

Uptake of gaseous aromatic hydrocarbons by non-growing ice crystals

Elke Fries^{a,*}, Werner Haunold^a, Wolfgang Jaeschke^a, Ines Hoog^b,
Subir K. Mitra^b, Stephan Borrmann^{b,c}

^a*Institut für Atmosphäre und Umwelt, J.W. Goethe-Universität Frankfurt am Main, AG Atmosphärische Umweltforschung, Georg-Voigt-Str. 14, D-60325 Frankfurt, Germany*

^b*Institut für Physik der Atmosphäre, J.G.-Universität, Becherweg 21, 55099 Mainz, Germany*

^c*Max-Planck Institut für Chemie, Abt. Luftchemie, 55020 Mainz, Germany*

Received 14 September 2005; received in revised form 20 March 2006; accepted 24 March 2006

Abstract

Laboratory studies were performed in a walk-in cold chamber to investigate the uptake of aromatic hydrocarbons by non-growing ice crystals at -20°C . Dendritic ice crystals were grown by vapor deposition and exposed to organic gases (benzene, toluene, ethylbenzene, *m/p*-xylene, *o*-xylene, *n*-propylbenzene, 4-ethyltoluene, 1,3,5-trimethylbenzene, *tert*-butylbenzene, 1,2,4-trimethylbenzene, and 1,2,3-trimethylbenzene) at gas-phase concentrations between 2.8 and $33.1\ \mu\text{g m}^{-3}$. During all exposure experiments, the gas/air stream was maintained at ice saturation to avoid ice crystal growth or evaporation. An analytical method comprising of solid-phase-micro-extraction followed by gas chromatography/mass spectrometry (SPME/GC–MS) was applied, which allows detection of organic compounds in melted ice at $0.025\ \text{ng g}_{\text{ice}}^{-1}$. The SPME/GC–MS method was an appropriate tool to determine the uptake of organic compounds by ice crystals at the applied gas-phase concentrations. However, it was not possible to detect any of the test substances in ice samples after exposure. No adsorption could be detected by increasing gas-phase concentrations. Neither increasing exposure time nor lowering flow rate of the carrier gas caused detectable adsorption effects of aromatic compounds on ice. Our results indicate that adsorption of aromatic hydrocarbons is either insignificant or highly reversible at -20°C . These findings are consistent with reversible adsorption processes reported already for many oxygenated organic compounds like alcohols, acids, and aldehydes. Although the specific surface area of dendritic ice crystals is large, the results of our study demonstrate that gas uptake by ice surfaces is negligible for the removal of aromatic hydrocarbons in the atmosphere. This is an indication that the occurrence of aromatic hydrocarbons in precipitation cannot be explained by surface adsorption. There must be another accumulation process leading to concentrations of aromatic hydrocarbons found in field studies which is still unknown.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Aromatic hydrocarbons; Ice crystals; Uptake; SPME; Adsorption

1. Introduction

Aromatic hydrocarbons like benzene, toluene, ethylbenzene, and xylenes (BTEX) have been

*Corresponding author. Tel.: +49 69 79822911;
fax: +49 69 79828548.

E-mail address: e.fries@kristall.uni-frankfurt.de (E. Fries).

detected in air at higher altitudes due to vertical transport processes (Prévot et al., 2000; Karl et al., 2001; Li et al., 2005). Those compounds are mainly emitted from automobile traffic and solvents to the atmosphere (Brocco et al., 1997). Emissions of aircraft exhaust also contain aromatic hydrocarbons from unburnt fuel (Slemr et al., 2001). BTEX have been also measured in rain and snow at a wide concentration range of low ppt to low ppb levels (Ligocki et al., 1985; Czuczwa et al., 1988). The wet removal of organic chemicals, which depends on the properties of the compound and the type of precipitation, has been reviewed by Scott (1981) and Eisenreich et al. (1981). These authors have proposed that wet removal of gaseous organic compounds is an equilibrium process between the gas and the aqueous phases and follows Henry's law (H). However, snow contains concentrations of aromatic hydrocarbons which require air concentrations higher than those usually measured (Czuczwa et al., 1988). An uptake of organic gases by the surfaces of ice crystals could be possible explanation for the underestimation of concentrations of organic compounds in rain and snow. Vapor adsorption depends strongly on the specific surface of the sorbent (Pennell et al., 1992). The adsorption equilibrium can be described by an adsorption coefficient K (Goss, 1993) as follows:

$$K = \frac{\{\text{mg of substance/surface area of sorbent (cm}^2)\}}{\{\text{mg of substance/volume of gas phase (cm}^3)\}}. \quad (1)$$

Knowledge on the interactions between ice crystals in tropospheric ice clouds and contrails and between inorganic and organic gases are important for interpretation of chemical reactions, precipitation formation, global transport mechanisms, and climate change. Deshler et al. (1994) found ice particles with radii 2–5 μm at temperatures several degrees above the stratospheric ice frost point. These field observations could be explained by a surface film of nitric acid trihydrate (NAT), which may kinetically hinder the evaporation of ice (Peter et al., 1994; Biermann et al., 1998). Organic pollutants from the exhaust of jet engines decrease evaporation rates of ice crystals implying an increase in the lifetime of polluted ice clouds (Diehl and Mitra, 1998).

Many previous laboratory studies have investigated adsorption of different organic compounds like alcohols, acids, aldehydes and various hydro-

carbons on ice surfaces using coated wall flow tubes (Abbatt et al., 1992; Winkler et al., 2002; Bartels-Rausch et al., 2005), Knudson flow reactors (Caloz et al., 1997; Hudson et al., 2002), or inverse gas chromatography (Goss, 1993; Hoff et al., 1995; Roth et al., 2004). Many of these studies have dealt with adsorption in terms of the free energy behavior of the adsorbate as a function of its distance from the solvent surface. At temperatures around 0 °C, similar adsorption enthalpies for ice and water have been observed for non-polar organic compounds like *n*-alkanes, chlorobenzenes, xylenes, and furans (Orem and Adamson, 1969; Goss, 1993; Hoff et al., 1995). There are also many theoretical studies calculating interactions between water molecules of ice surfaces and organic molecules (Allouche, 1999; Picaud and Hoang, 2000; Compoin et al., 2002; Lei and Wania, 2004). However, the understanding of the relevant processes is not as complete as for the adsorption of organic compounds on aerosol particles (Pankow, 1987), soil (Nguyen et al., 2005), or minerals (Goss and Eisenreich, 1996). Due to the great variability of temperature, relative humidity, ice surface area, gas partial pressures, aerosol number concentration, and composition in ice clouds, in-situ determination of the partitioning of organics between the gas and the ice phase is rather difficult. The collective influence of the pollutants must be also regarded considering the high variety of organic molecules with different physical and chemical properties in the atmosphere.

The uptake of chemicals by ice mainly depends on the shape (Keyser and Leu, 1993). Schaff and Roberts (1998) reported different interactions of organic compounds with amorphous and crystalline ice surfaces, based on differences in the density of free surface OH groups, surface area porosity, and permeability.

Based on previous experiments on the uptake of inorganic compounds by dendritic ice crystals (Mitra et al., 1990; Diehl et al., 1995, 1998) in this paper, a new experimental method is presented to evaluate the importance of the uptake of organic compounds by non-growing dendritic ice crystals. Inside a walk-in cold chamber (WCC), ice crystals were exposed to different aromatic hydrocarbons (benzene, toluene, ethylbenzene, *m/p*-xylene, *o*-xylene, *n*-propylbenzene, 4-ethyltoluene, 1,3,5-trimethylbenzene (1,3,5-TMB), *tert*-butylbenzene, 1,2,4-trimethylbenzene (1,2,4-TMB), and 1,2,3-trimethylbenzene (1,2,3-TMB)) at different gas-phase concentrations, flow rates of the carrier gas,

and exposure times. The uptake of the organic gases was quantified by detecting these compounds in melted ice crystals after exposure by a sensitive method composed of solid-phase-micro-extraction (SPME) followed by gas chromatography/mass spectrometry (GC/MS).

2. Experimental methods

2.1. Ice crystal growth

Dendritic ice crystals were grown in a diffusion chamber. The growth procedure is illustrated in Fig. 1. The top of a glass aquarium (0.25 m × 0.40 m × 0.25 m) was covered with an aluminum-extruded heatsink (0.5 SA DIN1748, Fischer, Germany), which provides a heat exchanger and a sample substrate. The aquarium was filled to a level of 2 cm with deionized water and placed into a 2 m × 2 m WCC. The WCC temperature was maintained at -20°C . The water was kept constantly at $+15^{\circ}\text{C}$ by covering the bottom of the aquarium with a heater mat (a). To increase heat exchange, the diffusion chamber was put below a fan inside the WCC. Dendritic ice crystals were deposited from water vapor onto the extruded heatsinks (b). The growth time was 20 h. Afterwards, the ice crystals were removed from the diffusion chamber

and placed on nine stainless-steel screen inserts 0.10 m in diameter (c). The stainless-steel mesh of the screen inserts had a grid size of 0.0014 m. Each insert was covered with approximately 3 g of ice crystals in one layer. All screen inserts were placed in a (self-constructed) stainless-steel flow reactor, which measured 0.40 m in length and 0.10 m in diameter (d, e).

2.2. Experimental setup

Six exposure experiments were performed in the WCC under the conditions of atmospheric pressure and a temperature of -20°C . The gas flow diagram outside and inside the WCC is shown in Fig. 2. Ambient air served as a carrier gas and was pumped with 50 L min^{-1} into a Teflon tube through a cleaning device equipped with two activated carbon filters and one Teflon filter. By means of this cleaning device, organic compounds and aerosol particles were removed to avoid background contamination. After passing the cleaning device, only N_2 , O_2 , CO_2 , and H_2O were assumed to be present in air. The removal efficiency of the cleaning device was determined by analyzing BTEX before and after passing through the cleaning device. During one separate experiment, the total particle concentration of the carrier gas was measured by a

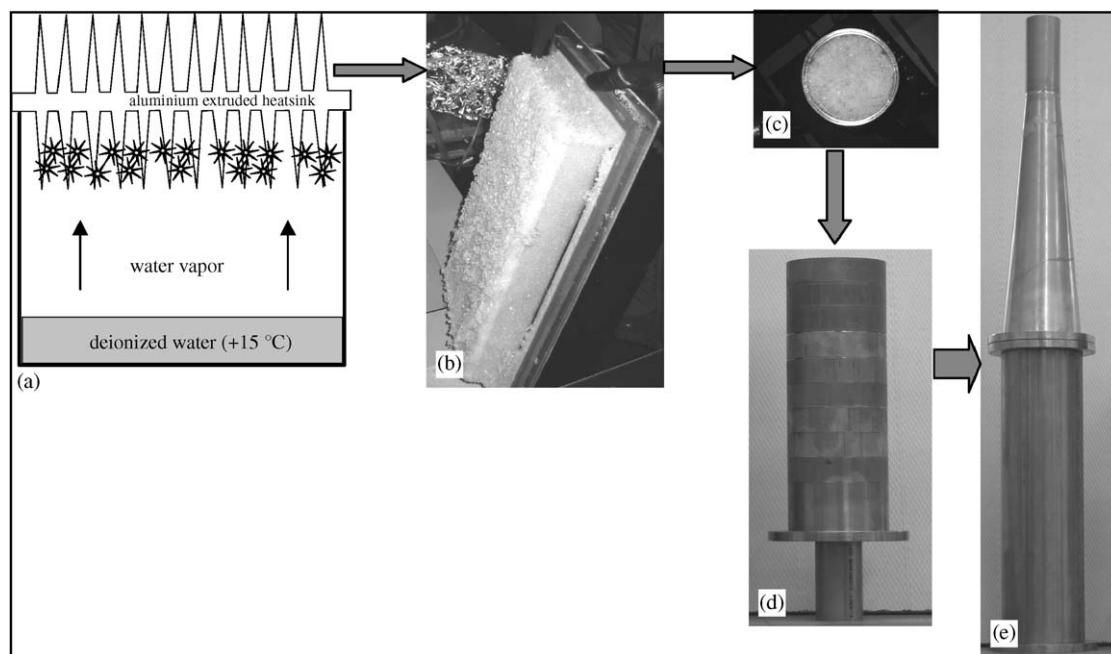


Fig. 1. Crystal growth procedure and placement of artificial ice crystals in the flow reactor (a: crystal growth; b, c: ice crystal harvesting; d, e: flow reactor).

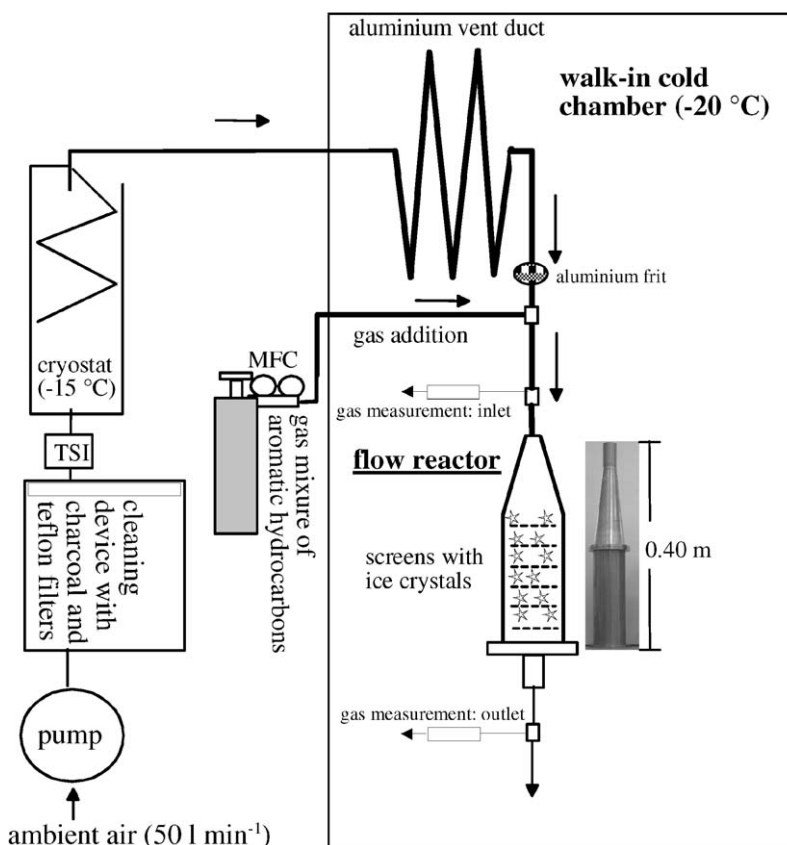


Fig. 2. Experimental setup and gas flow diagram of exposure experiments in a walk-in cold chamber at -20°C .

condensation particle counter (model TSI 3022). After passing the cleaning device, all particles were removed from the carrier gas. During the exposure experiments, the TSI was removed to avoid contamination of the system with butanol vapor. Prior to the addition of organic gases, the carrier gas stream was cooled to -15°C by passing it through a cryostat outside the WCC (see Fig. 2). Moisture was removed by a cold trap (glass loop) to saturate the carrier gas with respect to ice at -15°C . Entering the WCC, the temperature of the air stream was lowered to -20°C . To keep the air stream saturated at -20°C , the air was passed through 20 m of a helical flexible aluminium vent duct (System 300AC, Lindab Germany) with a diameter of 0.05 m (see Fig. 2). Moisture was removed by retaining the formed tiny ice crystals in the aluminium vent duct. In addition, supercooled droplets were removed with an aluminium frit located 0.30 m upstream of the flow reactor (see Fig. 2). At a distance of 0.20 m, a gaseous mixture of aromatic hydrocarbons (BTEX, *n*-propylbenzene, 4-ethyltoluene, 1,3,5-TMB, *tert*-butylbenzene, 1,2,4-

TMB, 1,2,3-TMB) was added to the saturated carrier stream through a heated pipe ($+15^{\circ}\text{C}$) to avoid condensation and crystallization of the organic gases. The flow velocities of the gas standard mixture were adjusted by a mass flow controller and were 12.5, 25, and 50 L min^{-1} . The ambient air/gas mixture entered the flow reactor through an interface of 0.05 m in diameter. With Reynolds numbers around 900, the gas flow inside the reactor was assumed to be laminar.

2.3. Gas standard preparation

The parent aromatic hydrocarbon mixture was prepared gravimetrically by mixing $180\ \mu\text{L}$ of BTEX, *n*-propylbenzene, 4-ethyltoluene, 1,3,5-TMB, *tert*-butylbenzene, 1,2,4-TMB, and 1,2,3-TMB. The most important physical and chemical parameters of these compounds are shown in Table 1. With water solubility below 1780 mg L^{-1} and vapor pressures higher than 0.23 kPa, the compounds have low polarities and high volatilities. All certified chemicals were purchased from

Table 1
Physical and chemical parameters of selected aromatic hydrocarbons

	MW (g mol ⁻¹)	<i>S</i> at +25 °C (mg L ⁻¹)	<i>P</i> at +25 °C (kPa)	<i>H</i> at +25 °C <i>c</i> _{gas} / <i>c</i> _{water}
Benzene	78	1780	12.60	0.22
Toluene	92	526	3.80	0.27
Ethylbenzene	106	169	1.30	0.32
<i>m/p</i> -xylene	106	161	1.10	0.29
<i>o</i> -xylene	106	178	0.90	0.21
<i>n</i> -propylbenzene	120	52	0.45	0.43
4-ethyltoluene	120	95	0.40	0.20
1,3,5-TMB	120	48	0.33	0.36
<i>Tert</i> -butylbenzene	134	30	0.29	0.54
1,2,4-TMB	120	57	0.27	0.25
1,2,3-TMB	120	72	0.23	0.16

MW = molecular weight, *S* = water solubility, *P* = vapor pressure, *H* = Henry Law constant.

Sigma-Aldrich at the highest purity of 99.9%. Parent aromatic mixture (25 µL) was mixed with high-purity synthetic air to form the daughter gas standard in a gas cylinder with a volume of 10 L at a nominal pressure of 0.01 kPa. The resulting gas-phase concentrations in the daughter gas mixture (µg m⁻³) were: 1.8 (benzene), 1.3 (toluene), 1.1 (ethylbenzene), 1.9 (*m/p*-xylene), 1.0 (*o*-xylene), 0.7 (*n*-propylbenzene), 0.7 (4-ethyltoluene), 0.7 (1,3,5-TMB), 0.6 (*tert*-butylbenzene), 0.8 (1,2,4-TMB), and 0.8 (1,2,3-TMB).

2.4. Gas-phase analysis

During all exposure experiments, concentrations of aromatics in the gas phase were measured at the inlet and the outlet of the flow reactor (see Fig. 2). The gas/air mixture was pumped with approximately 10 L min⁻¹ through glass sampling tubes packed with activated charcoal (Dräger) for 1 h. A sampling tube consisted of two layers: one sampling layer and one following layer. During sampling, aromatic hydrocarbons were adsorbed by the sampling layer. The following layer ensured that the adsorption capacity of the sampling layer did not exceed the breakthrough volume. After approximately 1 h, sampling tubes were removed. In the laboratory, analytes were desorbed from the sampling layer by adding 750 µL of carbon disulfide (CS₂) (Sigma-Aldrich, 99.9%). Stock solution (25 µL) of 1-chlorooctane (200 mg L⁻¹ in methanol) was added as an internal standard (IS). Samples were extracted in an ultrasonic bath for 10 min. One-microliter aliquot of each CS₂ extract was manually injected into the GC-injector using a split

mode of 1:10. The injector temperature was kept at 260 °C. The GC (Thermoquest CE Instruments Trace GC2000Series) was supplied with a 60 m DB-624 capillary column (Agilent Technologies) with an ID of 0.32 mm and a film thickness of 1.8 µm. Helium served as carrier gas. The column flow was set at 1 mL min⁻¹. The GC oven temperature was first held at 50 °C for 2 min, then increased to 190 °C at a rate of 10 °C min⁻¹ and finally held for 20 min at the final temperature. Data acquisition, processing, and instrument control were performed using Excalibur software (Thermoquest). Detection of the analytes was performed by a Thermoquest Finnigan Voyager MS in the electron impact positive ion and full scan mode (scan range 50–600). Quantification was accomplished by external standard calibration. For this purpose, five sampling tubes with activated charcoal were spiked with 50, 25, 10, 5, and 1 µL of a standard mixture of aromatic hydrocarbons (100 mg L⁻¹ in methanol). The detection limit was 0.25 ng m⁻³ for all aromatic compounds with relative standard deviations between 5% and 15%. In addition, six sampling tubes were analyzed without addition of a standard to determine background concentrations of aromatic hydrocarbons. Mean background concentration was 0.255 µg m⁻³ for toluene, 0.029 µg m⁻³ for ethylbenzene, 0.048 µg m⁻³ for *m/p*-xylene, and 0.022 ng m⁻³ for *o*-xylene. The SD values of the blanks varied between 0.0004 and 0.023 µg m⁻³. For benzene, *n*-propylbenzene, 1,3,5-TMB, 1,2,3-TMB, 4-ethyltoluene, and 1,2,4-TMB, no background concentrations were detected during gas-phase analysis. Background concentrations during gas-phase analysis resulted mainly from CS₂ and must

be subtracted from the concentrations measured in inlet and outlet samples.

2.5. Ice phase analysis

After each exposure experiment, ice crystals were removed manually from each screen insert and filled into separate glass vials sealed up with an aluminum-coated septum (Supelco). The ice sample volumes varied between 2.1 and 4.2 g. Subsequently, samples were transported to the laboratory and melted immediately before analysis. Five microliter of 1-brom-2-chlorethane (200 mg L^{-1} in water) was added as an IS to each sample. Concentrations of aromatic hydrocarbons in melted ice were determined by a sensitive method based on SPME followed by GC/MS (Achten et al., 2001). The HS-SPME apparatus consists of a $100 \mu\text{m}$ polydimethylsiloxane (PDMS) coating on 1 cm of fiber mounted on the syringe needle of the fiber holder (Supelco). Before starting the extraction, the fiber was drawn into the needle of the syringe, and the needle was used to penetrate the septum of the sealed vials. The fiber was then introduced into the headspace of the analyzed sample by depressing the plunger. The temperature of the analyte solution was kept constantly at $+35^\circ\text{C}$ by putting the vial in a water quench filled up with 3 cm of water. The sample holder was connected to a cryostat maintained at $+5^\circ\text{C}$. Samples were stirred at $890\text{--}900 \text{ rev min}^{-1}$ during analysis. Once adsorbed, VOCs were thermally desorbed from the fiber coating by inserting the fiber immediately into the GC injector kept at 260°C using the splitless mode. The fiber remained in the injector for 10 min. After this reconditioning time, all compounds were removed from the fiber. The GC (Thermoquest CE Instru-

ments Trace GC2000 Series) was equipped with a 60 m DB-624 capillary column (Agilent Technologies) with an ID of 0.32 mm and a film thickness of $1.8 \mu\text{m}$. Helium served as the carrier gas. The column flow was set at 1 mL min^{-1} . The GC oven temperature program was as follows: 50°C for 2 min, then heating at $10\text{--}190^\circ\text{C}$, and finally 20 min at 190°C . Data acquisition, processing, and instrument control were performed using Excalibur software (Thermoquest). Detection of the analytes was accomplished by a Thermoquest Finnigan Voyager mass spectrometer in the electron ionization positive ion and full scan mode (scan range $50\text{--}600$). The detection limits were defined at a signal-to-noise ratio of 10:1.

3. Results and discussion

The gas-phase concentrations during exposure experiments were measured at the inlet and the outlet of the flow reactor. BTEX concentrations measured in the gas phase at the outlet and the inlet of the flow reactor are shown in Table 2. Concentrations of gaseous organic compounds during experiments were between 2.8 and $33.1 \mu\text{g m}^{-3}$. The concentrations of all organic gases during experiments were in similar range of aromatic hydrocarbons occurring under environmental conditions in ambient air. The removal efficiency of the cleaning device was tested by sampling outside air before and after passing through the cleaning device. In Fig. 3, air concentrations of BTEX, 1,3,5-TMB, and 1,2,3-TMB before and after passing the cleaning device and resulting removal efficiencies are shown. Concentrations in ambient air without activated charcoal filters were $0.5 \mu\text{g m}^{-3}$ (benzene), $0.8 \mu\text{g m}^{-3}$ (toluene),

Table 2
Experimental conditions and gas phase concentrations of aromatic hydrocarbons ($\mu\text{g m}^{-3}$) during exposure experiments 1–6

No.	T_{WCC} ($^\circ\text{C}$)	Exposure time (min)	Flow rate of the carrier gas (m s^{-1})	c_{gas} benzene in/out ($\mu\text{g m}^{-3}$)	c_{gas} toluene in/ out ($\mu\text{g m}^{-3}$)	c_{gas} ethylbenzene in/out ($\mu\text{g m}^{-3}$)	c_{gas} m/p- xylene in/out ($\mu\text{g m}^{-3}$)	c_{gas} o-xylene in/out ($\mu\text{g m}^{-3}$)
1	-20	60	0.10	7.4/6.1	4.4/4.3	3.0/2.8	5.3/5.0	2.4/2.3
2	-20	60	0.10	15.6/14.4	12.5/10.6	10.1/8.9	17.5/15.3	7.9/7.1
3	-20	60	0.10	33.1/30.0	31.3/27.5	27.0/24.6	24.0/22.1	24.3/22.7
4	-20	60	0.05	13.3/10.1	9.4/9.0	6.2/5.9	5.4/5.1	5.5/5.0
5	-20	120	0.05	24.7/20.0	20.0/16.5	15.0/10.9	12.7/9.8	12.4/9.4
6	-20	180	0.05	27.7/22.8	23.0/21.2	16.9/15.6	14.7/14.0	14.2/13.3

No. = number of experiment, T_{WCC} = chamber temperature, c = concentration.

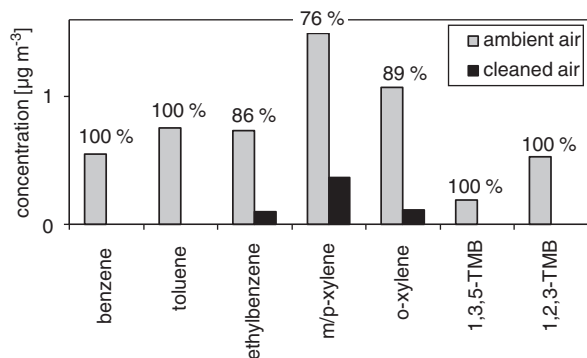


Fig. 3. Concentrations of selected aromatic hydrocarbons in ambient and cleaned air used as carrier gas for the exposure experiments and removal efficiencies of the cleaning device.

$0.7 \mu\text{g m}^{-3}$ (ethylbenzene), $1.5 \mu\text{g m}^{-3}$ (*m/p*-xylene), $1.1 \mu\text{g m}^{-3}$ (*o*-xylene), $0.2 \mu\text{g m}^{-3}$ (1,3,5-TMB), and $0.5 \mu\text{g m}^{-3}$ (1,2,3-TMB). After passing the cleaning device, concentrations decreased to $0.1 \mu\text{g m}^{-3}$ (ethylbenzene), $0.4 \mu\text{g m}^{-3}$ (*m/p*-xylene), and $0.1 \mu\text{g m}^{-3}$ (*o*-xylene). Benzene, toluene, 1,3,5-TMB, and 1,2,3-TMB were not detected in ambient air after passing the cleaning device. The corresponding removing efficiencies of the cleaning device for aromatic hydrocarbons varied between 76% and 100%.

To verify the applicability of the SPME/GC-MS method for determination of the uptake of organic compounds on ice surfaces, detection limits of the analytical method are discussed concerning the work of Goss (1993). The author determined the adsorption behavior of organic compounds by retention of the test substances on a GC-column filled with ice. He estimated an averaged relative gas-phase concentration of the substances in the column between 10^{-3} and 10^{-5} . Assuming a surface area of ice at $500 \text{ cm}^2 \text{ g}^{-1}$, he measured an adsorption coefficient (K) of 0.0027 cm for *m*-xylene on ice at -15°C . According to this K value, we calculated the expected concentrations of the tested compounds in ice by Eq. (1) at the minimum and maximum gas-phase concentration used during our experiments of 2.8 and $33.1 \mu\text{g m}^{-3}$, respectively. By normalizing the concentrations in ice using a specific surface area of $500 \text{ cm}^2 \text{ g}^{-1}$ estimated by Goss (1993), the expected concentrations of the tested compounds in ice are in the range of 0.004 – $0.045 \text{ ng g}_{\text{ice}}^{-1}$. Since our exposure experiments were performed with dendritic ice crystals, the specific area of Fassnacht et al. (1999) of $1820 \text{ cm}^2 \text{ g}^{-1}$ is assumed to be more adequate. Using this specific surface area, expected concentrations in ice are

between 0.015 and $0.164 \text{ ng g}_{\text{ice}}^{-1}$. The detection limit of the SPME/GC-MS method was $0.025 \text{ ng g}_{\text{ice}}^{-1}$ for ethylbenzene, *m/p*-xylene, *o*-xylene, 1,3,5-TMB, 1,2,4-TMB, and 1,2,3-TMB, $0.125 \text{ ng g}_{\text{ice}}^{-1}$ for toluene, and $0.500 \text{ ng g}_{\text{ice}}^{-1}$ for benzene. The expected values of aromatic hydrocarbons in ice are mostly above the detection limits of the analytical method, except for benzene. This demonstrates that the SPME/GC-MS method is an appropriate tool to measure the uptake of organic compounds under our experimental conditions.

Ice crystals grown in the diffusion chamber were checked for background contamination. The mean background concentrations of aromatic hydrocarbons in blanks were $0.5 \text{ ng g}_{\text{ice}}^{-1}$ for benzene, $2.7 \text{ ng g}_{\text{ice}}^{-1}$ for toluene, $0.4 \text{ ng g}_{\text{ice}}^{-1}$ for ethylbenzene, $1.3 \text{ ng g}_{\text{ice}}^{-1}$ for *m/p*-xylene, $0.1 \text{ ng g}_{\text{ice}}^{-1}$ for *o*-xylene, $0.02 \text{ ng g}_{\text{ice}}^{-1}$ for *n*-propylbenzene, 1,3,5-TMB and 1,2,3-TMB, and $0.04 \text{ ng g}_{\text{ice}}^{-1}$ for 4-ethyltoluene and 1,2,4-TMB. The SD values of the blanks varied between 0.006 and $0.189 \text{ ng g}_{\text{ice}}^{-1}$. In Table 1 the physical parameters of the compounds are summarized. The standard deviations showed a positive correlation with vapor pressures of the compounds. High vapor pressures of the compounds favor analytical losses during SPME-fiber transfer to the GC-injector resulting in lower reproducibility of the analytical method. Background concentrations during ice analysis resulted from laboratory air and IS addition and must be subtracted from the concentrations measured in ice samples.

The experimental conditions of the six exposure experiments are summarized in Table 2. During all experiments, the temperature of the WCC was kept at -20°C . In experiments 1, 2 and 3, gas-phase concentrations of aromatic hydrocarbons varied between 2.8 and $33.1 \mu\text{g m}^{-3}$. Exposure time and flow rate of the ambient air stream was 60 min and 0.10 m s^{-1} , respectively. At all gas-phase concentrations, it was not possible to detect aromatic compounds in ice after background subtraction. This indicates lower values of K than the minimum detectable values given by the detection limits of the analytical method. Therefore, exposure time was enhanced from 60 to 120 min and finally to 180 min during experiments 4, 5 and 6. Gas-phase concentrations of aromatics were between 5.9 and $27.7 \mu\text{g m}^{-3}$. Simultaneously, the flow rate was lowered to 0.05 m s^{-1} to enhance reaction time (see Table 2). Again, it was not possible to detect significant concentrations of aromatic hydrocarbons in ice above detection limits which indicates

values of K below the minimum detectable values. However, the method is applicable to detect adsorption of organic compounds in the extent reported by Goss (1993), it was not possible to detect any of the test compounds in ice samples after exposure. Neither increasing exposure time nor lowering the flow rate caused a detectable adsorption effect of aromatics in ice. Our results indicate that adsorption of non-polar aromatic hydrocarbons is either insignificant or highly reversible. The experimental conditions of the crystal growth environment were similar to conditions of the upper troposphere. So, our results are an indication that surface adsorption of organic compounds by ice is not a relevant process in the upper troposphere. However, concentrations of test substances in the gas phase were higher at the inlet than at the outlet of the flow reactor. Due to the absence of compounds in ice, the concentration decrease in the gas phase must be attributed to an imprecise determination of different sample volumes during air/gas sampling.

The results of the present study are in fair agreement with previous conclusions for the adsorption of some oxygenated organic molecules on ice surfaces at lower temperatures. For temperatures between -73 and -33 °C, the uptake of methanol, acetone, and formaldehyde on an ice-coated flow tube was insignificant and fully reversible (Winkler et al., 2002). Hudson et al. (2002) determined small surface coverage (10^{10} molecules cm^{-2} for methanol and acetone and $< 5 \times 10^9$ molecules cm^{-2} for acetaldehyde) at -63 °C, a negative temperature dependence, and a high adsorption reversibility. The results of our study do not indicate any positive correlation of adsorption with molecular weight or partial pressure as has been reported for oxygenated organic species like alcohols, acids, and aldehydes (Sokolov and Abbatt, 2002; Winkler et al., 2002; Dominé and Rey-Hanot, 2002; Hudson et al. 2002). The absence of adsorption even in spite of the high specific surface area of the artificial dendritic ice crystals can be explained with the low polarity of aromatic hydrocarbons. For these compounds, adsorption processes could only be due to weak physio-adsorption processes which have been reported to be highly reversible (Schaff and Roberts, 1998). Iijima et al. (1999) observed no removal of toluene by snow crystals due to low toluene polarity.

On the surface of pure ice, the presence of a quasi-liquid layer has been well known for decades

(for review see Dash et al, 1995). At high partial gas pressures, the quasi-liquid layer is expected to continuously thicken with time, allowing additional gas to be dissolved, which promotes further melting. Surface melting induced by higher partial pressures of HCl and HNO₃ (Diehl et al., 1995, 1998; Lee et al., 1999). There is evidence in the literature for dissociation of HCl and HNO₃ in the liquid-like ice surface, which explains why higher amounts adsorb than can be predicted. (Mitra et al., 1990; Kroes and Clary, 1992; Diehl et al., 1995; Zondlo et al., 1996). In our exposure experiments, the gas-phase concentrations were in the lower ppb range where the solid phase of ice must be thermodynamically stable. An enhanced uptake of aromatics due to melting processes at the ice surface could not be observed. Diffusion of HNO₃ into the ice crystal has also been observed to some extent (Diehl et al., 1995; Thibert and Dominé, 1998). The chemical and physical parameters of organic aromatic compounds do not favor dissociation and diffusion processes on ice surfaces.

4. Conclusions

We performed laboratory studies to investigate the uptake of aromatic hydrocarbons by dendritic ice surfaces at low gas-phase concentrations. The selected compounds constitute a representative group of volatile organic compounds with low water solubility. SPME/GC-MS is an appropriate tool to determine adsorption coefficients of the organic compounds by measuring those compounds in melted ice. Our uptake experiments demonstrate no importance of surface adsorption on ice for organic gases. The high specific surface area of dendritic ice crystals does not favor surface adsorption of organic compounds on ice. One possible explanation could be high reversibility of adsorption due to high vapor pressure and low water solubility. These findings are contrary to the results for inorganic compounds reported previously. Due to our results, effects of adsorption on ice surfaces on atmospheric transport processes and precipitation chemistry must be estimated to be very low for volatile organic compounds. It can be concluded that below-cloud scavenging of aromatic hydrocarbons by falling snowflakes at equilibrium conditions can be neglected for volatile organic compounds with lower water solubility. Adsorption is not the relevant uptake process responsible for the occurrence of such compounds in rain and snow. We

suggest further laboratory experiments to simulate adequately heterogeneous processes under ambient atmospheric conditions. In-cloud scavenging may be a possible removal process and laboratory experiments with growing ice crystals are recommended.

Acknowledgments

Financial support from the Deutsche Forschungsgemeinschaft (DFG) under grant numbers JAE350/1 and MI481/4-1 is kindly acknowledged. We would like to thank Prof. Dr. Wilhelm Püttmann for using his GC/MS lab. We also thank Dr. Ralf Kurtenbach for preparing the gas standard mixture, Dr. Karoline Diehl for fruitful discussions, and two anonymous reviewers for their helpful comments.

References

- Abbatt, J.P.D., Beyer, K.D., Fucaloro, A.F., McMahon, J.R., Wooldridge, P.J., Zhang, R., Molina, M.J.J., 1992. Interactions of HCl vapor with water-ice: Implications for the stratosphere. *Journal of Geophysical Research* 97, 15819–15826.
- Achten, C., Kolb, A., Püttmann, W., 2001. Sensitive method for determination of methyl-tert-butyl ether (MTBE) in water by use of headspace-SPME/GC-MS. *Fresenius' Journal of Analytical Chemistry* 371, 519–525.
- Allouche, A., 1999. Quantum studies of acetylene adsorption on ice surfaces. *Journal of Physical Chemistry A* 103, 9150–9153.
- Bartels-Rausch, T., Huthwelker, Th., Gäggeler, H.W., 2005. Atmospheric pressure coated-wall-flow-tube study of acetone adsorption on ice. *Journal of Physical Chemistry A* 109, 4531–4539.
- Biermann, U.M., Crowley, J.N., Huthwelker, T., Moortgat, G.K., Crutzen, P.J., 1998. FTIR studies on lifetime prolongation of stratospheric ice particles due NAT coating. *Geophysical Research Letters* 25, 3939–3942.
- Brocco, D., Fratarcangeli, R., Lepore, L., Petricca, M., Ventrone, I., 1997. Determination of aromatic hydrocarbons in urban air of Rome. *Atmospheric Environment* 31, 557–566.
- Caloz, F., Fenter, F.F., Tabor, K.D., Rossi, M.J., 1997. Design and Construction of a Knudsen cell reactor for the study of heterogeneous chemical reactions over the temperature range 130–750 K: performance and limitations. *Review of Scientific Instruments* 68, 3172–3179.
- Compoint, M., Toubin, C., Picaud, S., Hoang, P.N.M., Girardet, C., 2002. Geometry and dynamics of formic and acetic acids adsorbed on ice. *Chemical Physics Letters* 365, 1–7.
- Czuczwa, J., Leuenberger, C., Giger, W., 1988. Seasonal and temporal changes of organic compounds in rain and snow. *Atmospheric Environment* 22, 907–916.
- Dash, J.G., Fu, H., Wettlaufer, J.S., 1995. The premelting of ice and it's environmental consequences. *Reports on Progress in Physics* 58, 116–167.
- Deshler, T., Peter, Th., Müller, R., Crutzen, P.J., 1994. The lifetime of lee wave-induced ice particles in the Arctic stratosphere. I. Balloonborne observations. *Geophysical Research Letters* 21, 1327–1330.
- Diehl, K., Mitra, S.K., 1998. A laboratory study on the effects of the kerosene-burner exhaust on the ice nucleation and the evaporation rate of ice crystals. *Atmospheric Environment* 32, 3145–3151.
- Diehl, K., Mitra, S.K., Pruppacher, H.R., 1995. A laboratory study of the uptake of HNO₃ and HCl vapor by snow crystals and ice spheres at temperatures between 0 and –40 °C. *Atmospheric Environment* 29, 975–981.
- Diehl, K., Mitra, S.K., Pruppacher, H.R., 1998. A laboratory study on the uptake of HCl, HNO₃ and SO₂ gas by ice crystals and the effect of these gases on the evaporation rate of the crystals. *Atmospheric Research* 47–48, 235–244.
- Dominé, F., Rey-Hanot, L., 2002. Adsorption isotherms of acetone on ice between 193 and 213 K. *Geophysical Research Letters* 29, 1873.
- Fassnacht, S.R., Innes, J., Kouwen, N., Soulis, E.D., 1999. The specific surface area of fresh dendritic snow crystals. *Hydrological Processes* 13, 2945–2962.
- Eisenreich, S.J., Looney, B.B., Thornton, J.D., 1981. Airborne organic contaminants in the Great Lakes ecosystem. *Environmental Science and Technology* 15, 30–38.
- Goss, K.-U., 1993. Adsorption of organic vapors on ice and quartz sand at temperatures below 0 °C. *Environmental Science and Technology* 27, 2826–2830.
- Goss, K.-U., Eisenreich, S.J., 1996. Adsorption of VOCs from the Gas Phase to different minerals and a mineral mixture. *Environmental Science and Technology* 20, 2135–2142.
- Hoff, J.T., Wania, F., Mackay, D., Gillham, R., 1995. Sorption of non-polar organic vapors by ice and snow. *Environmental Science and Technology* 29, 1982–1989.
- Hudson, P.K., Zondlo, M.A., Tolbert, M., 2002. The interaction of methanol, acetone, and acetaldehyde with ice and nitric acid-doped ice: implications for cirrus clouds. *Journal of Physical Chemistry A* 106, 2882–2888.
- Iijima, K., Kobiyama, M., Hanaoka, Y., Kawamura, M., Toda, H., 1999. Adsorbability of contaminants from air by snow cooling systems. Paper for the Eighth Indoor Air99 Conference in Edinburgh, Scotland.
- Karl, T., Crutzen, P.J., Mandl, M., Staudinger, M., Guenther, A., Jordan, A., Fall, R., Lindlinger, W., 2001. Variability lifetime relationship of VOCs observed at the Sonnblick Observatory 1999-estimation of HO densities. *Atmospheric Environment* 35, 5287–5300.
- Keyser, L.F., Leu, M.T., 1993. Surface areas and porosities of ices used to simulate stratospheric clouds. *Journal of Colloid Interface Science* 155, 137–145.
- Kroes, G.J., Clary, D.C., 1992. Adsorption of HCl on ice under stratospheric conditions—a computational study. *Geophysical Research Letters* 19, 1355–1358.
- Lee, S.H., Leard, D.C., Zhang, R.Y., Molina, L.T., Molina, M.J., 1999. The HCl+ClONO₂ reaction rate on various water ice surfaces. *Chemical Physics Letters* 315, 7–11.
- Lei, D.Y., Wania, F., 2004. Is rain or snow a more efficient scavenger of organic chemicals? *Atmospheric Environment* 38, 3557–3571.
- Li, Y., Campana, M., Reimann, S., Schaub, D., Stemmler, K., Staehlin, J., Peter, T., 2005. Hydrocarbon concentrations at

- the alpine mountain site Jungfrauoch and Arosa. Atmospheric Environment 39, 1113–1127.
- Ligocki, M.P., Leuenberger, C., Pankow, J.F., 1985. Trace organic compounds in rain-II. Gas scavenging of neutral organic compounds. Atmospheric Environment 19, 1609–1617.
- Mitra, S.K., Bart, S., Pruppacher, H.R., 1990. A laboratory study on the scavenging of SO₂ by snow crystals. Atmospheric Environment 9, 2307–2312.
- Nguyen, T.H., Goss, K.-U., Ball, W.P., 2005. Polyparameter linear free energy relationships for estimating the equilibrium partition of organic compounds between water and the natural organic matter in soils and sediments. Environmental Science and Technology Critical Review 39 (4), 913–924.
- Orem, M.W., Adamson, A.W., 1969. Physical adsorption of vapor on ice. II. N-alkanes. Journal of Colloid Interface Science 31, 278–286.
- Pankow, J.F., 1987. Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. Atmospheric Environment 21, 2275–2283.
- Pennell, K.D., Rhue, R.D., Rao, P.S.C., Johnston, C.T., 1992. Vapor phase sorption of *p*-xylene and water on soils and clay minerals. Environmental Science and Technology 26, 756–763.
- Peter, Th., Crutzen, P.J., Müller, R., Deshler, T., 1994. The lifetime of leewave-induced ice particles in the Arctic stratosphere. II. Stabilization due to NAT-coating. Geophysical Research Letters 21, 1331–1334.
- Picaud, S., Hoang, P.N.M., 2000. Adsorption of acetone molecules on proton ordered ice. A molecular dynamics study. Journal of Chemical Physics 112, 9898–9908.
- Prévot, A.S.H., Dommen, J., Bäumle, M., 2000. Influence of road traffic on volatile organic compound concentrations in and above a deep Alpine valley. Atmospheric Environment 34, 4719–4726.
- Roth, C.M., Goss, K.-U., Schwarzenbach, R., 2004. Sorption of diverse organic vapors to snow. Environmental Science and Technology 38, 4079–4084.
- Schaff, J.E., Roberts, J.T., 1998. The adsorption of acetone on thin films of amorphous and crystalline ice. Langmuir 14, 1478–1486.
- Scott, B.C., 1981. Modelling wet deposition. In: Eisenreich, S.J. (Ed.), Atmospheric Pollutants in Natural Waters. Ann Arbor Science, Ann Arbor, MI, pp. 3–21.
- Slemr, F., Giehl, H., Habram, M., Slemr, J., Schlager, H., Schulte, P., Haschberger, P., Lindermeir, E., Doppelheuer, A., Plohr, M., 2001. In-flight measurement of aircraft CO and nonmethane hydrocarbon emission indices. Journal of Geophysical Research 106 (D7), 7485–7494.
- Sokolov, O., Abbatt, J.P.D., 2002. Adsorption to ice of *n*-alcohols (ethanol to 1-hexanol), acetic acid and hexanal. Journal of Chemical Physics 106, 775–782.
- Thibert, E., Dominé, F.J., 1998. Thermodynamics and kinetics of the solid solution of HNO₃ in ice. Journal of Physical Chemistry B 102, 4432–4439.
- Winkler, K., Holmes, N.S., Crowley, J.N., 2002. Interaction of methanol, acetone and formaldehyde with ice surfaces between 198 and 223 K. Physical Chemistry Chemical Physics 4, 5270–5275.
- Zondlo, M.A., Barone, S.B., Tolbert, M.A., 1996. Uptake of HNO₃ on ice under upper tropospheric conditions. Geophysical Research Letters 24 (11), 1391–1394.