantitative extraction of 80 VOCs in cloud water. The method has been optimized to determine the best repeatability and detection limit for most of the compounds (hydrophobic and hydrophilic). According to SBSE theory, at equilibrium the distribution coefficients of the analytes between the aqueous matrix and coated film of the stir bar (PDMS) are correlated with the corresponding octanol–water partitioning coefficients (Kpdms/w vs Ko/w). Hydrophobic compounds, characterized by a high octanol–water distribution coefficient (Kow), are extracted from water by SBSE with a high recovery. However, hydrophilic compounds, with a low Kow, are recovered in low yield but which can be improved by adding a salt such as sodium chloride to the sample. We solve the problem by performing two extractions, with and without added salt, to optimize the separate recoveries of hydrophilic and hydrophobic compounds (sequential SBSE).

First speciation of volatile organic compounds (VOCs) in cloud droplets sampled at the puy de Dôme research site are presented here including alkenes, alkanes, aromatics compounds, isoprene, terpenes, halocarbons, some aldehydes and ketones.