

Correction to “Development of a Mechanism for Nitrate Photochemistry in Snow”

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We have discovered an error in the calculation of the volume fraction of the QLL. This error resulted from a misinterpretation of eq 1 from Cho et al.¹ used to calculate the fraction of the QLL $\phi_{\text{H}_2\text{O}}(T)$ compared to the bulk solid

$$\phi_{\text{H}_2\text{O}}(T) = \frac{m_{\text{H}_2\text{O}}RT_f}{1000 \cdot H_f^0} \frac{T}{T_f - T} C_T^0 \quad (1)$$

with $m_{\text{H}_2\text{O}}$ the molecular weight of water, R the gas constant, T_f the water freezing temperature in K, and H_f^0 the melting enthalpy of water. According to Cho et al.¹ the last term C_T^0 represents the total bulk solute concentration, and not the total solute concentration in the QLL as stated in the original paper. Therefore, instead of the derived eq 3 of the original paper, eq 1 must be applied to calculate the QLL fraction depending on solute concentration and temperature. This fraction is then used to transform bulk into QLL concentrations and vice versa. Table 1 shows a summary of the corrected QLL fractions calculated with eq 1 and derived NO_3^- and NO_2^- concentrations for all experiments.

However, it must be noted that the derived concentrations of NO_2^- in batches 1 and 2 and NO_3^- in batches 3 and 4 and in the natural snow are higher than their solubility in water. According to Seidell² mixtures of water and NaNO_3 and NaNO_2 , show concentrations of 6 and 5.3 M, respectively, at their eutectic points observed at temperatures of approximately -18 and -20 °C. We used the concentrations at the eutectic points to impose upper limits on the initial NO_3^- and NO_2^- concentrations in the liquid fraction. We further reduced the initial concentrations taking into account the presence of either NO_2^- or NO_3^- . On the basis of measured solubilities of NaNO_3 and NaNO_2 in ternary mixtures with water,² maximum solubilities were further reduced by $0.2[\text{NO}_3^-]$ in the case of NO_2^- for batches 1 and 2 and by $0.5[\text{NO}_2^-]$ in the case of NO_3^- for

batches 3 and 4 and the natural snow experiment. Table 1 shows the estimated initial NO_3^- and NO_2^- concentrations used for further calculations. It is assumed that the non-QLL fractions were precipitated in the form of either NaNO_3 or NaNO_2 and that they did not participate in the photochemical reactions.

The optimization procedure to obtain the best fit for the unknown reaction and transfer rate coefficients k_1 , k_2 , k_4 , k_{10} , and k_{13} as described in the original paper depends on the QLL concentrations. Therefore, the entire optimization procedure was repeated, delivering new numbers for the rate coefficients. The same procedure and restrictions were applied as described in the original paper. The newly derived coefficients are summarized in Table 2.

Figure 1 in the original paper is replaced by Figure 1 here, showing an updated comparison of observed and simulated NO_3^- and NO_2^- concentration in the QLL using the corrected liquid fractions and the newly optimized reaction rate coefficients summarized in Table 2. The figure shows that the proposed mechanism is still able to reproduce the overall behavior of NO_3^- and NO_2^- in the snow and the observed concentration–time profiles. The overall errors between observed and simulated concentrations correspond to 24% for nitrate and 92% for nitrite resulting in an average error of 58%.

Apparently, the new procedure splitting the NO_3^- and NO_2^- into a portion in the QLL taking part in the reactions and in a solid portion not participating in the reactions introduces additional uncertainty for the optimization procedure. This is expressed by the obtained rate coefficients, which are significantly different from the results in the original manuscript. To address this point, we performed further sensitivity tests to give more information on the reliability of the obtained rates. For example, we tested by how much the different rate constants can be varied to increase the overall error from 58 to 59%. Such a small change

Table 1. Summary of the Liquid Fraction $\phi_{\text{H}_2\text{O}}(T)$ Calculated According to Eq 1 and Derived NO_3^- and NO_2^- Concentrations in the QLL for the Experiments with Artificial and Natural Snow^a

	batch 1	batch 2	batch 3	batch 4	natural snow
$\phi_{\text{H}_2\text{O}}(T)$	1.32×10^{-6}	5.23×10^{-7}	1.17×10^{-6}	1.08×10^{-6}	2.41×10^{-6}
$[\text{NO}_3^-]_{\text{bulk}} 10^{-6} \text{ M}$	0.76	1.66	10.8	9.97	22.6
$[\text{NO}_3^-]_{\text{derived}} \text{ M}$	0.57	3.17	9.30	9.27	9.38
$[\text{NO}_3^-]_{\text{QLL}} \text{ M}$	0.57	3.17	5.9	5.9	6.0
$[\text{NO}_2^-]_{\text{bulk}} 10^{-6} \text{ M}$	11.8	3.28	0.16	0.18	0.14
$[\text{NO}_2^-]_{\text{derived}} \text{ M}$	8.87	6.27	0.14	0.17	0.057
$[\text{NO}_2^-]_{\text{QLL}} \text{ M}$	5.2	4.7	0.14	0.17	0.057

^a Concentrations in italic type were reduced according to concentrations at the eutectic points (see text).

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Table 2. Summary of the Calculated Rate Coefficients for the Reactions 1, 2, 4, 10, and 13 after Optimization with the Corrected QLL Concentrations

k_1	$1.3 \times 10^{-5} \text{ s}^{-1}$
k_2	$1.3 \times 10^{-4} \text{ s}^{-1}$
k_4	$1.5 \times 10^{-3} \text{ s}^{-1}$
k_{10}	41 s^{-1}
k_{13}	410 s^{-1}

of the overall error allows the variation of the rate constants k_2 , k_4 , k_{10} , and k_{13} by ± 30 – 40% . A similar increase in the average error is only reached if the rate constant k_1 is changed by a factor of 7. Therefore, the obtained rate constant for k_1 is much less reliable than the other rate constants. In contrast, the overall error increases quickly with a change in the size of the solidified fraction. A small increase of 2% of the size of the non-QLL reservoir augments the overall error to 59%, whereas a reduction in the solid fraction always reduces the overall error. Part of this behavior is due to the method of the error calculation, which corresponds to average relative error based on the observed values. For example, nitrite concentrations in batch 1 decrease to small values in the experiments. The introduced reservoir in batch 1 always leads to higher NO_2^- concentrations in the simulations at $t > 2$ h, which in turn correspond to very high relative errors. As a result, reducing the size of the reservoir always leads to a decrease in the calculated relative errors. We further addressed the question of the impact of the reservoir by performing additional optimizations under different conditions for the reservoir. This concerned optimizations either without or with larger fixed reservoirs and a further optimization with a flexible reservoir, where NO_3^- and NO_2^- can be transferred from the solid state back into the QLL according to the upper limit of the solubility. All optimizations including a reservoir resulted in rate constants within the range presented above, whereas the optimization without a reservoir yielded rate constants similar to

the original manuscript with the exception of the rate constant k_4 that increased significantly in this case. Nevertheless, in all cases the observed concentration–time profiles were reasonably well reproduced by the simulated results, indicating that the assumption of a chemical mechanism in the snow similar to the mechanism in the aqueous phase seems to be quite robust. In fact, further recent experimental studies concerning the photochemistry of 2-nitrobenzaldehyde,³ the reactive uptake of ozone and the formation of reactive bromine,⁴ and Norrish type I reactions of dibenzyl ketones⁵ support this general hypothesis. Furthermore, Thomas et al.⁶ presented recently a snow chemistry module coupled to a 1-D atmospheric chemistry model. For the chemical mechanism they used the full aqueous phase mechanism normally used for the description of chemical processes in the aqueous phase and in aerosols. They found good agreement between observations of NO_x and reactive bromine on top of the Greenland ice sheet and the results of their coupled model.⁶

The effect of simplifying the mechanism as proposed in the original paper was verified by deleting reactions 9, 11, and 12. The maximum difference for the simulated NO_3^- and NO_2^- concentrations between the full and the simplified mechanism always remains below 0.5% except for NO_2^- in batch 2, where the difference increased to 1.5%.

Because the liquid fraction and the new rate coefficients also influence the calculated initial H_2O_2 and HCHO concentrations for the natural snow experiment, the optimization procedure for this case was also repeated. The corrected QLL concentrations are $[\text{H}_2\text{O}_2]_{\text{QLL}} = 11.6 \text{ M}$ and $[\text{HCHO}]_{\text{QLL}} = 0.225 \text{ mM}$ corresponding to $28.3 \text{ } \mu\text{M}$ (963 ppbw) and $5.4 \times 10^{-10} \text{ M}$ (0.016 ppbw) in the bulk snow. Like discussed in the original manuscript, the simulations are much less sensitive to the HCHO than to the H_2O_2 concentrations. Figure 2 of the original manuscript is replaced by the new Figure 2, showing a comparison of the simulated NO_3^- and NO_2^- concentrations with and without H_2O_2 and HCHO with the above-mentioned initial concentrations. With these corrected values, discrepancies between measured and

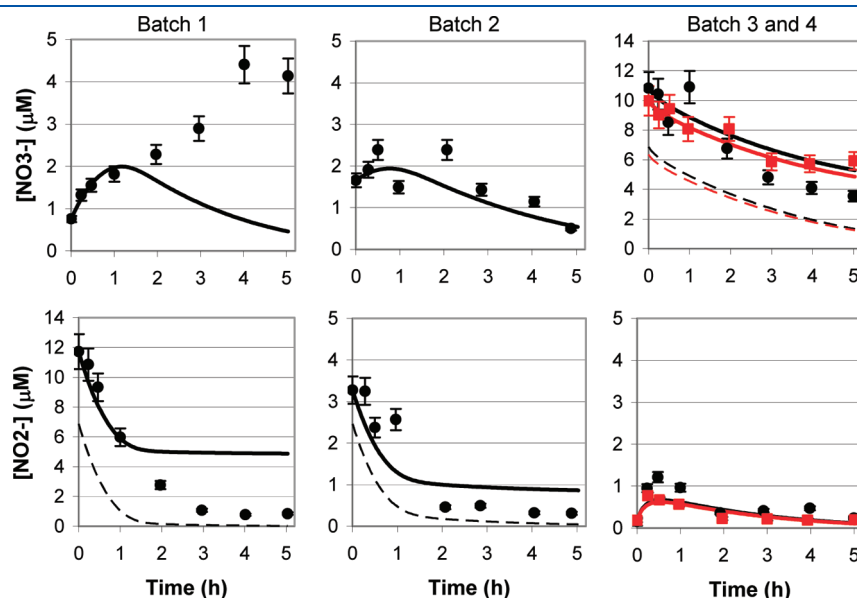


Figure 1. Comparisons of observed NO_3^- (top row) and NO_2^- (bottom row) concentrations in laboratory experiments performed with four batches of artificial snow (black dots for batch 1–3 and red squares for batch 4) with the simulations using the full chemical mechanism containing 16 reactions (solid lines in black for batches 1–3 and in red for batch 4). In the cases with fixed solid fractions of NO_2^- (batches 1 and 2) and NO_3^- (batches 3 and 4), the concentrations in the liquid fraction are shown by dashed lines. Concentrations are given for the bulk concentrations.

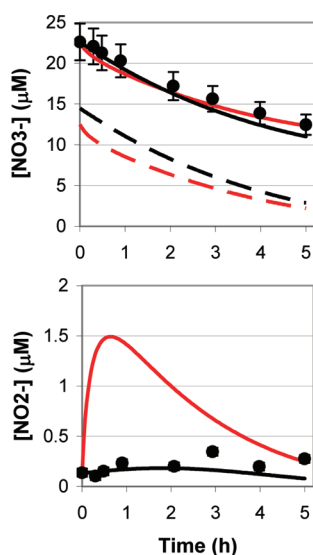


Figure 2. Comparisons of observed NO_3^- (left) and NO_2^- (right) concentrations in laboratory experiments performed with natural snow with simulated concentrations obtained with the simplified mechanism containing 13 reactions (red lines) and with the complete mechanism containing 18 reactions describing N-chemistry plus H_2O_2 and HCHO chemistry (black lines). The NO_3^- concentrations in the liquid fraction are shown by dashed lines. Concentrations are given for the bulk concentrations.

modeled nitrate and nitrite concentrations in the natural snow experiment amount to 9% and 39%, respectively. In the case of NO_2^- the error is higher than in the original paper. The calculated initial concentrations are still consistent with the usual range of concentrations measured in the snow as discussed in the original manuscript.

In summary, similar to conclusions in the original manuscript, the used hypotheses and assumptions to represent the reactive fraction in the snow remain very uncertain. Although this is a critical issue for a better understanding of chemical processes in the snow or ice at temperatures close to the melting point, available information on the size and the properties of the liquid fraction remains very limited and a question of debate (see, for example, refs 7 and 8 and references therein). Our results here demonstrate that under a wide variety of the properties (e.g., volume of the liquid fraction, fractionation between solid and liquid, transfer from the solid to the liquid fraction) the overall behavior of NO_3^- and NO_2^- can be captured using an aqueous phase mechanism. However, a precise determination of rate constants specific for conditions in snow and ice is not possible on the basis of the presented experiments. Therefore, further improved experiments under defined conditions (e.g., better constrained photolysis rates) would be highly desirable. Moreover, experiments using advanced techniques like cavity ring-down spectroscopy, chemiluminescence, and chemical ionization mass spectrometry to detect photochemical products in the gas phase as used by Abida et al.⁹ and Abida and Osthoff¹⁰ may help to refine chemical mechanisms in snow and ice.

Finally, Table 1 of the original paper contains three typing errors. Reaction 14 should read $\text{O}(^3\text{P})(+\text{O}_2) \rightarrow \text{O}_3$ with a rate constant of $1.2 \times 10^6 \text{ s}^{-1}$. Reaction 15 should read $\text{NO}_2^- + \text{O}(^3\text{P}) \rightarrow \text{NO}_3^-$.

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NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on November 3, 2011. Josué Bock, an author of the original paper, was erroneously included as an author of the Correction. The Correction is the work of Hans-Werner Jacobi only, and its scientific content has not been approved by Josué Bock. The revised version was published on December 5, 2011.