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Importance of the surface reaction $OH + Cl^-$ on sea salt aerosol for the chemistry of the marine boundary layer – a model study

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Abstract. The reaction of the hydroxyl radical with chloride on the surface of sea salt aerosol producing gas phase Cl_2 and particulate OH^- and its implications for the chemistry of the marine boundary layer under coastal, remote, and very remote conditions have been investigated with a numerical model. This reaction had been suggested by Laskin et al. (2003) to play a major role in the sulfur cycle in the marine boundary layer by increasing the sulfate production in sea salt by O_3 oxidation due to the additional production of alkalinity in the particle. Based on literature data a new “best estimate” for the rate coefficient of the reaction was deduced and applied, showing that the additional initial sulfate production by this reaction is less than 1%, therefore having only a minor impact on sulfate production. Even though the gas phase concentration of Cl_2 increased strongly in the model, the concentration of Cl radicals increased by less than 5% for the “best guess” case. Additional feedbacks between the cycles of chlorine and sulfur in the marine boundary layer are discussed as well as a two-stage acidification of large fresh sea salt aerosol.

1 Introduction

Aerosol particles play a key role in the climate system of the Earth because they can scatter radiation directly and influence the properties of cloud particles and therefore exert an indirect forcing on climate. Furthermore, they influence the hydrological cycle by changing cloud properties. Over clean oceans cloud condensation nuclei (CCN) are mainly sea salt and sulfate particles. The origin of sulfate particles in the marine boundary layer (MBL) is transport from continents and formation of new particles from sulfur-containing precursors. Apart from their own role as CCN, sea salt aerosol, which is mainly produced by bursting bubbles at the ocean surface (e.g. Woodcock et al., 1953), can also influence the chemical and microphysical properties of other aerosol particles by taking up and releasing chemically reactive compounds including sulfur and halogen compounds.

The natural marine cycle of sulfur is dominated by the emissions of dimethyl sulfide (DMS) (see e.g. Charlson et al., 1987), which is produced by organisms in the oceans and subsequently emitted to the atmosphere where it is oxidized in the gas phase by OH, NO_3, Cl, and BrO and in the aqueous phase by O_3. Sulfuric acid (H_2SO_4) is the only gas phase product of DMS that can form new aerosol particles whereas all other products only add to the mass of pre-existing aerosol (see e.g. Hoppel, 1987 and discussion in von Glasow and Crutzen, 2004). Additionally, the presence of sulfate in particles often increases the hygroscopicity of many aerosol particles (e.g. Seinfeld and Pandis, 1998).

A key factor in determining the importance of sulfur particles on microphysical processes and climate feedbacks as suggested for example by Charlson et al. (1987) is the fraction of DMS-products that form new aerosol particles or lead to the growth of existing particles, potentially increasing their ability to form droplets. Sea salt particles are very soluble and, due to their relatively large size, have short lifetimes of 1–2 days. Therefore the uptake of DMS-derived sulfur products by sea salt particles can be viewed as a short-cut in the marine sulfur cycle because of the rapid deposition of these compounds back to the ocean (e.g. von Glasow and Crutzen, 2004). Furthermore the change in hygroscopicity due to uptake of sulfate is small for sea salt.

SO_2 is a product of the oxidation of DMS. The fate of SO_2 depends on the abundance of the gas phase oxidant OH and the uptake to and oxidation in particles. The reaction rate coefficient for the aqueous phase oxidation of S(IV) (=$SO_{2,aq} + HSO_3^- + SO_3^{2-}$) by O_3 increases by about 6 orders of magnitude between pH 2 and 6 making it only important for pH values greater than 6 (e.g. Seinfeld and Pandis, 1998).

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The pH of freshly emitted sea salt aerosol is close to that of sea water of about 8.2 (e.g. Riley and Skirrow, 1965). Due to the presence of HCO_3^- in sea water and therefore also in sea salt aerosol, the particle pH is buffered (see e.g. Chameides and Stelson, 1992), meaning that the uptake of acids changes the pH only after this buffer has been depleted. Until the particle is acidified, the reaction of S(IV) + $O_{3,aq}$ is very efficient and constitutes a strong source for S(VI) ($=H_2SO_{4,aq} + HSO_4^- + SO_4^{2-}$) (e.g. Penkett et al., 1979; Hoffmann, 1986; Sievering et al., 1991). The production of non sea salt sulfate (nss-SO_4^{2-}) in this reaction and the uptake of other acids (HNO_3, HCl) lead to a decrease in the pH and the oxidation rate of S(IV) which is then dominated by H_2O_2 (e.g. Penkett et al., 1979) and the hypohalous acids HOBr and HOCl (Vogt et al., 1996). A detailed comparison of the different oxidation pathways in sea salt aerosol can be found in von Glasow et al. (2002b) and von Glasow and Crutzen (2004).

Direct and indirect determinations of the pH of supermicron particles which are usually dominated in the MBL by sea salt aerosol showed the following results: Hawaii, clean conditions 4.5–5.4 (Pszenny et al., 2004), Atlantic (50° N–17° S) 3.5–4.25 (Keene et al., 2005), Bermuda, (moderately polluted): 3.5–4.6 (Keene and Savoie, 1998, 1999; Keene et al., 2002), East Coast of U.S., (moderately to heavily polluted): 2.7–3.9 (Keene et al., 2004). As these are filter measurements, the sampling cannot separate single particles so that these numbers average over particles of different age and therefore different depletion of the bicarbonate buffer and chemical aging.

Recently it has been speculated by Laskin et al. (2003) that the reaction of gas phase OH with chloride on the surface of sea salt particles can lead to a significant delay in the acidification of sea salt particles by the production of alkalinity via the net reaction:

$$OH_g + Cl^- \longrightarrow 0.5\, Cl_{2,g} + OH^- \qquad (1)$$

This net reaction had been suggested by Knipping et al. (2000) based on variety of laboratory experiments, molecular dynamics, and kinetic modeling with the simplified system of pure NaCl particles. The enrichment of halides on the surface has further been investigated in molecular dynamics simulations by e.g. Jungwirth and Tobias (2001, 2002) and in the laboratory by e.g. Ghosal et al. (2000, 2005) and Liu et al. (2004). The focus of these papers was the release of Cl_2 to the gas phase. Laskin et al. (2003) could show the presence of elevated OH^- concentrations on the surface of NaCl particles that had reacted with OH.

The idea of Laskin et al. (2003) of the importance of Reaction (1) for the atmospheric sulfur cycle has been challenged by Keene and Pszenny (2004) based on their measurements of (bulk) aerosol pH and that acidity sources other than SO_2 were neglected by Laskin et al. (2003). Sander et al. (2004) criticized the atmospheric conditions that Laskin et al. (2003) had chosen for their extrapolation and expecially the fact that uptake limitations for OH had been ignored by Laskin et al. (2003). In their reply Laskin et al. (2004) stressed that the proposed mechanism will not keep sea salt particles alkaline under all conditions but that it rather modulates the rate of titration of the alkalinity. They also mention the possibility of formation of OH at the particle surface from the photolysis of NO_3^-. Alexander et al. (2005) analyzed the isotopic signature of sulfate in the Indian Ocean which can be used to deduce the oxidation pathways. A comparison of their data with global model runs showed that including the alkalinity formation mechanism by Laskin et al. (2003) leads to large inconsistencies between model and field data, implying that Reaction (1) plays only a minor role for the sulfur budget in the Indian Ocean MBL.

In general, Reaction (1) can only be of importance in regions where the gas phase acidity is high enough to eventually acidify the particles. In regions where this is not the case, i.e. where particles do not get more acidic than pH≈6, the oxidation of S(IV) by O_3 will always dominate, so that an additional source of alkalinity will have no effect. The focus of this study is the temporal evolution of the sea salt aerosol pH to be able to identify regions/conditions where Reaction (1) can have an effect by yielding "excess" nss-SO_4^{2-} due to the production of additional alkalinity in the particles. In order to accomplish this, the change of the pH in fresh sea salt particles of different sizes that evolve in the presence of sulfate and aged sea salt particles is calculated with a numerical box model under conditions typical for coastal regions, the remote MBL, and the very remote Southern Ocean. Furthermore, effects on the sulfur cycle and the release of Cl_2 to the atmosphere are quantified.

In Sect. 2 the numerical model is described, whereas in Sect. 3 the effects on sea salt particle pH and the oxidation of sulfur and in Sect. 4 the effects on gas phase chlorine are discussed.

2 Model description and setup

For this study the model MISTRA (von Glasow et al., 2002a,b; von Glasow and Crutzen, 2004) was used which is a model of the MBL. Microphysical processes are treated in detail and a major focus is on the interaction of gas phase and particulate phase (sea salt and sulfate aerosol) chemistry. Photolysis frequencies are calculated online with the model of Landgraf and Crutzen (1998). The chemical mechanism contains the most important reactions of O, H, C, N, S, Cl, and Br both in the gas and particulate phase. MISTRA is a one-dimensional model, in this study, however, it was run in the box-model mode. It was initialized with data from the lowest level of 1-D runs that were used for a numerical spin-up of the system.

2.1 “Mono-disperse” sea salt aerosol bin

The standard approach in the model is to consider one bin for the chemistry of sulfate particles and a second bin for sea salt particles. Especially in the case of sea salt this implies averaging over not only a range of particle sizes but especially particle ages. The pH – and therefore the chemistry – of sea salt particles is, as already mentioned, a strong function of time. As one focus of this paper is to investigate the influence of Reaction (1) on the pH, a way had to be found to explicitly take the particle age into account. To achieve this, a third chemical bin for fresh sea salt of a “discrete” radius was introduced which additionally allows to investigate the effect of particle size. This bin evolves in the presence of aged sulfate and sea salt particles and can, for example, also be acidified by HCl that had been released from older sea salt particles via acid displacement. The choice of the number and width Δr of this bin is important to ensure a realistic simulation. One cannot simply assume a particle density of 1 part. cm^{-3} for this size bin as this would drastically overestimate the total mass of sea salt for large radii and therefore change the chemistry completely. In principle, Δr should be approaching zero in order to model particles of a discrete size, but technically the number of particles for $\Delta r \rightarrow 0$ equals zero for any given size distribution (e.g. Seinfeld and Pandis, 1998). Here, the width of the radius bin was chosen as $\Delta r=0.1r$. Tests with $2\Delta r$ showed hardly any impacts on the results whereas the choice of $3\Delta r$ resulted in noticeable changes in the gas phase indicating that too much additional mass was present in this additional size bin. Therefore, using $\Delta r=0.1r$ ensures that the overall chemistry in the model is unchanged by the presence of this addition additional aerosol bin. The contribution of the “mono-disperse” sea salt aerosol bin to the total sea salt mass is a few tenths of a percent for all runs except for those with $r=1\,\mu$m where it is about 4–6%. In the following, this third aerosol size bin is referred to as the “mono-disperse” sea salt aerosol bin. The number of particles in this bin was taken from the size distribution of the lowest layer of a 1-D run of MISTRA (z=5 m). The chemistry and physics of this bin are treated in exactly the same way as in the other bins.

2.2 Implementation of the surface reaction

The rate coefficient of Reaction (1) is critical for this study. It depends on the transport of OH to the particle's surface and the reaction probability of OH with Cl^- at the surface. The usual expression for the mass transfer coefficient k_t for non-reactive uptake of gas molecules to the surface of a particle is (Schwartz, 1986):

$$k_t = \left(\frac{r^2}{3D_g} + \frac{4r}{3\bar{v}\alpha}\right)^{-1}, \qquad (2)$$

with the particle radius r, the mean molecular speed $\bar{v}=\sqrt{8RT/(M\pi)}$ (M is the molar mass), the accommodation coefficient α, and the gas phase diffusion coefficient D_g. D_g is approximated as $D_g=\lambda\bar{v}/3$ (e.g. Gombosi, 1994, p. 125) using the mean free path length λ. The effects of gas phase diffusion are more important for larger particles, therefore it has to be taken into account in the discussion of sea salt aerosol which span the size range from about 100 nm to several 10 μm. The error in the reactive uptake rate coefficient when gas phase diffusion limitations are ignored is only about 30% for r=0.1 μm and α=0.24 (110% for α=1), whereas it is already a factor of 2.6 (7.7) for r=0.6 μm and a factor of 14.6 (57.1) for r=1 μm.

A mathematical expression for a surface reaction can be found by replacing the accommodation coefficient α in Eq. (2) with the reaction probability γ. This ensures that limitations by gas phase diffusion and the specifics of the respective reaction are taken into account. If γ is taken from a laboratory experiment one has to ensure that gas phase diffusion limitations are not implicitly included twice as a net reaction probability might already include this effect.

Knipping and Dabdub (2002) re-evaluated the results from the laboratory study of Knipping et al. (2000) that was done with mono-disperse particles with radii of about 75 nm, indicating that gas phase diffusion limitations were small. They suggested the following expression for the reaction probability for the net Reaction (1):

$$\gamma = 0.02\gamma'[Cl^-]=0.04[Cl^-], \qquad (3)$$

where the concentration of chloride ions is given in mol l^{-1}. According to Knipping and Dabdub (2002) the value of the parameter γ' is chosen as 2. For typical chloride concentrations in sea salt particles of about 6 mol l^{-1} the resulting γ=0.24. The extrapolation of Laskin et al. (2003) assumed γ=1, also without taking gas phase diffusion limitations into account. Using a reaction probability of γ=1 without any restrictions assumes that every collision between an OH molecule and the particle surface leads to a reaction with Cl^- independent of the Cl^- concentration. Assuming that expression (3) gives the correct reaction probability if gas phase diffusion is unimportant, we can replace α in Eq. (2) with γ according to Eq. (3) to calculate the reaction rate including gas phase diffusion. Use of Eq. (3) also implies that only a fraction of the total Cl^- is available for the surface reaction as expressed by the factor 0.04,

As Reaction (1) is a surface reaction, the concentration of the aqueous phase reactants that have to be used strictly are those at the surface which might differ from those in the bulk of the particles. For Cl^- this is not critical as the change in its bulk concentration due to the surface reaction is small and, by using expression (3) for the calculation of γ, the surface enrichment of Cl^- is taken into account. Note that the surface enrichment in Cl^- is caused by the polarizability of the ions (Jungwirth and Tobias, 2002). According to the molecular dynamics calculations of Jungwirth and Tobias (2002)

Table 1. Initial mixing ratios of gas phase species (in nmol mol^{-1}; OH concentration in molec cm^{-3}).

species	coastal	remote MBL	Southern Ocean
O_3	43.0	18.0	12.0
OH	7.5×10^6	3.4×10^6	3.7×10^6
NO_x	0.145	0.004	0.0016
HNO_3	0.11	0.0011	0.0001
PAN	0.08	0.001	0.01
NH_3	0.11	0.1	0.1
H_2O_2	0.9	0.235	0.14
SO_2	0.1	0.085	0.07
H_2SO_4	0.0008	0.0003	0.0002
DMS	0.08	0.11	0.12
CH_4	1700.0	1700.0	1670.0
CO	190.0	68.0	44.0
C_2H_6	1.4	0.5	0.23
HCHO	0.36	0.12	0.13
HCl	0.34	0.025	0.01

it is maintained against aqueous phase diffusion. The production of OH^- in Reaction (1) occurs only in the layer that is directly accessible to OH molecules from the gas phase which will not be more than a few Ångstrom. The timescales for aqueous phase diffusion (complete mixing of a particle) is given by (e.g. Schwartz, 1986):

$$\tau = \frac{r^2}{\pi^2 D_a}, \qquad (4)$$

so it is about 10^{-4} s for a particle with r=1 μm. The surface reaction occurs on time scales a lot shorter than this but it is constrained to a very shallow layer. Diffusion out of this layer is very fast so that it is not expected that a gradient in pH develops outside this surface region.

The measurements of Laskin et al. (2003) and Gaspar et al. (2004) are indicative of an enrichment in the surface density of OH^- in NaCl crystals after exposure to OH. Unfortunately, the authors were not able to get detailed depth profile information of the samples and therefore no information about the depth of this surface layer is available. Furthermore, they could only analyze the reacted particles after recrystallization which might have impacted the depth profile by expulsion of ions to the surface that do not fit into the NaCl lattice.

2.3 Overview of model runs

Throughout this paper the term “case” is used for the different assumptions about the surface reaction and the term “scenario” for the different initial and boundary conditions. The different cases are set up to explore the importance of uptake limitations and the use of expression (3) versus a reaction probability of unity. The following cases are explored in this paper:

- case 1: no surface reaction
- case 2: γ=0.02γ'[Cl^-]=0.04[Cl^-], with gas phase diffusion limitation. This is considered to be the “best guess” case.
- case 3: γ=0.02γ'[Cl^-]=0.04[Cl^-], no gas phase diffusion limitation; same as in Knipping and Dabdub (2002).
- case 4: γ=1, with gas phase diffusion limitation, all particulate Cl^- is available for surface reaction.
- case 5: γ=1, no gas phase diffusion limitation, all particulate Cl^- is available for surface reaction; same as in Laskin et al. (2003).

The following chemical scenarios for the background atmosphere in which the fresh sea salt particles evolve are used, the concentrations and mixing ratios of the main species are listed in Table 1:

- Coastal: This scenario is based on various data from the PEM-tropics campaigns (e.g. Gregory et al., 1997) to simulate semi-polluted air over the ocean, as is the case for example in coastal regions. The concentration of sea salt aerosol is 13 μg m^{-3}, air temperature is 14°C.
- Remote MBL: With this scenario typical remote MBL conditions are simulated, the concentration of sea salt aerosol is 13 μg m^{-3}, air temperature is 14°C. It is based on various measurements, see von Glasow and Crutzen (2004).
- Southern Ocean: This scenario is meant to simulate the pristine regions of the MBL and is based on measurements from the Cape Grim Baseline Station (Ayers et al., 1995, 1997a,b, 1999; Monks et al., 1998, 2000). The concentration of sea salt aerosol is 34 μg m^{-3}, air temperature is 17°C.

All runs were made for relative humidities of 75%, therefore all particles are aqueous because they are produced as sea water droplets and the crystallization humidity is about 45%. Furthermore, the runs are for summer conditions in order to maximize [OH] and therefore the potential importance of Reaction (1). Model start is at local noon, all runs are integrated for 6 h. For the 1-D model runs from which the information for the initialization of the runs presented here was taken, a spin-up of one day was used. As Reaction (1) is dependent on photolysis to produce OH, no night time evaluation of this reaction is necessary. The focus of this study is the early evolution of fresh sea salt particles and in all presented runs the fresh sea salt particles get acidified within 6 h so that this duration of the model runs is sufficiently long.

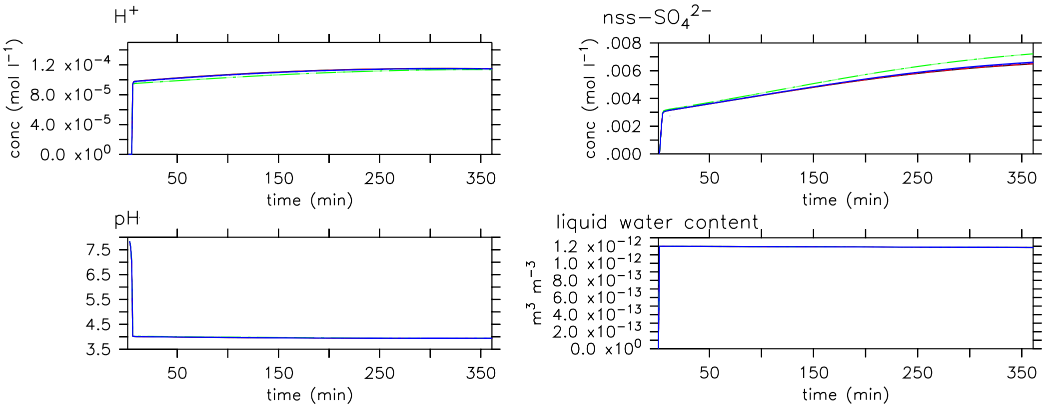

Fig. 1. Temporal evolution of the concentrations of H$^+$ and S(VI) as well as the pH and liquid water content for scenario "coastal" in the "mono-disperse" particle bin for r=1 μm. Case 1 – black, solid line, case 2 – red, dashed line, case 3 – blue, dotted line, case 4 – blue, solid line, case 5 – green, dash-dotted line. Note, that most lines except for case 5 overlap. The abscissa is time since model start in minutes.

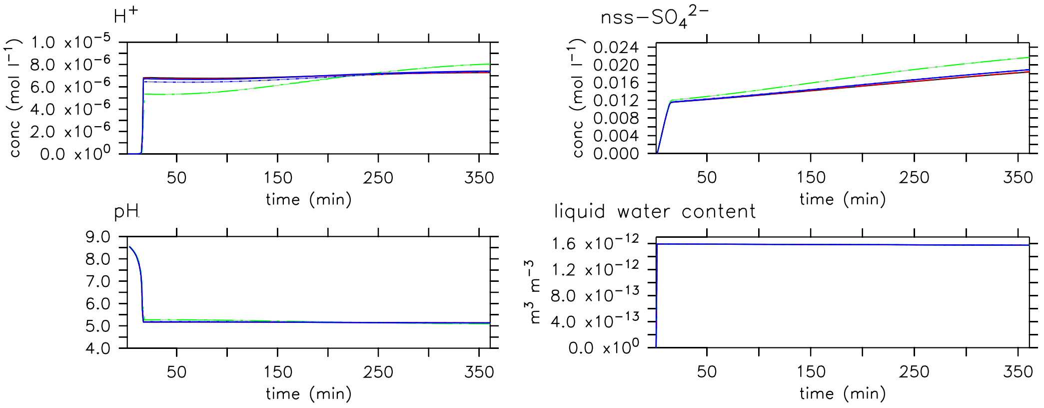

Fig. 2. Same as Fig. 1 but for scenario "remote MBL" in the "mono-disperse" particle bin for r=1 μm.

If the available gas phase acidity is not enough to deplete the bicarbonate buffer, the oxidation of S(IV) by ozone will always dominate, so there is no need to study the effect of additionally produced alkalinity via surface reactions under these conditions.

3 Effects on sea salt pH and the sulfur cycle

As already mentioned, the additional alkalinity produced in the surface reaction of OH with Cl$^-$ can extend the time during which rapid production of S(VI) via the reaction S(IV) + O_3 is important. Therefore, the timing of the acidification of the "mono-disperse" sea salt aerosol bin is critical for this process.

In the following the term "buffering time" is used for the time it takes to acidify the particles (see Table 2), here taken to be the time when the pH remains almost constant, i.e. when the HCO_3^- buffer is being depleted. The delay in acidification due to alkalinity production by the surface reaction is refered to as "additional buffering time" and can also be found in Table 2. The amount of additional S(VI) that is produced before the particles get acidified is shown for each case in Table 3. Only for particles with radii greater than 1 μm the "additional buffering time" is of noticable magnitude, it is strongest in case 5.

Figure 1 shows the evolution with time of [S(VI)], pH, [H$^+$], and the liquid water content in the "mono-disperse" sea salt aerosol bin for a radius of r=1 μm. The very short additional buffering time is too small to be discernable on that plot. The amount of sulfate being produced during the acidification is almost the same, the proton concentration is only in case 5 different from case 1. Figure 2 shows the same for the remote MBL scenario, again the additional buffering time is too small to be observed in any case, the difference in initial S(VI) production is only about 4% in case 5 and less than 1% or smaller in all other cases.

Table 2. Buffering time in the "mono-disperse" sea salt aerosol bin for case 1 for all scenarios and additional buffering time (BT) for cases 2–4 compared to case 1 (in minutes).

radius		coastal	remote MBL	Southern Ocean
0.1 μm	case 1: buffering time	3	3	4
	case 2: additional BT	<1	<1	<1
	case 3: additional BT	<1	<1	<1
	case 4: additional BT	<1	<1	<1
	case 5: additional BT	<1	<1	<1
0.6 μm	case 1: buffering time	4	10	12
	case 2: additional BT	<1	<1	<1
	case 3: additional BT	<1	<1	<1
	case 4: additional BT	<1	<1	<1
	case 5: additional BT	<1	<1	2
1.0 μm	case 1: buffering time	6	17	23
	case 2: additional BT	<1	<1	<1
	case 3: additional BT	<1	<1	1
	case 4: additional BT	<1	<1	<1
	case 5: additional BT	<1	1	2
5.0 μm	case 1: buffering time	65	210	245
	case 2: additional BT	<1	<1	<1
	case 3: additional BT	1	5	6
	case 4: additional BT	<1	<1	<1
	case 5: additional BT	5	18	21

As the small changes are hard to read from Figs. 1 and 2, the difference of nss-SO_4^{2-} produced during the acidification compared to the case without the surface reaction is also shown in Table 3. It is obvious that the amount of this "additional initial nss-SO_4^{2-} production" is very small. In case 2, the "best guess", this amount is never more than 1% compared to the case without the surface reaction. Only in case 5 up to 11% additional nss-SO_4^{2-} is predicted; please remember that this case is ignoring gas-phase diffusion limitations and assumes that all particulate Cl$^-$ is available for the surface reaction with a reaction probability of unity, therefore clearly overestimating the effect of the surface reaction. In summary, this shows, that the suggestion of Laskin et al. (2003) for the relevance of Reaction (1) for the sulfur cycle in the MBL is clearly overestimating its importance.

A surprising feature is, that in the cases including the surface reaction the S(VI) concentration at the end of the model run is greater than in case 1 (see Figs. 1 and 2). The increase is in general small but for case 5 it amounts to about 20%. Nevertheless, this effect is relatively small in absolute terms (case 5: 2.9 pmol mol^{-1}, expressed as pseudo-gas phase mixing ratio) because very little particle mass is associated with the "mono-disperse" sea salt bin. The increase is caused by feedbacks between the cycles of halogens and sulfur. Due to the increase of reactive chlorine in the gas phase (see Sect. 4), the gas phase reaction DMS + Cl is increased, yielding about 1.2, 0.2, and 2.8 pmol mol^{-1} more SO_2 in case 5 in the scenarios, "coastal", "remote MBL", and "Southern Ocean", respectively. Furthermore, HOCl is increased in both the gas and aqueous phase, leading to an increase in the aqueous phase production of nss-SO_4^{2-} by reaction of HOCl with S(IV). Under some conditions, a decrease of the particle pH below the pH in case 1 (as explained below) causes the release of more bromine from the particles and the associated feedbacks with the sulfur cycle (see e.g. von Glasow and Crutzen, 2004).

Table 3. Relative increase of the production of nss-S(VI) during the particle acidification in the "mono-disperse" sea salt particle bin for cases 2–5 compared to the run without the surface reaction (case 1). Note, that the amount of nss-S(VI) in 5.0 μm aerosol particles is only 10% of that in particles with radii of 0.6 and 1.0 μm.

radius		coastal	remote MBL	Southern Ocean
0.1 μm	case 2	0%	0.7%	1.0%
	case 3	0%	0.8%	1.5%
	case 4	0%	1.9%	3.2%
	case 5	0%	6.5%	9.0%
0.6 μm	case 2	0.1%	0.2%	0.3%
	case 3	0.5%	0.9%	1.3%
	case 4	0.2%	0.3%	0.5%
	case 5	3%	4.0%	6.0%
1.0 μm	case 2	0.1%	0.2%	0.3%
	case 3	0.1%	1.1%	2.0%
	case 4	0.2%	0.3%	0.4%
	case 5	3%	4.5%	6.0%
5.0 μm	case 2	0.8%	0.1%	0%
	case 3	1.8%	2.2%	2.0%
	case 4	0.2%	0.1%	0%
	case 5	9.0%	11%	9.0%

Figures 2 and 3 also show that the proton concentration can increase above (and the pH decrease below) that of case 1, again most pronounced in case 5. The decrease of the pH in the "mono-disperse" sea salt aerosol bin below the value from the case without surface reaction never happens in the "coastal" scenarios, but in the "remote MBL" and "Southern Ocean" scenarios it happens in all cases. This effect is caused by feedbacks from the gas phase: the gas phase product of the surface reaction is Cl_2 which photolyzes rapidly to two chlorine radicals. Under non-polluted conditions most Cl radicals react with CH_4 yielding the acid HCl, as do most other reactions of the Cl radical. As the surface reaction is occurring not only on the "mono-disperse" sea salt aerosol but also on aged sea salt particles, most of the Cl_2 – and the resulting HCl - that stems from the surface reaction comes from older, acidified particles. Therefore, the alkalinity produced in Reaction (1) can be exceeded by the uptake of the indirect product of the surface reaction, HCl, that had been

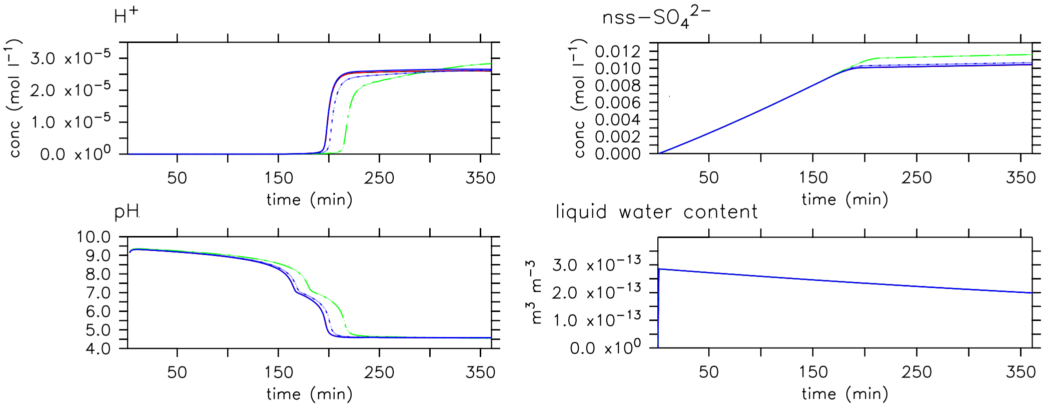

Fig. 3. Same as Fig. (1) but for scenario "remote MBL" in the "mono-disperse" particle bin for r=5 μm.

released from older particles. The net production of alkalinity can therefore be expressed by the number of the Cl radicals produced from Cl_2 that stems from the surface reaction that do not react (e.g. with CH_4) to yield the acid HCl in the gas phase.

In coastal regions the fraction of Cl radicals that do not yield HCl upon reaction – for example with simple alkenes and some biogenic hydrocarbons (Finlayson-Pitts and Pitts, 2000) – is higher than in other marine regions. For the discussion of sea salt acidification, this is, however, only of limited importance, as in these regions usually enough gas phase acidity from anthropogenic sources (e.g. NO_x or SO_2 emissions) is available. Exceptions might be regions where strong alkaline dust plumes are mixed with air masses containing high loadings of e.g. alkenes or biogenic VOCs. In the coastal scenarios presented here, the gas phase acidity is always high enough to rapidly acidify the sea salt particles.

In all model runs with "mono-disperse" sea salt aerosol of r=5 μm the particles get acidified in two steps (see Figs. 3 and 4), which is mainly caused by the large mass of the individual particle. Initially, the S(IV)-oxidation and H^+ production rates are about constant until the HCO_3^- buffer is depleted to about 10^{-3} of its initial concentration (in Fig. 4 after about 170 min.). Then the pH starts to change rapidly - the first step in the acidification – which is drastically slowing down both the S(IV)-oxidation and H^+ production rates. Even though the reaction rate of S(IV) with O_3 is reduced, it is still fast enough to dominate the acidification until finally $[HCO_3^-]$ has been reduced to about 10^{-5} of its initial value (in Fig. 4 after about 207 min), at which point $[HCO_3^-]$ and $[H^+]$ remain constant. Now, the particle is roughly in equilibrium with the gas phase and no further drastic changes in the pH occur. Under the conditions of the scenarios described in this paper, the acidification of the particle is dominated by sulfate production, the uptake of HNO_3 plays only a minor role. Note, that for each molecule of SO_4^{2-}, which is the dominant S(VI)-species under these conditions, being produced from $SO_{2,aq}$, two protons are released. Due to their smaller mass, the absolute amount of HCO_3^- in smaller particles is a lot less, so that the decrease of $[HCO_3^-]$ of 10^{-3} to 10^{-5} of its initial value occurs so rapidly that no stepwise acidification can be observed.

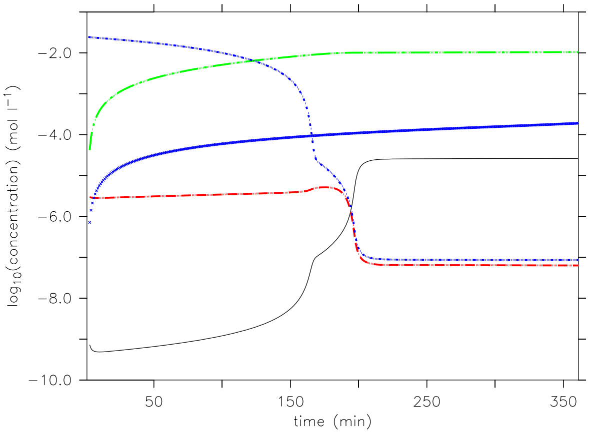

Fig. 4. Temporal evolution of the concentrations of H^+ (black, solid line), HCO_3^- (blue, dotted line), S(IV) (red, dashed line), S(VI) (green, dash-dotted line), and NO_3^- (blue, thick solid line) in run "remote MBL", case 1, r=5 μm. The abscissa is time since model start in minutes.

As already mentioned in the introduction, Laskin et al. (2004) suggested, based on Salvador et al. (2003), that a possible surface enrichment of NO_3^- might provide an in situ source for OH formation through photolysis thereby circumventing gas phase diffusion limitations during uptake for OH. The aqueous phase photolysis of NO_3^- produces not only OH but also OH^- which would neutralize the proton that was released during dissociation of HNO_3. This implies that the surface reaction of OH with Cl^- would be a net source of alkalinity. The concentration of NO_3^- in ocean water is only

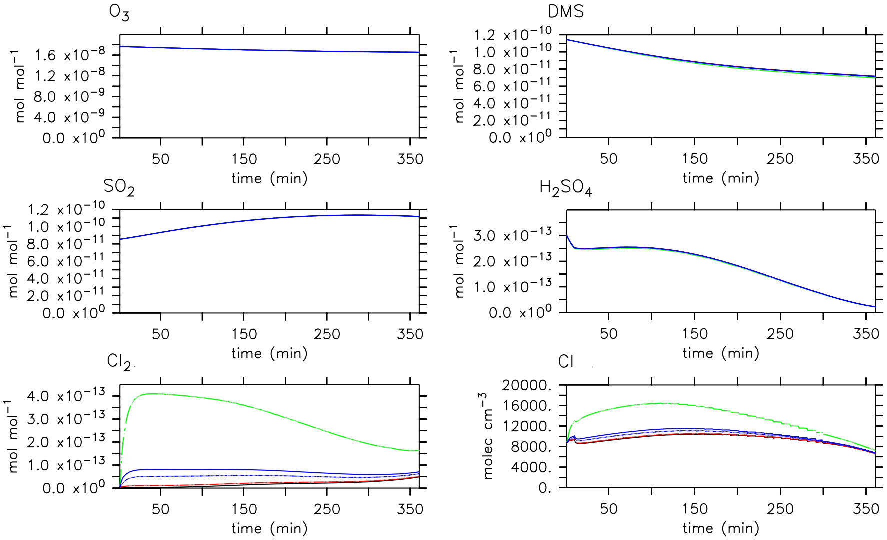

Fig. 5. Temporal evolution of the most important gas phase compounds for scenario 'remote MBL". Case 1 – black, solid line, case 2 – red, dashed line, case 3 – blue, dotted line, case 4 – blue, solid line, case 5 – green, dash-dotted line. Note, that most lines except for Cl_2 and Cl overlap. The abscissa is time since model start in minutes.

about 10^{-6} mol l^{-1}, too small to play any role in airborne sea salt aerosol, therefore the HNO_3 has to come from the gas phase. Then, however, it is also being subjected to gas phase diffusion limitations during uptake. In this case, this effect is not important as the photolysis of NO_3^- is rather slow ($J \approx 4 \times 10^{-7}$ s^{-1}), about a factor of 1/1500 slower than uptake (calculated for r=1 μm). Therefore even a possible increase in the quantum yield of NO_3^- due to a reduced "cage-effect" at the surface would not make this reaction fast enough to be of importance in the early stages of aerosol acidification. Note, that a more recent study showed that contrary to the earlier expectations, NO_3^- does not segregate to the surface but remains in the bulk (Dang et al., 2006).

4 Effects on the chlorine cycle

So far, mainly the aqueous phase products and consequences of Reaction (1) have been discussed. The gas phase product as measured by Knipping et al. (2000) is Cl_2 which rapidly photolyzes to two Cl atoms. Remember that Reaction (1) occurs during daytime only. The main interest in gas phase chlorine in the MBL is for the acidity budget (HCl), the production of HOCl for the aqueous phase oxidation of S(IV), and the oxidation of CH_4, some higher organics and DMS by the chlorine atom.

In the model the increase in gas phase Cl_2 is large, between several ten percent and a factor of 260 in the scenarios discussed here (see Table 4 and Fig. 5) but the mixing ratio remains in all cases below 1 pmol mol^{-1}. This increase, however, is not reflected in a corresponding increase in the Cl atom concentration which, as already mentioned, is the most relevant and reactive inorganic chlorine species; for the "best-guess" case 1 the increase is below 5%. The Cl concentration is on the order of 10^4 molec cm^{-3} for all cases including the one without the surface reaction, which is consistent with most, but not all determinations of chlorine atom concentrations in the MBL (e.g. Wingenter et al., 1996, 1999; Singh et al., 1996), that are all indirect. The reason for this seeming mismatch in the behavior of Cl_2 and Cl is that in the model Cl_2 is only a minor source for Cl atoms, photolysis of BrCl and HOCl and in the coastal scenarios also the reaction of HCl with OH are more important. Therefore it can be concluded that the impact of Reaction (1) on the chlorine budget in the MBL is indeed present but limited. Note, that most additional chlorine in the model stems from the release of the aged sea salt particles and not the "mono-disperse" fresh sea salt aerosol.

5 Conclusions

The surface reaction of OH with chloride on sea salt aerosol was studied with a numerical box model focusing on the time evolution of freshly emitted sea salt particles. Several assumptions for the rate coefficients under different atmospheric conditions were investigated. A discussion of the kinetic limitations of this reaction showed that a unity reaction probability as previously assumed by Laskin et al. (2003) is too high as it ignores gas phase diffusion and a dependency on the chloride concentration and neglects a previous assessment of the rate coefficient Knipping and Dabdub (2002). The photolysis of NO_3^- as an in situ source for OH molecules

Table 4. Maximum relative difference in gas phase Cl_2 and Cl as compared to the respective run without the surface reaction (case 1).

radius		coastal		remote MBL		Southern Ocean	
		ΔCl_2	ΔCl	ΔCl_2	ΔCl	ΔCl_2	ΔCl
0.1 μm	case 2	26%	1.3%	3.8×	1.6%	8.5×	3.4%
	case 3	2.2×	7.0%	14×	7.0%	37×	15.5%
	case 4	3.6×	14.0%	24×	13.0%	29×	7.0%
	case 5	13×	65.0%	110×	62.0%	205×	70.0%
0.6 μm	case 2	37%	1.2%	5.0×	1.4%	10.4×	4.2%
	case 3	3×	7.0%	22×	7.7%	48×	19.0%
	case 4	5.5×	14.0%	36×	12.8%	35×	7.5%
	case 5	23.5×	70.0%	185×	65.0%	260×	85.0%
1.0 μm	case 2	37%	1.2%	4.7×	1.4%	10×	4.0%
	case 3	3×	7.0%	23×	7.8%	48×	18.5%
	case 4	5.5×	14.0%	36×	13.0%	34×	7.4%
	case 5	23.5×	70.0%	185×	65.0%	260×	85.0%
5.0 μm	case 2	35%	1.1%	4.7×	1.3%	9.4×	3.7%
	case 3	2.85×	8.0%	21×	7.2%	45×	17.0%
	case 4	5.5×	15.0%	36×	12.8%	34×	7.0%
	case 5	23×	70.0%	180×	65.0%	245×	78.0%

in the particles could be shown to be unimportant for the delay in acidification.

Laskin et al. (2003) suggested that Reaction (1) might play a major role in the sulfur cycle in the MBL by delaying the acidification (i.e. increasing the buffering time) of sea salt aerosol and therefore allowing the very fast oxidation of S(IV) by O_3 to continue. This study showed that in model runs with realistic rate coefficients for the surface reaction, the additional alkalinity was not sufficient to significantly increase the initial production of S(VI) in fresh sea salt particles.

Some unexpected features and feedbacks could also be observed in the model like a step-wise acidification of larger sea salt particles. Furthermore, the total amount of nss-S(VI) increased esp. for (unrealistically) high reaction rates for the surface reaction. High reaction rates of the surface reaction increase gas phase chlorine. Chlorine, in turn, oxidizes DMS and therefore increases the available amount of sulfur in the MBL.

Outside of polluted regions, where usually significant amounts of gas phase acidity are available anyways, the main product of chlorine reactions in the gas phase is HCl. This reduces the net effect of Reaction (1) on acidity and its main effect is a redistribution of acidity from aged to fresh sea salt particles.

In general, an increase in halogen compounds increases the cycling of sulfur in the MBL. If nss-S(VI) is formed in sea salt aerosol this will speed up the removal of sulfur to the ocean as the lifetime of sea salt aerosol is generally lower than that of sulfate aerosol (see e.g. von Glasow and Crutzen, 2004; Alexander et al., 2005).

One motivation behind the study by Laskin et al. (2003) was to resolve an apparent mismatch in SO_2 and nss-S(VI) between models and measurements which they tried to explain with the surface reaction of OH with Cl^-. In the context of this study, uncertainties in the oxidation mechanism of DMS as e.g. highlighted by Lucas and Prinn (2002, 2005) and von Glasow and Crutzen (2004) or other halogen reactions like the oxidation of DMS by BrO (Toumi, 1994) or the aqueous phase oxidation of S(IV) by hypohalous acids (Vogt et al., 1996) are more likely to explain this mismatch (see also discussion in von Glasow et al., 2002b; von Glasow and Crutzen, 2004).

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