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Introduction and Motivation

Levoglucosan, is an important marker compound for biomass burning processes. It usually represents a large fraction of the water-soluble organic carbon in atmospheric particles influenced by combustion processes. But, how stable is this marker compound in the atmosphere? Two studies in 1988 and 2000 measured the stability of levoglucosan towards sunlight under ambient conditions and towards the acid-catalyzed hydrolysis (1,2). In both studies no degradation of levoglucosan was observed. These studies are cited until today as reference for the atmospheric stability of levoglucosan. However, particle phase or gas phase oxidation processes of levoglucosan with atmospheric radicals are not yet characterized. Due to the lack of kinetic data, detailed studies on the reactivity of levoglucosan with OH, NO₃, and SO₄⁻ radicals in aqueous solutions have been performed in this study (3). The experimental data were implemented into a parcel model describing the microphysics and the multiphase chemistry to investigate the degradation fluxes of levoglucosan in cloud droplets and in deliquescent particles. The model calculations show that levoglucosan can be oxidized readily by OH radicals and that these oxidation reactions are as fast as that of other alcohols in the tropospheric multiphase system. The conclusion of this study concerning the stability of levoglucosan in the troposphere was recently confirmed in a aerosol chamber study (4).

Table 1: Measured second order rate constants (k_{rad}) and activation parameter for the reaction of levoglucosan with OH, NO₃, and SO₄⁻ in aqueous solution.

Radical	$k_{\text{rad}, 298\text{K}}$ [M ⁻¹ s ⁻¹]	E_A [kJ/mol]	A [M ⁻¹ s ⁻¹]	ΔH^\ddagger [kJ/mol]	ΔG^\ddagger [kJ/mol]	ΔS^\ddagger [J/K mol]
OH	$(2.4 \pm 0.3) \cdot 10^9$	9.0 ± 2.9	$(8.7 \pm 0.4) \cdot 10^{10}$	6.5 ± 2.1	19.6 ± 7.3	$-(43.8 \pm 2.1)$
NO ₃	$(1.6 \pm 0.2) \cdot 10^7$	17.8 ± 2.6	$(2.3 \pm 0.1) \cdot 10^{10}$	15.4 ± 2.2	31.7 ± 5.9	$-(54.9 \pm 2.4)$
SO ₄ ⁻	$(5.2 \pm 0.8) \cdot 10^7$	9.0 ± 3.0	$(2.1 \pm 0.1) \cdot 10^9$	6.6 ± 2.2	28.9 ± 11.4	$-(74.8 \pm 4.3)$

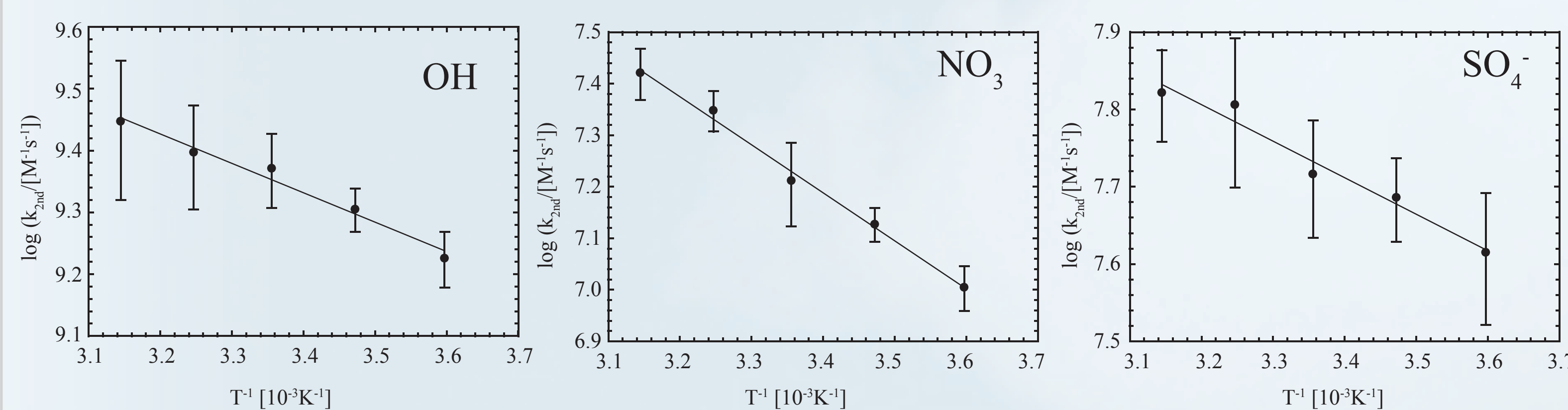


Figure 1: Arrhenius plots ($\log k_{\text{rad}}$ vs. $1/T$) for the measured radical reactions in aqueous solution.

As can be seen in Table 1, levoglucosan is rapidly oxidized by atmospheric free radicals in aqueous solution similar to mono- and polyfunctional alcohols. The temperature dependent measurements (Table 1 and Figure 1) show a linear dependency between the logarithmic rate constants and the inverse temperature.

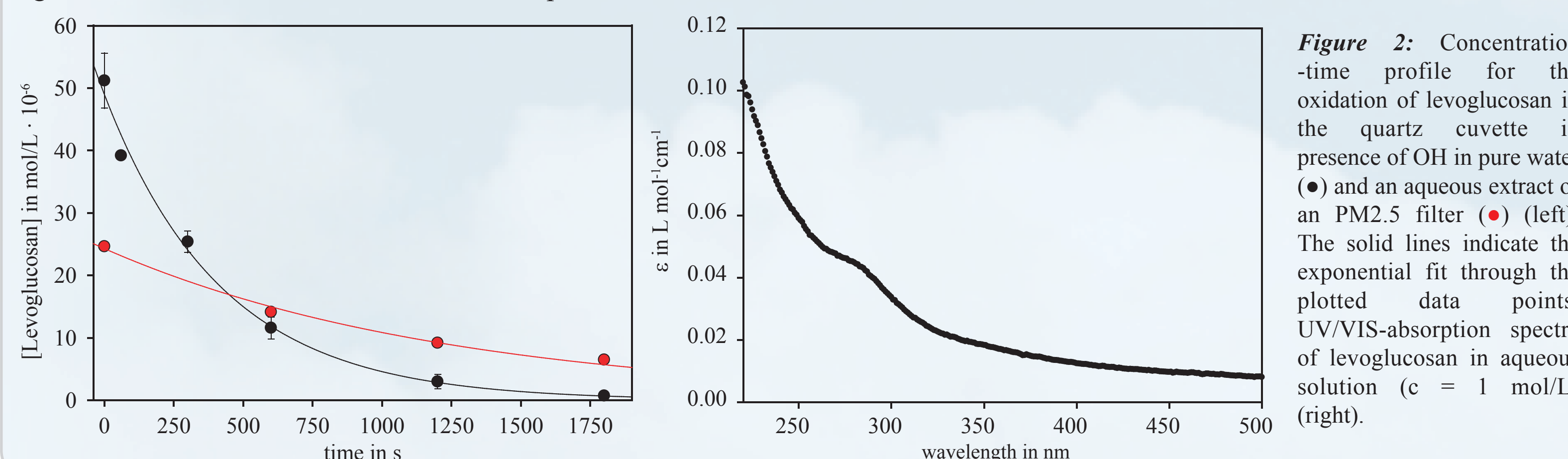
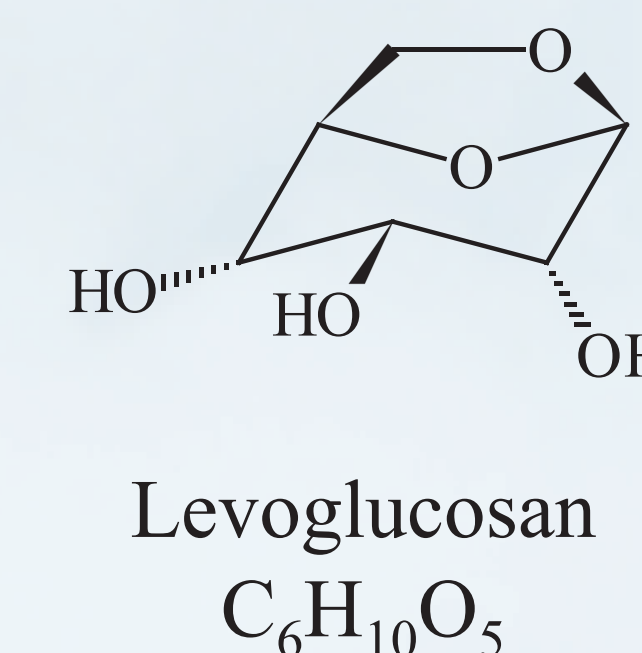


Figure 2: Concentration-time profile for the oxidation of levoglucosan in the quartz cuvette in presence of OH in pure water (●) and an aqueous extract of an ambient PM2.5 filter (●) (left). The solid lines indicate the exponential fit through the plotted data points. UV/VIS-absorption spectra of levoglucosan in aqueous solution ($c = 1 \text{ mol/L}$) (right).

Laboratory studies

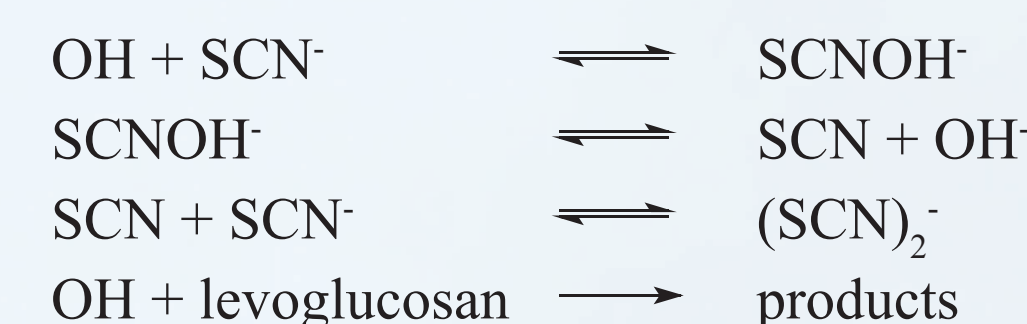
■ Kinetic measurements of OH, NO₃, and SO₄⁻ radical reactions with levoglucosan in aqueous solution

- Laser flash photolysis technique (5)
- Temperature dependent measurements $278\text{K} \leq T \leq 318\text{K}$ with $\Delta T = 10\text{K}$
- Conditions of pseudo first order
- Radical sources:
 - OH: $\text{H}_2\text{O}_2 + \text{hv} (\lambda = 248 \text{ nm}) \rightarrow 2\text{OH}$
 - SO₄⁻: $\text{K}_2\text{S}_2\text{O}_8 + \text{hv} (\lambda = 248 \text{ nm}) \rightarrow 2\text{SO}_4^{\cdot-}$
 - NO₃: $\text{K}_2\text{S}_2\text{O}_8 + \text{hv} (\lambda = 248 \text{ nm}) \rightarrow 2\text{SO}_4^{\cdot-}$
 - SO₄⁻ + NO₃⁻ $\rightarrow \text{SO}_4^{2-} + \text{NO}_3^{\cdot}$



• Kinetic measurements using continuous-wave (cw) laser (5)

OH: Kinetic studies on OH radical reactions were performed applying a competition kinetic method using thiocyanate (SCN⁻) as reference system.



Measurements of the (SCN)₂⁻ formation as a function of the levoglucosan concentration were done using a cw-laser at $\lambda = 473 \text{ nm}$.

SO₄⁻: Direct measurement of the SO₄⁻ radical decay as a function of the levoglucosan concentration using a cw-laser at $\lambda = 473 \text{ nm}$.

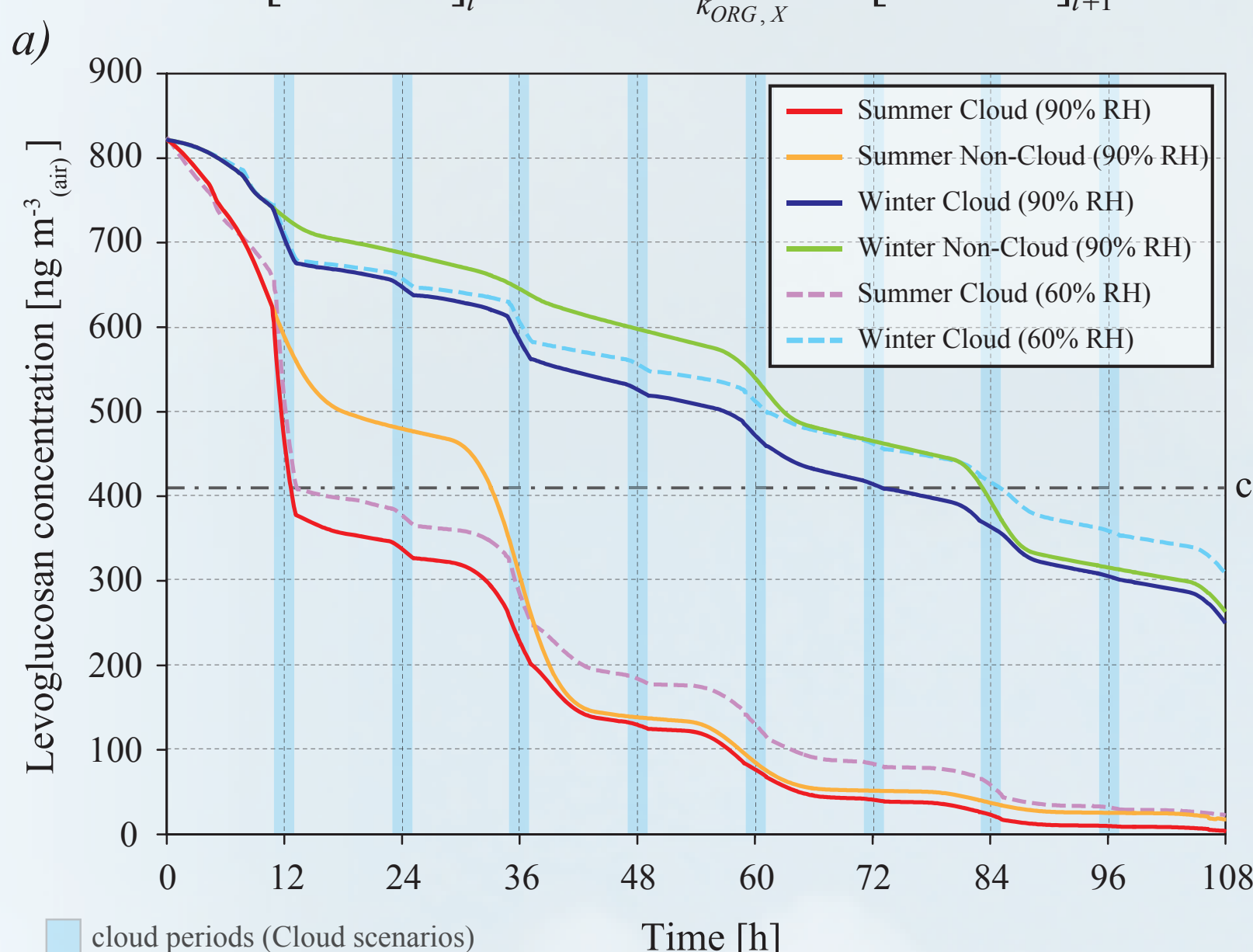
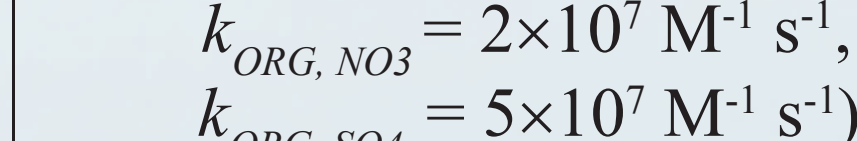
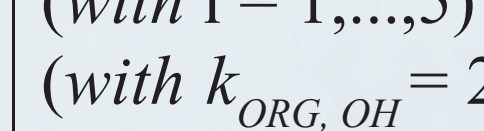
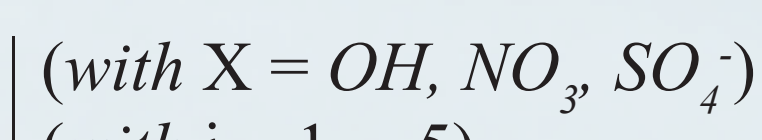
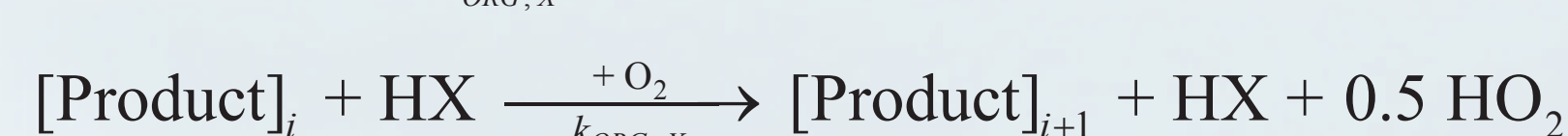
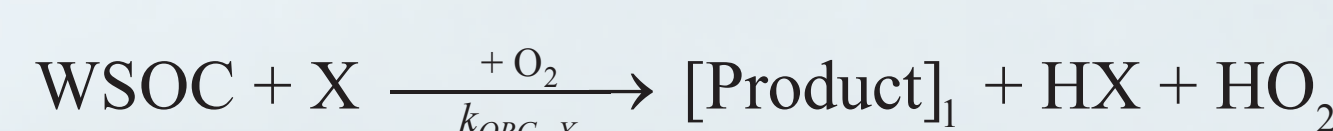
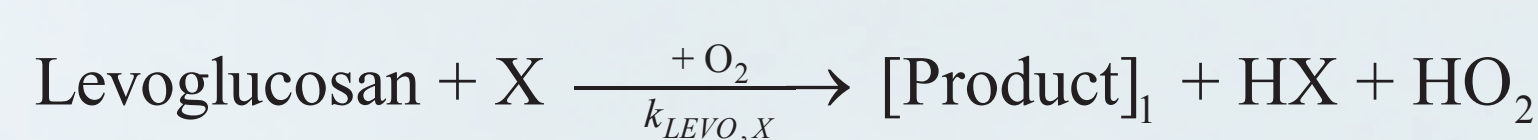
NO₃: Direct measurement of the NO₃ radical decay as a function of the levoglucosan concentration using a cw-laser at $\lambda = 635 \text{ nm}$.

■ Investigations on the stability of levoglucosan in pure water and an aqueous PM2.5 filter extract (3)

- Solutions containing levoglucosan ($4.5 \times 10^{-5} \text{ M}$) and H₂O₂ ($1 \times 10^{-4} \text{ M}$) were irradiated by a Hg/Xe lamp in a quartz cuvette.
- A long-pass filter (WG 280) was applied to simulate the solar spectral range.
- The decay of levoglucosan was measured as a function of the lamp exposure time both in the presence and in the absence of H₂O₂ using a high-performance anion-exchange chromatography system with a pulsed amperometric detector.
- The black dots in Figure 2 show the measured levoglucosan degradation profile in pure water as well as an exponential fit of the data points. The decay of levoglucosan follows first-order kinetics. On the basis of the data the half-lifetime of levoglucosan in the absence of other reactants was calculated to be $t_{1/2} = 338 \text{ s}$.
- Furthermore, a rate constant for the levoglucosan decay in the absence of H₂O₂ was determined. In presence of light only a rate constant of $k_{\text{st}} = 6.4 \times 10^{-5} \text{ s}^{-1}$ was determined. The reason for this decay remains unclear, since levoglucosan absorbs almost no light above $\lambda = 280 \text{ nm}$ (Figure 2).
- The red dots in Figure 2 show the measured levoglucosan degradation profile in an aqueous extract of an ambient PM2.5 filter sample as well as an exponential fit of the data points. The decay of levoglucosan in presence of other water soluble reactants and H₂O₂ ($1 \times 10^{-4} \text{ M}$) follows again first-order kinetics. The filter sample was collected on Dec 17th, 2007, at the village of Seiffen, Saxony, Germany ($50^\circ, 38', 50'' \text{ N}$, $13^\circ, 27', 08'' \text{ E}$, 647 m asl). Seiffen is known for the wooden handcraft industry. In the filter sample high concentrations of levoglucosan (830 ng m^{-3} for PM2.5) and other biomass-burning tracer compounds such as methoxyphenols were found. On the basis of the data in Figure 2 the half-lifetime of levoglucosan in presence of other water soluble reactants was calculated to be $t_{1/2} = 884 \text{ s}$.
- The kinetic data obtained as well as ambient data from Seiffen were subsequently used as input parameters to model the lifetime of levoglucosan in the troposphere as shown in the following.

Modeling studies

The SPectral Aerosol Cloud Chemistry Interaction Model (SPACCIM; (6)) was applied to investigate the radical oxidation of levoglucosan in the atmospheric aqueous phases and its influence on the lifetime of levoglucosan. The adiabatic air parcel model simulations were done for summer and winter conditions, simulating high and low photochemical activity. For both conditions, model runs were performed for both non permanent cloud scenarios (Summer Cloud and Winter Cloud) considering chemical aerosol cloud interactions and non-cloud scenarios (Summer Non-Cloud and Winter Non-Cloud) which describe chemical interactions under deliquescent particle conditions only. For the scenarios Summer Cloud and Winter Cloud, an air parcel moves along a predefined trajectory passing 8 cloud events (4 times at noon and 4 times at midnight) for about 2 hours each so that the air mass is subjected to a typical tropospheric in-cloud residence time of about 15% (7). For non-cloud periods, an intermediate aqueous aerosol state is considered at 90% RH. Additionally, a second non-cloud scenarios with a lower RH (60%) was simulated in order to illustrate the effect of the aerosol water content on the degradation of levoglucosan. It is noted that non-ideal effects of concentrated aqueous solutions were ignored in the model calculations. In SPACCIM, the complex multiphase chemistry mechanism RACM MIM2ext (revised and extended Regional Atmospheric Chemistry Model + Mainz Isoprene Mechanism 2) / CAPRAM 3.0i (Chemical Aqueous Phase Radical Mechanism) (8) was applied. Additionally, an aqueous degradation sequence (see below) of levoglucosan and the water soluble organic carbon (WSOC) was added to the CAPRAM 3.0i mechanism. The measured kinetic data were used for the description of the radical oxidation pathways of levoglucosan. The corresponding values for the WSOC oxidation by the radicals have been estimated from the results presented by (5).



- Aqueous-phase oxidations can substantially influence the levoglucosan concentrations in the atmosphere (τ_a values at 90% RH were about 12.7h, 33.1h, 72.8h and 83.2h for Summer Cloud, Summer Non-Cloud, Winter Cloud and Winter Non-Cloud, respectively)

- Degradation of levoglucosan is much faster in the tropospheric aqueous droplets than postulated in former studies (2, 9) that considered non radical reactions only

- Daytime aqueous-phase chemistry is a very effective sink for levoglucosan (see Figure 3)

- Mean levoglucosan degradation fluxes of about $7.2 \text{ ng m}^{-3} \text{ h}^{-1}$ (average over 108 hours) in the Summer Cloud and about $4.7 \text{ ng m}^{-3} \text{ h}^{-1}$ in the Winter Cloud case

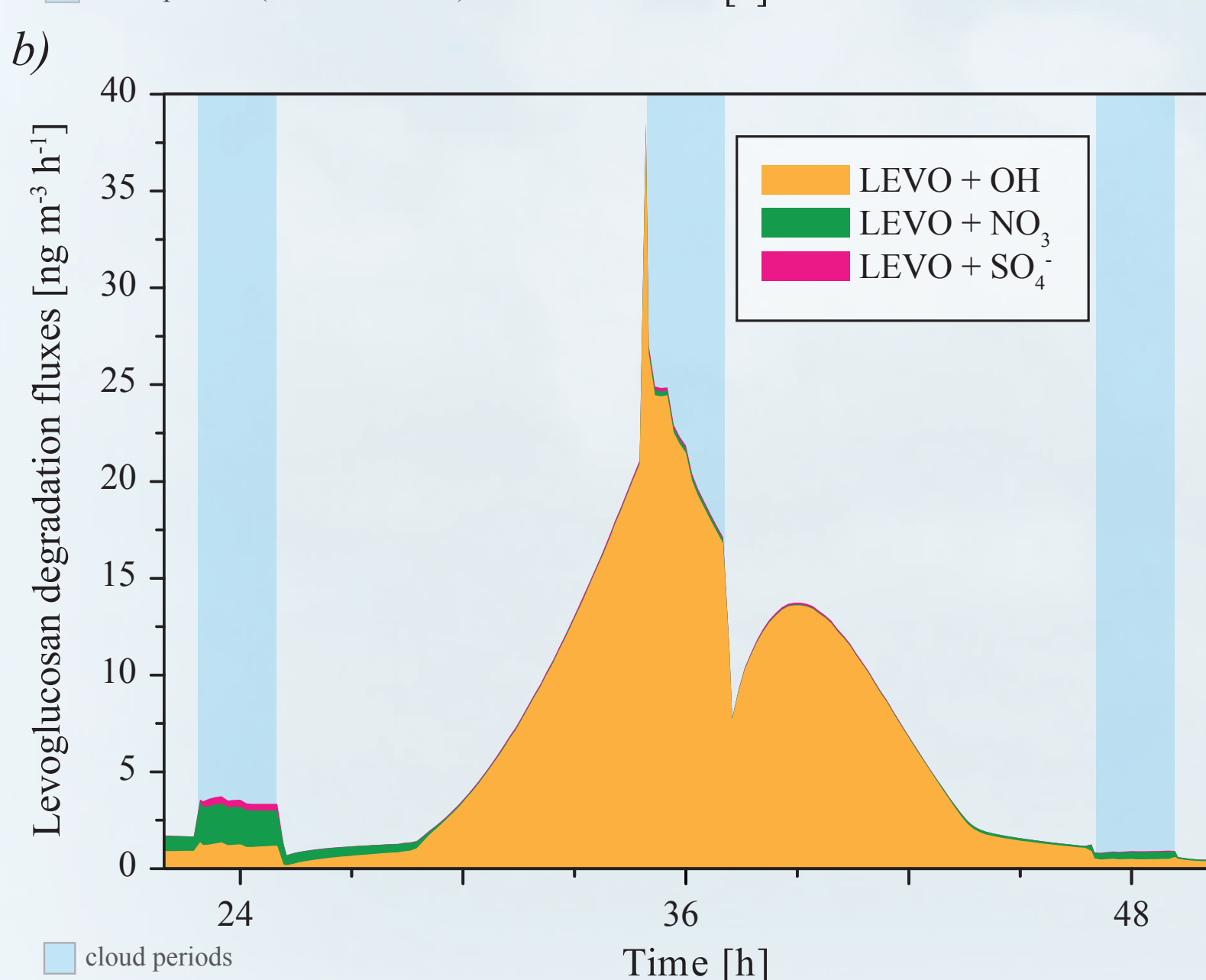
- Degradation in clouds show even higher mean fluxes, ranging up to $17.5 \text{ ng m}^{-3} \text{ h}^{-1}$ for Summer Cloud and $7.5 \text{ ng m}^{-3} \text{ h}^{-1}$ for Winter Cloud case

- Also free radical chemistry in deliquescent particles represents a considerable sink for levoglucosan

- Integrative calculations show that the radical-driven oxidation of levoglucosan proceeds by approx. 42%/27% in the clouds and 58%/73% in the deliquescent particles (Summer Cloud/ Winter Cloud case).

- OH radical represents the dominating oxidant for levoglucosan under both cloud and deliquescent particle conditions (see Figure 3)

Figure 3: (a) Modeled aqueous-phase levoglucosan concentrations in $\text{ng m}^{-3}(\text{air})$ over the simulation time for the six model scenarios Summer Cloud, Summer Non-Cloud, Winter Cloud, Winter Non-Cloud, Summer Cloud (60% RH) and Winter Cloud (60% RH). The grey dash dotted line marks the time of half-initial-value concentration $c_{1/2}$. (b) Modeled aqueous-phase chemical degradation mass fluxes (chemical sinks by different radical oxidants) of levoglucosan in $\text{ng m}^{-3} \text{ h}^{-1}$ (second day of the model simulation for the Summer Cloud case).



■ Sensitivity studies

Based on the obtained results of the base cases (Summer Cloud and Winter Cloud), chemical sensitivity studies on levoglucosan degradation were performed with regards to (1) the soluble iron fraction and (2) the initial H₂O₂ concentration. Simulations were performed for the Summer and Winter Cloud cases with different concentrations of water-soluble iron and the initial H₂O₂, respectively (see Table 2 and Figure 4).

Table 2: Overview of the sensitivity studies (Fe1 represents the "base case").

Sensitivity case	Scaling factor	Particle mass fraction of the water-soluble iron / Initial H ₂ O ₂ concentration
Fe1/H1	100 %	0.001456 % / 1.0 ppb
Fe2/H2	50 %	0.000728 % / 0.5 ppb
Fe3/H3	10 %	0.000146 % / 0.1 ppb

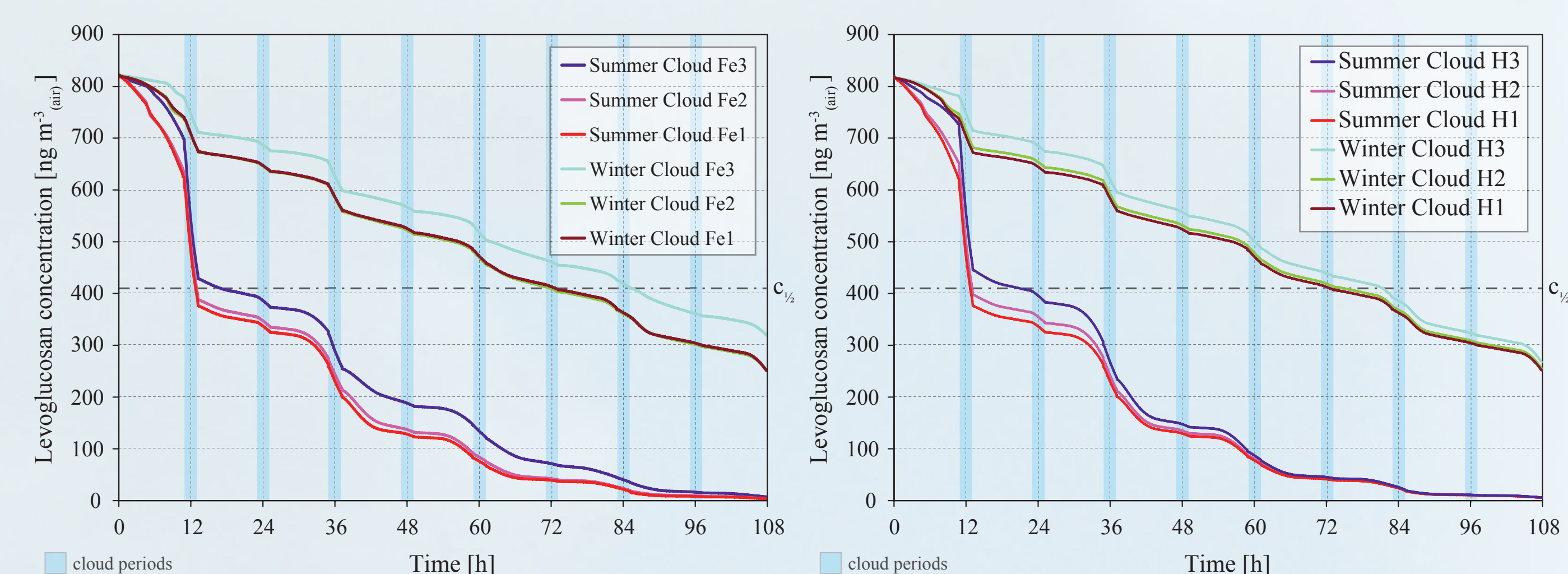


Figure 4: Modeled aqueous-phase levoglucosan concentrations in $\text{ng m}^{-3}(\text{air})$ as a function of the simulation time modeled with different water-soluble iron contents (left) and different initial H₂O₂ concentrations for the Summer Cloud and Winter Cloud cases.

Summary and Conclusion

Levoglucosan, an important molecular marker for biomass burning, represents an important fraction of the water soluble organic carbon (WSOC) in atmospheric particles influenced by residential wood burning and wildfires. Even if levoglucosan is widely used in source apportionment studies only few studies investigated the atmospheric stability of this tracer compound so far. Furthermore, oxidation processes by free radicals in aqueous particles are not yet considered as a potential sink reaction for this highly water soluble compound. Therefore, detailed kinetic studies on the reactivity of levoglucosan towards three important atmospheric free radicals (OH, NO₃ and SO₄⁻) in aqueous solutions were performed for the first time using the laser flash photolysis technique. Laboratory studies on the stability of levoglucosan were done both in the presence and absence of other water soluble reaction partners. Furthermore, the experimental data were implemented into the parcel model SPACCIM in order to study the degradation fluxes of levoglucosan in cloud droplets and aqueous particles considering a detailed microphysics and multiphase chemistry. The model calculations, performed under different conditions, show that levoglucosan can be oxidized readily by OH radicals in the tropospheric aqueous phase. Mean degradation fluxes of about $7.2 \text{ ng m}^{-3} \text{ h}^{-1}$ in summer and $4.7 \text{ ng m}^{-3} \text{ h}^{-1}$ in winter were calculated. Model calculations demonstrate that under certain atmospheric conditions the oxidation of levoglucosan can be as fast as that of other atmospherically relevant organic compounds and it may not be as stable as previously thought in the atmosphere particularly under high relative humidity conditions.

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