

**Importance of
mineral cations and
organic aerosols**

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Importance of mineral cations and organics in gas-aerosol partitioning of reactive nitrogen compounds: case study based on MINOS results

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Received: 4 October 2005 – Accepted: 21 November 2005 – Published: 19 December 2005

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Abstract

The partitioning of reactive nitrogen compounds between the gas and the aerosol phase, as observed during the MINOS (Mediterranean INTensive Oxidant Study) campaign in Crete, Greece, in July and August 2001, has been studied with three thermodynamic gas-aerosol equilibrium models (EQMs) of different chemical complexity: ISORROPIA, which is limited to the ammonium sulfate-nitrate-sodium-chloride-water-system, SCAPE2, which also includes mineral elements (calcium, magnesium and potassium), and EQSAM2, which additionally accounts for organic acids. The different EQMs, as applied at the same level of complexity, generally produce comparable results within the range of measurement uncertainties (on average within ~10%), although they differ considerably in particular aspects. Model simulations of three distinct air pollution episodes during MINOS show that organic acids (lumped) and soluble mineral cations need to be included in EQMs to accurately simulate the gas-aerosol partitioning of ammonia and nitric acid.

1. Introduction

The MINOS (Mediterranean INTensive Oxidant Study) campaign (Lelieveld et al., 2002; Salisbury et al., 2003) took place in summer 2001 (28 July till 21 August) with the objective to study the chemical and transport processes that cause the relatively high pollution concentrations often encountered in the Mediterranean lower atmosphere (Fig. 1).

The measurements provided evidence of a remarkably high level of air pollution from the surface to the top of the troposphere up to 15 km altitude. Most pollution was observed in the lower 4 km, originating from both western and eastern Europe (Lelieveld et al., 2002; Traub et al., 2003). During MINOS the observations at Finokalia were strongly influenced by the transport of air pollution from SE-Europe. The sources include industrial activity, traffic, forest fires, agricultural and domestic burning. Since the Mediterranean region has only few clouds in summer, the solar radiation levels are high

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so that noxious reaction products are formed in photochemical smog. The consequent air pollution includes ozone, various aerosol precursor gases and acidic or hygroscopic aerosol particles with distinct chemical composition.

The most abundant aerosol precursor gases are ammonia (NH_3), sulfuric acid (H_2SO_4) and nitric acid (HNO_3). While NH_3 is an end product of soil biogenic activity, being enhanced emitted by farming and fertilization, H_2SO_4 and HNO_3 form acids and are oxidation products from gas-phase photochemistry. H_2SO_4 derives from sulfur dioxide (SO_2) and HNO_3 from NO_x ($\text{NO}_2 + \text{NO}$), i.e. trace gases released from combustion processes, e.g. in fossil energy production and traffic. Additional aerosol precursor gases include hydrochloric acid (HCl) and various condensable organic acids (R-COOH). While sulfuric and nitric acid in the Mediterranean region mainly originate from anthropogenic activities, the origin of organic acids is manifold and less clear; a certain fraction originates from anthropogenic activity and, depending on the season, from natural sources such as forests and coastal ecosystems.

The corresponding ions are ammonium (NH_4^+), sulfate (SO_4^{2-}), bisulfate (HSO_4^-), nitrate (NO_3^-), chloride (Cl^-), and organics (R-COO^-). Except for NH_4^+ these are anions associated with gas-aerosol partitioning and the formation and growth of secondary aerosols (i.e. formed within the atmosphere), while the major cations are mainly of natural origin (primary aerosols), present in the coarse mode particles and not undergoing gas-aerosol partitioning (but liquid-solid partitioning). Most important are sodium (Na^+) originating mainly from bubble bursting sea spray, calcium (Ca^{2+}), magnesium (Mg^{2+}) and a minor fraction of potassium (K^+) which originate from mineral dust, e.g. Saharan dust. The major mineral cations present in the fine mode largely originate from anthropogenic activity, including NH_4^+ , the cation of NH_3 , and "pyrogenic" potassium (K^+) from biomass burning.

The anions are neutralized by cations through various reaction pathways, being important for various reasons. Firstly, trace gases that have a short lifetime of a day or less can re-partition into the aerosols, which have a much longer lifetime of about a week depending on size, composition and meteorological conditions. For instance,

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NH₃ reacts with H₂SO₄ to form stable ammonium sulphate salts that are mostly confined to the aerosol fine mode. Secondly, the salts are more-or-less hygroscopic, so that the aerosols interact with natural and anthropogenic gases by various heterogeneous reactions that take place on aqueous or dry aerosol surfaces.

5 The present study addresses the influence of mineral cations and organic acids on the gas-aerosol partitioning of reactive nitrogen compounds in the Mediterranean lower atmosphere. We focus on nitrate and ammonium as they are the two dominant nitrogen-containing compounds in aerosol particles, mainly of anthropogenic origin.

While it has been demonstrated that nitrate is mainly present in the form of ammonium nitrate e.g. in northwestern and central Europe, previous size fractionated aerosol measurements conducted in the Mediterranean have indicated the near-absence of submicron nitrate (Bardouki et al., 2003). The high hydroxyl (OH) levels occurring in the area during summer (up to 2·10⁷ molecules/cm³), in conjunction with the relatively high NO_x concentrations and the lack of precipitation, promote the build-up of HNO₃ from gas phase reactions (Berresheim et al., 2003). Once HNO₃ is formed, it is most likely captured by coarse mode (D ≥ 1.2 μm) sea-salt and dust particles, leading to a depletion of aerosol nitrate in the fine mode (D < 1.2 μm). On the other hand, ammonium nitrate may be formed during night in case of excess ammonia; however, since this salt is thermodynamically not stable, it can evaporate during the day whereby the aerosol precursor gases NH₃ and HNO₃ are likely to condense on pre-existing and larger aerosol particles. As a consequence, some anthropogenic air pollutants may not (or only during night) be confined to the fine aerosol mode but rather interact with larger particles which might be of natural origin such as sea salt and mineral dust aerosol.

25 To study the gas-aerosol partitioning of these compounds by considering the major sea salt (Na⁺, Cl⁻) and mineral (Ca²⁺, Mg²⁺, K⁺) elements, we employ the available and widely used thermodynamic gas-aerosol equilibrium models ISORROPIA (Nenes et al., 1998) and SCAPE2 (Kim et al., 1995; Meng et al., 1995). Since ISORROPIA and SCAPE2 do not include organic acids – ISORROPIA is limited to the ammonium-

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sulfate-nitrate-sodium-chloride-water-system, and SCAPE2 additionally includes major crustal elements (Ca^{2+} , Mg^{2+} , K^+) – we further apply EQSAM2, which derives from EQSAM (Metzger, 2000; Metzger et al., 2002a, b). EQSAM2 includes lumped organic acids and mineral cations (Na^+ , Ca^{2+} , Mg^{2+} , K^+), as well as an extended description of gas-liquid-solid partitioning by accounting for the various mineral salt compounds based on theoretically derived activity coefficients and single solute molalities. For a description of EQSAM2 we refer to Metzger (2005)¹ and Metzger and Lelieveld (2005)².

2. Measurements

2.1. HNO_3 and NH_3

The technique used for the sampling of atmospheric HNO_3 and NH_3 is based on the nebulization/reflux principle (Cofer et al., 1985; Sciare and Mihalopoulos, 2000). The Cofer sampler was running with an average flow rate of 16 L min^{-1} and the sampling step was 2–3 h. After sampling the aliquots for HNO_3 and NH_3 analysis were kept refrigerated at 4°C in the dark and analyzed within a month period using Ion Chromatography (see details below). The detection limit for a mean sampling volume of 3 m^3 was found to be $20 \text{ pmol}\cdot\text{mol}^{-1}$ and the precision was estimated to be 15%.

2.2. Aerosol sampling and analysis

Bulk aerosol samples were collected on $0.5 \mu\text{m}$ PTFE filters running in parallel with the Cofer sampler. In total, 226 aerosol samples were collected during the sampling period and subsequently analyzed for the main anions and cations by Ion Chromatography.

¹Metzger, S.: Reformulating Aerosol Thermodynamics, Atmos. Chem. Phys. Discuss., to be submitted, 2005.

²Metzger, S. and Lelieveld, J.: Technical note: New version of the equilibrium simplified aerosol model (EQSAM2), Atmos. Chem. Phys. Discuss., to be submitted, 2005.

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To obtain an impression of the distribution of aerosols over the fine and coarse mode, we also collected aerosol samples in parallel on Stack Filter Units (SFUs). The 50% cut-point diameter (D50) of the 8 μm pore size filter was estimated to be of the order of $1.2 \pm 0.1 \mu\text{m}$ E.A.D. More details can be found at Sciare et al. (2005).

For the analysis of anions (chloride: Cl^- ; bromide: Br^- ; nitrate: NO_3^- ; sulfate: SO_4^{2-} ; oxalate: $\text{C}_2\text{O}_4^{2-}$) a Dionex AS4A-SC column with ASRS-I suppressor in auto-suppression mode of operation was used and isocratic elution at 2.0 ml min^{-1} of $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ eluent. Organic anions were analyzed using a Dionex DX-500 Ion Chromatograph with an AS11 analytical column and NaOH (0.1–3.5 mM) as eluent in the gradient mode. For the cations (sodium: Na^+ ; ammonium: NH_4^+ ; potassium: K^+ ; magnesium: Mg^{2+} and calcium: Ca^{2+}) a CS12-SC column was used with CSRS-I suppressor. Separation was achieved under isocratic conditions with 20 mM MSA eluent and flow rate of 1.0 ml min^{-1} : The reproducibility of the measurements was better than 2% and the detection limit ranged from around 5 ppb for the main anions and cations to below 0.2 ppb for the major organic anions. More details on the analytical technique can be found in Kouvarakis and Mihalopoulos (2002).

To support the modeling study, major low molecular weight (LMW) organic anions, being weak acids, were lumped together according their protonation constant, as they might be neutralized (deprotonated) by the presence of sufficient alkaline material, for instance, in the case of potassium or excess ammonia.

According to Trebs et al. (2005) equivalent moles were calculated as a first approximation assuming that mono-, di-, and tricarboxylic acids form the respective mono-, di-, and tri-ammonium salts, which means that they may donate all H^+ to be neutralized by bases such as ammonia (NH_3), which forms the cation ammonium (NH_4^+), or the organic acids might be neutralized by other cations (Na^+ , Ca^{2+} , Mg^{2+} , K^+). Although it is difficult to estimate the degree of acid dissociation (the pH of the sampled aerosol is not known), we assume that full acid dissociation of ammonium salts occurred, since excess of NH_3 was available at the site. Organic acids are therefore added to the ionic charge balance accounting for the total of carboxylic groups.

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During MINOS the following classes of organic acids were measured: monocarboxylic (formate, acetate and propionate), dicarboxylic (oxalate, succinate and glutarate) and ketocarboxylic (pyruvate). The above measured organic species account for the majority (more than 80%) of the organic acids existing in the aerosol phase (Kawamura et al., 1996; Kawamura and Sakaguchi, 1999; Krivacsy et al., 2001) and concurrent measurements during the campaign (Roemp et al., manuscript in preparation) confirm this conclusion.

3. Model description

The gas-aerosol partitioning of inorganic and organic aerosol compounds is modeled assuming thermodynamic and chemical equilibrium. The gas-aerosol equilibrium models partition the major aerosol precursor gases and aerosol compounds between the gas-, liquid-, or solid aerosol phase based on the total of aerosol precursor gases and aerosol compounds. The aerosol precursor gases are ammonia (NH_3), sulfuric acid (H_2SO_4), nitric acid (HNO_3), hydrochloric acid (HCl), and condensable organic acids (R-COOH), the latter being lumped together according to the total of carboxylic groups. The corresponding ions are ammonium (NH_4^+), sulfate (SO_4^{2-}), bisulfate (HSO_4^-), nitrate (NO_3^-), chloride (Cl^-), and lumped organics (R-COO^-), respectively. For each aerosol species the aerosol precursor gases and anions are added (i.e. $\text{NH}_3+\text{NH}_4^+$, $\text{H}_2\text{SO}_4+\text{SO}_4^{2-}+\text{HSO}_4^-$, $\text{HNO}_3+\text{NO}_3^-$, $\text{HCl}+\text{Cl}^-$, $\text{R-COOH}+\text{R-COO}^-$) and the total is used as input in the gas-aerosol models together with the total of the corresponding (major) cations, i.e. sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^+).

The gas-aerosol equilibrium models (re-)partition the anions based on stoichiometric neutralization reactions with the cations, assuming chemical equilibrium, so that stronger acids drive the weaker acids out of the aerosol phase. For instance, chloride and nitrate anions are replaced by sulfate anions, since sulfuric acid is stronger than nitric or hydrochloric acid. Chlorine release from the aerosol particles will follow the

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formation of nitrate. Organic acids are assumed to be weaker than the considered inorganic acids and are therefore driven out of the aerosol phase in case of insufficient cations. Similarly, ammonium is driven out of the aerosol phase (in form of ammonia) in the presence of mineral cations. Since mineral cations originate mainly from primary production (e.g. wind blown dust or sea spray) they are therefore present in the coarse rather than the fine aerosol particles, thus strongly determining the particle size distribution, which again affects the gas-aerosol partitioning due to the ionic composition.

To take size distribution effects into account, we consider in this study simply a bimodal aerosol size-spectrum with two major aerosol modes, i.e. the fine ($D < 1.2 \mu\text{m}$) and coarse ($D \geq 1.2 \mu\text{m}$) mode. For each mode, we calculate gas-aerosol equilibrium partitioning based on size-segregated aerosol compounds that derive from the measured ion concentrations in the two modes. To study the gas-aerosol partitioning we use the thermodynamic equilibrium models (EQMs) ISORROPIA (Nenes et al., 1998), SCAPE2 (Meng et al., 1995), which derives from SCAPE (Kim et al., 1995), and EQSAM2 (Metzger and Lelieveld, 2005²), which derives from EQSAM (Metzger, 2000; Metzger et al., 2002a). The gas-aerosol partitioning represented by EQSAM2 is schematically described in Fig. 2.

The EQMs calculate the gas-aerosol equilibrium partitioning based on the following assumptions. First of all, aerosol particles are assumed to be in thermodynamic and chemical equilibrium and internally mixed. While the latter assumption might be questionable under certain conditions, i.e. for coarse mode particles that originate from mineral dust (see discussion section), the equilibrium assumption is justified especially for fine particles. Smaller particles have shorter equilibration time-scales than larger particles due to a larger surface to volume ratio. The equilibrium timescales are then in the range of minutes to one hour for the conditions considered (Meng and Seinfeld, 1996), which is much shorter than the measurement intervals of about 2–3 h. However, also the coarse particles can be regarded as internally mixed (and hence in equilibrium), if salt compounds are predominant. For instance, sea salt particles are hygroscopic (due to the presence of MgCl_2), so that the salt compounds take up enough water vapor

to deliquesce as soon as the relative humidity (*RH*) exceeds the relative humidity of deliquescence (RHD). At RHD, the aerosol particle is then assumed to be a saturated solution of the inorganic salt compound(s) with the salts completely dissociated into the anion-cation pairs.

5 Another simplification is that the set of chemical reactions that needs to be solved for a certain aerosol composition is reduced by dividing the entire concentration range into certain concentration domains (aerosol types) and sub-domains (RHD regimes), which match the actual aerosol composition. This framework is common to all EQMs used, see e.g. Metzger (2000), Metzger et al. (2002a), and the references therein.

10 While EQSAM2 currently captures the equilibrium partitioning of the $\text{H}_2\text{SO}_4/\text{HSO}_4^-/\text{SO}_4^{2-}$ - $\text{HNO}_3/\text{NO}_3^-$ - $\text{NH}_3/\text{NH}_4^+$ - HCl/Cl^- - $\text{R-COOH}/\text{R-COO}^-$ - Na^+ - Ca^{2+} - Mg^{2+} - K^+ - H_2O -system (Fig. 2), SCAPE2 and ISORROPIA do not include organics, and ISORROPIA does not either include mineral cations except sodium. However, it is common to all EQMs that they calculate temperature (*T*) and *RH* dependent gas-liquid-solid aerosol partitioning. This includes crystallization (or the deliquescence and dissociation into ions) of salt compounds, if the *RH* drops below (or exceeds) the RHD of the salt compound or of the mixture of salts (then called MRHD – mutual relative humidity of deliquescence). The EQMs finally compute the aerosol composition for a certain *T*, *RH* and the total of the gas and aerosol concentrations, based on the gas-liquid-solid, or gas-liquid, or gas-solid partitioning (either of one depending on *T*, *RH* and the input concentrations), including the corresponding solid and/or ionic compositions, the aerosol associated water mass and other derived aerosol properties (e.g. pH, or ionic strength of the solution) which are difficult to measure.

4. Results

25 The MINOS measurements taken at Finokalia, Crete, in the southern Aegean Sea (Fig. 1) were analyzed with the gas-aerosol partitioning models for the MINOS core period, i.e. 1–18 August 2001. This core period can be subdivided into three different

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periods, i.e. two humid periods interrupted by a dry period:

- Period I (1 August–6 August 2001) was dominated by moderate winds from north-northwesterly direction, bringing humid air enriched with high levels of sea salt from central and western Europe over the Ionian Sea to Crete.
- Period II (6 August–12 August 2001) was dominated by subsidence, depositing pre-dominantly mineral dust from Saharan outbreaks, which was mixed or partly coated with biomass-burning air pollution.
- Period III (12 August–18 August 2001) was dominated by moderate winds from north-northeasterly direction bringing again humid air with high levels of sea salt particles though in this case from eastern Europe over the Aegean Sea to Crete. Similarly to period II, the air was mixed with pollution from biomass-burning.

4.1. Observations

For the three different periods that characterize the MINOS campaign, time evolutions of the air temperature (T) and the relative humidity (RH) are shown in Fig. 3, together with fine mode ($D < 1.2 \mu\text{m}$) non-sea-salt potassium (nss-K^+); the latter is conceived to be an indicator for biomass burning pollution.

The three different periods can also be characterized by the pollution levels of atmospheric aerosols and their ionic composition. In particular, the concentration levels of cations are characteristic. Time averages for the three different periods, including the time averages over all periods of the observed aerosol and aerosol precursor gas concentrations in units of nanomole per cubic meter of air [nmol/m^3] are shown for the fine and coarse mode in Fig. 4. The major mineral cations (Na^+ from sea salt aerosols, Ca^{2+} , Mg^{2+}) are present in the coarse mode (more than 95% of the total concentration) which indicates their natural origin. The major mineral cation present in the fine mode is, besides NH_4^+ (more than 95% of the total concentration), pyrogenic potassium K^+ (more than 70% of the total concentration; Sciare et al., 2005).

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The measurements further indicate that the major anthropogenic air pollutants are distributed over both the aerosol fine and coarse mode. For instance nss-SO_4^{2-} is mainly present in the aerosol fine mode in contrast to aerosol nitrate, which is confined to coarse mode particles. For a further discussion of the measurements, we refer to Salisbury et al. (2003), and Sciare et al. (2005). In the following we focus on the gas-aerosol partitioning modeling of reactive nitrogen compounds.

4.2. Modeling

To study the T and RH dependent equilibrium partitioning of reactive nitrogen compounds of the observed $\text{H}_2\text{SO}_4/\text{HSO}_4^-/\text{SO}_4^{2-}$ - $\text{HNO}_3/\text{NO}_3^-$ - $\text{NH}_3/\text{NH}_4^+$ - HCl/Cl^- - Na^+ - Ca^{2+} - Mg^{2+} - K^+ - H_2O -system, including lumped organic acids (R-COOH), we separate this complex aerosol system into five chemical systems for the fine (F1-F5) and the coarse (C1-C5) aerosol mode, according to Table 1. Chemical system F1/C1 excludes all mineral cations, F2/C2 accounts for sodium, F3/C3 additionally accounts for Ca^{2+} , Mg^{2+} , K^+ as equivalent sodium, F4/C4 explicitly treats all mineral cations (SCAPE2 and EQSAM2 only) and F5/C5 also accounts for additional anions from lumped organic acids (EQSAM2 only).

This separation allows investigating the gas-aerosol partitioning of nitrogen compounds and the sensitivity to the choice of the aerosol chemical subsystem. This is achieved by different constraints on the ionic composition, i.e. by subsequently including more and more cations and anions. This separation further allows comparing the results of differently complex equilibrium models (ISORROPIA, SCAPE2, EQSAM2) at different levels of complexity. While the models are only comparable if applied at the same level of complexity, i.e. for the aerosol chemical systems F1/C1 and F2/C2, and with some restrictions also for F3/C3, the model comparison at different levels of complexity (F4/C4 and F5/C5) focuses on the relative importance of individual aerosol components for the gas-aerosol partitioning of nitrogen compounds.

The most complex chemical system (F5/C5) is given by including all measurements.

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However, only EQSAM2 matches the chemical system F5/C5, as it includes mineral cations and (lumped) organic acids in addition to the inorganic ammonium-sulfate-nitrate-water aerosol system (F1/C1), which is common to all EQMs. ISORROPIA also includes the major sea salt compounds, thus describing the chemical system F2/C2, but it does not include mineral cations (Ca^{2+} , Mg^{2+} , K^+) nor organic acids. SCAPE2 in turn includes the major mineral cations (Na^+ , Ca^{2+} , Mg^{2+} , K^+) but also no organic compounds, thus describing chemical system F4/C4. Nevertheless, mineral cations can be considered by all three models, if mineral cations are added as “ Na^+ -equivalent” to the sodium (e.g. 1 mole of Mg^{2+} as 2 mole Na^+). This so-called equivalent sodium approach (Moya et al., 2001) yields chemical system F3/C3 (Table 1), which should be considered however as an approximation only, because of inconsistencies in the RHDs (see discussion section).

4.2.1. Gas-liquid-solid partitioning

To study the gas-aerosol partitioning of size-fractionated nitrogen compounds, we first investigate in this section the relative importance of the choice of the chemical system and of the modeling approach (application of different EQMs). Since ammonia is the relatively weakest base, its cation ammonium is driven out of the aerosol phase in the presence of sufficient mineral cations. Ammonium is hence an ideal indicator for a sensitivity study of the gas-aerosol partitioning of size-fractionated nitrogen compounds. We therefore first address the ammonium partitioning (Fig. 5), defined as the concentration ratio of ammonium to the total of ammonia and ammonium and calculated from time averages (over all periods) of observed and predicted ammonia and ammonium concentration for fine and coarse mode particles and for all chemical systems (Table 1). Note that the partitioning is expressed in percent, which can result in large values pertaining to small concentrations, thus highlighting small differences, which underscores discrepancies between models and observations. Note further that Fig. 5 also allows a comparison of the different model predictions of the three EQMs (ISORROPIA, SCAPE2, EQSAM2) with each other and with the observations for both

the coarse and fine modes.

The observations (marked as CF in Fig. 5) show that on average 73% of the ammonium partitioned into the fine mode (F), while only about 13% partitioned into the coarse mode (C). However, the EQMs underestimate the ammonium partitioning for all chemical systems except for F5 (EQSAM2) and C1 (all EQMs). This underestimation increases as more mineral cations (Na^+ , Ca^{2+} , Mg^{2+} , K^+) are considered (F1-F5 and C1-C5). The increasing underestimation of the ammonium partitioning is most pronounced in SCAPE2 and EQSAM2 (for EQSAM2 except F5/C5) as both explicitly include all mineral cations; for ISORROPIA the values are approximately constant (F2-F5 and C2-C5), since mineral cations except sodium (i.e. Ca^{2+} , Mg^{2+} , K^+) are not explicitly accounted for in the model framework in contrast to SCAPE2 and EQSAM2.

On the other hand, if all mineral cations (Na^+ , Ca^{2+} , Mg^{2+} , K^+) are omitted, i.e. chemical system C1, all EQMs largely overestimate the amount of ammonium partitioned into the coarse mode. Interestingly, this is not the case for the same chemical system if applied to the fine mode (F1). Obviously, insufficient anions of the ammonium-sulfate-nitrate-water-system are available for neutralization by ammonia to get a sufficient amount of ammonium into the aerosol phase (F1). Only if the additional anions from (lumped) organic acids are taken into account in the modeling framework of EQSAM2, ammonium sufficiently partitions into the aerosol phase. The predicted average ammonium partitioning is then comparable to the observations within 1–2% for both the aerosol fine and coarse mode (F5/C5).

Nevertheless, all three EQMs give, within the measurement uncertainty of approximately 10%, comparable results for the ammonium partitioning predictions if applied at the same level of complexity, i.e. for the chemical systems F1/C1 and F2/C2, and with the above mentioned restrictions also for F3/C3. However, the model comparison at different levels of complexity (F4/C4 and F5/C5) indicates that it is important for the gas-aerosol partitioning of nitrogen compounds to consistently include mineral cations and organic acids, since only the predictions are comparable to the observations, if both mineral cations and organic acids are considered (F5/C5).

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4.2.2. Aerosol system F1/C1 compared to F5/C5

In this section we investigate the time evolution of the gas-aerosol partitioning of size-fractionated ammonium compounds over the three different periods (Period I–III). According to the previous section, we focus on the ammonium partitioning. Figure 6 shows the time series of the observed ammonium concentrations (in nmol/m^3 air) for the aerosol fine and coarse mode, together with the model predictions by ISORROPIA, SCAPE2 and EQSAM2 for the chemical systems F1/C1 and F5/C5, which exclude and include mineral cations (Na^+ , Ca^{2+} , Mg^{2+} , K^+) and organic acids, respectively.

Firstly Fig. 6a and c confirms that all three EQMs are in an excellent agreement if applied at the same level of complexity (F1/C1). However, they fail to predict the observed aerosol fine and coarse mode ammonium concentrations for all three periods. The only exception is the relatively good prediction of fine mode ammonium fraction for period I. Since all three EQMs also give similar results for system F5 and period I, it indicates that mineral cations and organic acids are unimportant for the ammonium partitioning for period I (fine aerosol mode). Obviously, for this period the fine mode is well represented by chemical system F1 since sulfate is the predominant anion, being predominantly neutralized by ammonium as a result of the limited availability of mineral cations (Fig. 4a).

For periods II and III the situation considerably differs as both are affected by biomass burning, i.e. with pyrogenic potassium in the aerosol fine mode. As a result, ammonium is driven out of the aerosol phase by the additional potassium cations, which preferentially neutralize the inorganic anions. Only if additionally organic anions are considered, ammonium is predicted in the aerosol phase. This is accomplished by the model predictions of EQSAM2 (chemical system F5, Fig. 6b). Since EQSAM2 is the only thermodynamic model that consistently includes mineral cations and lumped organic acids in this comparison, the results of Fig. 6b) do not improve for the other EQMs compared to Fig. 6a). Instead, the results become worse for SCAPE2 as this model only considers additional cations (Ca^{2+} , Mg^{2+} , K^+) but no organic acids, so that

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even more ammonium is driven out of the aerosol phase. In contrast, the results of ISORROPIA do not change, as these additional cations are not considered.

The situation is similar for the coarse mode (Figs. 6c and d), except that all EQMs largely overestimate the ammonium concentrations, if all mineral cations are omitted (chemical system C1, Fig. 6c). This is in strong contrast to the fine mode (Fig. 6a). Mineral cations are predominant in the coarse mode for all periods (Fig. 4b). A further consequence of this is that SCAPE2 hardly predicts any coarse mode ammonium if all mineral cations are considered for all periods, while the predictions of ISORROPIA mainly fail for the relatively dry period II. The reason is that for this period the sea salt concentrations are relatively low and the concentrations of cations from mineral (Saharan) dust high (chemical system C5, Fig. 6d). For the two humid periods with high sea salt concentrations (period I and III) the coarse mode simulations with ISORROPIA compare relatively well for the wrong reasons, i.e. only because both mineral cations and lumped organic acids are neglected in the modeling approach. However, both seem to be important for the gas-aerosol partitioning of reactive nitrogen compounds for certain Mediterranean conditions (period II and III).

4.2.3. Sensitivity to organic acids and mineral cations (F5/C5)

In this section we focus on the sensitivity of the gas-aerosol partitioning of reactive nitrogen compounds to the concentrations of organic acids and mineral cations. We first focus on the ammonium concentrations, for which we discuss only the fine mode. Ammonium is predominantly present in the fine mode and in competition with pyrogenic potassium, which is the predominant mineral cation in the fine mode as shown above (Fig. 4a).

To account for a potential disequilibrium for coarse mode particles due to the longer equilibration timescales of larger particles (smaller surface to volume ratio) or the unknown amount of insoluble matter (especially of mineral dust particles), we also study the sensitivity of coarse mode nitrate to the insoluble fraction of mineral cations from coarse mode sea salt and mineral dust.

Figure 7a shows similar to Fig. 6b time series of the measured ammonium concentrations (in nmol/m^3 air) for the aerosol fine mode (chemical system F5), together with the model results with ISORROPIA, SCAPE2 and EQSAM2, while Fig. 7b shows the associated scatter plots (model versus observations). In addition, the results of EQSAM2* are shown, which equals EQSAM2, except for the input concentrations of lumped organic acids (see below).

In contrast to EQSAM2 (see discussion of Fig. 6b), the predicted concentrations of fine mode ammonium by EQSAM2* are, according to Figs. 7a and b, much closer to the results of ISORROPIA and SCAPE2 for period II and III, only due to differences in the input concentrations of lumped organic acids, which were lower during all periods for EQSAM2* (discussion follows). In particular the high ammonium concentrations, which are confined to the biomass burning periods (II-III), are only reproduced by EQSAM2. Note that the correlation coefficients (R) given in the legends need not necessarily to be consistent with the scatter shown in Fig. 7b. The reason is that the correlation coefficient is mainly phase sensitive (i.e. $R=1$ means that the values occur at the same time), while the scatter (slope) shows the error in amplitude (i.e. a zero error or one-by-one slope if the predicted values are identical to the observed values at a certain time).

Obviously, there is a threshold value for the input concentration of lumped organic acids at which the ammonium is predicted in the aerosol phase in amounts as observed. This threshold value can be determined by the difference between total anions and cations, by accounting for the observed ammonium concentrations. For instance, for this study the required input concentration (threshold value) of the lumped organic acids – needed to balance the aerosol ammonium with respect to the observed concentration – has been estimated to best match the observed ammonium concentration for each period, by running EQSAM2 in the so-called reverse approach (see Metzger and Lelieveld, 2005²). From this sensitivity study the following values

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of Lumped Organic Acids (LOA) in percentage of the total (estimated) organic matter (OM) have been deduced for EQSAM2:

I. Period (1 August 2001, 10:00 hr–6 August 2001, 16:00 hr):

– fine mode: 10% of OM as LOA

II. Period (6 August 2001, 16:00 hr–12 August 2001, 19:00 hr):

– fine mode: 70% of OM as LOA

III. Period (12 August 2001, 19:00 hr–18 August 2001, 10:00 hr):

– fine mode: 70% of OM as LOA

For this modeling study we have assumed that the measured LOA (Fig. 4a), with values extracted by Sciare et al. (2005), account for approximately 10% of the total however not measured organic matter that might also include humic-like substances (HULIS). For EQSAM2* we used the measured LOA values, i.e. for all three periods LOA=10% of the total (estimated) OM.

The considerably larger amount of lumped organic acids, required to balance the observed fine mode ammonium during the two periods affected by biomass burning (i.e. period II and III), thus provides an indication of the fraction of additional organic matter, e.g. HULIS, which may be important in addition to the lumped organic acids considered. Assuming that the extracted organic acids are Water Soluble Organic Compounds (WSOC) that roughly account for 10% of the total organic matter (as mentioned above), additionally 60% of the OM would be subject to neutralization by ammonium, which might be HULIS. This fraction would therefore behave as the WSOC fraction that consist of the low molecular weight (LMW) organic acids given in Sect. 2, which have been lumped together according to the modeling results discussed in Trebs et al. (2005).

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Similarly to Fig. 7a, Fig. 8a shows the time series of measured nitrate concentrations (in nmol/m^3) for the aerosol coarse mode (chemical system C5), together with the model predictions by ISORROPIA, SCAPE2, EQSAM2, while Fig. 8b shows the associated scatter plots (model versus observations). In addition the results of EQSAM2* are shown, which equals EQSAM2 except for the input concentrations of mineral cations for the aerosol coarse mode, which differ (see below).

The time series of the aerosol nitrate (Fig. 8a) shows that the observed nitrate partitioning follows the *RH* relatively well (compare with Fig. 3) for the coarse mode, in contrast to aerosol ammonium (Fig. 7a). Nitric acid partitions largely into the aerosol phase under humid conditions, which is less well captured by the models including additional mineral aerosol compounds, i.e. they largely overestimate coarse mode nitrate. In particular Figs. 8a and b show that – from all models that have been applied to the same input concentrations, i.e. ISORROPIA, SCAPE2, EQSAM2* – the model predictions of ISORROPIA are in best agreement with the observations for coarse mode nitrate, since mineral cations from mineral dust are neglected. Since only ISORROPIA neglects cations from mineral dust, the deviations compared to other model predictions are most pronounced for period II, mainly due to the relatively low aerosol load of coarse mode sodium from sea salt (Fig. 4b). Only EQSAM2 yields a similarly close agreement with the observations (Fig. 8b) by considering the cations from mineral dust. In contrast to EQSAM2, the predicted concentrations of coarse mode nitrate by EQSAM2* are closer to the predictions of SCAPE2 for the entire period and in particular for period II and III, i.e. according to Figs. 8a and b. Similar to the sensitivity of aerosol ammonium to the concentration of organic acids, aerosol nitrate appears to be quite sensitive to the overall concentration of mineral cations. In particular the additional mineral cations from mineral dust leads especially for the dry period, which was influenced by Saharan dust (period II), to too high concentrations of coarse mode nitrate, compared to the observation.

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Obviously, not all of the measured mineral cations are required to neutralize the nitric acid to form nitrate. Similar to the required input concentration (threshold value) of the lumped organic acids, needed to balance the aerosol ammonium with respect to the observed concentration, the critical concentration of mineral cations has been determined to best match the observed nitrate concentration for each period by running EQSAM2 in the so-called reverse approach. In this way we implicitly account for the unknown insoluble matter (cations), or the amount of cations not available to neutralize nitric acid due to long equilibration time-scales, or due to the possibility that nitric acid might just have been absorbed on the surface of mineral dust particles, still not being neutralized. From this sensitivity study the following values have been deduced for EQSAM2, while we used for EQSAM2*, consistently with all other EQMs and for all periods, the total concentration of measured cations according to Fig. 4b:

I. Period (1 August 2001, 10:00 hr–6 August 2001, 16:00 hr):

– coarse mode: 4% of OM as LOA, 60% of Na⁺, 20% of Ca²⁺ and Mg²⁺

II. Period (6 August 2001, 16:00 hr–12 August 2001, 19:00 hr):

– coarse mode: 8% of OM as LOA, 60% of Na⁺, 20% of Ca²⁺ and Mg²⁺

III. Period (12 August 2001, 19:00 hr–18 August 2001, 10:00 hr):

– coarse mode: 8% of OM as LOA, 60% of Na⁺, 20% of Ca²⁺ and Mg²⁺

According to Fig. 4, aerosol nitrate is largely confined to the coarse mode, in contrast to ammonium that is mainly present in the fine mode. In particular the model results (Fig. 8b) are much closer to the observations for coarse mode nitrate for period I, with fewer discrepancies between the models compared to the results for period II and III, indicating that aerosol nitrate is mostly neutralized by sodium and less by other cations. The differences in the models predictions of EQSAM2 and EQSAM2* and the fact that the results of EQSAM2 are closer to the observations for period II and III compared

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to EQSAM2* (and the other EQMs), indicate that not all measured mineral cations neutralized nitric acid. Hence, the predictions of EQSAM2* are closer to SCAPE2 as both consider mineral cations, but both deviate most from the observations compared to EQSAM2 and ISORROPIA. This is in particular the case for the dry period, being strongly influenced by Saharan dust aerosols that lead to a significant contribution of mineral cations from mineral dust (in particular Ca^{2+} and Mg^{2+}).

According to the results in Fig. 8, however, not either all of the measured sodium neutralized the observed nitric acid during the two humid periods (I and III), influenced predominantly by coarse sea salt aerosol. The additional – although small – amount of non-sodium cations (in particular Ca^{2+} and Mg^{2+}) lead to too high nitrate concentrations if all sodium is considered in the neutralization reactions, as the results of SCAPE2 and EQSAM2* indicate. Even for the case where we have neglected any additional mineral cations (Ca^{2+} , Mg^{2+} and K^+) except sodium, the predicted nitrate concentrations are too high if all sodium is considered for the neutralization reactions, as indicated by the results of ISORROPIA. Obviously, not all sodium cations are required to neutralize nitric acid, even for the two humid periods (I and III), which indicates that for these cases sea salt particles might have consisted of an insoluble sodium chloride core, which did not equilibrate with nitric acid within the measurement interval of two hours. Approximately 40% of the sea salt particles (moles m^{-3} air) were not internally mixed but rather coated by non-neutralized nitric acid, possibly associated with an organic film.

5. Discussion and conclusions

The gas-aerosol partitioning of reactive nitrogen compounds, observed during the MINOS measurement campaign in Crete, Greece (Fig. 1), appears to be rather complex (Fig. 2) as the Mediterranean lower atmosphere is influenced by various periods with different levels of air pollution and distinct chemical composition. For instance, the core phase of the MINOS measurement campaign (1–18 August 2001) can be characterized

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by three different sub-periods, i.e. basically two humid periods with high levels of sea salt aerosol interrupted by a dry period with high levels of mineral dust aerosol, while the two last periods were additionally influenced by biomass burning pollution (Fig. 3). The different levels of atmospheric aerosols and their ionic composition, and in particular the concentration levels of cations, can be used to characterize the different periods of air pollution. For instance, the concentration levels of cations are important for the gas-aerosol partitioning of reactive nitrogen compounds as they determine the neutralization level of acidic particles, which in turn determines the gas-aerosol partitioning of volatile or semi-volatile aerosol compounds, the hygroscopic growth, or the aerosol precursor gas concentration.

The measurements (Fig. 4) show that the most important mineral cations are mainly present in the coarse mode, which indicates their natural origin, i.e. sodium from sea salt, and calcium, magnesium and a minor fraction of potassium from wind blown mineral dust (e.g. for period II from Saharan dust). In contrast, the major mineral cations present in the fine mode originated mainly from anthropogenic activities, i.e. ammonium and pyrogenic potassium. However, the main gaseous anthropogenic air pollutants, i.e. ammonia, nitric acid and organic acids, were as abundant as their natural counterparts and distributed over both the aerosol fine and coarse mode. For instance ammonia partitioned mainly into the fine mode, while nitric acid partitioned mainly into the coarse mode. This actually contradicts the assumption sometimes made that anthropogenic air pollutants are mainly confined to the aerosol fine mode, while natural air pollutants mainly occur in the coarse mode.

To study the temperature (T) and relative humidity (RH) dependent gas/aerosol equilibrium partitioning of reactive nitrogen compounds of the observed $H_2SO_4/HSO_4^-/SO_4^{2-}-HNO_3/NO_3^- -NH_3/NH_4^+ -HCl/Cl^- -Na^+ -Ca^{2+} -Mg^{2+} -K^+ -H_2O$ -system, including lumped organic acids ($R-COOH$) (Fig. 2), we have divided this complex aerosol system into five chemical systems for the fine (F1-F5) and coarse (C1-C5) aerosol mode, according to Table 1. This has been achieved by different constraints on the ionic composition, i.e. by subsequently including additional cations and anions.

This distinction allowed a comparison of EQMs at different levels of complexity (ISORROPIA, SCAPE2, EQSAM2). Our results show that the models yield comparable results (on average within ~10%, approximately the measurement uncertainty) if they are applied at the same level of complexity involving chemical systems F1/C1-F3/C3 of Figs. 5 and 6a, c).

Note, however, that the so-called equivalent sodium approach, which yields chemical system F3/C3 (Table 1), should be regarded as an approximation only, because of inconsistencies in the RHDs. For instance, the RHD of Na_2SO_4 is 93% and higher than of MgSO_4 , which is 86%, while the RHD of NaHSO_4 is 52% and thus lower than that of MgSO_4 . In the case of the equivalent sodium approach, these differences in the RHDs will cause differences in the liquid/solid partitioning, which subsequently affects the gas-aerosol partitioning of nitrogen compounds. This picture becomes even more complicated as EQSAM2 and ISORROPIA consider deliquescence relative humidities of mixed salts (Nenes et al., 1998, and Metzger et al., 2005²), since they are generally lower than the RHDs of the individual salt compounds, which are only considered in SCAPE2 (Kim et al., 1995). Nevertheless, the models agree within 10% also for the equivalent sodium approach (F3/C3 of Fig. 5), which indicates that these differences are of secondary importance for the gas-aerosol partitioning of reactive nitrogen compounds. More important is the consistent inclusion of major aerosol components, as shown by the model comparison at different levels of complexity (F4/C4 and F5/C5).

Figures 5 and 6b, d reveal the relative importance of mineral cations and organic acids for the gas-aerosol partitioning of nitrogen compounds. For instance, our results show that (lumped) organic acids are required to correctly balance fine and coarse mode ammonium (Fig. 7). The reason is that ammonia is driven out of the aerosol phase if mineral cations are considered but not additional acids from organics, which is the case for ISORROPIA and SCAPE2 (Figs. 6a, c versus Figs. 6b, d). The situation becomes worse for the case of low sea salt concentrations and relatively high concentrations of cations from mineral (Saharan) dust (chemical system C5, Fig. 6d). However, for the two humid periods with high sea salt concentrations (period I and III)

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the coarse mode predictions of ISORROPIA compare relatively well, but for the wrong reason, i.e. only because of the fact that both mineral cations and lumped organic acids are neglected in the modeling approach, although both seem to be important for the gas-aerosol partitioning.

This result is consistent with the findings of Trebs et al. (2005), which came to the same conclusion, however, for another extreme regime of air pollution, i.e. biomass burning of effluents over the tropical rainforest that has been investigated from 12 September to 14 November 2002 within the framework of LBA-SMOCC (Large-Scale Biosphere Atmosphere Experiment in Amazonia – Smoke Aerosols, Clouds, Rainfall, and Climate: Aerosols From Biomass Burning Perturb Global and Regional Climate).

Our results further show that the consideration of major coarse mode mineral cations is important in order to balance aerosol nitrate as observed. For period I and III, the consideration of sodium from sea salt aerosol is most important, while accounting for the additional major cations calcium and magnesium from mineral dust leads, in particular for period II, to an overestimation of aerosol nitrate by SCAPE2 and EQSAM2* (Fig. 8). This indicates that only a soluble fraction of mineral cations is in chemical and thermodynamic equilibrium with inorganic and organic acids. The fraction of mineral cations that did not neutralize the acids has most likely not been in equilibrium, i.e. insoluble coarse mode particles on which acids condensed without being neutralized, yielding externally rather than internally mixed aerosols. This fraction has been estimated by a sensitivity study to be approximately 80% for the measured calcium and magnesium (percentage in terms of moles per cubic meter air), by using the reverse approach option of EQSAM2. In this case the model is constrained by observed nitrate and nitric acid concentrations to predict the amount of mineral cations that are required to balance the model predictions for aerosol nitrate with the observations. From this sensitivity study it further appears that approximately 40% of the major mineral cation from sea salt (Na^+) did not neutralize nitric acid, since also the predictions of ISORROPIA, which neglects all mineral cations except sodium, slightly overestimates aerosol nitrate for all periods consistently with the other EQMs. Only EQSAM2 correctly

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balances the aerosol nitrate if we account for the previously determined insoluble fraction (forward approach). The fraction of nitric acid that remained un-neutralized is given by the difference of EQSAM2 and EQSAM2*; EQSAM2* is identical to EQSAM2 except that all mineral cations have been considered for the nitrate partitioning. EQSAM2* therefore predicts for all periods higher aerosol nitrate concentrations than EQSAM2, consistently with SCAPE2.

We thus conclude that consistently including inorganic and (lumped) organic acids together with (soluble) mineral cations and ammonium is most important in aerosol composition modeling studies, even if we can currently realize this only in a simplified manner. Certainly, such a simplified approach is associated with uncertainties, e.g. lumping organic acids based on the total of carboxylic groups, and ignoring the possibility that part of the organic acids are semi-volatile (we have treated them as non-volatile), or the fact that we have simplified the activity coefficient calculation by deriving the activity coefficients of semi-volatile compounds directly from the *RH*. Additional uncertainties arise from the use of filter measurements in particular for semi-volatile aerosol compounds such as ammonium nitrate, which was however not an important compound for this study (at least not during daytime), or the various assumptions made about the RHDs and the lack of knowledge on MRHD for mixed inorganic and organic salt solutions. Nevertheless, our simplified approach provides a first and reasonably realistic evaluation of the gas-aerosol partitioning of reactive nitrogen compounds in the Mediterranean region.

Acknowledgements. This work was supported by the PHOENICS project (<http://phoenics.chemistry.uoc.gr>), financed by the European Union (EVK2-CT-2001-00098). We thank C. Oikonomou for the IC measurements and J. Sciare for providing the partitioning between the fine and coarse mode of the main anions and cations and the OM values. N. Mihalopoulos thanks the Ministry of Education through Pythagoras II project for financial support.

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- Bardouki, H., Liakakou, H., Economou, C., Sciare, J., Smolík, J., Ždímal, V., Eleftheriadis, K., Lazaridis, M., and Mihalopoulos, N.: Chemical composition of size resolved atmospheric aerosols in the eastern Mediterranean during summer and winter, *Atmos. Environ.*, 37, 195–208, 2003.
- Berresheim, H., Plass-Dülmer, C., Elste, T., Mihalopoulos, N., and Rohrer, F.: OH in the coastal boundary layer of Crete during MINOS: Measurements and relationship with ozone photolysis, *Atmos. Chem. Phys.*, 3, 639–649, 2003, [SRef-ID: 1680-7324/acp/2003-3-639](#).
- Cofer, W. R., Collins, V. G., and Talbot, R.: Improved aqueous scrubber for collection of soluble atmospheric trace gases, *Environ. Sci. Technol.*, 19, 557–560, 1985.
- Kawamura, K., Kasukabe, H., and Barrie, L.: Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in Arctic aerosols: One year of observations, *Atmos. Environ.*, 30, 1709–1722, 1996.
- Kawamura, K. and Sakaguchi, F.: Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics, *J. Geophys. Res.*, 104, 3501–3509, 1999.
- Kim, Y. P. and Seinfeld, J. H.: Atmospheric gas/aerosol equilibrium III. Thermodynamics of crustal elements Ca²⁺, K⁺, and Mg²⁺, *Aerosol Sci. Technol.*, 22, 93–110, 1995.
- Kouvarakis, G. and Mihalopoulos, N.: Seasonal variation of dimethylsulfide in the gas phase and of methanesulfonate and non-sea-salt sulfate in the aerosol phase measured in the Eastern Mediterranean atmosphere, *Atmos. Environ.*, 36, 929–938, 2002.
- Kouvarakis, G., Doukelis, Y., Mihalopoulos, N., Rapsomanikis, S., Sciare, J., and Blumthaler, M.: Chemical, physical and optical characterization of aerosol during PAUR II experiment, *J. Geophys. Res.*, 107, 814, doi:10.1029/2000JD000291, 2002.
- Krivacsy, Z., Hoffer, A., Sarvari, Z., Temesi, D., Baltensperger, U., Nyeki, S., Weingartner, E., Kleefeld, S., and Jennings, S. G.: Role of organic and black carbon in the chemical composition of atmospheric aerosol at European background sites, *Atmos. Environ.*, 35, 6231–6244, 2001.
- Lelieveld, J., Berresheim, J. H., Borrmann, S., Crutzen, P. J., Dentener, F. J., Fischer, H., Feichter, J., Flatau, P. J., Heland, J., Holzinger, R., Kormann, R., Lawrence, M. G., Levin, Z., Markowicz, K. M., Mihalopoulos, N., Minikin, A., Ramanathan, V., de Reus, M., Roelofs, G.

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Meng, Z., Seinfeld, J. H., Saxena, P., and Kim, Y. P.: Atmospheric gas/aerosol equilibrium. IV: Thermodynamics of carbonates, *Aerosol Sci. Technol.*, 23, 131–154, 1995.

Meng, Z. and Seinfeld, J. H.: Time scales to achieve atmospheric gas/aerosol equilibrium for volatile species, *Atmos. Environ.*, 30, 2889–2900, 1996.

Metzger, S. M.: Gas/Aerosol Partitioning: A simplified Method for Global Modeling, PhD thesis, University Utrecht, The Netherlands, ISBN: 90-393-2510-3, <http://www.library.uu.nl/digiarchief/dip/diss/1930853/inhoud.htm/>, 2000.

Metzger, S. M., Dentener, F. J., Lelieveld, J., and Pandis, S. N.: Gas/aerosol partitioning I: a computationally efficient model, *J. Geophys. Res.*, 107(D16), doi:10.1029/2001JD001102, 2002a.

Metzger, S. M., Dentener, F. J., Jeuken, A., Krol, M., and Lelieveld, J.: Gas/aerosol partitioning II: global modeling results, *J. Geophys. Res.*, 107(D16), doi:10.1029/2001JD001103, 2002b.

Moya, M., Ansari, A. S., and Pandis, S. N.: Partitioning of nitrate and ammonium between the gas and particulate phases during the 1997 IMADA-AVER study in Mexico City, *Atmos. Environ.*, 35, 1791–1804, 2001.

Nenes, A., Pilinis, C., and Pandis, S. N.: Isorropia: A new thermodynamic model for multiphase multicomponent inorganic aerosols, *Aquat. Geochem.*, 4, 123–152, 1998.

Salisbury, G., Williams, J., Holzinger, R., Gros, V., Mihalopoulos, N., Vrekoussis, M., Sarda-Estève, R., Berresheim, H., von Kuhlmann, R., Lawrence, M., and Lelieveld, J.: Ground-based PTR-MS measurements of reactive organic compounds during the MINOS campaign in Crete, July–August 2001, *Atmos. Chem. Phys.*, 3, 925–940, 2003, [SRef-ID: 1680-7324/acp/2003-3-925](https://doi.org/10.5194/acp-3-925-2003).

Sciare, J. and Mihalopoulos, N.: A new technique for sampling and analysis of atmospheric dimethylsulfoxide (DMSO), *Atmos. Environ.*, 34, 151–156, 2000.

Sciare, J., Bardouki, H., Moulin, C., and Mihalopoulos, N.: Aerosol sources and their contribution to the chemical composition of aerosols in the Eastern Mediterranean Sea during summertime, *Atmos. Chem. Phys.*, 3, 1–12, 2003a, [SRef-ID: 1680-7324/acp/2003-3-1](https://doi.org/10.5194/acp-3-1-2003).

Sciare, J., Cachier, H., Oikonomou, K., Ausset, P., Sarda-Estève, R., and Mihalopoulos, N.:

Characterization of Carbonaceous Aerosols during the MINOS campaign in Crete, July–August 2001: a multi-analytical approach, *Atmos. Chem. Phys.*, 3, 1743–1757, 2003b, [SRef-ID: 1680-7324/acp/2003-3-1743](#).

5 Sciare, J., Oikonomou, K., Cachier, H., Mihalopoulos, N., Andreae, M. O., Maenhaut, W., and Sarda-Estève, R.: Aerosol mass closure and reconstruction of the light scattering coefficient over the Eastern Mediterranean Sea during the MINOS campaign, *Atmos. Chem. Phys.*, 5, 2253–2265, 2005, [SRef-ID: 1680-7324/acp/2005-5-2253](#).

10 Traub, M., Fischer, H., de Reus, M., Kormann, R., Heland, J., Ziereis, H., Schlager, H., Holzinger, R., Williams, J., Warneke, C., de Gouw, J., and Lelieveld, J.: Chemical characteristics assigned to trajectory clusters during the MINOS campaign, *Atmos. Chem. Phys.*, 3, 459–468, 2003, [SRef-ID: 1680-7324/acp/2003-3-459](#).

15 Trebs, I., Metzger, S., Meixner, F. X., Helas, G., Hoffer, A., Andreae, M. O., Moura, M. A. L., da Silva Jr., R. S., Slanina, J., Rudich, Y., Falkovich, A., and Artaxo, P.: The NH_4^+ - NO_3^- - Cl^- - SO_4^{2-} - H_2O system and its gas phase precursors at a rural site in the Amazon Basin: How relevant are crustal species and soluble organic compounds?, *J. Geophys. Res.-Atmos.*, 110(D07303), doi:10.1029/2004JD005478, 2005.

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Table 1. Aerosol chemical systems considered in the different equilibrium models.

Fine	Coarse	Model*	Aerosol system
F1	C1	1, 2, 3	$\text{H}_2\text{SO}_4/\text{HSO}_4^-/\text{SO}_4^{2-}-\text{HNO}_3/\text{NO}_3^--\text{NH}_3/\text{NH}_4^+-\text{H}_2\text{O}$
F2	C2	1, 2, 3	$\text{F1/C1} + \text{HCl/Cl}^- - \text{Na}^+$
F3	C3	1, 2, 3	$\text{F2/C2} + (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+) \text{ as equivalent Na}^+$
F4	C4	1, 2	$\text{F2/C2} + \text{Ca}^{2+} + \text{Mg}^{2+} \text{ K}^+$
F5	C5	1	$\text{F4/C4} + \text{organic acids}$

* 1 = EQSAM2, 2 = SCAPE2, 3 = ISORROPIA

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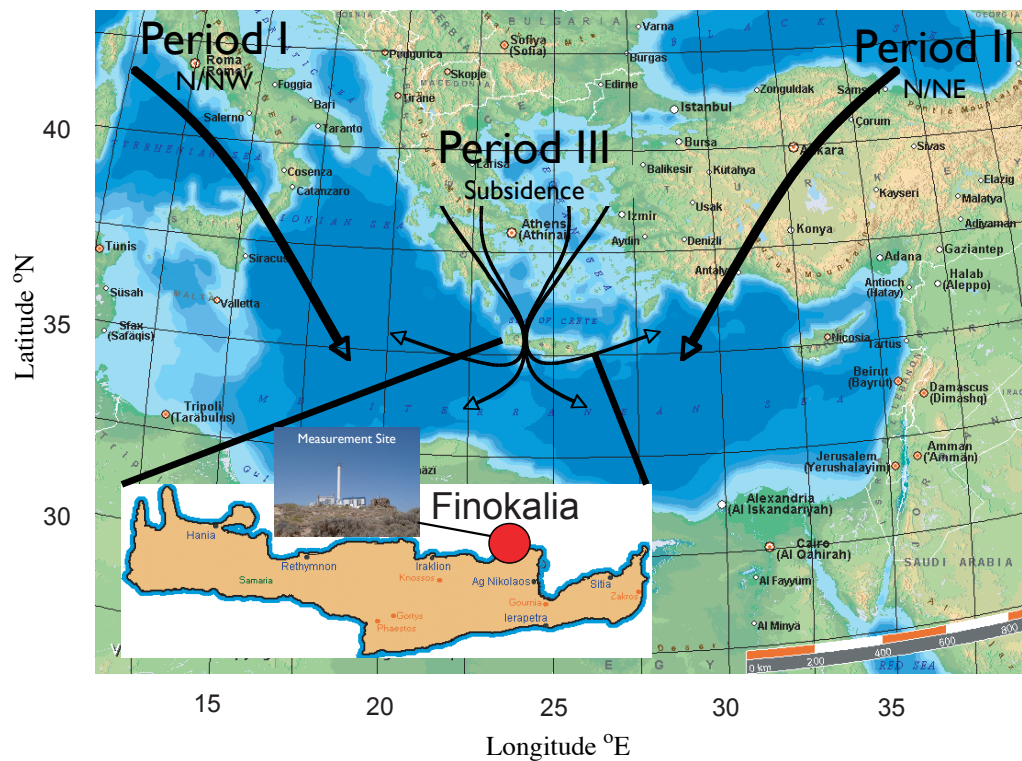


Fig. 1. Map of the eastern Mediterranean region, Crete and Finokalia station where the MINOS campaign was performed.

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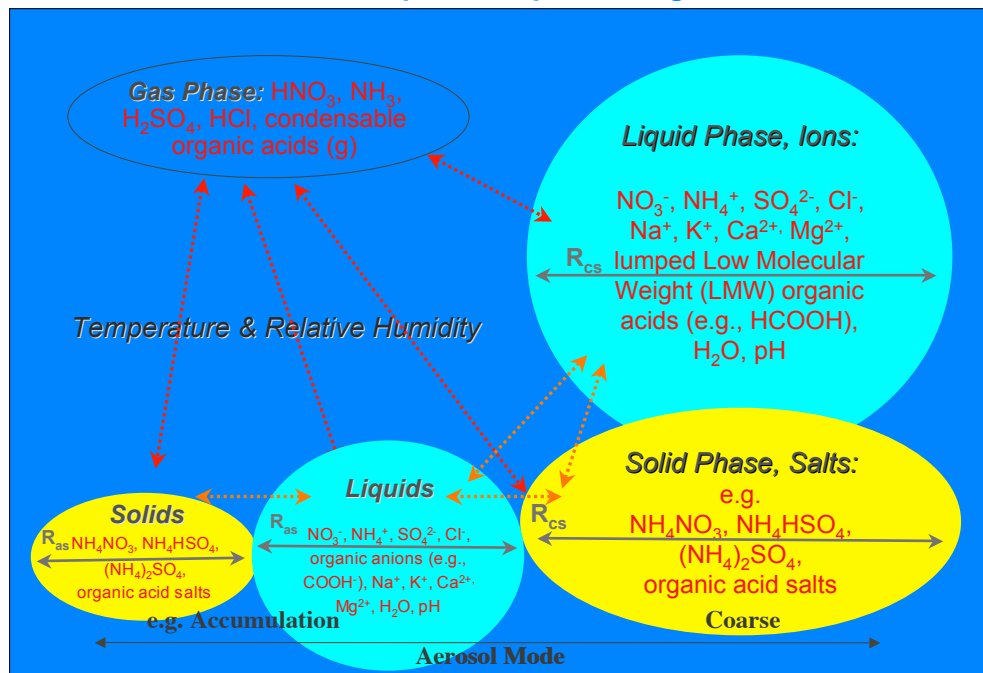


Fig. 2. Schematic description of the compounds and gas-aerosol partitioning processes included in EQSAM2.

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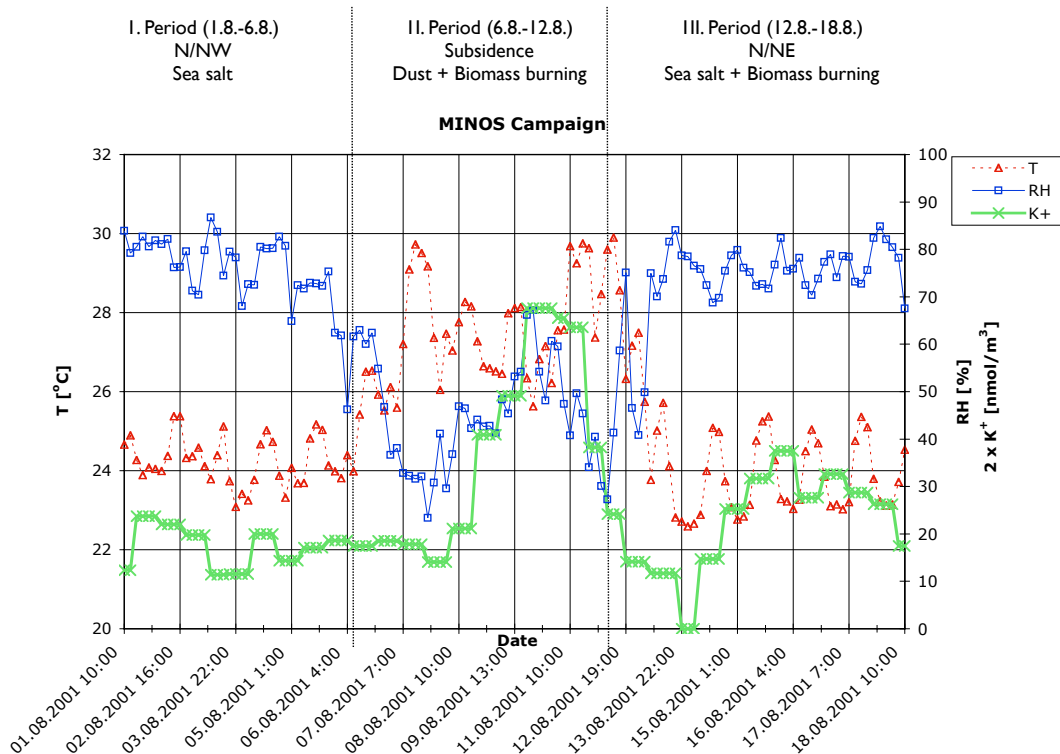


Fig. 3. Temperature (T), relative humidity (RH) and potassium (K^+) time evolution during the MINOS campaign for three different air pollution periods: Period I (1 August–6 August 2001) dominated by sea salt, period II (6 August–12 August 2001) dominated by mineral dust and biomass-burning air pollution, period III (12 August–18 August 2001) dominated by sea salt and biomass-burning air pollution. Note that potassium concentrations [nmol/m³], used as indicator for biomass burning, are scaled by a factor of two.

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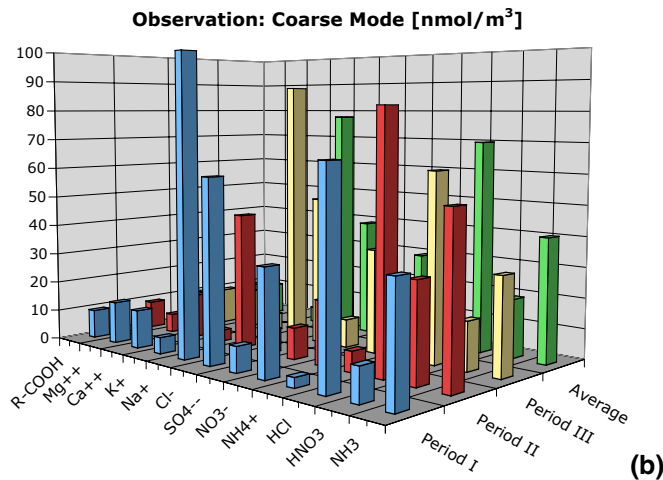
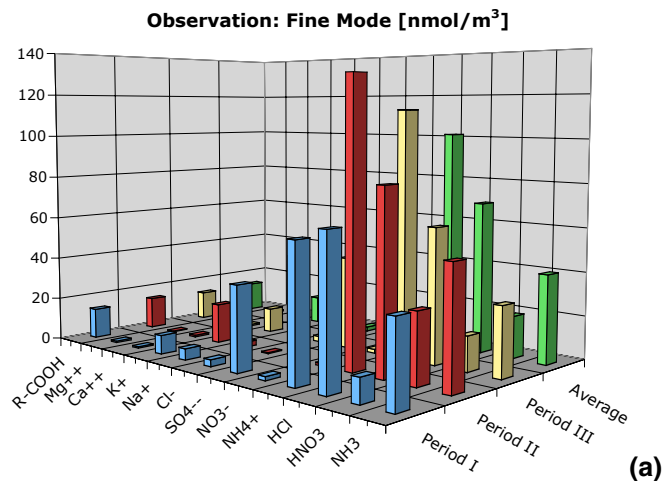


Fig. 4. Time averages of observed aerosol precursor gas and aerosol concentrations [nmol/m³] for the three different periods as defined in Fig. 3. Panel (a) shows the aerosol fine mode, and panel (b) the coarse mode aerosol.

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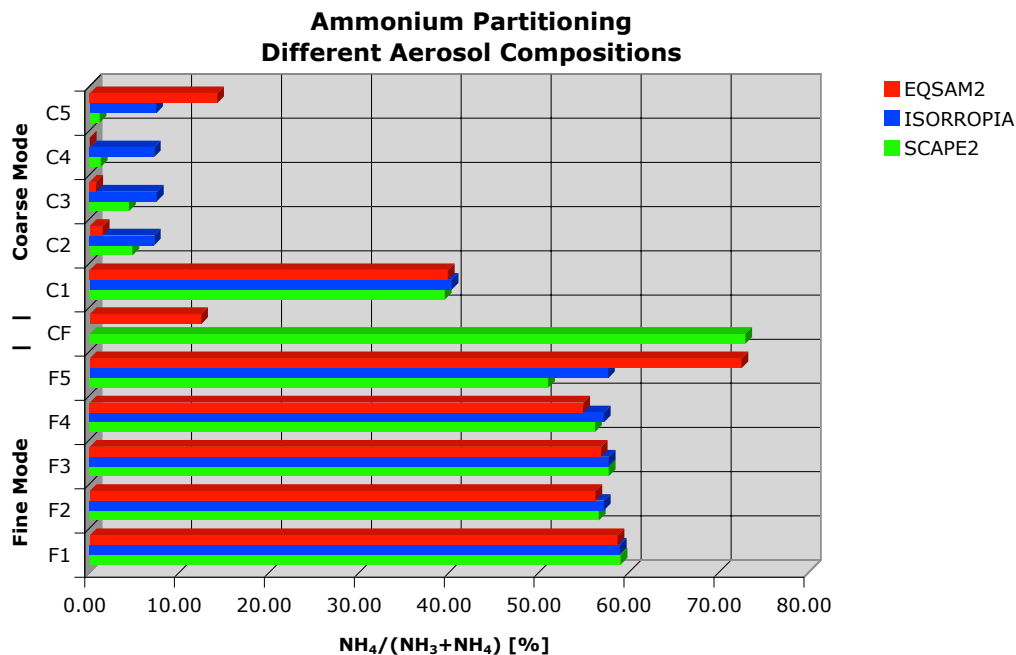
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	F1	F2	F3	F4	F5	CF	C1	C2	C3	C4	C5
EQSAM2	58.70	56.26	56.86	54.89	72.48	12.41	39.83	1.44	0.71	0.01	14.15
ISORROPIA	58.96	57.18	57.74	57.18	57.67		40.25	7.15	7.45	7.15	7.40
SCAPE2	59.06	56.65	57.75	56.22	50.99	72.91	39.48	4.77	4.36	1.24	1.12

Fig. 5. Time averages of observed and model calculated ammonium partitioning (ratio of aerosol ammonium and ammonium plus ammonia) [%] for the fine (F) and coarse (C) aerosol mode and for all aerosol systems (F1-F5 and C1-C5) given in Table 1. For each system, all three model predictions are shown: from top to bottom EQSAM2 (red), ISORROPIA (blue) and SCAPE2 (green), whereas the observations (CF) are shown in the middle between the two aerosol modes starting from top to bottom with the coarse (C, red) and fine (F, green) modes.

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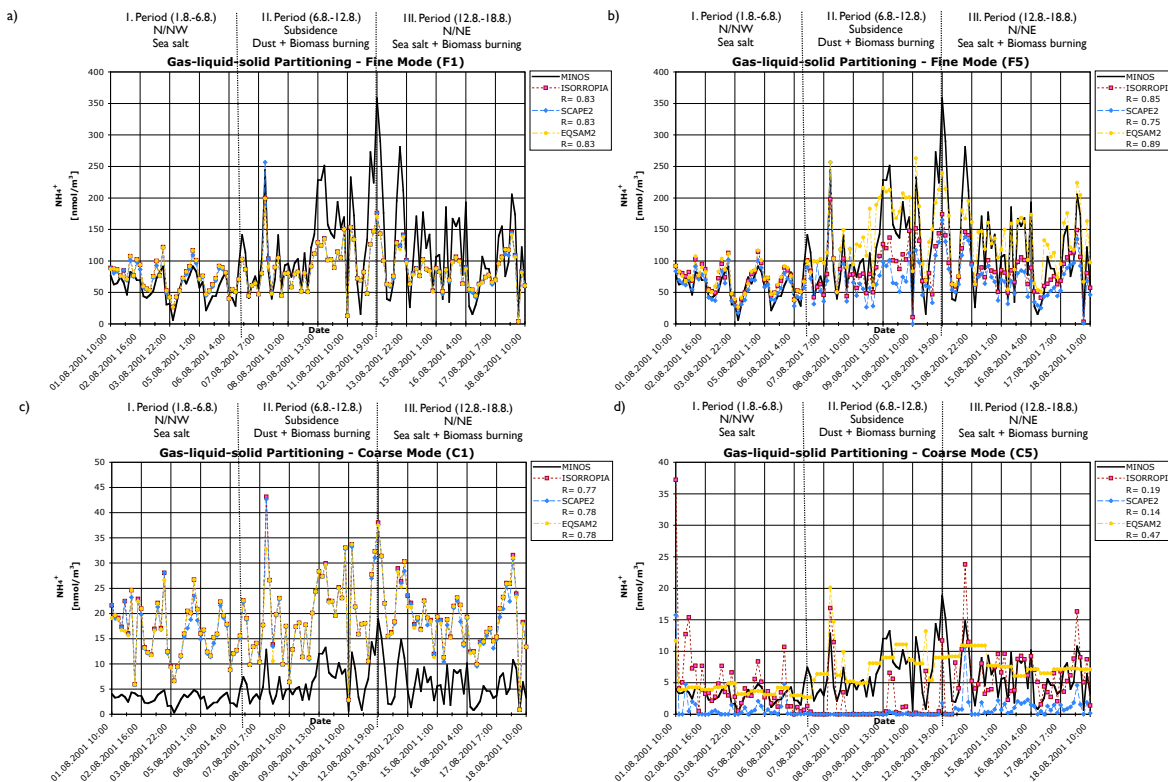


Fig. 6. Time series of measured (black solid line) fine mode aerosol ammonium (panels **a** and **b**) [nmol/m^3] and coarse (panels **c** and **d**) mode ammonium [nmol/m^3] for two different aerosol systems: The reduced chemical system (panels **a** and **c**) neglecting all cations except ammonium (F1/C1) and the most complete chemical system (F5/C5) (panels **b** and **d**) including mineral cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}). For each model the correlation coefficient (R) is given. The model results are obtained with ISORROPIA (purple, dashed line with closed squares), SCAPE2 (blue, long dashed line with closed diamonds), EQSAM2 (gold, short-long dashed line with closed circles).

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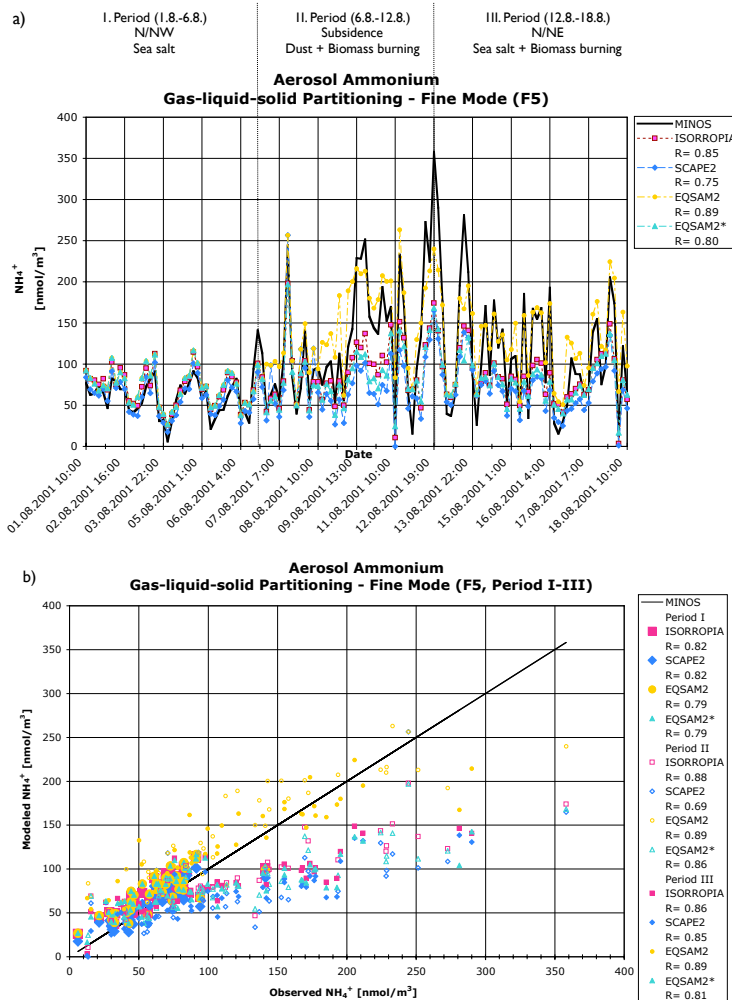
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Fig. 7.

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Fig. 7. Time series of measured (black solid line) and calculated fine mode aerosol ammonium (panel **a**) [nmol/m^3] with the corresponding scatter plot (panel **b**) (model predictions versus observations) for the most comprehensive chemical system (F5/C5). The correlation coefficients (R) are given in the legends and the colors and symbols of the three models (ISORROPIA, SCAPE2, EQSAM2) are the same as in Fig. 6. The additional model EQSAM2* (turquoise, short-long-dotted dashed with closed triangles) is the same as EQSAM2 except for the input concentrations of mineral cations and lumped organic acids. See text for details. Note the different symbols for the scatter plot that indicate each period, i.e. large closed symbols are used for period I, small open symbols for period II and small closed symbols for period III. The symbols are the same as in panel (a). The correlation coefficients (R) are given in the legend of panel (b) for each period and model, while panel (a) shows the entire period (and each model).

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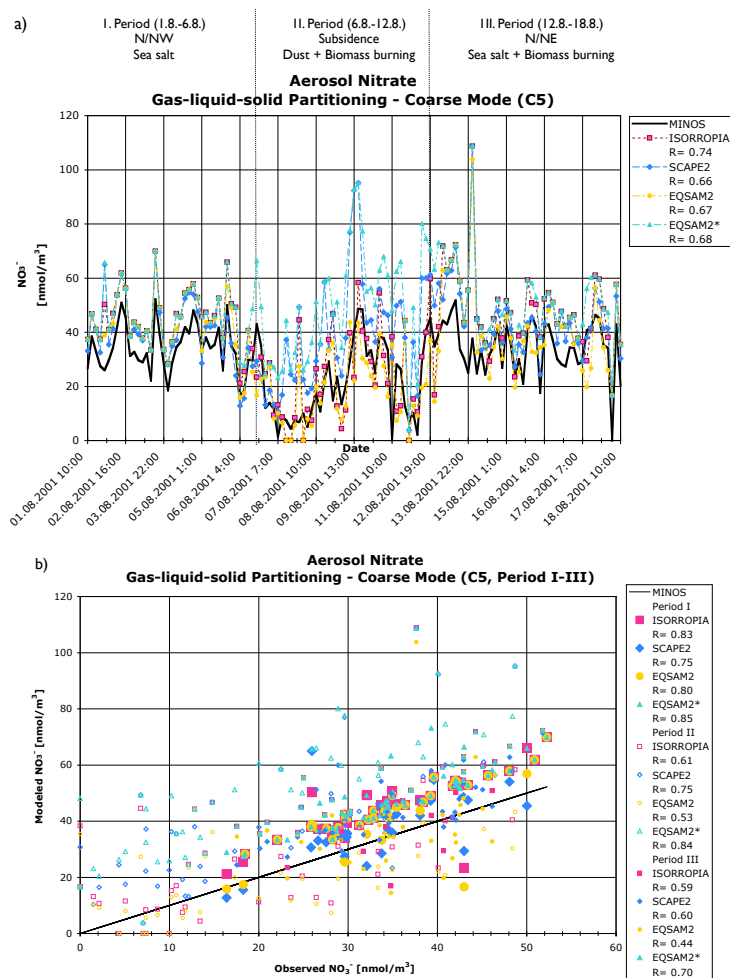


Fig. 8. Time series of measured (black solid line) and calculated coarse mode aerosol nitrate (panel a) [nmol/m³] and the corresponding scatter plot (panel b), analogous to Fig. 7.

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