Gas-aerosol relationships of H\textsubscript{2}SO\textsubscript{4}, MSA, and OH:
Observations in the coastal marine boundary layer at Mace Head, Ireland

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[1] Atmospheric concentrations of gaseous sulfuric acid (H\textsubscript{2}SO\textsubscript{4}), methane sulfonic acid (MSA), and hydroxyl radicals (OH) were measured by chemical ionization mass spectrometry (CIMS) during the second New Particle Formation and Fate in the Coastal Environment (PARFORCE) campaign in June 1999 at Mace Head, Ireland. Overall median concentrations in marine background air were 1.5, 1.2, and 0.12 \text{ng/cm\textsuperscript{3}}, respectively. H\textsubscript{2}SO\textsubscript{4} was also present at night indicating significant contributions from nonphotochemical sources. A strong correlation was found between daytime OH and H\textsubscript{2}SO\textsubscript{4} levels in clean marine air suggesting a fast local production of H\textsubscript{2}SO\textsubscript{4} from sulfur precursor gases. Steady state balance calculations of ambient H\textsubscript{2}SO\textsubscript{4} levels agreed with measured concentrations if either very low H\textsubscript{2}SO\textsubscript{4} sticking coefficients (0.02–0.03) or sources in addition to the SO\textsubscript{2}/OH reaction were assumed. Overall, variations in ambient H\textsubscript{2}SO\textsubscript{4} levels showed no correlation with either the tidal cycle or ultrafine particle (UFP) concentrations. However, on particular days an anticorrelation between H\textsubscript{2}SO\textsubscript{4} and UFP levels was occasionally observed providing evidence for the contribution of H\textsubscript{2}SO\textsubscript{4} to new particle formation and/or particle growth. Gaseous MSA concentrations were inversely correlated with dew point temperature reflecting a highly sensitive gas-particle partitioning equilibrium of this compound. The present observations seriously question the general use of MSA as a conservative tracer to infer the relative production yield of H\textsubscript{2}SO\textsubscript{4} from dimethylsulfide (DMS) oxidation. MSA/H\textsubscript{2}SO\textsubscript{4} concentration ratios typically ranged between 0.06 and 1.0 in marine air at ground level. Measured diel OH profiles showed a significant deviation from concurrent variations of the ozone photolysis frequency. They also showed up to 1 order of magnitude lower values compared to OH concentrations calculated with a simple photochemical box model. These differences were most pronounced during particle nucleation events occurring on sunny days around noon and at low tide. The present results suggest that both the oxidation capacity and the particle formation potential in the coastal boundary layer were significantly affected by reactions of unknown compounds prevailing in this type of environment.

INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere-composition and chemistry; KEYWORDS: gas-to-particle conversion, hydroxyl radical, sulfuric acid, methane sulfonic acid, coastal marine boundary layer


1. Introduction

[2] Nucleation theory predicts that gaseous sulfuric acid is a direct precursor and major source of atmospheric submicrometer sulfate particles [Kulmala et al., 2000a, 1998; Jaeger-Voirol and Mirabel, 1989; Shaw, 1989; Doyle, 1961]. Within a size range of approximately 0.1–1 \text{µm} diameter these particles can effectively reduce incoming solar radiation, either by direct backscattering (direct forcing) or by increasing cloud albedo (indirect forcing) [Schwartz, 1996; Kiehl and Briegleb, 1993; Charlson et al., 1987]. However, present estimates are still uncertain with respect to both the contribution of H\textsubscript{2}SO\textsubscript{4} to new particle formation and the magnitude of the sulfate-induced climate forcing [Kulmala et al., 2000a, 1998; Schwartz...
and Andrae, 1996; Intergovernmental Panel on Climate Change (IPCC), 1996]. A major reason for these uncertainties is the paucity of sensitive and time-resolved measurements of atmospheric HSO₄ concentrations which have become possible only in recent years with the development and application of chemical ionization mass spectrometry (CIMS) [Berresheim et al., 2000, 1995b, 1993; Weber et al., 1999, 1998, 1997; Reiner et al., 1998; Jefferson et al., 1998; Tanner et al., 1997; Eisele and Tanner, 1993, 1991; Arnold and Fabian, 1980].

[3] Present model calculations suggest that new particle formation in the marine boundary layer (MBL) is primarily induced by HSO₄ condensation in conjunction with water vapor and at least one more (stabilizing) compound such as ammonia, NH₃ (ternary nucleation theory) [Korhonen et al., 1999; Weber et al., 1999; Marti et al., 1997; Van Dingenen and Raes, 1993]. The dominant source of HSO₄ in the background MBL is believed to be oxidation of dimethyl sulfoxide (CH₃S(O)₂; DMS) by the hydroxyl radical (OH) yielding different intermediate and end products such as SO₂, dimethyl sulfone, methane sulfonic acid, and HSO₄ methan sulfonic acid, dimethyl sulfone, respectively [Davis et al., 1991; Sorensen et al., 1996; Berresheim et al., 1995a]. The fractional yield of HSO₄ as an end product of DMS oxidation depends critically on temperature and atmospheric NOₓ (= NO + NO2) and HOₓ (=OH + HO2) levels and on the scavenging of SO₂ by sea salt or cloud droplets. In the marine boundary layer a significant fraction of sulfate-containing submicrometer particles may also be produced by mechanical breakup of sea-salt particles [O’Dowd et al., 1997]. Therefore concurrent measurements of HSO₄ concentrations and of aerosol size spectra and chemical composition are required to reveal the relative contribution of both sources (HSO₄ production and sea-salt fractionation) to the submicrometer particle budget in the MBL. Methane sulfonic acid (CH₃(SO₂)OH; MSA) also has some potential of contributing to new particle formation. However, its saturation vapor pressure with respect to the aqueous phase is about 10⁻²⁸ mmHg [Kreidenweis and Seinfeld, 1988; Hoppel, 1987].

[4] Measurements of OH concentrations are highly desirable to provide a better understanding of both atmospheric photochemical processes and particle nucleation mechanisms and a better precision in corresponding model simulations. Recently, O’Dowd et al. [1999] reported OH measurements in the MBL at Mace Head indicating a correlation between atmospheric OH levels and newly formed ultrafine particle (UFP, 3–10 nm diameter) concentrations. If corroborated by further measurements, this relationship may also have general implications for the atmospheric oxidation capacity in the coastal marine environment.

[5] The EU-funded project New Particle Formation and Fate in the Coastal Environment (PARFORCE) was specifically designed to study the occurrence and mechanin of new particle formation in coastal marine air including measurements of a broad range of both aerosol and gas phase related parameters (see the overview article by O’Dowd et al. [2002a]). The atmospheric chemistry research division of the German Weather Service (Deutscher Wetterdienst, DWD) participated in the 1999 June campaign of project PARFORCE at Mace Head, Ireland (53°20’N, 9°54’W). Atmospheric OH, HSO₄, and MSA concentrations were measured in real time to address the aforementioned scientific objectives. In this paper we present the corresponding results and evaluate observed variations in OH, HSO₄, and MSA concentrations in relation to the occurrence and intensity of particle nucleation events, aerosol number concentrations and chemical composition, and meteorological processes.

2. Experiment

[6] Atmospheric HSO₄, MSA, and OH concentrations were measured by chemical ionization mass spectrometry (CIMS) based on methods previously developed by Tanner et al. [1997] and Eisele and Tanner [1993]. The system was installed and shipped to the Mace Head station in a mobile field laboratory (container owned by DWD). To minimize direct sampling of sea spray, the container was deployed on a small hill approximately 300 m from the shoreline (near the Mace Head cottage laboratory). All three compounds were measured continuously between June 5 and 30 (JD 156–181) with short interruptions due to maintenance or rain. The DWD system and its present performance have been described in detail by Berresheim et al. [2000]. A brief outline of the measurement techniques is given here. Ambient air is sampled at 10 L min⁻¹ into the ion reaction region of the system where neutral sample molecules are ionized at atmospheric pressure by charge transfer reactions with NO₃ core ions. The NO₃ ions are produced in a separate sheath gas by a radioactive ²¹⁴Am source and are subsequently focused by electrical fields to the sample flow axis. HSO₄ and MSA molecules directly react with NO₃ yielding the corresponding HSO₄⁻ and MSA⁻ product ions. To measure OH, excess ³⁴SO₂ is added to the sample flow before the ionization region. The SO₂ completely titrates the sampled OH within approximately 20 ms producing heavy isotope H₃₂SO₄⁻ molecules which in turn react with NO₃ to produce H₄SO₄⁻ product ions. These differ from the H₅SO₄⁻ ions derived from ambient HSO₄ by two mass units. However, for specific studies explained in detail in the next section, ³₂SO₂ was occasionally used as OH titrant gas. The OH background signal is produced by adding high-purity propane to the sample air/SO₂ mixture such that all OH is now scavenged by reaction with propane instead of SO₂. With only ³₂SO₂ present in the mixture the corresponding signal should be equal to the H₄SO₄⁻ signal contributed from ambient HSO₄. A fraction of the remaining NO₃⁻ ions and the newly formed product ions are forced by electrical fields through a 200 μm diameter aperture into a differentially pumped vacuum region where they are first stripped of neutral ligand molecules, then mass-filtered by a quadrupole (at approximately 2 × 10⁻⁵ hPa pressure), and finally detected by an electron multiplier. The individual concentrations of HSO₄, MSA, and OH are determined from the corresponding product ion to NO₃⁻ signal ratios and a calibration factor which is valid for all three components. F was frequently determined during the campaign using a calibration unit which emits filtered UV light at λ = 185 nm into the airflow in front of the sample tube. The UV light photolyses ambient air water vapor yielding concentrations of OH in the 10⁻¹⁰–10⁻⁹ molecules cm⁻³ range which are calculated based on the known H₂O absorption cross section [Cantrell et al., 1997] and concurrent measurements of [H₂O] using a chilled mirror dew point hygrometer (Michell Instruments). At 5 min signal integration the overall 2 σ precisions, accuracies, and detection limits for the HSO₄ and MSA measurements are 30%, 39%, and 3 × 10⁴ molecules cm⁻³, and for the OH measurements are 48%, 54%,
and $5 \times 10^6$ molecules cm$^{-3}$, respectively [Berresheim et al., 2000]. H$_2$SO$_4$, MSA, and OH concentrations were measured at 30 s time resolution. H$_2$SO$_4$ and OH were measured in alternating cycles. Since our primary objective was to study the relationship between H$_2$SO$_4$ and UFP number concentrations, H$_2$SO$_4$ was measured in the first part of the campaign (June 5–11; JD 156–162) for up to 55 min h$^{-1}$, and OH was measured for only 5 min h$^{-1}$. Thereafter, the measurement strategies were varied as follows: June 11–16 (JD 162–167): H$_2$SO$_4$ continuous, no OH measurements; June 17 (JD 168): H$_2$SO$_4$ and OH measurements alternating at 30 s intervals; June 18–19 (JD 169–170): rain, no measurements; June 20–25 (JD 171–176): H$_2$SO$_4$ and OH measurements alternating at 5 min intervals; June 26–30 (JD 177–181): H$_2$SO$_4$ and OH measurements alternating at 30 s intervals. MSA was always measured in conjunction with either H$_2$SO$_4$ or OH. For OH titration, $^{33}$SO$_2$ was used instead of $^{34}$SO$_2$ between June 21 and 28 (JD 172–179).

Ancillary measurements included meteorological parameters, ozone photolysis frequency $j_{O(1D)}$ (filter radiometry; Meteorologie Consult), and ambient concentrations of NO and NO$_2$ (model 42 chemiluminescent analyzer, Thermo Environmental and Scintrex LMA-3 analyzer, respectively). Ambient SO$_2$ was measured by an instrument system [Hansson et al., 2000] using wetted parallel plate denuders (PPD) similar to the one described by Dasgupta et al. [1997]. The PPD was coupled on-line to ion chromatography for analysis of atmospheric HNO$_3$ and SO$_2$ as nitrate and sulfate ions, respectively. With time resolution of 20 min the detection limits for both gases were 6 parts per trillion by volume (pptv; 1 pptv = 2.67 x $10^6$ molecules cm$^{-3}$ at 0°C, 1013 hPa). The system has been tested for memory effects and for losses of both gases in the sampling line. The total error of the SO$_2$ analysis is estimated to be 50% at ambient levels <60 pptv and 20% above 60 pptv. Additional losses in the sampling line due to sea spray interferences were found to correspond to ≤40 pptv.

3. Results and Discussion

3.1. H$_2$SO$_4$

Figure 1a shows the results of the H$_2$SO$_4$ measurements for the whole campaign period, and a statistical summary is given in Table 1. Overall, H$_2$SO$_4$ concentrations in marine air masses were comparable to previous observations at Cheeka Peak, a coastal research station at similar latitude (48°18′N, 124°37′W) on the U.S. Pacific coast [Berresheim et al., 1993; Eisele and Tanner, 1993]. The measured values showed a regular diurnal cycle consistent with the photochemical production of H$_2$SO$_4$. In marine air the average noontime maximum was $1.0 \times 10^7$ cm$^{-3}$, and nighttime values were low but still significant (average: $0.9 \times 10^6$ cm$^{-3}$; Table 1). In polluted air, concentrations as high as $1.1 \times 10^7$ cm$^{-3}$ were measured. The extremely high concentrations on June 24 and June 25 (JD 175 and 176; Figure 1a) were probably caused by local sulfur emissions from domestic peat fires in nearby residences. This is supported by concurrently observed high NO$_x$ and CO levels. The short midday pollution episode on June 28 (JD 179) was due to emissions from the C-130 research plane crossing over Mace Head at low level.

The diurnal cycle of H$_2$SO$_4$ showed no general correlation in time with the tidal cycle, and thus with particle nucleation events which occurred almost exclusively during low tide [O’Dowd et al., 2002a, 2002b]. A detailed inspection of the corresponding data sets was carried out to check for a possible relationship between short-term variations of H$_2$SO$_4$ and UFP concentrations. Two examples are shown in Figure 2 presenting a close-up view of high time-resolution measurements of H$_2$SO$_4$ and total particle concentrations (>3 nm diameter), the latter measured with the UCPC instrument at the cottage laboratory. The data were recorded during a strong and a weak nucleation event (June 12 (JD 163) and June 17 (JD 168), respectively), both occurring at low tide. From the differential measurements at the shore laboratory (particles in the size range between 3 and 10 nm diameter) it can be concluded that the particle size spectrum was dominated by UFP during both events. On June 12 (Figure 2a) the highest particle concentrations (7–8 $\times 10^5$ cm$^{-3}$) were observed between 950 and 1000 UTC coinciding approximately with mid low-tide conditions. During the main particle formation event, H$_2$SO$_4$ concentrations were still relatively low (2–3 $\times 10^6$ cm$^{-3}$), while UFP levels were extremely high compared to noontime values. Figure 2a demonstrates that under such conditions an anticorrelation between both H$_2$SO$_4$ and UFP levels may be detectable, e.g., in this case at 920, 955, 1020, and 1040 UTC. These observations provide some evidence for the participation of H$_2$SO$_4$ in new particle formation and/or particle growth. However, for the whole period between 9 and 11 UTC the anticorrelation between both data sets was statistically weak ($r = 0.27$, $n = 120$). Corresponding data analyses for other event periods
in which \( H_2SO_4 \) concentrations were relatively higher and UFP levels relatively lower showed little or no indications for a relationship between both data sets (Figure 2b). For the total campaign period we conclude that (1) elevated \( H_2SO_4 \) concentrations alone were not sufficient to trigger detectable UFP formation, the latter being strongly correlated with the occurrence of low tide [O’Dowd et al., 2002a, 2002b] and (2) short-term variations in \( H_2SO_4 \) and UFP levels showed no systematic relationship during particle nucleation events. These results are consistent with current model interpretations suggesting that \( H_2SO_4 \) was the dominant precursor for newly formed particles, yet the growth of these particles into detectable sizes above 3 nm diameter was dominated by the agglomeration of one or more unknown (possibly organic) compounds [Kulmala et al., 2002; O’Dowd et al., 1999].

To better understand the importance of \( H_2SO_4 \) in the new particle formation process, it is instructive to compare measured and calculated \( H_2SO_4 \) concentrations. On the basis of such a comparison, Birmili et al. [2000] estimated a rate for the turnover of \( H_2SO_4 \) molecules into new particles on the order of \( 10^4 \) molecules cm\(^{-3}\)/s for nucleation events observed at Hohenpeissenberg, Germany. This “\( H_2SO_4 \) nucleation loss rate,” \( J_{H2SO4} \), was considered equivalent to an estimated particle production rate of 3 particles cm\(^{-3}\)/s. In the following, we will take a similar approach by assuming a steady state balance between the \( SO_2 + OH \) reaction as the only source and condensation to the existing aerosol surface as well as new particle formation as the only sinks of \( H_2SO_4 \):

\[
k[SO_2][OH] = k_{CS}[H_2SO_4] + J_{H,SO_4},
\]

where \( k = 8.5 \times 10^{-13} \) cm\(^3\)/molecule\(^{-1}\)/s\(^{-1}\) at 298 K [DeMore et al., 1997]. The pseudo first-order rate constant \( k_{CS} \) for the \( H_2SO_4 \) condensational sink is calculated by the Fuchs-Sutugin equation [Fuchs and Sutugin, 1970] using the measured aerosol size distribution, corrected for ambient humidity conditions by a particle growth factor (g.f., equal to ratio of ambient “wet” to measured “dry” particle diameter). A critical parameter in the expression for \( k_{CS} \) is the \( H_2SO_4 \) accommodation coefficient \( \alpha \) which has a value \( \leq 1 \). The concept of condensation sink and the effect of the \( H_2SO_4 \) accommodation coefficient \( \alpha \) on it have been investigated in more detail by Kulmala et al. [2000b] and Dal Maso et al. [2002]. The condensation sink is significantly smaller if \( \alpha < 1 \). However, theoretical studies indicate that \( \alpha \) is typically near unity [Clement et al., 1996].

<table>
<thead>
<tr>
<th>Compound Statistics</th>
<th>All Data</th>
<th>24-Hour(^a)</th>
<th>Minimum, Night(^c)</th>
<th>Maximum, Day</th>
</tr>
</thead>
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<tr>
<td><strong>H2SO4</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median</td>
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<td>1.46</td>
<td>0.84</td>
<td>10.14</td>
</tr>
<tr>
<td>Mean</td>
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<td>2.60</td>
<td>0.90</td>
<td>10.42</td>
</tr>
<tr>
<td>s.d.</td>
<td>7.80</td>
<td>2.50</td>
<td>0.44</td>
<td>3.92</td>
</tr>
<tr>
<td>( n ) (5 min)</td>
<td>3371</td>
<td>1764</td>
<td>784</td>
<td>16</td>
</tr>
<tr>
<td><strong>MSA</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>0.80</td>
<td>1.20</td>
<td>0.35</td>
<td>5.58</td>
</tr>
<tr>
<td>Mean</td>
<td>1.82</td>
<td>2.10</td>
<td>1.01</td>
<td>8.51</td>
</tr>
<tr>
<td>s.d.</td>
<td>2.65</td>
<td>2.86</td>
<td>1.60</td>
<td>6.45</td>
</tr>
<tr>
<td>( n ) (5 min)</td>
<td>4868</td>
<td>2405</td>
<td>1025</td>
<td>21</td>
</tr>
<tr>
<td><strong>OH</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median</td>
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<td>0.12</td>
<td>−0.14</td>
<td>2.51</td>
</tr>
<tr>
<td>Mean</td>
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<td>0.49</td>
<td>−0.11</td>
<td>2.64</td>
</tr>
<tr>
<td>s.d.</td>
<td>2.12</td>
<td>0.80</td>
<td>0.18</td>
<td>0.49</td>
</tr>
<tr>
<td>( n ) (5 min)</td>
<td>1176</td>
<td>488</td>
<td>318</td>
<td>11</td>
</tr>
</tbody>
</table>

\(^a\) Units are in \( 10^6 \) molecules cm\(^{-3}\); s.d., standard deviation; \( n \), number of data.

\(^b\) Only days without major data gaps.

\(^c\) Time, 2100-0300 UTC.

Table 1. Statistical Summary of the 5-Minute Integrated Concentrations Measured at Mace Head, June 5–30, 1999\(^a\)

![Figure 2a](image1.png)

**Figure 2a.** High-time resolution (1 min) fluctuations of aerosol particle concentrations (>3 nm diameter; UCPC) and concurrently measured \( H_2SO_4 \) and MSA molecular concentrations on (a) June 12 and (b) June 17, 1999. Data are shown for periods when new particle formation events occurred at low tide.
calculated $\text{H}_2\text{SO}_4$ values were consistently lower than the measured values by approximately 1 order of magnitude which according to equation (1) would correspond to a negative $J_{\text{H}_2\text{SO}_4}$. Even considering maximum uncertainty estimates for $[\text{OH}]$, $[\text{SO}_2]$, and $k_{\text{CS}}$, the resulting negative differences between calculated and measured $\text{H}_2\text{SO}_4$ concentrations are still large. A major error resulting from a systematic undermeasurement of OH concentrations can be excluded due to frequent calibrations and extensive tests of the CIMS technique before and during the field campaign. Also, this would have resulted in an equal undermeasurement of $\text{H}_2\text{SO}_4$, and thus a corresponding error in the $\text{H}_2\text{SO}_4$ balance calculation (equation (1)) would have cancelled out. As shown in Figures 3a and 3b, the measurements can be approximately matched using very low $\text{H}_2\text{SO}_4$ accommodation coefficients in the range of $\alpha = 0.02 - 0.03$. This would correspond to atmospheric lifetimes of $\text{H}_2\text{SO}_4$ between 50 and 110 min with respect to aerosol scavenging ($1/k_{\text{CS}}$). Previous laboratory studies suggested $\alpha$ values lower than 1, especially in the presence of organic aerosol particles or inorganic particles coated by organic films ($\alpha = 0.2 - 0.8$ [Jefferson et al., 1997]; $\alpha = 0.02 - 0.09$ [Van Dingenen and Raes, 1991]). Thus we believe the choice of $\alpha$ represents the largest uncertainty in our present calculations preventing an estimate for $J_{\text{H}_2\text{SO}_4}$, by the simple approach taken here. It is possible that $\alpha$ covers a large range of values depending on the chemical nature of the aerosol surface which may strongly determine the corresponding $\text{H}_2\text{SO}_4$ uptake efficiency. However, based on the recent critical literature and model evaluation of this subject by Clement et al. [1996] and our own observations discussed in the following sections, we conclude that $\alpha$ values for $\text{H}_2\text{SO}_4$ as low as in Figure 3 were rather unlikely and atmospheric $\text{H}_2\text{SO}_4$ lifetimes were much shorter than estimated here with respect to the marine aerosol prevalent at Mace Head.

[12] It is conceivable that $\text{H}_2\text{SO}_4$ may have had major sources in addition to the $\text{SO}_2+\text{OH}$ reaction which have not been accounted for in equation (1). This is also supported by the significant presence of $\text{H}_2\text{SO}_4$ at night during most of the measurement period (average: $0.9 \times 10^6 \text{ cm}^{-3}$; Figure 1a and Table 1). In contrast, nighttime OH levels were below the detection limit (for a discussion of the slightly negative nighttime OH signals, see Berresheim et al. [2000]). Significant contributions to $\text{H}_2\text{SO}_4$ from the reaction of $\text{SO}_2$ with an oxidant other than OH have also been observed in continental air at Hohenpeissenberg, Germany [Berresheim et al., 1999]. The presence of this unknown oxidant in ambient air can be detected by using $^{32}\text{SO}_2$ instead of $^{34}\text{SO}_2$ for the OH measurement. As explained in section 2, the OH background signal should then equal the signal obtained from measuring ambient $\text{H}_2\text{SO}_4$. However, relatively higher signals were often recorded at Hohenpeissenberg with the observed signals showing a maximum difference around nighttime. We speculate that ozone reactions with unsaturated hydrocarbons may be responsible for this contribution, perhaps via the formation of intermediate stable Criegee biradicals which could oxidize $\text{SO}_2$ to $\text{H}_2\text{SO}_4$ [Horie and Moortgat, 1991; Cox and Penkett, 1972, 1971]. Preliminary tests in our home laboratory have shown that this source could explain the observed nighttime $\text{H}_2\text{SO}_4$ levels and may contribute as much as 20% to the corresponding maximum daytime levels. In the marine environment, similar processes may exist, perhaps involving different hydrocarbons and resulting oxidant species. During the 1999 PARFORCE campaign, $^{32}\text{SO}_2$ was used as titrant gas between June 21 and 28

**Figure 3.** Measured (solid line) and calculated (dashed lines) concentrations of $\text{H}_2\text{SO}_4$ shown for coastal atmospheric background conditions on (a) June 17 and (b) June 27, 1999. Steady state calculations of $\text{H}_2\text{SO}_4$ were based on equation (1) assuming different values for the $\text{H}_2\text{SO}_4$ sticking coefficient $\alpha$, a negligible $\text{H}_2\text{SO}_4$ nucleation loss rate ($J_{\text{H}_2\text{SO}_4} = 0$), measured particle size distributions (corrected for ambient relative humitudes), and (c) measured $\text{SO}_2$ (mixing ratio in parts per trillion by volume (pptv)) and OH concentrations. The measured profiles were approximated using $\alpha = 0.03$ (Figure 3a) and $\alpha = 0.02$ (Figure 3b), respectively (see text for further details). On both days, new particle formation events occurred around midday hours.

[11] For practical reasons, we first assume $J_{\text{H}_2\text{SO}_4} = 0$ in equation (1) and calculate the $\text{H}_2\text{SO}_4$ concentrations from the ratio $k[\text{SO}_2][\text{OH}]$/$k_{\text{CS}}$ using the corresponding measured $\text{SO}_2$ and OH concentrations. Any exceedence of the measured by the calculated $\text{H}_2\text{SO}_4$ values may then be interpreted as the fraction of $\text{H}_2\text{SO}_4$ which has been transformed into new particles corresponding to a positive nonzero value of $J_{\text{H}_2\text{SO}_4}$. Typical examples for the results obtained from the 1999 PARFORCE campaign are shown in Figures 3a and 3b for June 17 (JD 168) and June 27 (JD 178). Best estimates for the corresponding g.f. values were used in the calculations, and $\alpha$ was varied from 0.01 to 1. The results obtained for $\alpha = 1$ are in sharp contrast to previous field studies in which the measured $\text{H}_2\text{SO}_4$ concentrations were either matched or exceeded by the calculated values assuming $\alpha = 1$ [Birmili et al., 2000; Weber et al., 1997]. For the present measurements in the coastal marine atmosphere at Mace Head the corresponding
signal differences and also a significant diel variation. At night this contributed to nighttime contributions by the reaction of SO₂ with the nitrate radical (NO₃) are considered to be negligible. This reaction would have yielded H₂SO₄ levels of less than 2.5 × 10¹⁰ cm⁻³ assuming an ambient NO₃ concentration of 1 × 10⁻⁴ cm⁻³ [Allan et al., 2000] and a corresponding reaction rate constant <1 × 10⁻¹⁶ cm³ s⁻¹ [Atkinson et al., 1997].

Similar results were obtained on most other days of the campaign. However, one major exception was the night of June 23–24 (JD 174–175) when man-made fires were visible in the larger vicinity of Mace Head and ambient SO₂ concentrations increased to more than 5 × 10¹⁰ cm⁻³ [Hansson et al., 2000]. As shown in Figure 4b, the corresponding ambient H₂SO₄ levels also increased and even more so the OH background signal such that the difference in the respective H₂SO₄ values reached a maximum of 8 × 10⁶ cm⁻³ at 110 UTC. These observations indicate that anthropogenic sources may significantly amplify non-OH oxidation of SO₂.

[13] Introducing an additional source term in equation (1) representing the reaction of SO₂ with the unknown oxidant may perhaps explain the observed nighttime H₂SO₄ levels in coastal background air but not the large differences obtained between calculated and measured daytime H₂SO₄ concentrations assuming α = 1 (Figures 3a and 3b). Based on our present knowledge of typical concentrations of atmospheric sulfur compounds [e.g., Berresheim et al., 1995a], halogen radicals [Carpenter et al., 1999; Rudolph et al., 1996; Keene et al., 1996], and reaction rate constants [DeMore et al., 1997] pertinent to daytime background MBL conditions we conclude that significant contributions to the observed H₂SO₄ levels in addition to the SO₂+OH reaction may have only derived from the oxidation of dimethyl disulfide (DMDS) or DMS by OH or possibly BrO [Grenfell et al., 1999] yielding intermediate products other than SO₂, such as, e.g., SO₃ which rapidly combines with water vapor to H₂SO₄ [Lin and Chameides, 1993]. For example, by assuming α = 1 and J₃H₂SO₄ = 0 and introducing k'[DMDS]/OH as a second source term into equation (1) we can estimate the DMDS concentration required to obtain agreement between calculated and measured H₂SO₄ concentrations. In the case of June 17 (JD 168) a DMDS mixing ratio of 3.5 ± 1 pptv would be sufficient to match the difference between measured and calculated H₂SO₄ concentrations shown in Figure 3a (based on k2 = 2.4 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ at 289 K [DeMore et al., 1997]). Of course, this is a minimum estimate since it implicitly assumes a 100% yield of H₂SO₄ from the reaction of DMDS with OH and no major formation of SO₃ as an intermediate product. However, on the basis of measured values of α = 0.3–0.7 [Jefferson et al., 1997] and DMDS levels up to 2.5 pptv (measured at Mace Head in September 1998 [Grenfell et al., 1999]) it appears that DMDS oxidation could have significantly contributed to the H₂SO₄ concentrations observed in coastal marine air. Additional contributions from H₂S or CS₂ are unlikely since both compounds are oxidized by OH to form SO₂ as the dominant intermediate product [Berresheim et al., 1995a]. Also, elevated H₂S emissions during low tide would have produced a tidal pattern in the H₂SO₄ diel cycle, which, however, was not observed. Previously, Jefferson et al. [1998] measured H₂SO₄ and OH at a coastal site in Antarctica. They could explain only 12% of the observed H₂SO₄ assuming that the only source of H₂SO₄ was OH oxidation of SO₂ derived from DMS. They also speculated that DMDS oxidation may have significantly contributed to the observed H₂SO₄ levels.

[14] Finally, as further discussed in the next section, our
measurements do not indicate a major downward transport of 
H$_2$SO$_4$ into the MBL from upper altitudes. All H$_2$SO$_4$ data 
were systematically analyzed for possible short-term correla-
tions with dew point temperature, wind direction, $j_{O(1D)}$ and 
SO$_2$, MSA, and OH concentrations. On most days, H$_2$SO$_4$
levels were photochemically driven and correlated mainly with 
SO$_2$, OH, and $j_{O(1D)}$. Occasionally, satellite peaks of H$_2$SO$_4$
were observed in the morning or late afternoon hours on type 
I or type II days (e.g., at 900 UTC on June 27, Figures 3b and 
4a). These could largely be explained by elevated SO$_2$ levels 
which in turn did not appear to originate from upper altitudes 
but possibly from ships passing by offshore. However, between 
1317 and 1327 UTC on June 28 (JD 179), ground-level H$_2$SO$_4$
concentrations increased sharply from background values of 
$1 \times 10^7$ cm$^{-3}$ to $5 \times 10^7$ cm$^{-3}$ during a low-level over-
flight of the C-130 research plane over the station (flight altitude 
approximately 50 m).

3.2. MSA

[15] Gaseous MSA concentrations were relatively high 
compared to H$_2$SO$_4$ (Figure 1b) and previously measured val-
ues near the U.S. Pacific coast [Berresheim et al., 1993; Eisele 
and Tanner, 1991]. The overall median concentration ($0.8 \times 
10^6$ cm$^{-3}$) was only about a factor of 2 lower than the corre-
sponding H$_2$SO$_4$ value, and selecting only type I and type II 
days, the median MSA/H$_2$SO$_4$ concentration ratio was as high 
as 0.82 (Table 1). Like H$_2$SO$_4$, MSA reached maximum levels 
on most days around midday and was still significantly present 
at night (in the $10^5$ cm$^{-3}$ range).

[16] Average hourly MSA/H$_2$SO$_4$ ratios were calculated for 
all type I and type II days and are shown in Figure 5. In this 
figure the corresponding average values for each hour have 
been compiled to produce a composite diel profile of the MSA/
H$_2$SO$_4$ ratio for clean air conditions. The results ranged from 
approximately 0.06 to 1.0 with the highest values occurring in 
late afternoon and evening hours (17–24 UTC). In some 
nights, short-term peaks with ratios up to 12 were observed. By 
comparison, aerosol fine particle MS$^+$/NS$^-$ ratios showed a 
similar range (0–0.8) on type I and II days. However, a diel 
variation corresponding to that of the gas phase ratios was not 
observed. The conspicuous increase of the MSA/H$_2$SO$_4$ ratio 
during late daytime hours resulted from decreasing H$_2$SO$_4$ and 
concurrently increasing MSA concentrations. At other times, 
MSA levels dropped almost instantaneously to very low values, 
even during midday hours. A corresponding example is shown 
in Figure 6 including diel variations of both MSA and the dew 
point temperature (top panel). Clearly several periods can be 
identified exhibiting a strong anticorrelation between MSA 
and dew point levels. As previously observed in the coastal 
environment of Antarctica [Davis et al., 1998; Jefferson et al., 
1998], fluctuations in ground-level dew point temperature of 
several degrees Celsius over periods of <2 hours may be in-
dicative for turbulent vertical exchange of lower MBL air (rela-
tively moist) with upper MBL or free tropospheric air (rela-
tively dry). On such occasions, strong variations in MSA/ 
H$_2$SO$_4$ ratios comparable to the present results were observed 
in the coastal atmosphere of Antarctica (Palmer Station, 
64°46′S, 64°03′W), not only during daytime but also at night. 
Davis et al. [1998] concluded that a significant fraction of MSA 
measured at surface level was produced from DMS oxidation.
at higher altitudes and entrained into the lower MBL by intensive vertical mixing due to wind shear and/or jumps in thermodynamic stability between different layers.

[17] During the June 1999 campaign at Mace Head, ambient MSA levels were often highly variable including nighttime. Generally, rapid changes in the boundary layer structure were observed [Kunz et al., 2002; de Leeuw et al., 2002] which could have induced this high variability in MSA levels. On some days the photochemically driven diel pattern of MSA was so disturbed that it became unrecognizable, e.g., on June 28 (JD 179) and June 29 (JD 180) as shown in Figure 6. On both of these days, strong MSA peaks coincident with significant dew point temperature minima were observed at 1030 UTC and 1300 UTC on June 28, and between 630 and 740 UTC on June 29 (Figure 6). Under daylight conditions some of the short-term peaks in the MSA concentration also indicated a positive correlation with global irradiance and air temperature (e.g., at 1300 UTC on June 28, and between 700 and 800 UTC on June 29) reflecting a corresponding fluctuation in cloud coverage over the area. Under such conditions, with dew point (and relative humidity) values decreasing and ambient temperature increasing, atmospheric gaseous MSA concentrations may have been enhanced by both photochemical formation as well as direct evaporation of MSA from aerosol particles. This leads to the conclusion that the partitioning of MSA between the gas and liquid/aerosol phase was very sensitive to ambient relative humidity and temperature. Short-term changes in the corresponding MSA vapor pressure were probably responsible for the considerable fluctuations in MSA levels observed at night and overlapped with photochemical production of MSA at daytime.

[18] Other “nonphotochemical” variations observed in ambient MSA levels, in particular during episodes lasting longer than about 2 hours, resulted from large-scale mixing of different air masses in association with synoptic frontal systems. One example is shown in Figure 6 for 1450 UTC on June 28. At that time a warm front over the open ocean approaching Ireland pushed relatively moist air into the study area, and the local horizontal wind direction changed within just 10 min from about 280° to 200°. Thereafter, the wind direction progressively changed back to westerly and northwesterly (300°) flow with dew point levels decreasing again and MSA concentrations steadily increasing to maximum values occurring between 1800 and 1900 UTC. Two explanations for the observed changes in MSA levels during this episode may seem likely: (1) The ocean area to the southwest of Mace Head produced significantly lower emissions of DMS resulting in lower atmospheric MSA concentrations than over areas in WNW direction, and/or (2) gaseous MSA was more efficiently scavenged in the relatively moist southwesterly air by wet deposition to particles and the sea surface.

[19] In contrast to MSA, gaseous H$_2$SO$_4$ concentrations were not significantly elevated when the dew point temperature decreased. As mentioned earlier, MSA has a much higher saturation vapor pressure than H$_2$SO$_4$. Consequently, MSA is expected to have a lower loss rate due to aerosol scavenging and a higher atmospheric lifetime in the gas phase compared to H$_2$SO$_4$. Also, MSA should condense preferably on larger aerosol particles than H$_2$SO$_4$ which indeed has been corroborated by previous measurements of the particle size distributions of the respective ionic components methanesulfonate (MS$^-$) and non-sea-salt sulfate (NS$_{2}$SO$_4$) in aerosol particles [e.g., Pszenny, 1992]. Assuming a value of 0.12 for MSA [De Bruyn et al., 1994] and 0.5 for H$_2$SO$_4$, Jefferson et al. [1998] estimated the MSA lifetime to be 4–7 times longer than that of H$_2$SO$_4$. Applying the same values to our PARFORCE data set, we calculate respective lifetimes of 20–40 min for MSA and 3–10 min for H$_2$SO$_4$ in the coastal marine atmosphere of Mace Head.

[20] On the basis of only the results obtained from our stationary ground-level measurements it is not possible to quantitatively distinguish between individual contributions to gaseous MSA levels from horizontal and vertical mixing processes (ranging over microscales, mesoscales, and synoptic scales), gas/particle partitioning, and photochemical production from DMS oxidation. The complex overlap of these different processes (including intermittent precipitation and fog episodes) may also explain the total lack of correlation found between the MSA and aerosol MS$^-$ concentrations (r = 0.0; see Allen et al. [2000] for preliminary results of the aerosol ion measurements during the PARFORCE campaign). On the other hand, as shown in Figures 2a and 2b, some direct evidence was found for short-term anticorrelations between MSA and UFP levels indicating a contribution of MSA to (most likely) UFP growth, however, to a lesser extent than in the case of H$_2$SO$_4$. Also, a strong positive correlation between MSA and H$_2$SO$_4$ variations was found for the period of the intensive particle event on June 12 (Figure 2a: r = 0.95). During the less intensive event on June 17 the correlation was relatively weaker, yet still significant (Figure 2b: r = 0.41).
Table 2. Chemical Reaction Mechanism for the Box Model Used in the OH Simulations

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction Rate Constant $k^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_3 + h\nu \rightarrow O(^1D) + O_2$</td>
<td>$1.8E-12 \times \exp(-1370/T)^b$</td>
</tr>
<tr>
<td>$NO_2 + h\nu \rightarrow NO + O_3$</td>
<td>$0.78 \times 1.8E-11 \times \exp(107/T) + 0.21 \times 3.2E-11 \times \exp(67/T)$</td>
</tr>
<tr>
<td>$H_2O_2 + h\nu \rightarrow OH + OH$</td>
<td>$2.2E-10$</td>
</tr>
<tr>
<td>$CH_2O + h\nu \rightarrow HO_2 + HO_2 + CO$</td>
<td>$1.3E-13 \times (1 + 0.6 \times P/1013) \times (300/T)$</td>
</tr>
<tr>
<td>$CH_2O + h\nu \rightarrow CO + H_2$</td>
<td>$1.9E-12 \times \exp(-1000/T)$</td>
</tr>
<tr>
<td>$CO + OH \rightarrow CO_2 + O_2$</td>
<td>$7.7E-12 \times \exp(-2100/T)$</td>
</tr>
<tr>
<td>$OH + HO_2 \rightarrow H_2O_2 + H_2O$</td>
<td>$k_0 = 5.85E-23 \times T^{-3.4}, k_\text{c} = 2.0E-12$</td>
</tr>
<tr>
<td>$OH + SO_2 \rightarrow SO_3 + HO_2 + M$</td>
<td>$2.4E-15$</td>
</tr>
<tr>
<td>$SO_3 + H_2O \rightarrow H_2SO_4$</td>
<td>$4.8E-11 \times \exp(250/T)$</td>
</tr>
<tr>
<td>$HO_2 + NO \rightarrow OH + NO_2$</td>
<td>$3.4E-12 \times \exp(270/T)$</td>
</tr>
<tr>
<td>$H_2O_2 + OH \rightarrow HO_2 + O_2$</td>
<td>$1.4E-14 \times \exp(-600/T)$</td>
</tr>
<tr>
<td>$OH + HO_2 \rightarrow H_2O_2 + O_2$</td>
<td>$[2.2E-13 \times \exp(600/T) + 1.9E-33 \times [M] \times \exp(980/T)] \times [1 + 1.4E-21 \times [H_2O] \times \exp(2200/T)]$</td>
</tr>
<tr>
<td>$H_2O_2 + OH \rightarrow H_2O + HO_2$</td>
<td>$2.9E-12 \times \exp(-160/T)$</td>
</tr>
<tr>
<td>$OH + NO_2 + M \rightarrow HNO_2 + M$</td>
<td>$k_0 = 3.9E-23 \times T^{-3.4}, k_\text{c} = 2.3E-9 \times T^{-0.6}$</td>
</tr>
<tr>
<td>$CH_4 + OH \rightarrow CH_3 + HO_2$</td>
<td>$2.3E-12 \times \exp(-1765/T)$</td>
</tr>
<tr>
<td>$CH_2O + NO \rightarrow CH_2O + HO_2 + NO_2$</td>
<td>$4.2E-12 \times \exp(180/T)$</td>
</tr>
<tr>
<td>$CH_2O + HO_2 \rightarrow CH_2OOH + O_2$</td>
<td>$3.8E-13 \times \exp(780/T)$</td>
</tr>
<tr>
<td>$CH_2O + CH_3O_2 \rightarrow CH_2O + CH_2O + HO_2 + HO_2$</td>
<td>$7.5E-14 \times \exp(190/T)$</td>
</tr>
<tr>
<td>$CH_2O + CH_3O_2 \rightarrow CH_2O + CH_2O + CH_2OH$</td>
<td>$1.5E-13 \times \exp(190/T)$</td>
</tr>
<tr>
<td>$CH_2O + CH_3O_2 \rightarrow products$</td>
<td>$2.5E-14 \times \exp(190/T)$</td>
</tr>
<tr>
<td>$CH_2O + OH \rightarrow CH_3 + H_2O$</td>
<td>$1.9E-12 \times \exp(90/T)$</td>
</tr>
<tr>
<td>$CH_2O + OH \rightarrow HO_2 + CO + H_2O$</td>
<td>$8.6E-12 \times \exp(20/T)$</td>
</tr>
</tbody>
</table>

$^a$ Units: s$^{-1}$ for unimolecular, cm$^{-3}$ molecule$^{-1}$ s$^{-1}$ for bimolecular, and cm$^{-6}$ molecule$^{-2}$ s$^{-1}$ for termolecular reactions.

$^b$ Read 1.8E-12 as 1.8 $\times 10^{-12}$.

3.3. OH

[21] Overall, ambient OH concentrations showed a diurnal photochemical cycle throughout the PARFORCE campaign. With the exception of high-pollution periods (June 25, 26, and the C-130 overflight on June 28), OH daytime maximum values were rather low in clean marine air (median: 2.5 $\times 10^6$ cm$^{-3}$; Figure 1c and Table 1). Detailed inspection of the data showed that on some days OH levels deviated strongly from tracking concurrent variations in measured ozone photolysis frequencies. In the following discussion, we explore the hypothesis that OH was rapidly consumed by highly reactive compounds present in the coastal marine atmosphere. Ambient concentrations of such compounds may be particularly high during low-tide periods due to emissions from exposed tidal soils and decaying marine organisms (e.g., algae, seaweed). Corresponding reactions with OH may not only be relevant to the oxidation capacity but also to the mechanism of new particle formation and growth in coastal marine air. Our hypothesis is supported by recent observations and model studies suggesting that one or more unknown chemical species may be responsible for the rapid growth of newly formed particles observed at low tide [O’Dowd et al., 1999]. On the basis of the results obtained in the present study these considerations can be further substantiated as shown by the example in Figure 7. On June 17 (JD 168) the tide was at a minimum around midday, and a particle nucleation event occurred between about 1100 and 1500 UTC (see also Figure 2b). During this period, relatively clean air was advected from the ocean by westerly winds. Sunny and almost cloud-free conditions prevailed throughout the day yielding a smooth diel variation of the ozone photolysis frequency $j_{O_3(1,0)}$. In contrast, OH concentrations measured between approximately 1000 and 1730 UTC showed a strong deviation from the diel profile of $j_{O_3(1,0)}$. A linear regression calculation between both data sets based on 5 min average values ($n = 46$) yielded a coefficient of determination of $r^2 = 0.72$. Therefore on this day only $\pm 72\%$ of the variability in OH can be explained by the variability in ozone photolysis (following Ehhalt and Rohrer [2000]). On all other days with OH measurements (except during pollution episodes) the average was $85 \pm 5\%$. No indications were found in instrumental, meteorological, or measured chemical parameters explaining the odd variation of OH levels on June 17. Similar observations have previously been reported by O’Dowd et al. [1999]. These authors speculated about a causal relationship between reduced OH and UFP concentrations during particle nucleation events.

[22] On first view the results shown in Figure 7 suggest a crude correlation between total particle (UCPC, >3 nm diameter) and OH concentrations during the midday and early afternoon hours. However, a closer inspection of the data revealed, for example, an anticorrelation around 1054 UTC, a time lag of approximately 9 min between the decrease of OH and particle concentrations at 1214 UTC and 1223 UTC, respectively, and a nearly simultaneous decrease in the levels of both compounds at 1307 UTC. The best (linear and logarithmic) fits between both data sets for this period yielded a regression coefficient of only $r = 0.3$.

[23] A much better correlation was found between the corresponding OH and $H_2SO_4$ concentrations ($r = 0.50$ for 1100–1500 UTC; $r = 0.78$ for all data, 953–1717 UTC). OH and $H_2SO_4$ levels were also well correlated on other days of the
campaign with regression coefficients ranging between $r = 0.51$ (June 27 (JD 178), 600–1800 UTC) and $r = 0.73$ (June 29 (JD 180), 600–1800 UTC). Both data sets obtained on June 17 are plotted in Figure 7 together with the corresponding SO$_2$ and MSA values. The results demonstrate that H$_2$SO$_4$ production occurred rapidly in the coastal boundary layer and was primarily determined by OH. The second H$_2$SO$_4$ maximum at 1400 UTC also coincided with maximum SO$_2$ concentrations. The dominant source for both compounds at that time was presumably DMS oxidation as suggested by the corresponding peak in MSA concentrations. Downward transport of MSA from upper altitudes was negligible on June 17 based on observed dew point temperature values. By comparison, the morning OH and H$_2$SO$_4$ peak concentrations observed at 1000 UTC were not mirrored by a corresponding MSA peak value indicating a minor contribution from local DMS oxidation to the corresponding H$_2$SO$_4$ levels.

To verify our hypothesis that unknown reactive compounds may have significantly reduced ambient OH concentrations on June 17 (and possibly other days), we calculated the diel cycle of OH for this day based on a simple photochemical box model. The basic equations and reaction rate constants pertaining to the model are compiled in Table 2. Previous measurements of OH diel profiles at Hohenpeissenberg, Germany, have been successfully simulated using the same model approach including days before and after the PARFORCE campaign. Measured photolysis frequencies were verified using the model System for Transfer of Atmospheric Radiation (STAR) developed by Ruggaber et al. [1994]. In the OH simulations, best fit values for the individual photolysis frequencies were used resulting from a power curve approximation of the actually measured values in the form of $j = A \exp(-B/\cos\theta)$, with $AB$ equal to fitting coefficients and $\theta$ equal to zenith angle. Measured values for pressure, temperature, and CO, NO, and H$_2$O concentrations were directly used as input parameters. For clear-sky days the corresponding results showed about 15–20% difference between noontime measured and (STAR) modeled $j_{\text{OH}(D)}$ values and <15% difference between measured and modeled OH concentrations. As an example, Figure 8a demonstrates the generally good agreement between the OH measurements at Hohenpeissenberg and the corresponding model results for the midday and afternoon hours of July 30, 1999. On the other hand, this example also shows how the model can help to identify and evaluate potential malfunctions of the CIMS system as occurred on that day during the morning hours when the system suffered from detector instabilities resulting in overly high measured OH values.

In sharp contrast to the Hohenpeissenberg “background continental air” simulations, the results obtained for the “background coastal air” of June 17 (JD 168; Figure 8b) show a large discrepancy between modeled and observed OH concentrations differing by an average factor of 8.2 ±2.2. For similar, yet slightly cloudier conditions encountered on June 27 (JD 178) the respective values differed by a factor of 6.4 ±2.3. These results clearly indicate that major sink mechanisms for OH prevail in the coastal marine atmosphere which are not accounted for in the present model. The consumption of OH by reactive compounds is most pronounced when the concentrations of both OH and the corresponding reactants reach maximum levels at the same time. We conclude that at Mace Head this may be the case on relatively cloud-free days such as June 17 and June 27 when low tide occurs at noontime hours. Overall, our results suggest a potentially strong link between the oxidation capacity and particle nucleation probability in the coastal marine atmosphere at Mace Head.

4. Summary and Conclusions

During the PARFORCE campaign at Mace Head in June 1999, H$_2$SO$_4$ concentrations were highly correlated with OH levels in coastal marine air. Both compounds showed a pronounced diurnal cycle driven by photochemistry. In contrast, daytime MSA concentrations rarely exhibited a “pure” photochemical behavior. On most days of the campaign, pronounced secondary MSA maxima were observed in the morning, afternoon, or even nighttime hours. These peaks were caused either by vertical or horizontal advection of air enriched in MSA and/or by reevaporation of MSA from aerosol particles exposed to relatively warmer and drier air masses. In conclusion, our results strongly suggest that the aerosol methanesulfonate concentration is not a conservative tracer for deriving an estimate of the aerosol non-sea-salt sulfate concentration produced by the oxidation of DMS.

During individual periods when new particle formation occurred, some observational data showed an anticorrelation between H$_2$SO$_4$ and ultrafine particle concentrations pointing...
toward a contribution of H$_2$SO$_4$ to particle formation and/or growth. Overall, however, no conclusive evidence was found for such a relationship, possibly because H$_2$SO$_4$ was always present during daytime at concentrations much higher than the critical levels required for inducing new particle formation [Kulmala et al., 2000a, 1998]. Most obvious in this respect was the lack of a correlation between the H$_2$SO$_4$ diurnal cycle and the tidal cycle, the latter being clearly related with the timing of new particle formation events [O’Dowd et al., 2002a, 2002b]. Owing to its relatively higher vapor pressure, MSA may have only contributed significantly to particle growth but not particle formation.

[28] Steady state calculations of diel H$_2$SO$_4$ profiles resulted in much lower values compared to measured concentrations when considering the SO$_2$+OH reaction as the only source of H$_2$SO$_4$. Most likely an additional major source exists in coastal regions such as relatively fast reactions of DMDS or DMS with OH and/or halogen radicals yielding H$_2$SO$_4$ without SO$_2$ as an intermediate product. In this way, reactive sulfur compounds such as DMDS may significantly contribute to new particle formation [e.g., Kreidenweis et al., 1991].

[29] A strong deviation of ambient OH concentrations from simple photochemical steady state model results was observed. Measured OH concentrations were significantly lower than calculated values. These discrepancies were most pronounced under clear-sky conditions for noontime OH levels in coincidence with a low-tide/new particle formation event. No explicit hydrocarbon or halocarbon chemistry was included in the model (except for methane oxidation). The present results suggest that OH levels in the coastal marine atmosphere may be significantly affected by reactions with chemical compounds playing only a minor role in the background continental atmosphere. Furthermore, these reactions may not only have major implications for the oxidation capacity but also for the particle formation potential in the coastal marine boundary layer.

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