Name of research institute or organization:

Institut für Atmosphäre und Umwelt, Universität Frankfurt, Germany

Title of project:

Volatile organic compounds (VOC) in air, snow and ice crystals at high alpine research station Jungfraujoch during CLACE 5

Project leader and team:

Dr. Elke Fries, Prof. Dr. Wolfgang Jaeschke, Prof. Dr. Wilhelm Püttmann, project leaders
Karsten Sieg, Dr. Elena Starokozhev

Project description:

Introduction and work package

Anthropogenic volatile organic compounds (VOC) are emitted from automobile traffic and aircraft exhaust (aromatic hydrocarbons) and from solvent production and use (aromatic hydrocarbons and halocarbons) (i.e. Slemr et al., 2001).
Snowfall has the potential to significantly contribute to the deposition of airborne organic contaminants by washing out the aerosol particles and adsorbing gas phase molecules (Franz, 1994).
Most of the studies of organic contaminants in snow from high altitudes in Europe have dealt with semi-volatile organic compounds recognized as persistent organic pollutants (POPs) (see for review Daly and Wania, 2005), whereas VOC have been mostly measured in snow from urban sites.
During the Cloud and Aerosol Characterization Experiment CLACE 5 in February-March 2006 quasi-continuous measurements of VOC in air, snow and ice crystals were carried out at the Sphinx laboratory at the alpine research station Jungfraujoch (3580 m asl) to determine the influence of in-cloud scavenging on the occurrence of VOC in snow.
In addition, during CLACE 5 snow samples and aerosol samples were collected for our project partners of the Sonderforschungsbereich 641 "die troposphärische Eisphase" from MPI Mainz and Mainz university and for the analytical chemistry group of Augsburg university.

Results

VOC in air were measured with an online-gas chromatographic system (AirmoVOC) with a temporal resolution of 60 min. Median concentrations of benzene, toluene, ethylbenzene, m/p-xylenes, and o-xylene in air samples were between 5 and 266 ng m^{-3}.
VOC were also measured in snow and ice collected directly in-cloud. A self-made snow collector was installed at the Sphinx laboratory. During snow events freshly fallen snow and ice crystals were collected and filled into 20 ml brown glass vials sealed with screw caps. To avoid contamination through storage and transport vials were protected through an aluminium plate on both sides of the septum. Field blanks were prepared during snow sampling. The frozen snow samples were transported to the laboratory in a freezing box and melted right before analysis. Fluorobenzene was added to each sample as an internal standard. Concentrations of VOC in the melted

ice were determined by a sensitive method based on a self-controlled Solid-Phase-Dynamic-Extraction (SPDE) followed by gas chromatography /mass spectrometry (GC/MS). VOC were allowed to adsorb on a syringe coated with a mixture of polydimethylsiloxan (PDMS) and activated charcoal (AC). After extraction, the syringe was drawn into the GC injector and analytes were desorbed thermally at 230 °C. Results from the occurrence of VOC in snow were also compared to the results from CLACE 4 in 2005.
Benzene and alkylated benzenes, chlorinated hydrocarbons and monoterpenes were identified in snow samples. During CLACE 4 (2005), particularly the biogenic compounds α-pinene, ß-pinene and limonene show enhanced concentrations in March than in February. This may reflect increased local emission rates of these compounds as winter gives way to spring. Lower concentrations of VOC were detected in samples collected from snow events without preceding precipitation free days before sampling. Generally there is a tendency in the results that higher concentrations are found after longer precipitation free periods, suggesting that higher concentrations in snow may be caused by the washout effect of precipitation. No dependence of concentrations of VOC in snow on the days of the week could be observed. During CLACE 4 (2005) concentrations of most of the VOC were higher than during CLACE 5 (2006). During the snow sampling performed in CLACE 4, the wind direction was predominately from the Northeast and the wind speeds high. In contrast, during the sampling of CLACE 5 the wind came from the south-south west with much lower wind speeds. Lower concentrations in 2005 could be explained by different transport processes of organic gases from the surrounding valleys to Jungfraujoch. High concentration variations of VOC in snow samples taken at the same time at the same place demonstrate a heterogeneous nature of snow which causes variable distribution of VOC in snow. Scavenging ratios (Wg) were determined by relating the gas constant times the ambient temperature to the Henry´s Law constant of the individual compound. Values of Wg varied between 0.1 (limonene) and 5.1 (1,2,3-TMB). From these scavenging ratios and the concentration of VOC measured in snow average concentrations of VOC in air at equilibrium conditions were calculated. Predicted air concentrations between 3 $\mu g\ m^{-3}$ and 42,928 $\mu g\ m^{-3}$ were higher than measured ones. These results demonstrate concentrations of VOC in snow are well above that expected for equilibrium with air. This is an indication that snow scavenges VOC very efficiently and that VOC are accumulated in snow.

References

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Slemr F, Giehl H, Habram M, Slemr J, Schlager H, Schulte P, Haschberger P, Lindermeir E, Dopelheuer A, Plohr M., In-flight measurement of aircraft CO and nonmethane hydrocarbon emission indices. J Geophys Res 2001; 106 (D7): 7485-7494.

Key words:
Organic compounds, SPDE, snow, GC/MS, air

Internet data bases:

http://www.meteor.uni-frankfurt.de/b8.htm

Collaborating partners/networks:

Project partners of the SFB 641 from the universities Frankfurt, Mainz and Darmstadt, and the MPI Mainz

Scientific publications and public outreach 2006:

Refereed journal articles

Fries, E., Sieg, K., Jaeschke W., Püttmann, W., Winterhalter, R., Williams, J., Moortgat, G. (2007): Occurrence of VOC in snow and ice in spring at Jungfraujoch (46.6°N, 8.0°E) in 2005 and 2006 during CLACE 4 and 5. Submitted to the special issue "Research at Jungfraujoch: Top of Science" in Science of the Total Environment.

Sieg, K., Fries, E., Püttmann, W. (2007): Analysis of BTEX and Aldehyde with solid-phase dynamic extraction from melted snow water; in prep. For submission to Journal of Chromatography A.

Winterhalter, R., Williams, J., Fries, E., Sieg, K., Moortgat, G.K. (2007): Concentrations of higher dicarboxylic acids in fresh snow samples collected at Jungfraujoch during CLACE 5. in prep. For submission to Journal of Environmental Chemistry.

Conference papers

Sieg, K., Fries, E., Starokozhev, E., Heurich, B, Püttmann, W., Jaeschke W. (2006): Volatile organic compounds (VOC) in air and in snow / ice at high alpine research station Jungfraujoch during Clace 5; poster presentation during the conference "Top of science", Interlaken 2006.

Winterhalter, R., Williams, J., Fries, E., Sieg, K., Moortgat, G.K. (2007): Concentrations of dicarboxylic acids in freshly precipitated snow samples at the high altitude research station Jungfraujoch during CLACE 5. Presentation at the European Geosciences Union General Assembly 2007, 15.4. - 20.4.2007, Vienna.

Address:

Institut für Atmosphäre und Umwelt
Johann Wolfgang Goethe - Universität
Georg-Voigt-Straße 14
D-60325 Frankfurt am Main

Contacts:

Dr. Elke Fries
Tel.: +49 69 798 22911
Fax: +49 69 798 28548
e-mail: E. Fries@kristall.uni-frankfurt.de