



Seasonal variability of the formation of particle sulfur species (sulfate and methanesulfonate) over the Eastern Mediterranean: a modeling approach

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Aim

The present study aims (i) to improve our understanding on the mechanism of particulate sulfur formation and methanesulfonate (MS) in the Eastern Mediterranean, and particularly to investigate the importance of the gas phase versus the heterogeneous reactions leading to MS and nss-SO₄²⁻ formation, and (ii) to evaluate the relative contributions from biogenic and anthropogenic sources to the S budget.

Approach

To investigate the mechanism of particulate sulfate formation in the area and its seasonal variability, sulfur dioxide, hydroxyl radical, sulfate and rate constant of condensational sink (kcs) observations are combined with the sulfate size segregated measurements and zero-dimensional model results. A chemical box model coupled offline with an aerosol-cloud model has been used. The chemical box model is appropriate for simulations of boundary layer chemistry taking

into account C₁-C₅ hydrocarbon chemistry as well as sulfur oxidation in the troposphere. The aerosol model is capable of simulating all basic aerosol processes, including (parameterized) nucleation, condensational growth of aerosol particles by both non-volatile and semi-volatile trace gases, coagulation, cloud droplet activation and deactivation, as well as aqueous-phase reactions taking place in hygroscopic aerosol particles or in cloud droplets.

Introduction

Experimental

The measurements

All measurements reported here have been at Finokalia (35°24'N, 25°60'E), a remote coastal site on the north east side of the island where the monitoring station of the University of Crete is situated. A detailed dataset collected during the MINOS experiment that has been conducted from 28 July to 22 August 2001 Lelieveld et al. (2002) has been used for the summer investigations. This dataset includes the following key species: dimethyl sulfide (DMS), dimethyl sulfoxide (DMSO), gaseous sulfur dioxide (SO₂) and bulk aerosol (SO₄²⁻ MS⁻), sulfuric acid (H₂SO₄), methanesulfonic acid (MSA) and hydroxyl radicals (OH), as well as meteorological parameters and size-segregated aerosol.

For the investigation of the other seasons, seasonal average values were used as input to the chemical model. These values are: nitrogen monoxide (NO), nitrogen dioxide (NO₂), ozone (O₃), carbon monoxide (CO), which were measured every 5 minutes. Sulphur dioxide (SO₂) corresponds to 2 days average. Furthermore, size-segregated mass measurements were used as input in the aerosol model.



The site

Special meteorological conditions dominate the area year around (intensive sun light, high temperatures etc) and enhance photochemistry. The site is mostly under the influence of NW, N, NE winds.

<http://finokalia.chemistry.uoc.gr>

The models

To archive our aims, a chemical box model and an aerosol box model have been used. The chemical box model is used to evaluate the contribution of anthropogenic relative to biogenic sources to the S budget and the importance of heterogeneous and gas-phase reaction for the sulfur cycle. In addition, the aerosol model complements the analysis and describes explicitly the gas – aerosol partitioning.

Chemical box model description

The commercial available software FACSIMILE (Curtis and Sweetenham, 1988), which uses automatic time step selection and error control, was used to solve the differential equation with a high accuracy required for chemistry studies. The chemistry model is a condensed chemical mechanism (about 300 chemical reaction and 140 chemical species). It is able to simulate marine boundary layer photochemistry of ozone, water vapor, nitrogen oxides, carbon monoxide and volatile organics (Tsigaridis and Kanakidou, 2002; Vrekoussis et al., 2004) as well as gas-phase chemistry of sulfur. In addition to background O₃/NO_x/OH/CO and CH₄ chemistry, it also takes into account the oxidation chemistry of C₁ – C₅ hydrocarbons including isoprene (Tsigaridis and Kanakidou, 2002; Vrekoussis et al., 2004) and biogenic sulfur oxidation mechanisms (Sciare et al., 2000). Oxidation of volatile organic compounds (VOC) by all major three oxidants (O₃, OH and NO₃) is considered when applicable.

Aerosol model description

The aerosol model used in the simulations is a Lagrangian model box, which follows an air parcel in the boundary layer. In the model, the aerosol number size distribution is prescribed by a specified number of modes that may overlap with each other. Depending on the application, each mode is further divided into 10 – 100 bins. For the present study 39 bins have been considered. The model is initialized by assuming that the modes are log-normally shaped and that aerosol particles in the same modes have the same chemical composition. Therefore, the aerosol model was run with an aerosol size distribution consisting of three log-normal modes: an accumulation mode and supermicron sea-salt and dust modes. No Aitken or nucleation mode was considered, since the study focuses on simulating the mass size distributions of different aerosol components and very small fraction of the simulated components resides below the accumulation mode size range. During the simulation, various aerosol processes modify the “dry” diameter, chemical composition and number concentration of particles in every size bin. The “wet” diameter of particles in each size bin is calculated based on the particle hygroscopic properties in that size bin.

Two base-case simulations were performed, termed the DRY and WET simulation. In the DRY simulation, only condensation of gaseous H₂SO₄ and MSA were allowed to form particulate sulfate and MS. In the WET simulation, we included the oxidation of SO₂ to sulfate by O₃ in sea-salt particles, as well as the oxidation of DMSO to MSA by OH in both accumulation mode and sea-salt particles. For the summer case study, the model simulations covered a total of 120 hours starting from 00:00 on August 14 and ended at 24:00 on August 18.

Conclusions

First results – the summer time case

- Gas-phase H₂SO₄ formation followed by condensation can fully explain submicron nss-SO₄²⁻ within the modeling and experimental uncertainties (roughly 30%).
- Only about 10% of the supermicron nss-SO₄²⁻ can be explained by condensation of gas-phase H₂SO₄, the rest must be formed via heterogeneous pathways.
- SO₂ oxidation by O₃ in wet sea-salt particles may explain the supermicron nss-SO₄²⁻ only if sea-salt particles have substantially (up to 30 times) higher alkalinity than present in natural sea water. Another possible pathway is nss-SO₄²⁻ formation on dust particles which account for the majority of supermicron mass.
- Condensation of gaseous MSA can explain particulate MS when MSA mass accommodation coefficient on particle surfaces is greater than or equal to 0.3. From the laboratory experiments available in the literature this is highly unlikely.
- Aqueous-phase oxidation of DMSO by OH can easily explain observed levels of particulate MS.
- Biogenic sulfur emissions contribute 5–20% of the measured total sulfur in the aerosol phase, a figure in agreement with earlier studies performed in the eastern Mediterranean.

Further work

This work continuous with the investigation of the seasonal significance of the above conclusions. For this similar simulations for the area for the other seasons are performed based on monthly mean observations.

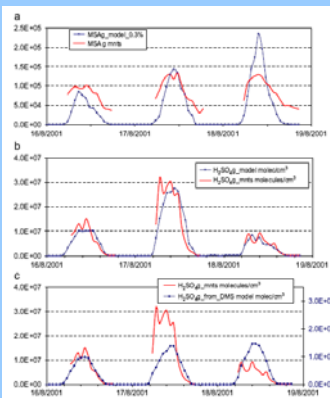
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Results and Discussion

chemistry simulation results

For the summer time MINOS campaign, the modeling effort has been limited to the period 14 – 18 of August 2001, when air masses were originating from N, NE sectors, typical wind pattern during summertime in the area, and there is a satisfactory amount of observations available.



The model satisfactorily simulates the daytime variation and the absolute concentrations of OH radicals although overall it underestimates the observations of OH radicals by about 8% and captures the order of magnitude of the NO₃ observations within the range of their variability. Therefore, it is able to simulate reasonably well both the gas-phase daytime and nighttime oxidation of DMS and SO₂ in the area.

MSA: Fig. 1a compares the simulated MSA levels to the measured ones (16 to 18th of August 2001) for the base simulation. This simulation has been performed using the measured DMS and OH levels. Since during night the observed MSA concentrations were below the detection limit, no MSA production from the DMS reaction with NO₃ is assumed in the model. The simulated MSA levels compare well with the modeled only when the yield of MSA from DMS oxidation by OH radicals is set to 0.003.

H₂SO₄: Fig. 1b compares the simulated H₂SO₄ levels to the measured ones. The simulation has been performed using the measured OH and SO₂ levels. The simulated H₂SO₄ levels compare very well with the observations (slope = 0.87, r² = 0.8).

Based on a yield of MSA from DMS oxidation of 0.3% that has been derived for the studied area from MSA observations and simulations, the H₂SO₄ levels originating from the DMS oxidation alone can be calculated. These levels are shown in Fig. 1c and correspond to the contribution of biogenic S to the total measured H₂SO₄ and SO₄²⁻ levels. The simulated biogenic H₂SO₄ levels range between 5–20% of the measured ones indicating a biogenic S contribution in good agreement with the mean values reported during summer by Kouvarakis et al. (2002).

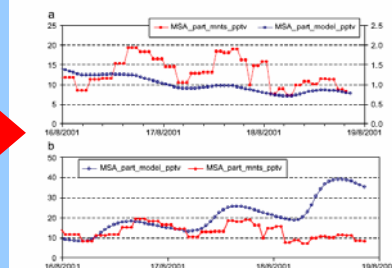


Fig. 2. Comparison between the modeled and measured MS. By considering the only gas-phase chemistry (for observations see data in the text and the model results are on the right) and the gas-phase and heterogeneous chemistry. Units are ng m⁻³.

MS: compares the simulated MS levels to the measured ones. It is clear that simulated MS levels are at least an order of magnitude lower than the observed ones indicating that gas-particle conversion of MSA plays a minor role on the measured MS levels. MSA may re-entrain into the gas phase at low relative humidity however such conditions were not occurred during the simulation period and they are quite rare during summer in the area.

It is clear from Fig. 2b that inclusion of heterogeneous reactions of DMSO and MSIA improve the agreement between the observed and simulated values of MS.

aerosol simulation results

Table 1

Measured and simulated (DRY base case) concentrations (ng m⁻³) of aerosol species

Compound	First impactor	Second impactor	Simulated
nss-SO ₄ (< 1 μm)	4290	3200	3900
nss-SO ₄ (1–10 μm)	640	340	38
MSA (< 1 μm)	48	17	5.6
MSA (1–10 μm)	3	–	0.2
Sea-salt (1–10 μm)	4000	2400	–
Dust (1–10 μm)	14,700	9800	–

Note that simulated sea-salt and dust concentrations were constrained to match the observations.

The concentrations of non-sea salt sulfate (nss-SO₄²⁻) and methane sulfate (MS) simulated in the DRY base case, together with the corresponding measured concentrations, are shown in Table 1. The uncertainties are 25 – 30 % for submicron nss-SO₄²⁻ about a factor of two for supermicron nss-SO₄²⁻ and up to a factor of three for MS.

The DRY simulation successfully predicts the concentration of submicron nss-SO₄²⁻ in measured air masses. Therefore condensation of gaseous sulfuric acid alone is able to explain the formation of submicron nss-SO₄²⁻ during the period considered here.

The simulated supermicron nss-SO₄²⁻ concentration is too low by roughly an order of magnitude, suggesting that reactions taking place either in wet sea-salt particles or on the surface of dust particles were the dominant source of supermicron nss-SO₄²⁻.

In case of MSA, the simulated concentration is too low by a factor of 3 – 10 depending whether we rely on the first or second impactor sample. Two potential reasons for this underprediction can be identified: either the mass accommodation coefficient of gaseous MSA on particle surface is substantially higher than assumed here, or, similar to supermicron nss-SO₄²⁻, particulate MSA was mainly formed by heterogeneous pathways.

Acknowledgments

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