**Atmospheric
Chemistry
and Physics
Discussions**

Distribution of VOCs between air and snow at the Jungfraujoch high alpine research station, Switzerland, during CLACE 5 (winter 2006)

E. Starokozhev[1], E. Fries[2], A. Cycura[3], and W. Püttmann[1]

[1]Institute of Atmospheric and Environmental Sciences, Dept. of Analytical Environmental Chemistry, J. W. Goethe-University Frankfurt/Main, Germany
[2]Institute of Environmental Systems Research, University Osnabrück, Germany
[3]Environment Monitoring Center, Orenburg State University, Russia

ACPD

8, 14347–14369, 2008

Distribution of VOCs between air and snow

E. Starokozhev et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄ | ►|
◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

E. Starokozhev et al.

Abstract

Volatile organic compounds (VOCs) were analyzed in air and snow samples at the Jungfraujoch high alpine research station in Switzerland as part of CLACE 5 (CLoud and Aerosol Characterization Experiment) during February/March 2006. The fluxes of individual compounds in ambient air were calculated from gas phase concentrations and wind speed. The highest flux values were observed for the aromatic hydrocarbons benzene (14.3 μg m^{-2}s^{-1}), 1,3,5-trimethylbenzene (5.27 μg m^{-2}s^{-1}), toluene (4.40 μg m^{-2}s^{-1}), and the aliphatic hydrocarbons i-butane (7.87 μg m^{-2}s^{-1}), i-pentane (3.61 μg m^{-2}s^{-1}) and n-butane (3.23 μg m^{-2}s^{-1}). The fluxes were used to calculate the efficiency of removal of VOCs by snow, and the effect of temperature on removal efficiency. The removal efficiency was calculated at $-24°$C ($-13.7°$C) and ranged from 37% (35%) for o-xylene to 93% (63%) for i-pentane. The distribution coefficients of VOCs between the air and snow phases were derived from published poly-parameter linear free energy relationship (pp-LFER) data, and compared with distribution coefficients obtained from the simultaneous measurements of VOC concentrations in air and snow at Jungfraujoch. The coefficients calculated from pp-LFER exceeded those values measured in the present study, which indicates more efficient snow scavenging of the VOCs investigated than suggested by theoretical predictions.

1 Introduction

Large quantities of a number of organic compounds enter the troposphere from a variety of sources. Some of these occur naturally, but most air pollutants are derived from human activities (anthropogenic) and can significantly change or impact the earth's natural life processes (Bidleman, 2001). Volatile organic compounds (VOCs) such as benzene, toluene, ethylbenzene and xylenes constitute an important group of anthropogenic organic compounds from combustion (vehicles, aircraft and fossil fuel power plants), fuel storage and transport, solvent usage and production, industrial emissions,

E. Starokozhev et al.

landfills and hazardous waste facilities (Zalel et al., 2008). Some VOCs are toxic (e.g. benzene, 1,3-butadiene) and many are ozone precursors (Dollard et al., 2007). VOCs are transformed and removed from the troposphere by chemical processes including photolysis, reaction with hydroxyl (OH) or nitrate (NO_3) radicals, and reaction with O_3
(National Research Council, 1991; Atkinson, 1995, 1997). It is well established that benzene and the alkylated benzenes react almost exclusively with OH radicals under the conditions prevalent in the lower troposphere (Atkinson, 1994). Secondary aerosol particles are formed from some organic compounds including toluene and pinenes (Odum et al., 1997; Kavouras et al., 1998; Kleindienst et al., 2004). As gases and ad-
sorbed on particles, some VOCs (e.g. i-alkanes, aromatic hydrocarbons) can be transported over long distances from source regions to higher layers of the troposphere, where they can persist for long periods of time (Gröllert and Puxbaum, 1998; Li et al., 2005).

The difference in atmospheric lifetimes of VOCs with respect to OH removal can be a useful tool to estimate the amount of photochemical processing in an advection flow (Monod et al., 2001). Other processes influencing the distribution pattern of VOCs are emission rates, mixing processes, dilution, and dry and wet deposition. The datasets obtained from automatic non-methane VOC monitoring may contain much additional information that could contribute to understanding of the processes and trends that govern dispersion and transformation of ambient pollutants (Zalel et al., 2008). At high latitudes and altitudes, the transformation and deposition of VOCs is significantly influenced by low temperatures, and in particular by the phase transition of water at temperatures below 0˚C (Lei and Wania, 2004). In the atmosphere at high altitudes, snow and ice represent an important compartment for storage and reactions of environ-
mentally relevant chemicals. Research has been conducted aimed at understanding the processes linked to the occurrence of organic pollutants in snow and ice (Roth et al., 2004) since organic pollutants were detected in snow in remote areas (Hoff et al., 1995; Wania et al., 1999) and at a high alpine site (Gröllert and Puxbaum, 1998).

Here we present the results of measurements of selected VOCs in ambient air

at the Jungfraujoch high alpine research station during field work associated with CLACE 5 (CLoud and Aerosol Characterization Experiment), undertaken in February/March 2006. As part of this research, quantitative characteristics of VOCs distribution between atmospheric phases during precipitation formation were investigated.

2   Background theory

High alpine sites are appropriate locations to determine background concentrations of VOCs in the free troposphere, since these locations are primarily influenced by the long range transport of ozone and its precursors (Pochanart et al., 2001; Zanis et al., 2000). However, the concentrations of air contaminants (e.g. VOCs and aerosols) at higher altitudes (>3000 m) have also been shown to be affected by polluted regions in alpine valleys (Prévot et al., 2000; Baltensperger et al., 1997a). Due to economic growth in Europe and construction of roads and tunnels in alpine regions, traffic and hence VOC emissions have increased markedly during the last decades, and are expected to increase further in the future (Prévot et al., 2000; Karl et al., 2001).

The environmental fate of VOCs is highly dependent on their partitioning in the atmosphere between gas and condensed phases like aerosols, rain, fog and snow. Such sorption processes can slow the long range transport of compounds in the atmosphere. Transformation processes are also significantly affected by VOC partitioning between phases. A good understanding of the thermodynamic partition equilibria of organic pollutants is therefore the basis for a good understanding of their fate (Goss, 2004).

The atmosphere of the Swiss Alps is a multicomponent and multiphase system, and water can be present in all three states of aggregation under climate conditions. The organic vapors are present in the atmosphere in insufficient amounts and can not generate own phases. They can sorb onto solid or liquid surfaces and form surface films from which substances exchange into all phases. To determine the distribution of organic substances between different phases of the system, it is necessary to assess the contribution of processes involving the dispersion and transformation of compounds in

ambient air, and their physical and chemical removal from the system. These processes are the transport of organic chemicals, their reactions with other compounds of the atmosphere (OH radicals, ozone, gaseous nitrogen oxides), and wet and dry deposition (Forrer et al., 2000; Rouviere et al., 2005).

In the Alps at higher altitudes, the transport of organic compounds from emission sources to higher altitudes in the troposphere is a complex process consisting of several stages: the elevation (vertical transport) of the contaminants from the sources to the upper troposphere, the horizontal transport of the compounds in the upper troposphere, precipitation scavenging of organic chemicals, and their deposition on alpine surfaces (Fig. 1). Any transported compound can be quantitatively described by its fluxes, following the procedure described by Dämmgen et al. (1997). The vertical flux (J_0) is directly proportional to the gradient of concentration of the substance ($_\Delta C$) between a source and a receptor, (Eq. 1):

$$J_0 \approx {_\Delta C}. \tag{1}$$

The horizontal flux (J_c) is described by convective diffusion, and is proportional to the concentration and velocity of the substance in the air flow (Eq. 2):

$$J_c = C_{air} v \tag{2}$$

where C_{air} is the concentration of VOC in the air ($\mu g \, m^{-3}$) and v is the velocity of the horizontal flux (m s^{-1}).
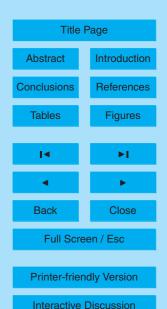
The flux of deposition (J_d) is difficult to describe quantitatively. Hydrocarbons distribute among the different compartments of the multiphase atmospheric system (gas phase, aqueous droplets, aerosol particles, ice, and snow crystals). Their partitioning depends upon their nature and concentration, and on meteorological conditions. The deposition flux can be described by the density (d) and intensity (I) of precipitation (Eq. 3):

$$J_d \approx I d. \tag{3}$$

Distribution of VOCs between air and snow

E. Starokozhev et al.

Since mixing is diffusion-controlled, the system is considered to be in dynamic equilibrium. The partitioning of organic substances between the gas and other phases can be described by the distribution coefficient (Eq. 4), which encompasses characteristics of all fluxes in the atmosphere:

$$K_{air/snow} = \frac{C_{air}}{C_{snow}} \tag{4}$$

where C_{snow} is the concentration of VOC in the precipitation ($ng\,L^{-1}$).

The distribution of VOCs between the atmospheric phases determines whether and how the chemicals will be scavenged by precipitation (Lei and Wania, 2004). The partitioning constant varies among different compounds, which allows assessment of the major trends for processes relevant to each substance. When $K_{air/snow}$ approaches infinity, the efficiency of the scavenging process of organic compounds by precipitation is low. On the other hand, active precipitation scavenging of the compound will take place when $K_{air/snow}$ approaches 0.

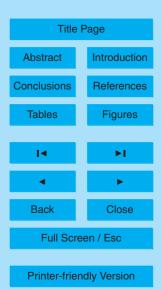## 3 Experimental section

3.1 Location and meteorology

The large scale topography of the Swiss Alps is along a NW-SE cross section which is characterized by two mountain ranges divided by the deep Rhone Valley (Fig. 2). The Jungfraujoch observation station (3580 m a.s.l., 46.55° N, 7.98° E) is situated on the northerly crest on a mountain saddle between the mountains Jungfrau (4158 m a.s.l.) in the west and Moench (4099 m a.s.l.) in the east. During autumn, winter and spring, the research station is in clouds in the free troposphere about 40% of the time, whereas there is a clear influence from the planetary boundary layer in summer (Baltensperger et al., 1997a; Zanis et al., 2000). Meteorological processes on different spatial and time scales are important in the interpretation of trace gas observations at high alpine

Distribution of VOCs between air and snow

E. Starokozhev et al.

sites during the whole year (Forrer et al., 2000). These processes may contribute to the export of anthropogenic pollution from the boundary layer to the free troposphere. Meteorological information including air temperature, wind direction, wind speed, relative humidity and global radiation during sampling was obtained from a monitoring station of the Swiss Meteorological Institute within the Swiss Air Pollution Network (NABEL).

3.2 Analytical methods

Hydrocarbons were measured by a GC-FID automatic sampling instrument (AirmoVOC HC2010) with an integration time of 60 min. The system was located in a laboratory at the top of the research station. The inlet of the GC system was a 1/8" stainless steel tube drawing outside air at $100\,ml\,min^{-1}$ from 5 m above the bottom. The air sample was pre-concentrated at room temperature in an adsorption tube packed with two adsorbents (3 cm Carbotrap B, 1 cm Carbosieve). The trapped components were desorbed by heating the adsorption tube to $250°C$ for 2 min, then transported by H_2 (5.0) to a cryofocusing unit. This unit consisted of a fused silica capillary tube packed with Carbopack and Envicarb X (2:1), which adsorbs hydrocarbons by CO_2 cooling at $-45°C$. After heating of the cryotrap to $350°C$, the organic compounds were injected into a fused silica capillary column (24 m×0.25 mm, BGB 2.5; film thickness 1 μm, stationary phase 2.5% phenylpolysiloxane and 97.5% methylpolysiloxane) for chromatographic separation. The temperature program for the chromatographic separation was as follows: $30°C$ for 20 min, increase by $3°C\,min^{-1}$ to $120°C$, increase by $5°C\,min^{-1}$ to $150°C$, 15 min at $150°C$. Flame ionization detection (FID) was used for quantitative analysis of organic trace compounds. Calibration of the system was performed with a thirty-component mixture produced and certified by NPL (National Physics Laboratory, UK). Hydrocarbons were identified based on their retention times. Accuracy values comprised the 2 sigma errors of calibration, the reproducibility of the measurements, and peak integration errors due to peak overlap and baseline noise. The detection limit was between 1 and 10 ppt, depending on the individual hydrocarbon. The precision of the instrument was below 15% and the accuracy below 10% for C5–C9, as found in

Distribution of VOCs between air and snow

E. Starokozhev et al.

several intercomparison campaigns for VOC measurements (Winkler, 2001).

Snow/ice was sampled during precipitation events using a custom built stainless steel collector installed on the measurement platform at the research station. A total of 27 snow/ice samples were collected from 20–26 February and 1–5 March 2006. Analysis of VOC in melted snow samples was performed by HS-SPDE (headspace solid phase dynamic extraction) and GC/MS (gas chromatography/mass spectrometry). The relative standard deviations varied between 5 and 15% for benzene and the alkylated benzenes. The sampling procedures, and the HS-SPDE and GC/MS analytical methods have been described in detail by Fries et al. (2008) and Sieg et al. (2008).

4 Results and discussion

4.1 VOC fluxes

To assess the influence of atmospheric transformation of organic compounds on their further behavior, it is necessary to consider the atmosphere as a thermodynamic system; this requires simultaneous investigation and comparison of the meteorological and physico-chemical parameters of the system. The following meteorological parameters simultaneously reflect the thermodynamic characteristics of the atmosphere: (i) temperature describes the conditions of gas and vapor components in the atmosphere, (ii) wind speed describes transport of compounds in the ambient air, (iii) relative humidity gives the concentration of water vapor in the air and allows prediction of the direction of condensation and evaporation processes in the system at any moment, and (iv) global radiation provides a measure of the additional energy influencing the degree of condensation and evaporation of water and organic compounds in the air.

The concentrations of organic substances in the gas phase and snow were selected as physico-chemical parameters of the system. Alkanes, alkenes and aromatic hydrocarbons were determined in the air samples during CLACE 5 (Fig. 3, Table 3). Data from four days of measurements were selected for investigation of the VOC distribu-

Distribution of VOCs between air and snow

E. Starokozhev et al.

Printer-friendly Version

Interactive Discussion

tion between the air and snow phases. Only on two of these days (24 February and 1 March) did significant snowfall take place. The two other days (11 and 12 March) were clear and sunny. The air temperature on the selected days was always far below 0°C, and varied from −12°C (24 February and 11 March) to −27°C (1 and 12 March). The meteorological regimes on 11 and 12 March were similar to those of 24 February and 1 March (Table 1). Thus, it is possible to consider the atmospheric conditions on 11 and 12 March as the initial state of the thermodynamic system "atmosphere", and the conditions on the 24 February and 1 March as the final state after the reaction (snow scavenging) took place. Analysis of the wind speed $(2-14\,\mathrm{m\,s^{-1}})$ during these days shows that there was a permanent transfer of the air mass in the atmosphere, forced by convection. Therefore, spatial homogeneity involves horizontal and vertical mixing processes (Baltensperger et al., 1997b), and the amounts of organic chemicals in the gas phase can be better described using their fluxes.

The fluxes of individual hydrocarbons detected in all air samples during CLACE 5, calculated using Eq. (2) are given in Fig. 3. The diagrams of the initial fluxes (J_c) show the highest values of the following hydrocarbons (in $\mu\mathrm{g\,m^{-2}\,s^{-1}}$) on 11 (12) March: benzene 14.3 (4.38), 1,3,5-trimethylbenzene 5.27 (1.79), toluene 4.40 (1.56), i-butane 7.87 (7.27), i-pentane 3.61 (3.40), and n-butane 3.23 (2.80). Insignificant concentrations (approximately 10% of the benzene concentration) of the following hydrocarbons were found in the ambient air on the same dates: 1,2,4-trimethylbenzene 1.49 (0.51), m/p-xylene 1.09 (0.28), o-xylene 1.02 (0.24), ethylbenzene 0.83 (0.45). OH-rate constants of these compounds are higher than for benzene and consequently the atmospheric lifetimes for these chemicals (8.4 h, 11.7 h, 20.3 h, and 1.63 days, respectively) are shorter than for benzene (9.4 days) (see Table 2). The high concentrations of alkanes in ambient air could be due to their long persistence in the atmosphere, with distant sources making a greater contribution to their concentrations than in the case of the faster reacting VOCs (Hellén et al., 2006).

The final flux values (J_c') for all hydrocarbons on 24 February and 1 March were lower than the initial flux values. One explanation for this is VOC removal by wet deposition.

Distribution of VOCs between air and snow

E. Starokozhev et al.

Distribution of VOCs between air and snow

E. Starokozhev et al.

However, the efficiency of washing out of selected compounds from the atmosphere varied widely (range 30–100%), which may be explained by different photochemical activity and interaction with water vapor. Benzene in the atmosphere should partition into the water phase to a greater extent than the other organic compounds investigated here, as it has the lowest Henry's constant. Toluene can be absorbed by the water phase, and will be transformed by reactions with components of the gas phase (e.g. OH-rate constants, see Table 2) more efficiently than benzene. Thus, the quantitative characteristics of the distribution of the investigated hydrocarbons between the air and snow phases in the atmosphere should be different.

The efficiency of scavenging of VOCs by snow was calculated, Eq. (5) as the difference between the initial (J_c) and final ($J_c^{'}$) flux values before and after wet deposition:

$$E = \frac{J_c - J_c^{'}}{J_c} 100\%.$$ (5)

The efficiency of removal of VOCs by snow events during CLACE 5 is shown in Fig. 4. The ranking of organic compounds according to their removal efficiency indicates a low dependency on their solubility in water (see Table 2). Thus isopentane and n-pentane, with very high values of Henry's law constants (50 and 56, respectively), were removed from the atmosphere by snow very effectively (60–90%). In contrast, o-xylene (Henry's constant=0.21) was removed with low efficiency (35–37%). The reason for these results could be that dissolution is not the major mechanism of uptake of VOCs by snow. The efficiency of snow removal of aromatic hydrocarbons was temperature dependent; the lower the ambient temperature at Jungfraujoch, the greater was the efficiency of washing out.

Thus, the highest removal efficiency values for all compounds were obtained at an ambient temperature of approximately −24°C. An increase in temperature to −13.7°C decreased removal efficiency by a factor of approximately two for some hydrocarbons including ethylbenzene and isobutene. The removal efficiency for benzene, toluene, n-pentane and n-butane decreased by an average of 20% with this temperature in-

crease (see Fig. 4). These finding validate the results of the uptake model of Fries et al. (2007) that revealed a higher uptake of aromatic hydrocarbons by ice crystals at lower temperatures.

⁵ According to Lei and Wania (2004), one possible explanation for this observation might be cold temperature removal of organic chemicals due to a reduction in vapor pressure with temperature, which consequently enhances air/ice partitioning. Another explanation could be that low temperatures (Hoff et al., 1995), the large size and specific surface area of snow/ice crystals (Franz and Eisenreich, 1998,) promote snow/ice-hydrocarbon interactions. Specific snow surface area is a key parameter determining ¹⁰ the capacity of snow for organic contaminants and is even higher during colder days (Burniston et al., 2007).

4.2 Determination of distribution coefficients

To estimate the distribution ratio of hydrocarbons between air and snow in the troposphere, their concentrations were determined in these phases during the CLACE 5 ¹⁵ campaign. Air and snow samples were collected at the same time so that the measured concentrations reflected the equilibrium distribution. Unfortunately, alkanes could not be quantified in snow samples using the chosen analytical method. However, Gröllert and Puxbaum (1998) reported a maximum ratio of 130 ($\frac{C_{snow}}{C_{air}}$) for scavenging of alkanes by snow at an elevated alpine site.

²⁰ Benzene, alkylated benzenes, chlorinated hydrocarbons and monoterpenes were quantified in snow samples, and benzene, toluene, m/p-xylene, o-xylene, ethylbenzene, 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene were also quantified in the air samples (see Table 3). For these latter seven compounds, the distribution coefficients ($K_{air/snow}$) were derived from measurements using Eq. (4) (Table 3). The distribution ²⁵ coefficients show a correlation with ambient temperature, with values of coefficients being higher for all compounds at −13.7°C than at −24°C (e.g. 5.3×10^{-3} and 4.8×10^{-3}, respectively, for benzene). Unexpectedly, the highest distribution coefficient values

were observed for benzene despite it having the highest water solubility ($1780\,\text{mg L}^{-1}$) among the analyzed monoaromatic hydrocarbons. The lowest distribution coefficient value was found for 1,2,4-trimethylbenzene (2×10^{-4}), which has a water solubility of $57\,\text{mg L}^{-1}$. The distribution coefficients of the other aromatic hydrocarbons at $-13.7°C$ were 3.6×10^{-4} for 1,3,5-trimethylbenzene, 4×10^{-4} for m/p-xylene, 4×10^{-4} for toluene, 3×10^{-4} for o-xylene, and 2.3×10^{-4} for ethylbenzene.

Several studies have reported hydrophobic VOCs in precipitation at higher concentrations than predicted from Henry's law constants and ambient atmospheric concentrations (Sato et al., 2006; Fries et al., 2008).

Lei and Wania (2004) proposed Eq. (6) for estimating the distribution coefficients of a wide range of organic compounds at temperatures below $0°C$.

$$K^{b}_{\text{air/snow}} = \frac{1}{A_I \cdot \rho_W \cdot K_{SA}} \qquad (6)$$

where A_I is the specific surface area in $\text{m}^2\,\text{g}^{-1}$ and ρ_w is the density of ice (g m^{-3}). K_{SA} is the sorption coefficient onto the snow surface ($\text{m}^3\,\text{m}^{-2}$), determined for a wide range of hydrophobic and hydrophilic organic substances at $-6.8°C$ (Roth et al., 2004).

The K_{SA} values have been extrapolated to a temperature of $-13.7°C$ for the compounds considered in the present study.

The distribution coefficients determined empirically and theoretically show the same pattern as described above (see Table 3). Comparison of the distribution coefficients derived from measurements during CLACE 5 ($K_{\text{air/snow}}$) with those values ($K^{b}_{\text{air/snow}}$) calculated using Eq. (6) shows good consistency for benzene (5.3×10^{-3} and 6.2×10^{-3}, respectively) and 1,3,5-trimethylbenzene (4.4×10^{-3} and 5.2×10^{-3}, respectively) (see Table 3). The small difference in coefficient values for these compounds indicates that their sorption onto the snow surface plays a significant role in their removal by snow. For 1,2,4-trimethylbenzene, o-xylene, , m/p-xylene, ethylbenzene and toluene the empirical coefficient values were 0.5×10^{-3}, 1.1×10^{-3}, 1.3×10^{-3}, 1.5×10^{-3} and 2.8×10^{-3}, respectively (Table 3). However, for the other aromatic hydrocarbons the distribution

coefficients calculated theoretically were one order of magnitude higher than the empirical values (see Table 2). One explanation for these differences may be the influence of processes other than dissolution and sorption on the removal of hydrocarbons by snow from the gas phase, as the calculated distribution coefficients ($K^b_{air/snow}$) consider adsorption of VOCs on the snow surface as the only important process during scavenging. For compounds with low water solubility and a low $K_{air/snow}$, such as 1,2,4-trimethylbenzene and o-xylene, removal from the air by snow adsorption alone is insignificant. For these compounds in particular, other processes such as particle scavenging should also be considered.
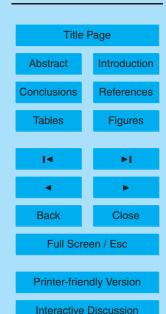
5 Conclusions

VOCs were measured in air and snow samples during CLACE 5 in the winter of 2006. The fluxes of individual organic compounds were measured under various atmospheric conditions, and from these fluxes the removal efficiency of the hydrocarbons by snow was calculated. The efficiency values of some investigated compounds (e.g. alkanes, m/p-xylene, and o-xylene) were inconsistent with their water solubility and volatility. The distribution coefficients between air and snow phases were derived for various aromatic hydrocarbons from measurements made during the present study, and from calculated values obtained from previous studies. The empirical and calculated distribution coefficients showed the same pattern, but the empirical coefficients for several hydrocarbons were one order of magnitude lower than the calculated values. One explanation for this may be the influence of processes other than dissolution and adsorption on the removal of hydrocarbons by snow from the ambient air. For compounds with low water solubility and a low distribution coefficient, removal from the air by snow adsorption alone is negligible. For these compounds in particular, other processes such as particle scavenging should also be considered. The measured distribution coefficients and the removal efficiencies showed a correlation with temperature, characterized by increased VOC removal by snow with decreasing ambient temperature.

◀ | ▶

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

References

Atkinson, R.: Gas-phase tropospheric chemistry of organic compounds, J. Phys. Chem., Ref. Data, Monograph, 2, 1–216, 1994.

Atkinson, R.: Gas phase tropospheric chemistry of organic compounds. In: Volatile Organic Compounds in the Atmosphere, edited by: Hester, R. E., Harrison, R. M., Issues, Environ. Sci. Technol., 4, The Royal Society of Chemistry, Cambridge, UK, 65–89, 1995.

Atkinson, R.: Gas-phase tropospheric chemistry of volatile organic compounds. 1. Alkanes and alkenes, J. Phys. Chem., Ref. Data, 26, 215–290, 1997.

Baltensperger, U., Gäggeler, H. W., Jost, D. T., Lugauer, M., Schwikowski, M., Weingartner, E., and Seibert, P.: Aerosol climatology at the high-Alpine site Jungfraujoch, Switzerland, J. Geophy. Res., 102(D16), 19 707–19 715, 1997a.

Baltensperger, U., Schwikowski, M., Jost, D. T., Nyeki, S., Gäggeler, H. W., and Poulida, O.: Scavenging of atmospheric constituents in mixed phase clouds at the high-alpine site Jungfraujoch part I: Basic concept and aerosol scavenging by clouds, Atmos. Environ., 32, 3975–3983, 1997b.

Bidleman, T. F.: Atmospheric processes, Environ. Sci. Technol., 22, 361–367, 2001.

Burniston, D. A., Strachan, W. J. M., Hoff, J. T., and Wania, F.: Changes in surface area and concentrations of semivolatile organic contaminants in aging snow, Environ. Sci. Technol., 41, 4932–4937, 2007.

Dämmgen, U., Grünhage, L., and Jäger, H.-J.: Description, assessment and meaning of vertical fluxes of matter within ecotopes: a systematic consideration, Environ. Pollut., 96, 249–260, 1997.

Dollard, G. J., Dumitrean, P., Telling, S., Dixon, J., and Derwent, R. G.: Observed trends in ambient concentrations of C2eC8 hydrocarbons in the United Kingdom over the period from 1993 to 2004, Atmos. Environ., 41, 2559–2569, 2007

Forrer, J., Rüttimann, R., Schneiter, D., Fischer, A., Buchmann, B., and Hofer, P.: Variability of trace gases at the high Alpine site Jungfraujoch caused by meteorological transport processes, J. Geophys. Res., 105(D10), 12 241–12 251, 2000.

Fries, E., Starokozhev, E., Haunold, W., Jaeschke, W., Hoog, I., Mitra, S. K., and Borrmann,

Distribution of VOCs between air and snow

E. Starokozhev et al.

S.: Laboratory studies on the uptake of aromatic hydrocarbons by ice crystals during vapor depositional crystal growth, Atmos. Environ., 41, 6156–6166, 2007.

Fries, E., Sieg, K., Püttmann, W., Jaeschke, W., Winterhalter, R., Williams, J., and Moortgat, G.: Benzene, alkylated benzene, chlorinated hydrocarbons and monoterpenes in snow ice in spring at Jungfraujoch (46.6° N, 8.0° E) during CLACE 4 and 5, Sci. Total. Environ., 391, 269–277, 2008.

Franz, T. P. and Eisenreich, S. J.: Snow scavenging of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in Minnesota, Environ. Sci. Technol., 32, 1771–1778, 1998.

Goss, K.-U.: The air/surface adsorption equilibrium of organic compounds under ambient conditions. Critical reviews, Environ. Sci. Technol., 34, 339–389, 2004.

Gröllert, C. and Puxbaum, H.: Lipid organic aerosol and snow composition at an elevated alpine site in the fall and spring season and scavenging ratios for single compounds, Water Air Soil Poll., 117, 157–173, 2000.

Hellén, H., Hakola, H., Pirjola, L., Laurila, T., and Pystynen, K.-H.: Ambient air concentrations, source profiles, and source apportionment of 71 different C2–C10 volatile organic compounds in urban and residential areas of Finland, Environ. Sci. Technol., 40, 103–108, 2006.

Hoff, J. T., Wania, F., Mackay, D., and Gillham, R.: Sorption of non-polar organic vapors by ice and snow, Environ. Sci. Technol., 29, 1982–1989, 1995.

Karl, T., Crutzen, P. J., Mandl, M., Staudinger, M., Guenther, A., Lordan, A., Fall, R., and Lindinger, W.: Variability lifetime relationship of VOCs observed at the Sonnblick Observatory 1999 – Estimation of HO densities, Atmos. Environ., 35, 5287–5300, 2001.

Kavouras, I. G., Mihalopoulos, N., and Stephanou, E. G.: Formation of atmospheric particles from organic acids produced by forests, Nature, 395, 683–686, 1998.

Kleindienst, T. E., Conver, T. S., McIver, C. D., and Edney, E. O.: Determination of secondary organic aerosol products from the photooxidation of toluene and their implication in ambient $PM_{2.5}$, J. Atmos. Chem., 47, 79–100, 2004.

Lei, D. L. and Wania, F.: Is rain or snow a more efficient scavenger of organic chemicals?, Atmos. Environ., 38, 3557–3571, 2004.

Li, Y., Campana, M., Reimann, S., Schaub, D., Stemmler, K., Staehelin, J., and Peter, T.: Hydrocarbon concentrations at the Alpine mountain sites Jungfraujoch and Arosa, Atmos. Environ., 39, 1113–1127, 2005.

Monod, A., Sive, B. C., Avino, P., Chen, T., Blake, D. R., and Rowland, F. S.: Monoratomatic

Distribution of VOCs between air and snow

E. Starokozhev et al.

compounds in ambient air of various cities: a focus on correlations between the xylenes and ethylbenzene, Atmos. Environ., 35, 135–149, 2001.

National Research Council, Rethinking the Ozone Problem in Urban and Regional Air Pollution, National Academy Press, Washington, DC, 1991.

Odum, J. R., Jungkamp, T. P. W., Griffin, R. J., Forstner, H. J. L., Flagan, R. C., and Seinfeld, J. H.: Aromatics, Reformulated Gasoline, and Atmospheric Organic Aerosol Formation, Environ. Sci. Technol., 31, 1890–1897, 1997.

Prévot, A. S. H., Dommen, J., and Bäumle, M.: Influence of road traffic on volatile organic compound concentrations in and above a deep Alpine valley, Atmos. Environ., 34, 4719–4726, 2000.

Roth, C. M., Goss, K.-U., and Schwarzenbach, R. P.: Sorption of diverse organic vapours to snow, Environ. Sci. Technol., 38, 4078–4084, 2004.

Sato, E., Matsumoto, K., Okochi, H., and Igawa, M.: Scavenging Effect of Precipitation on Volatile Organic Compounds in Ambient Atmosphere, B. Chem. Soc. Jpn., 79, 1231–1233, 2006.

Sieg, K., Fries, E., and Püttmann, W.: Analysis of BTEX and n-aldehydes (C6–C10) in melted snow water by use of solid phase dynamic extraction (SPDE) combined with GC/MS, J. Chromatogr. A, 1178, 178–186, 2008

Wania, F., Mackay, D., and Hoff, J. T.: The importance of snow scavenging of polychlorinated biphenyl and polycyclic aromatic hydrocarbon vapors, Environ. Sci. Technol., 33, 195–197, 1999.

Winkler, J., Blank, P., Glaser, K., Gomes, J. A. G., Habram, M., Jambert, C., Jaeschke, W., Konrad, S., Kurtenbach, R., Lenschow, P., Lörzer, J. C., Perros, P. E., Pesch, M., Prümke, H. J., Rappenglück, B., Schmitz, T., Slemr, F., Volz-Thomas, A., and Wickert, B.: Ground-based and airbonre measuremnts of nonmethane hydrocarbons in BERLIOZ: Analysis and selected results, J. Atmos. Chem., 42, 465–492, 2002.

Zalel, A. and Broday, Y. D. M.: Revealing source signatures in ambient BTEX concentrations, Eniviron. Pollut., doi:10.1016/j.envpol.2008.01.016, in press, 2008.

Zanis, P., Monks, P. S., Schuepbach, E., Penkett, S. A.: The role of in-situ photochemistry in the control of ozone during spring at the Jungfraujoch observatory (3580 m a.s.l.) – comparison of model results with measurements, J. Atmos. Chem., 37(1), 1–27, 2000.

Distribution of VOCs between air and snow

E. Starokozhev et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

◄◄	►►
◄	►
Back	Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 1. Meteorological parameters during CLACE 5 (2006).

Date	Sampling time	Wind speed ($m\,s^{-1}$)	Relative humidity (%)	Air temperature (°C)	Global radiation ($W\,m^{-2}$)
24 February	00:00	3.7	55.4	−16.4	0
	04:00	9.1	52.7	−16.5	0
	08:00	9.6	98.2	−14.5	102
	12:00	14.2	98.5	−13.7	312
	16:00	11.7	99.8	−13.7	78
	20:00	15.7	99.3	−14.2	0
1 March	00:00	8.1	100	−21.6	0
	04:00	7.9	97.5	−22.5	0
	08:00	9.9	100	−24.1	114
	12:00	4.2	98.7	−23.2	390
	16:00	2.7	78.8	−23.7	42
	20:00	2.9	52.8	−24.4	0
11 March	00:00	5.1	96.3	−17.8	0
	04:00	47.5	99.3	−17.8	0
	08:00	8.2	98.3	−18.3	126
	12:00	12.6	95.8	−17.7	516
	16:00	13.3	99.8	−13.7	78
	20:00	8.1	99.3	−16.2	0
3 March	00:00	7.5	100	−21.6	0
	04:00	6.5	99.8	−23.7	0
	08:00	6.7	100	−24.3	114
	12:00	5.6	100	−26.6	618
	16:00	5.6	99.1	−27.6	102
	20:00	2.1	46.6	−24.4	0

Table 2. Physico-chemical parameters of VOCs, measured in air samples during CLACE 5.

Compound	Molecular weight	Water solubility (mg/L)	H(25°C) (atmm^3/mole)	H(25°C) (dimensionless)	Boiling point (°C)	OH Rate constant (cm^3/molecule s)	Atmospheric lifetime[a]
isobutane	58	48.8	1.19	47.6	−11.7	2.34×10^{-12}	5 days
n-butane	58	61.2	0.95	38	−0.5	2.54×10^{-12}	4.6 days
isobutene	56	263	0.218	8.27	−6.9	5.14×10^{-11}	5.40 h
3 methylpentane	86	17.9	1.68	67.2	63.2	5.7×10^{-12}	2 days
2 methylpentane	86	14	1.71	68.4	60.2	5.6×10^{-12}	2.1 days
n-pentane	72	38	1.25	50	36	3.94×10^{-12}	2.9 days
isopentane	72	48	1.4	56	27.8	3.9×10^{-12}	3 days
n-hexane	86	9.5	1.8	72	68.7	5.61×10^{-12}	2.1 days
benzene	78	1780	0.00555	0.22	80.1	1.23×10^{-12}	9.4 days
toluene	92	526	0.00664	0.27	110.6	5.96×10^{-12}	1.9 days
o-xylene	106	178	0.00518	0.21	144.4	1.37×10^{-11}	20.3 days
m/p-xylene	106	161	0.00718	0.29	139.1	2.36×10^{-11}	11.7 days
ethylbenzene	106	169	0.00788	0.32	136.2	7.1×10^{-12}	1.6 days
1,3,5-TMB	120	48	0.00877	0.36	165	5.75×10^{-11}	4.9 h
1,2,4-TMB	120	57	0.00616	0.25	169	3.3×10^{-11}	8.42 h

[a] Assuming (OH)=10^6 rad cm^{-3} (Monod et al., 2001).

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Table 3. Concentrations of VOCs in air (C_{air}) and snow (C_{snow}) samples collected on 24 February and 1 March 2006, and distribution coefficients derived empirically ($K_{air/snow}$) and calculated from previous reports ($K^b_{air/snow}$).

Sampling time	24 February 2006 12:45			1 March 2006 14:50			
Ambient temperature	T=−13,7°C (259.3 K)			T=−24°C (249 K)			
	C_{air} $[\mu g\,m^{-3}]$	C^a_{snow} $[ng\,L^{-1}]$	$K_{air/snow}$	C_{air} $[\mu g\,m^{-3}]$	C^a_{snow} $[ng\,L^{-1}]$	$K_{air/snow}$	$K^b_{air/snow}$
benzene	0.37	69	0.0054	0.33	69	0.0048	0.0062
toluene	0.15	397	0.0004	0.19	558	0.0003	0.0028
o-xylene	0.05	166	0.0003	0.07	238	0.0003	0.0011
m/p-xylene	0.04	104	0.0004	0.06	169	0.0004	0.0013
ethylbenzene	0.04	172	0.0002	0.06	285	0.0002	0.0015
1,3,5-TMB	0.15	42	0.0036	0.23	68	0.0034	0.0052
1,2,4-TMB	0.04	203	0.0002	0.06	477	0.0001	0.0005

[a] Fries et al. (2008).
[b] Calculated using Eq. (4) by Lei and Wania (2004), and Eq. (5) by Roth et al. (2004), extrapolated to −13.7°C.

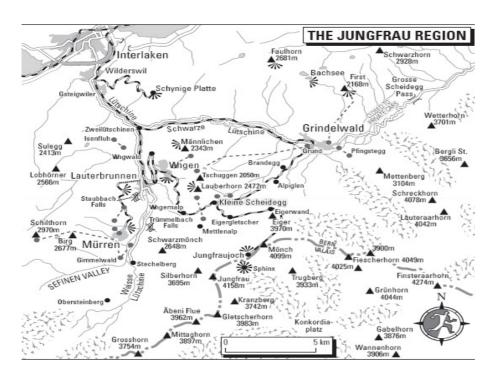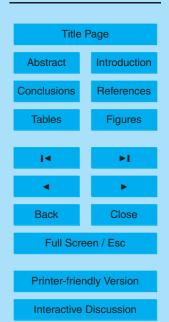**Fig. 1.** Physico-chemical transport model of organic compounds in the troposphere.

Fig. 2. Geographical setting of the Jungfraujoch high alpine research station, Switzerland (Rough Guides/Map published on http://Switzerland.isyours.com).
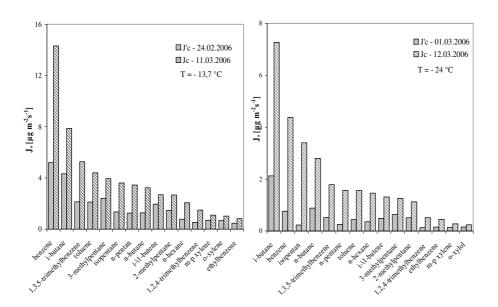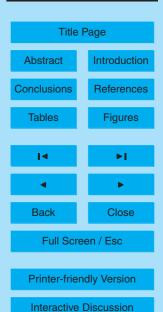
Fig. 3. Initial (J_c) and final ($J_c^{'}$) fluxes (after wet deposition) of VOCs in the ambient air at temperatures below 0°C during CLACE 5 (2006).

Fig. 4. Removal efficiency of VOCs by snow under various atmospheric conditions.