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Wind tunnel experiments on the retention of trace gases during riming: nitric acid, hydrochloric acid, and hydrogen peroxide

N. von Blohn[1], K. Diehl[1], S. K. Mitra[1], and S. Borrmann[1,2]

[1]Institute of Atmospheric Physics, Johannes Gutenberg University, Mainz, Germany
[2]Max Planck Institute of Chemistry, Mainz, Germany

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Correspondence to: N. von Blohn (vonblohn@uni-mainz.de)

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Abstract

Laboratory experiments were carried out in a vertical wind tunnel to study the retention of different atmospheric trace gases during riming. In the experiments, the rimed ice particles floated in a laminar air stream carrying a cloud of supercooled droplets with radii between 10 and 20 µm. Ice particles, dendritic ice crystals, and snow flakes with diameters between 6 mm and 1.5 cm were allowed to rime at temperatures between −5 and −12 °C where riming mainly proceeds in the atmosphere and with cloud liquid water contents between 1 and 1.5 g m^{-3} which are values typically found in atmospheric mixed phase clouds. Three trace species were investigated, nitric and hydrochloric acid, and hydrogen peroxide. They were present in the supercooled liquid droplets in concentrations from 1 to 120 ppmv, i.e. similar to the ones measured in cloud drops. The chemical analyses of the rimed ice particles allow to determine the trace species concentration in the ice phase. Together with the known liquid phase concentration the retention coefficients were calculated in terms of the amount of the species which remained in the ice phase after freezing. It was found that the highly soluble trace gases nitric and hydrochloric acid were retained nearly completely (98.6 ± 8 % and 99.7 ± 9 %, respectively) while for hydrogen peroxide a retention coefficient of 64.3 ± 11 % was determined. No influence of the riming temperature on the retention was found which can be explained by the fact that in the observed range of temperature and liquid water content riming proceeded in the dry growth regime.

1 Introduction

Precipitation in tropospheric mixed phase clouds where ice particles and supercooled liquid drops are simultaneously present is mostly initiated via the ice phase. Processes leading to the growth of ice particles to precipitation sizes are the diffusion of water vapor (Bergeron Findeisen process) and riming, i.e. the deposition of liquid droplets on ice particles such as frozen drops and ice crystals (Pruppacher and Klett, 1997).

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An important aspect of the riming process lies in the field of cloud chemistry: the retention of water-soluble trace gases during riming represents a way of scavenging via the ice phase. Only a fraction of the trace species is transferred from the impinging liquid droplets into the ice, the rest being released back into the gas phase. Thus, the retention of trace gases is affecting their partitioning between the phases, scavenging and life time, and their pathway in the atmosphere (e.g., Salzmann et al., 2007). In field measurements, higher amounts of trace species were found in rimed snow samples as in unrimed samples which confirm the importance of riming for precipitation chemistry in mixed phase clouds (e.g., Borys et al., 1988; Collett et al., 1991; Harimaya and Nakai, 1999). Laboratory studies support this conclusion because trace gases like SO_2, HNO_3, HCl, and NH_3 are taken up by ice crystals in significantly lower amounts than by water drops (e.g., Mitra et al., 1990; Diehl et al., 1995, 1998; Hoog et al., 2007). Thus, riming might be the major process to incorporate these trace gases into the ice phase.

The retention coefficients are affected by the characteristics of the trace gases (Stuart and Jacobson, 2003). Highly soluble gases such as HNO_3 and HCl are almost completely dissociated in water so that afterwards ions are hardly able to leave again from the liquid phase. This should lead to a high retention of these gases. In comparison, gases such as NH_3 or SO_2 are not that highly dissociated in water, while H_2O_2, for instance, is almost not dissociated but only dissolved in water. For these trace gases one would expect lower retention during riming. All the mentioned species were investigated earlier in several laboratory studies; however, these were leading to controversial results. Iribarne et al. (1983) measured a retention of 25 % for SO_2 while Lamb and Blumenstein (1987) found 1 to 12 % only. Later Iribarne et al. (1990) determined an even higher retention for SO_2 of 60 %. For H_2O_2, Iribarne and Physnov (1990) determined 100 % retention but Snider et al. (1992) measured 25 % only and Snider and Huang (1998) even 5 %. The uncertainties of measurements indicated by the authors were below 10 % (absolute values). Thus, these strongly deviating values were probably caused by differences in experimental conditions which were in some cases quite

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far from those occurring in the real atmosphere. Some of these studies were performed in a cloud chamber with impaction cylinders or rotating rods as riming objects; in others flat collecting surfaces were used. In some cases the rime surface was ventilated, in others not.

Thus, the goal of the present investigations was to study the riming process under simulated realistic atmospheric conditions: ice crystals and particles have been freely or at least captively floated in the Mainz vertical wind tunnel at their terminal velocities ensuring that the ventilation coefficient during the experiments has the correct magnitude. From these experiments and the subsequent chemical analyses of the melt water more precise retention coefficients with less uncertainty were expected. The measurements were performed in the wind tunnel with ice particles and snow flakes which grew by collecting supercooled droplets flowing by. The supercooled droplets with radii between 10 and 20 µm contained dissolved trace species. In the present study, nitric acid, hydrochloric acid, and hydrogen peroxide were used. The highly soluble gases nitric acid and hydrochloric acid were investigated at first where retention coefficients near 100 % were expected. This way earlier results could be confirmed for validation of the adopted experimental methods and for detailed error analysis. Afterwards, hydrogen peroxide was investigated for which earlier investigations gave widely differing retention coefficients. In a forthcoming study, the trace gases sulfur dioxide and ammonia will be considered.

2 Experimental methods

2.1 Vertical wind tunnel

The experiments were performed in the Mainz vertical wind tunnel which allows free levitation of hydrometeors (droplets, ice particles, ice crystals, snow flakes, hailstones) from micrometer to centimeter sizes at their respective terminal velocities in a vertical air stream. Single events can be observed under controlled temperatures between

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30 °C and −30 °C, dew points from −40 °C to saturation (ambient temperature) and wind speeds from 10 cm s^{-1} up to 40 m s^{-1}. For its entire range of air speeds the tunnel shows a turbulence level of less than 0.5 % (Vohl, 1989). More details of the wind tunnel design and construction can be found in Pruppacher (1988) and in the review articles of Szakáll et al. (2010) and Diehl et al. (2011).

The present experiments were carried out in a way similar to those carried out recently where the collection kernels of ice particles and riming droplets have been investigated (von Blohn et al., 2009). During the experiments presented here single ice particles or crystals, or snow flakes grew by collision within a cloud of supercooled droplets which was produced upstream of the observation section by an array of sprayers. The sprayers were installed on the walls of the mixing chamber of the wind tunnel to prevent freezing of the sprayer nozzles. Thus, the temperature of the droplets was above 0 °C when they entered the wind tunnel; however, by the time they reached the experimental section (after 2 to 3 s) their temperature was in equilibrium with the air temperature of the wind tunnel. The size spectrum of the cloud of liquid droplets was determined inside the experimental section with a Classical Scattering Aerosol Spectrometer Probe (CSASP, Particle Measuring Systems) and shows droplet radii between 4 and 22 µm with a median volume radius of approximately 15 µm (for more details see von Blohn et al., 2009). The conditions during the experiments were similar to those typical for riming in atmospheric mixed-phase clouds, i.e. temperatures from −5 to −12 °C and liquid water contents lying between 1 and 1.5 g m^{-3} (Pruppacher und Klett, 1997). It was shown that in these observed ranges of temperature and liquid water content the growth of the ice particles proceeds in the dry growth regime (von Blohn et al., 2009). That means despite the increase of the surface temperature of the rimed ice particles by the release of latent heat the surface temperature stays definitely below 0 °C. Therefore, liquid drops colliding with the ice particle freeze immediately after contact.

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2.2 Liquid phase concentrations

During the experiments described here, the liquid droplets contained defined concentrations of the trace gas to be studied (HNO_3, HCl, or H_2O_2). Non-volatile salts were added to the solution as tracers (Na_2SO_4, KH_2PO_4, or KNO_3). These tracers remained entirely within the droplets during freezing so that the amount of liquid water deposited on the ice particles could be determined afterwards, using the method of Iribarne and Physnov (1990). In that way errors caused by evaporation of the droplets could be compensated (details in next section). Table 1 shows the concentrations of gases and tracers in the droplet solutions during our experiments. As far as possible, the content of the trace gases in the liquid phase was chosen similarly to concentrations found in atmospheric cloud droplets. Field measurements of HNO_3 (measured as NO_3^- in cloud water) range from 0.5 to 100 ppmv with average values between 12 and 19 ppmv; cloud water concentrations of HCl (measured as Cl^-) are between 0.1 and 110 ppmv with mean values of 6 to 40 ppmv (e.g., Römer et al., 1985; Warneck, 2000; Pruppacher and Klett, 1997; Neal et al., 2007). Thus, for nitric and hydrochloric acid, the experimental liquid phase concentrations of 12 and 120 ppmv, and 17, 50, and 90 ppmv, respectively (see Table 1), were at the order of the average and maximum concentrations measured in cloud water. Regarding H_2O_2, cloud water concentrations are much lower with average values around 0.1 ppmv and maximum 0.5 ppmv (e.g., Sauer et al., 1996; Valverde-Canossa et al., 2005). In this case, the liquid phase concentrations used in the experiments, i.e. 1 and 10 ppmv (see Table 1) were up to one order of magnitude higher because lower liquid phase concentrations produced too low concentrations in rime ice leading to large uncertainties during analysis.

2.3 Experimental description

Performing the experiments with completely freely floating small ice particles as described in von Blohn et al. (2009) did not lead to good statistics for accurate results. The time periods to freely suspend frozen drops were too short to accumulate sufficient

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material that allows an acceptable level of accuracy in the analyses so that one would need to collect many ice particles into one sample. However, preliminary tests with HNO_3 and HCl indicated that this caused unavoidable large uncertainties in the measurements. Therefore, the experiments were performed mostly with captively or quasi-floating ice particles and crystals.

In a *first set*, experiments with all three trace species (HNO_3, HCl, or H_2O_2) were carried out with captively floating ice particles of about 8 mm in diameter which were tethered using a very thin nylon fiber. Thus, they were freely movable in the air stream while supported at their free fall velocities so that heat transfer between ice particle and environment could take place in a way similar to that occurring in the real atmosphere. Along the nylon fiber negligible heat conduction occurs so that the temperature of the ice particle was not affected by the connecting fiber. The ice particles were prepared inside the walk-in cold chamber of the Mainz wind tunnel laboratory in small moulds in a way that deionised and distilled water froze around the nylon fiber. Afterwards, in each case the ice particle was transferred to the wind tunnel inside an isolated box which was mounted at a connection port on the wind tunnel wall. From there it could be moved towards the centre of the tunnel while hanging from a thin rod. The ice particles were weighted before and after riming to determine the initial ice mass and the collected rimed mass to calculate the dilution of the collected sample. The captively floating ice particle was continuously exposed to a supercooled droplet cloud of the investigated solution and was allowed to rime for 15 to 20 min. Subsequently, the rimed graupel was taken out of the wind tunnel section and put into a small sample container. After melting it was ready to be analyzed. Simultaneously, a Teflon rod was rimed in the experimental section to get a pure rime ice sample without an ice core. From this reference sample the evaporation of the riming droplets on their way from the sprayers to the experimental section was determined via the tracer concentration.

In a *second set* of experiments, dendritic ice crystals were used. They were produced from deionised water in a deposition growth chamber installed inside the walk-in cold chamber (see, e.g., Diehl et al., 1998; Hoog et al., 2007). In case of the H_2O_2

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experiments, composites of ice crystals were assembled to yield large snow flakes of about 1 to 1.5 cm diameter. Each snow flake was transported to the wind tunnel lying on a coarse meshed net of extremely fine nylon fibers inside an isolated box. This box was mounted at the wind tunnel connection port, the net was moved into the centre of the tunnel, and the air speed in the tunnel was set in such a way that the snow flake was quasi-floating on the net. Thus, the wind speed was equal to the terminal velocity of the snow flake. When exposed to the riming droplets the snow flakes sampled a large number of supercooled droplets because of their large surface area which reduced measurement uncertainties during analysis. After a riming time of 15 to 20 min the net with the rimed snow flake was moved back into the insulation box and re-transferred to the walk-in could chamber avoiding contact with tunnel walls to minimize contamination. There it was put into a sample container where the rimed snow flake melted.

In case of HNO_3 and HCl the *second set* of experiments was performed with freely floating dendritic ice crystals of approximately 6 mm length. Each of them was transported to the wind tunnel lying on a fine net inside the insulation box. After the box was mounted at the tunnel, the net was moved into the centre of the wind tunnel and turned upside down so that the ice crystal fell off ending up freely floating in the air stream. After a riming time between one and two minutes, the ice crystal was extracted from the wind tunnel section with a cuvette that was brought into the experimental section through an air lock. To get enough material for a reasonable chemical analysis 3 to 5 rimed ice crystals had to be put together in one sample box. As a minimum amount of liquid is required for the analysis 500 µl pure distilled water was added to the samples. Because of this dilution these experiments could be performed only with the maximum concentrations of HNO_3 or HCl in the solution droplets (50 and 120 ppmv). In case of H_2O_2, even with higher concentrations in the liquid phase, the amount of retained material in the ice phase was below the detection limit.

As in the first set of experiments, pure rime ice samples were taken in the experimental section on a Teflon rod. From these reference samples both the dilution of the

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collected rimed snow flakes and the evaporation of the riming droplets were determined via the tracer concentration.

Summarizing, the riming experiments with HNO_3 and HCl were performed using captively floating ice particles and freely floating ice crystals. Experiments with H_2O_2 were performed with captively floating ice particles and quasi-floating snow flakes.

2.4 Chemical analyses and evaluation

The retention coefficients of HNO_3, HCl, and H_2O_2 were determined from the amount of the species in the melt water of the grown ice particles, crystals, or snow flakes, and the amount of the species in the supercooled liquid droplets. The amounts of the tracer materials (Na_2SO_4, KH_2PO_4, or KNO_3) in ice were used to correct errors caused by evaporation of droplets on their way from the sprayers to the experimental section. Nitrate, chloride, sulfate, and phosphate were determined by ion chromatography (DIONEX 2000i and DIONEX ICS-1000) using appropriate separation columns, suppressors, and eluents. Hydrogen peroxide was analyzed by high performance liquid chromatography (HPLC) equipped with a spectrofluorometric detector.

Regarding the liquid phase concentrations in the supercooled droplets, these were stable during the experiments in case of HNO_3 and HCl because they are completely dissolved and dissociated in the liquid and, therefore, do not easily desorb (Pruppacher and Klett, 1996). However, the situation was different with H_2O_2 dissolved in the supercooled droplets as it is not stable in the liquid phase but tends to desorb and degenerate due to break down in water and oxygen. Therefore, the liquid phase concentration had to be corrected. The maximal degeneration was to be expected just after the solution was sprayed out from the bottle container. The amount of reduction was determined from a detailed sprayer statistics before starting the riming experiments. The solution concentrations before entering the sprayers and directly after leaving the sprayers were compared so that the actual liquid phase concentration present during riming could be determined.

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In cases of HNO_3 and HCl, the retention coefficient was calculated from the concentration of the collected sample after riming C_{sample}, the liquid phase concentration C_{liq}, the collected mass of the rimed sample m_{sample}, the rime mass m_{rime}, the liquid phase concentration of the tracer $C_{trac,liq}$, and the concentration of the tracer in the reference sample $C_{trac,ref}$ according to the following equation

$$R = \frac{C_{sample}}{C_{liq}} \frac{m_{sample}}{m_{rime}} \frac{C_{trac,liq}}{C_{trac,ref}} \tag{1}$$

The second term on the right-hand side of Eq. (1) represents the dilution factor accounting for the dilution of the sample by the pure ice core, and the third term represents the evaporation factor due to changes of the liquid phase concentration by evaporation of the supercooled droplets.

In case of H_2O_2, the retention coefficient was calculated from the concentration of the collected sample after riming C_{sample}, the liquid phase concentration $C_{liq,spray}$, the concentration of the tracer in the reference sample $C_{trac,ref}$, the concentration of the tracer in the collected sample $C_{trac,sample}$, the liquid phase concentration of the tracer $C_{trac,liq}$, and the concentration of the tracer in the reference sample $C_{trac,ref}$ according to

$$R = \frac{C_{sample}}{C_{liq,spray}} \frac{C_{trac,ref}}{C_{trac,sample}} \frac{C_{trac,liq}}{C_{trac,ref}} \tag{2}$$

In the first term on the right-hand side of Eq. (2), C_{liq} was replaced with $C_{liq,spray}$ which means the liquid phase concentration measured directly after the sprayers. This way the liquid phase concentration was corrected because inside the sprayer nozzle the H_2O_2 concentration was reduced by degeneration. The second term on the right-hand side of Eq. (2) represents the dilution factor accounting for the dilution of the sample by the pure ice core, and the third term represents the evaporation factor due to changes of the liquid phase concentration by evaporation of the supercooled droplets.

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3 Experimental results

3.1 Nitric and hydrochloric acid

The retention coefficients of the HNO_3 experiments for captively floating ice particles are shown in Fig. 1 as a function of the ambient air temperature for two concentrations of HNO_3 in the riming droplets of 12 ppmv (black circles) and 120 ppmv (open circles). All values are around a retention coefficient of 1 within their errors and do not show any temperature dependence. In Fig. 2 the retention coefficients measured with freely floated ice crystals and a liquid phase concentration of 120 ppmv are given for an average temperature of $-10 \pm 2\,^{\circ}C$. All data are again spread around a retention coefficient of 1. In case of the HCl experiments, the results for the captively floated ice particles are plotted against the air temperature in Fig. 3. Two concentrations of the liquid phase concentration are explored, namely 17 ppmv (black circles) and 90 ppmv (open circles). Similar to the case of HNO_3 (see Fig. 1), all values are around the retention coefficient of 1 and no temperature dependence has been observed. Figure 4 shows the retention coefficients of freely floated rimed ice crystals and a liquid phase concentration of 90 ppmv for an average temperature of $-10 \pm 2\,^{\circ}C$ which were spread around 1, as it has been observed for HNO_3 (see Fig. 2).

The data points in Figs. 1 to 4 and all following figures represent one measurement each. The errors of the temperature measurements where $\pm 1.5\,^{\circ}C$; this value represents the standard deviation of the temperature during the riming time while the device error of the used temperature sensors was $0.25\,^{\circ}C$ only. In Table 2 the mean values of the retention coefficients determined by different techniques and with various liquid phase concentrations are listed with errors which were calculated using the Gaussian error computation. The following factors are taken into account for these calculations: device errors of the balances and the ion chromatographs, and calibration errors. The column on the right hand side gives the standard deviations of all sampled data from the mean values. For nitrate and hydrochloride acid, it can be seen from Table 2 that the estimated errors caused by the measurement techniques are higher than the

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standard deviations from the scatter of the data. In case of HNO_3 a retention coefficient of 0.95 ± 0.07 was determined for the captively floated ice particles with 12 ppmv liquid phase concentration and a value of 1.02 ± 0.08 with 120 ppmv liquid phase concentration. For the freely floated ice crystals with a HNO_3 liquid phase concentration of 120 ppmv a retention coefficient of 0.99 ± 0.08 was determined. Obviously there is no difference between the results using ice particles or ice crystals. The results obtained with higher liquid phase concentrations are slightly higher as the ones with lower liquid phase concentrations; however, the deviation lies within the measurement error. Thus, in spite of the differences in liquid phase concentrations or experimental methods, one average value has been derived from all data.

In the experiments of HCl with captively floated ice particles a retention coefficient of 1.01 ± 0.09 was measured with a liquid phase concentration of 17 ppmv and 0.97 ± 0.08 with a liquid phase concentration of 90 ppmv. For freely levitated ice crystals with an HCl liquid phase concentration of 90 ppmv a retention coefficient of 0.99 ± 0.08 was found. No significant differences between liquid phase concentrations or experimental methods were observed so that here, too, all data have been taken into account to yield an average value.

Finally, average values from all experimental techniques and liquid phase concentrations are 99 ± 8 % retention for HNO_3 and 100 ± 9 % for HCl. These numbers are in good agreement with the results of Iribarne and Physnov (1990) who found a retention coefficient of 95 % for HNO_3 and 100 % for HCl. These two trace gases are highly soluble in water and afterwards, strongly dissociated so that their release during freezing is hardly possible. Thus, retentions near 1 are to be expected which was also shown in the theoretical investigations of Stuart and Jacobson (2003, 2004). They concluded that chemicals with very high effective Henry's Law constants (such as nitrite and hydrochloric acid) are likely to be fully retained during riming under all freezing conditions. Thus, independent of the experimental techniques adopted in earlier investigations and those employed in the present studies, the results are very similar. The fact that the retention determined for HCl is always slightly higher than the one measured for HNO_3

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can possibly explained by the value of the effective Henry's Law constant. Stuart and Jacobson (2003) calculated these for dry growth riming (which has been observed in the present experiments, see von Blohn et al., 2009) and found an effective Henry's Law constant of 4.4×10^{15} for HCl and a somewhat lower value of 1×10^{13} for HNO_3.

3.2 Hydrogen peroxide

Experiments with H_2O_2 were performed with captively floating ice particles and with quasi-floating snow flakes. Figure 5 shows the retention coefficients determined with captively floated ice particles rimed with H_2O_2 solution droplets of two different concentrations (1 ppmv given as black circles, and 10 ppmv given as open circles) plotted against the ambient air temperature. The retention coefficients measured with quasi-floating snow flakes rimed with solution droplets containing 1 ppmv H_2O_2 as a function of temperature are shown in Fig. 6. For both cases, there is no noticeable temperature dependence. It can easily be seen from Figs. 5 and 6 that the scatter of the data is much higher than for the other two investigated trace gases. In Table 2 it is evident that the standard deviations affected by the scatter of the data are in the range of the errors caused by the measurement techniques and calculated using the Gaussian error computation.

The mean values of the retention coefficients for H_2O_2 are given in Table 2 as 0.74 ± 0.11 for 1 ppmv liquid phase concentration and 0.60 ± 0.10 for 10 ppmv liquid phase concentration. For the quasi-floated snow flakes rimed with 1 ppmv solution droplets a retention coefficient of 0.59 ± 0.10 was determined. It seems that the retention coefficients for lower concentrations are slightly above the values for higher concentrations but only in the case of captively floating ice particles. The retention of quasi-floating snow flakes measured with the lower liquid phase concentration does not confirm this observation. However, the deviations are still lying within the measurement error. Thus, independently of the experimental methods and liquid phase concentrations, an average value of the retention coefficients was determined to be 64 ± 11 % for H_2O_2.

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This value of H_2O_2 retention does not agree with any of the previous ones. We think the 100 % retention of Iribarne and Physnov (1990) is an overestimation. According to Stuart and Jacobson (2003, 2004) this could be expected for highly soluble and dissociative trace gases but the effective Henry's Law constant of H_2O_2 they determined was 1.5×10^7 and, thus, orders of magnitudes lower than the ones of HNO_3 and HCl. The 5 % retention determined by Snider and Huang (1998) was determined from the concentrations of H_2O_2 in field ice samples and the equilibrium concentration predicted by Henry's Law. However, it seems that this method underestimates the retention during the riming process. Finally, it appears that the 25 % retention of Snider et al. (1992) might be influenced by the specific conditions during their field measurements in stratiform orographic clouds. In comparison to earlier studies the new data were obtained from a simulation of the riming process closer to conditions occurring in the atmosphere. Therefore, the new average value might represent the retention coefficient applicable to models to simulate the effects of the ice phase on H_2O_2 gas concentration in the troposphere (e.g., Salzmann et al., 2007).

For all trace gases, varying the temperature did not lead to very different retention coefficients. This can be explained by the fact that in the observed ranges of temperature and liquid water content riming proceeded in the dry growth regime. That means liquid drops colliding with the ice particle freeze immediately after contact. As long as this is the case the retention coefficients do not show significant variations for different temperatures. In some cases with captively floating of graupels a slight reduction of the H_2O_2 retention coefficient was observed at the higher end of the temperature range. The rimed ice also showed a smoother surface indicating an onset of semi-dry growth. Thus, for wet growth conditions lower retention coefficients are to be expected.

4 Conclusions

In the present studies, laboratory experiments were performed at the Mainz vertical wind tunnel to investigate riming of individual freely floating ice particles. As several

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previous investigations resulted in controversial values of the retention coefficient, the goal was to simulate the riming process as close as possible to the atmosphere. While the ice particles were freely or at least captively or quasi-floating at their terminal velocities in the vertical air stream of the tunnel, the ventilation and, thus, the heat transfer proceeded in a realistic manner.

For nitric and hydrochloric acid retention coefficients near 100 % were expected because of their high solubility and dissociation in water. The results obtained with the wind tunnel experiments verified earlier results and confirmed the experimental methods. No significant differences were found between the use of ice particles and dendritic ice crystals as rimed ice. Additionally, the liquid phase concentrations did not have significant effects on retention. Furthermore, the results did not show a temperature dependence which was explained by the fact that in the observed range of temperature and liquid water content riming proceeded in the dry growth regime. For wet growth conditions where freezing proceeds more slowly lower retention coefficients are to be expected.

Therefore, average values for all investigated conditions were determined: 99 ± 8 % retention for nitric acid, 100 ± 9 % for hydrochloric acid, and 64 ± 11 % for hydrogen peroxide. The lower retention of H_2O_2 is to be expected because the effective Henry's Law constant of H_2O_2 is orders of magnitudes lower than the ones of HNO_3 and HCl. The latter value inhibits a step forward as the results from previous experiments ranged from 5 to 100 %. The new average value might represent the retention coefficient applicable to theoretically simulate the effects of the ice phase on H_2O_2 gas concentration in the troposphere.

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Table 1. Composition of the riming droplets with solved gases and salt tracers (errors ±3 % maximum).

nitric acid	solution 1	solution 2	solution 3
HNO_3	120 ppmv	12 ppmv	120 ppmv
Na_2SO_4 (tracer)	70 ppmv	10 ppmv	–
H_2SO_4 (tracer)	–	–	10 ppmv
hydrochloric acid	**solution 1**	**solution 2**	**solution 3**
HCl	90 ppmv	50 ppmv	17 ppmv
Na_2SO_4 (tracer)	120 ppmv	70 ppmv	20 ppmv
hydrogen peroxide	**solution 1**	**solution 2**	
H_2O_2	10 ppmv	1 ppmv	
KH_2PO_4 (tracer)	40 ppmv	–	
KNO_3 (tracer)	–	0.4 ppmv	
Na_2SO_4 (tracer)	–	0.8 ppmv	

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Table 2. Retention coefficients of nitric and hydrochloric acid and hydrogen peroxide.

	retention coefficient (average value with measuring error)	standard deviation (of all data)
nitric acid (HNO_3)		
ice particles captively floated		
12 ppmv	0.95 ± 0.07	0.04
120 ppmv	1.02 ± 0.08	0.04
ice crystals freely floated		
120 ppmv	0.99 ± 0.08	0.03
hydrochloric acid (HCl)		
ice particles captively floated		
17 ppmv	1.01 ± 0.09	0.05
90 ppmv	0.97 ± 0.08	0.04
ice crystals freely floated		
90 ppmv	0.99 ± 0.08	0.04
hydrogen peroxide (H_2O_2)		
ice particles captively floated		
1 ppmv	0.74 ± 0.11	0.11
10 ppmv	0.60 ± 0.10	0.16
snow flakes quasi-floated		
1 ppmv	0.59 ± 0.10	0.15

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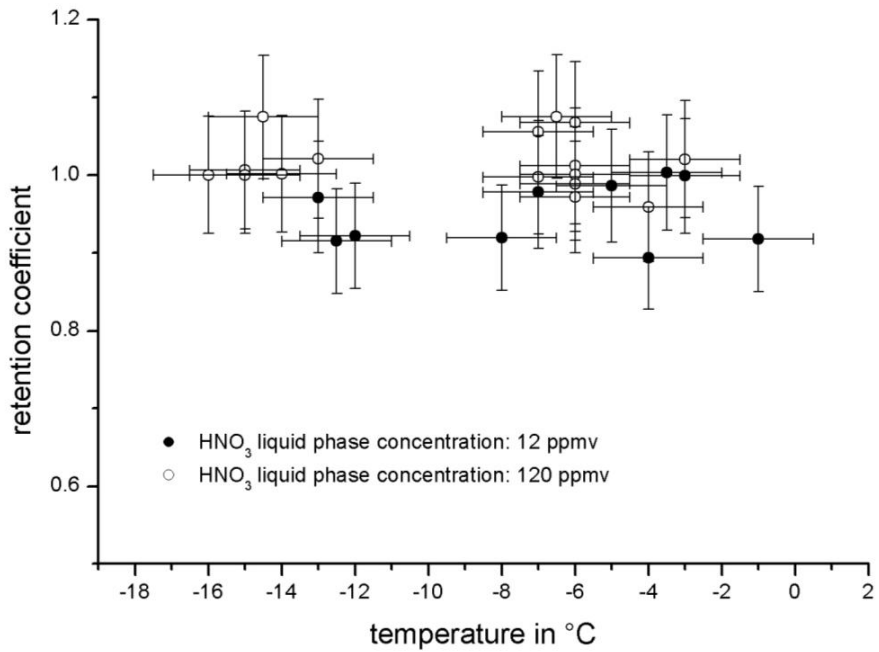

Fig. 1. Retention coefficient of HNO_3 as a function of ambient air temperature, determined with captively floating ice particles rimed with solution droplets of two concentrations (black circles: 12 ppmv, open circles: 120 ppmv).

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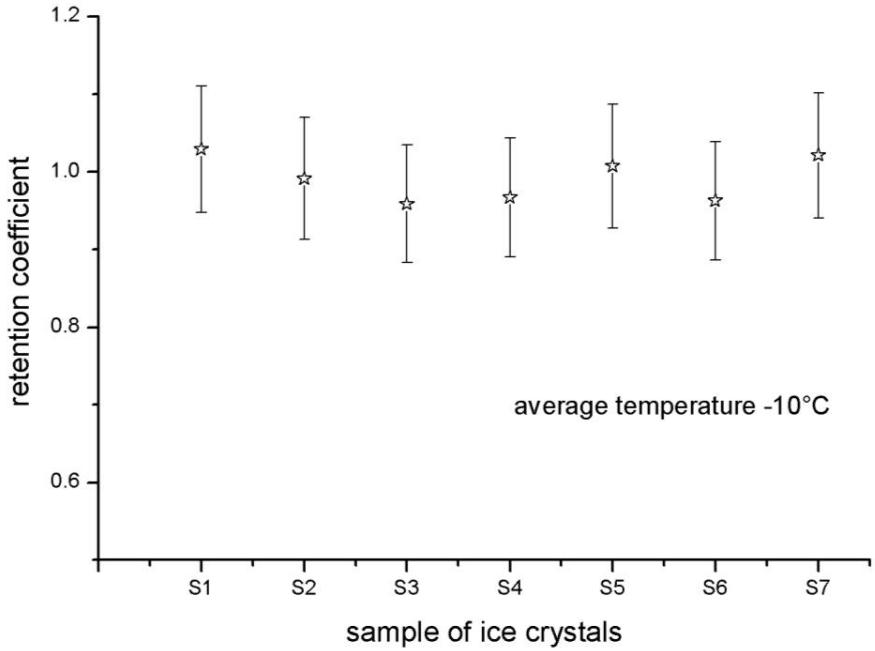

Fig. 2. Retention coefficient of HNO_3, determined with freely floated ice crystals rimed with solution droplets with a concentration of 120 ppmv. Several samples at an average air temperature of $-10 \pm 2\,^{\circ}C$.

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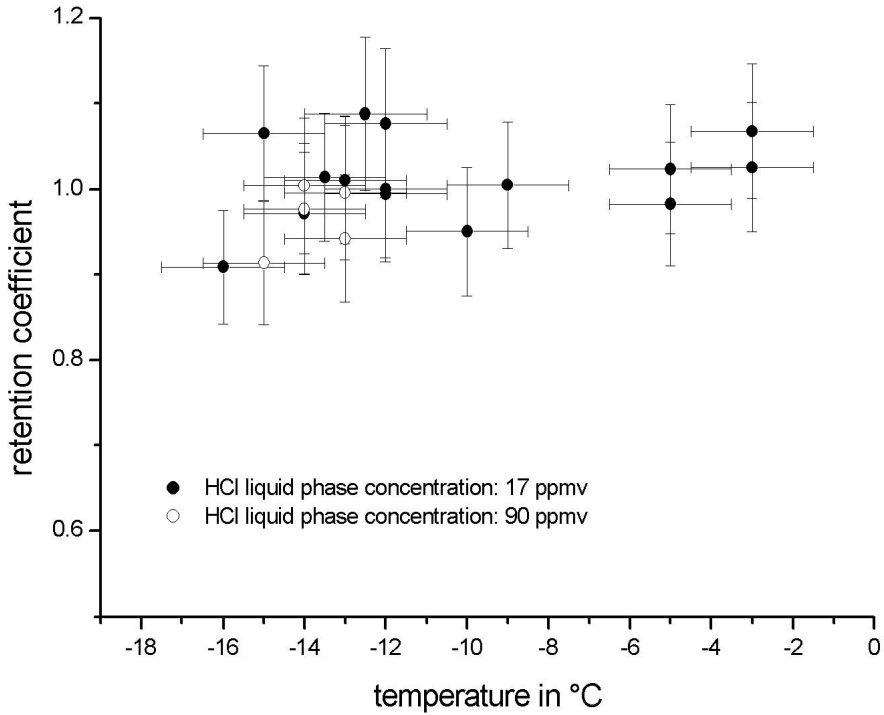

Fig. 3. Retention coefficient of HCl as a function of ambient air temperature, determined with captively floating ice particles rimed with solution droplets of two concentrations (black circles: 17 ppmv, open circles: 90 ppmv).

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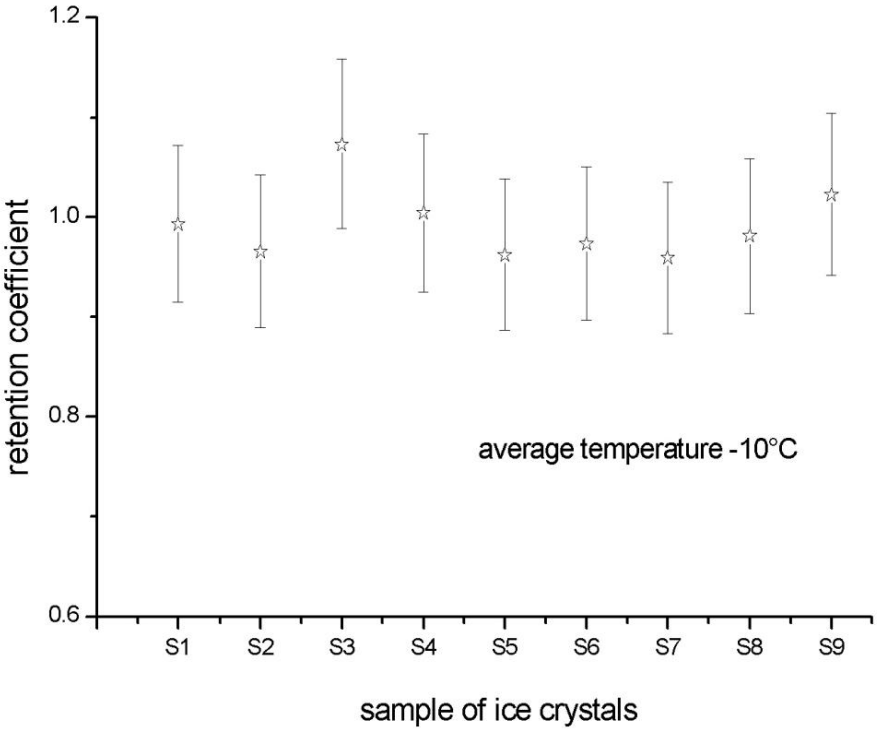

Fig. 4. Retention coefficient of HCl, determined with freely floated ice crystals rimed with solution droplets with a concentration of 90 ppmv. Several samples at an average air temperature of $-10 \pm 2\,^{\circ}C$.

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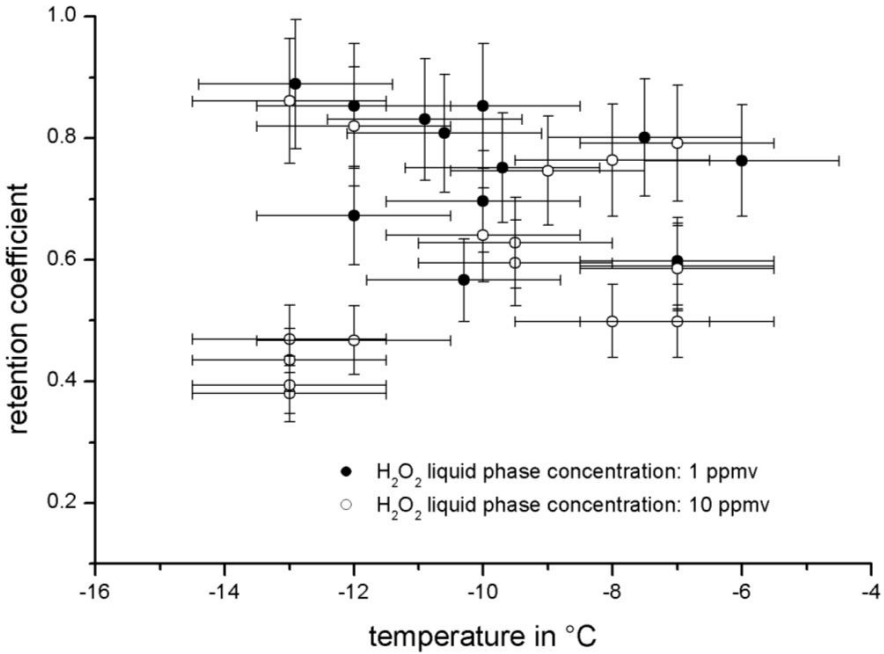

Fig. 5. Retention coefficient of H_2O_2 as a function of ambient air temperature, determined with captively floating ice particles rimed with solution droplets of two concentrations (black circles: 1 ppmv, open circles: 10 ppmv).

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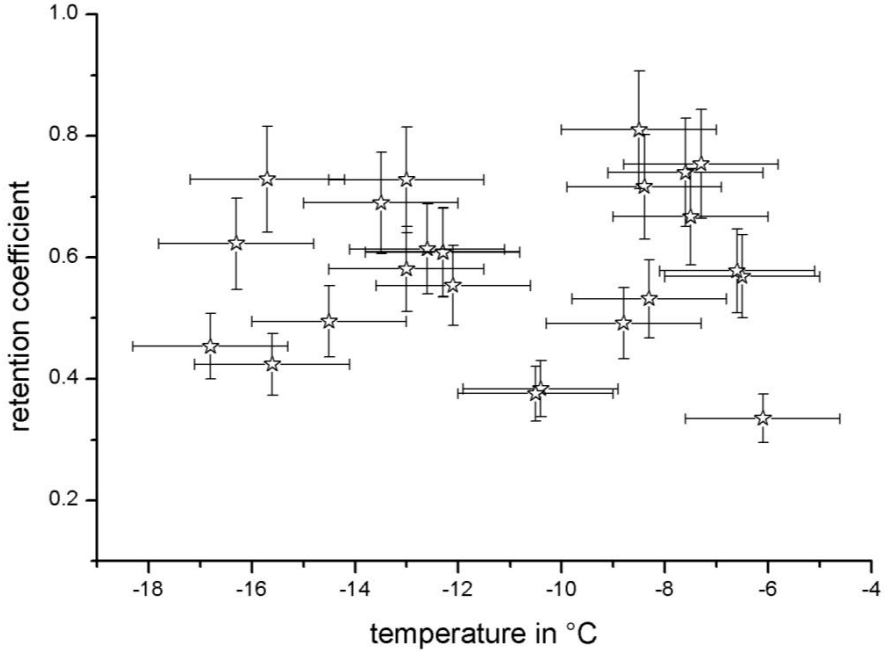

Fig. 6. Retention coefficient of H_2O_2 as a function of air temperature, determined with quasi-floating snow flakes rimed with solution droplets with a concentration of 1 ppmv.

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