

Particle water and pH
in the Eastern
Mediterranean

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Particle water and pH in the Eastern Mediterranean: sources variability and implications for nutrients availability

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Abstract

Particle water (LWC) and aerosol pH drive the aerosol phase, heterogeneous chemistry and bioavailability of nutrients that profoundly impact cloud formation, atmospheric composition and atmospheric fluxes of nutrients to ecosystems. Few measurements of in-situ LWC and pH however exist in the published literature. Using concurrent measurements of aerosol chemical composition, cloud condensation nuclei activity and tandem light scattering coefficients, the particle water mass concentrations associated with the aerosol inorganic (W_{inorg}) and organic (W_{org}) components are determined for measurements conducted at the Finokalia atmospheric observation station in the eastern Mediterranean between August and November 2012. These data are interpreted using the ISORROPIA-II thermodynamic model to predict pH of aerosols originating from the various sources that influence air quality in the region. On average, closure between predicted aerosol water and that determined by comparison of ambient with dry light scattering coefficients was achieved to within 8% (slope = 0.92, $R^2 = 0.8$, $n = 5201$ points). Based on the scattering measurements a parameterization is also derived, capable of reproducing the hygroscopic growth factor ($f(\text{RH})$) within 15% of the measured values. The highest aerosol water concentrations are observed during nighttime, when relative humidity is highest and the collapse of the boundary layer increases the aerosol concentration. A significant diurnal variability is found for W_{org} with morning and afternoon average mass concentrations being 10–15 times lower than nighttime concentrations, thus rendering W_{inorg} the main form of particle water during daytime. The average value of total aerosol water was $2.19 \pm 1.75 \mu\text{g m}^{-3}$, contributing on average up to 33% of the total submicron mass concentration. Average aerosol water associated with organics, W_{org} , was equal to $0.56 \pm 0.37 \mu\text{g m}^{-3}$, thus organics contributed about 27.5% to the total aerosol water, mostly during early morning, late evening and nighttime hours.

The aerosol was found to be highly acidic with calculated aerosol pH varying from 0.5 to 2.8 throughout the study period. Biomass burning aerosol presented the highest

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values of pH in the submicron fraction and the lowest values in total water mass concentration. The low pH values observed in the submicron mode and independently of air masses origin could increase nutrient availability and especially P solubility, which is the nutrient limiting sea water productivity of the eastern Mediterranean.

1 Introduction

Atmospheric particles have the ability to absorb significant amounts of water, which profoundly affects their physical and chemical properties (Khlystov et al., 2005), and impacts on atmospheric processes and health. Ambient concentrations of aerosol liquid water are controlled by the aerosol chemical composition, relative humidity (RH) and temperature, as it is largely in chemical equilibrium with the surrounding water vapor. Liquid water is ubiquitous and exceeds the total aerosol dry mass by 2 to 3 times on a global scale (Liao and Seinfeld, 2005). Therefore, the aerosol liquid water content (LWC) increases the particle size, affecting the particle lifetime and scattering efficiency. LWC and its strong dependence on relative humidity (RH) are the most important contributors to aerosol direct radiative cooling by aerosols (Pilinis et al., 1995). Numerous modeling studies suggest that reactions in aerosol liquid water are an important pathway of secondary organic aerosol (SOA) formation (Carlton and Turpin, 2013; Myriokefalitakis et al., 2011), thus playing an important role in the overall aerosol chemical composition. Aerosol water also has profound impact on the aerosol phase state, being able to transform semi-solid and viscous particles into a single liquid phase that rapidly equilibrates with its environment (Pöschl and Shiraiwa, 2015). This affects the timescale of heterogeneous reactions and ice nucleation. Despite the abundance and importance of LWC, it is not routinely measured, actual mass concentrations are uncertain, especially in the presence of organic compounds and model predictions of the property are often not evaluated (Nguyen et al., 2014).

Apart from the LWC, the pH of aqueous aerosols is another critically important aerosol property that drives many processes related to the aerosol chemical com-

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position and gas-aerosol partitioning (Guo et al., 2015; Surratt et al., 2007; 2010; Meskhidze et al., 2003; Eddingsaas et al., 2010; Myriokefalitakis et al., 2015). A direct measurement of aerosol pH in-situ is not possible; instead indirect proxies are commonly used to represent the particle acidity (Guo et al., 2015; Hennigan et al., 2015). The most frequently used proxy is the “ion balance”, where the charge balance of measurable anions and cations is calculated, with the exception of the hydronium and hydroxyl ions; a surplus of cations implies an alkaline aerosol and vice versa. Often it is implied that a larger value of the ion balance implies a stronger acidity/alkalinity. As shown by Hennigan et al. (2015) and Guo et al. (2015), the ion balance (and other similar proxies discussed in Hennigan et al., 2015) fail in general to represent the true aerosol pH; only meticulous measurement of semi-volatile species (such as ammonia/ammonium) and other aerosol chemical constituents, combined with appropriate thermodynamic calculations (e.g. with ISORROPIA-II; Fountoukis and Nenes, 2007) are able to realistically provide particle pH and LWC (Hennigan et al., 2015).

Directly linked to aerosol pH and LWC is the catalytic role of aerosol acidification on the bioavailability of nutrients contained within dust; upon deposition, increased availability of these nutrients may promote primary productivity in continental and marine ecosystems (e.g., Meskhidze et al., 2003; Nenes et al., 2011; Mahowald et al., 2008, 2009; Krishnamurthy et al., 2010). Acids (such as sulfuric and nitric) generated in the atmosphere from a variety of anthropogenic and biogenic sources, when mixed with mineral aerosols in sufficient amounts could lower the aerosol pH to values that increase the solubilities of Fe and P-containing minerals by several orders of magnitude (Stumm and Morgan, 1996; Shi et al., 2012). Nenes et al. (2011) have demonstrated that acidification can release considerable amounts of soluble phosphorus from soil-laden minerals (e.g., 81–96 % of the total P found in Saharan dust and soil). Apart from P, the transport and deposition of mineral dust is believed to be a major, if not the dominant source of Fe to the remote ocean (Jickells et al., 2005). With the incorporation of SO₂ in advected dust plumes and the subsequent acidification through heterogeneous oxidation, Meskhidze et al. (2003) concluded that in pH < 2, 1–2 % of the contained

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Fe would be mobilized within 3–5 days. Meskhidze et al. (2005) also demonstrated that sufficient acidification of Asian dust plumes could drive, upon deposition, a phytoplankton bloom in High Nitrate Low Chlorophyll regions of the North Atlantic. Solomon et al. (2009) also showed that simulated enhancements in particulate soluble iron driven by the chemical dissolution mechanism, can range from 0.5 to 6 %, which is consistent with observations over the North Pacific Ocean.

The Eastern Mediterranean, being at the nexus of three continents (Europe, Asia and Africa), receives air masses influenced by a spectrum of human (traffic, biomass burning and industry) and natural (dust and marine) sources. It is therefore an ideal location to study atmospheric acidification of aerosols; very few studies however to date have accomplished that. By combining aerosol chemical composition measurements in conjunction with cloud condensation nuclei (CCN) concentration and light scattering coefficient (σ_{sp}) measurements, we determine the water mass concentrations (LWC) of aerosols from various sources in the Eastern Mediterranean. These data are then used in combination with the ISORROPIA-II thermodynamic equilibrium model (Fountoukis and Nenes, 2007) to predict the aerosol pH for air masses that influenced air quality in the Eastern Mediterranean during the late summer and fall months of 2012.

2 Instrumentation and methods

2.1 Measurement site

Aerosol measurements were conducted at the Finokalia atmospheric observation station in Crete, Greece (35°20' N, 25°40' E, 250 m a.s.l.) between August and November 2012. The site (<http://finokalia.chemistry.uoc.gr/>) is a European supersite for atmospheric aerosol research and is part of the ACTRIS Network (Aerosols, Clouds, and Trace gases Research Infrastructure) (<http://www.actris.eu/>). The station is located at the northeastern part of the island of Crete, facing the Mediterranean Sea covering the whole northern sector. Being away from direct urban influence, the station is

et al., 2015). Concurrent black carbon (BC) measurements were performed on site using a seven-wavelength aethalometer (Magee Scientific, AE31) with a time resolution of 5 min. Based on previous studies at Finokalia, BC is found mainly on the fine aerosol fraction (Koulouri et al., 2008; Bougiatioti et al., 2014) hence these values are used in addition to the ACSM concentrations to calculate the dry aerosol mass of the PM₁ fraction.

Size-selected cloud condensation nuclei (CCN) measurements were obtained using a Droplet Measurement Technologies, Continuous Flow Streamwise Thermal Gradient CCN counter (CFSTGC). Particles of 60, 80, 100 and 120 nm were first size-selected by a differential mobility analyzer (DMA), split into two and one of these flows was introduced in the CCN counter. The total number of condensation nuclei (CN) was measured by a condensation particle counter (CPC; TSI 1772) situated downstream the first DMA. In the CCN counter, the activated droplets are sized and counted by an optical particle counter (OPC) after exiting the growth chamber. The instrument was operated in scanning flow CCN analysis mode (SFCA; Moore and Nenes, 2009), where the flow rate in the growth chamber changes over time, while a constant temperature difference is maintained. In that way the supersaturation changes continuously, providing activation spectra with a high temporal resolution. The flow rate was increased linearly between a minimum and a maximum flow rate and sigmoidal activation curves of CCN vs flow rate were recorded, with the inflection point of the sigmoid representing a critical activation flow, Q_{50} , that corresponds to a critical supersaturation, S^* , above which particles act as CCN. From the critical supersaturation and knowledge of the particle dry diameter, with the application of Köhler theory, the hygroscopicity parameter kappa (Petters and Kreidenweis, 2007) is obtained, which is then used to determine the LWC associated with organic components of the aerosol (Guo et al., 2015)

2.3 Determination of LWC from nephelometers

The particle water was inferred using the approach of Guo et al. (2015), where the ratio of the wet and dry PM₁ scattering coefficients (σ_{sp}) measured by the two neph-

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elometers is used. For this, the aerosol hygroscopic growth factor ($f(\text{RH})$) is calculated according to a well-established method based on the two scattering coefficients: $f(\text{RH}) = \sigma_{\text{sp}(\text{wet})} / \sigma_{\text{sp}(\text{dry})}$ (e.g. Sheridan, 2002; Magi, 2003; Kim et al., 2006). These scattering coefficients in ambient and dry conditions are proportional to the diameter of average surface $\overline{D_p}$ and the average scattering coefficients $\overline{Q_s}$, so that :

$$\overline{D_{p,\text{ambient}}} = \overline{D_{p,\text{dry}}} \sqrt{f(\text{RH}) \overline{Q_{s,\text{dry}}} / \overline{Q_{s,\text{ambient}}}} \quad (1)$$

Assuming that the two average scattering efficiencies are almost equal, LWC is then equal to the difference between ambient and dry particle volume, and by substitution of the dry diameter of average surface:

$$\overline{D_{p,\text{dry}}}^3 = \frac{m_p}{\left(\frac{\pi}{6}\right) \rho_p N_t} \quad (2)$$

where N_t is the total number concentration, ρ_p is the density of dry aerosol and m_p is the dry mass concentration, we arrive at the simplified expression of:

$$\text{LWC} = \left[f(\text{RH})^{1.5} - 1 \right] \frac{m}{\rho_p} \quad (3)$$

The simplification assumption that the dry and ambient scattering efficiencies are almost equal introduces an error in the derived LWC, which based on the detailed analysis of Guo et al. (2015), is of the order of 10 % at $\text{RH} = 76.4\%$, but can reach up to 21 % at $\text{RH} = 90\%$.

For this set of measurements the PM_{10} dry mass concentration is calculated from the sum of the ACSM constituents combined with the BC measurements. The particle density, ρ_p , was estimated from the particle composition from the ACSM ammonium, organics and sulfate, using an organic density of 1.35 g cm^{-3} as determined by Lee

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et al. (2010) for the same site during the summer of 2008, the density of ammonium sulfate (1.77 g cm^{-3}) and the equation:

$$\rho_p = \left[\frac{x_{a/s}}{\rho_{a/s}} + \frac{x_{org}}{\rho_{org}} \right]^{-1} \quad (4)$$

where $x_{a/s}$ is the mass fraction of ammonium sulfate and x_{org} is the mass fraction of the organics, and $\rho_{a/s}$ and ρ_{org} are the densities of ammonium sulfate and the organics, respectively. It must be noted that nitrate is not taken into account as its concentrations are very close to the limit of detection of the ACSM for the PM_1 fraction at the Finokalia site during the studied period. Particle density was calculated to be $1.56 \pm 0.08 \text{ g cm}^{-3}$ ($n = 6028$), with aerosol concentration ranging from 1.33 to $16.65 \mu\text{g m}^{-3}$ and average value of $5.62 \pm 3 \mu\text{g m}^{-3}$. The particle water calculated by this method is hereafter referred to as $f(\text{RH})_{\text{water}}$, with the uncertainty of this calculation being estimated to be 23 % (Guo et al., 2015).

2.4 LWC and pH prediction from chemical composition

The water vapor uptake by aerosol establishing equilibrium for ambient temperature and relative humidity conditions is influenced by both inorganic and organic components. LWC, therefore, is directly dependent on aerosol chemical composition and meteorological conditions, as well. As proposed by Guo et al. (2015) and explained below, we calculated the particle water associated with inorganics (W_{inorg}) and the particle water associated with organics (W_{org}). The sum of these two ($W_{inorg} + W_{org}$), equal to the total particle water, is then compared to the LWC determined by the two nephelometers.

First the particle pH was calculated by the thermodynamic model ISORROPIA-II for the PM_1 aerosol fraction. W_{inorg} was calculated based on a thermodynamic equilibrium between an inorganic aerosol ($\text{NH}_4\text{-SO}_4\text{-NO}_3\text{-Cl-Na-Ca-K-Mg-water}$) and its gas phase precursors. For the current analysis, the inputs to ISORROPIA-II are the inorganic ions measured by the ACSM with a 30 min time resolution (except for Cl which

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is at the detection limit of the instrument at the specific site), the average daily values for Na^+ , Cl^- , Ca^{2+} , K^+ and Mg^{2+} determined by ion chromatography analysis of PM_{10} filters, and RH and T measured by the ambient nephelometer probe. The use of daily values for the macromineral elements obtained from the filter analysis could introduce potential artifacts in the calculation, but is believed to be limited as almost 90 % of the fine fraction mass in the area can be attributed to ammonium sulfate and organics (Koulouri et al., 2008; Bougiatioti et al., 2009, 2013).

The contribution of the organic components to particle water (W_{org}) was determined from the organic hygroscopicity parameter (κ_{org}) from the observed CCN activities of the organic fraction (Cerully et al., 2015):

$$W_{\text{org}} = \frac{m_s}{\rho_s} \frac{\kappa_{\text{org}}}{\left(\frac{1}{\text{RH}} - 1\right)} \quad (5)$$

where m_s and ρ_s are the organic mass concentration from the ACSM and an organic density, respectively determined as described in Sect. 2.3.

Finally, the particle pH is calculated by the thermodynamic model ISORROPIA-II (Fountoukis and Nenes, 2007) based on the calculated equilibrium particle hydronium ion concentration in the aerosol. As ISORROPIA-II does not take into account the LWC associated with the organic aerosol, a recalculation of pH is made by considering the predicted particle hydronium ion concentration per volume of air (H_{air}^+) and the total predicted water ($W_{\text{inorg}} + W_{\text{org}}$) (Guo et al., 2015):

$$\text{pH} = -\log_{10} H_{\text{aq}}^+ = -\log \frac{1000 H_{\text{air}}^+}{W_{\text{inorg}} + W_{\text{org}}} \quad (6)$$

where the modeled concentrations for LWC and H_{air}^+ are $\mu\text{g m}^{-3}$, and H_{aq}^+ (mol L^{-1}) is the hydronium concentration in an aqueous solution and W_{inorg} and W_{org} are in $\mu\text{g m}^{-3}$. ISORROPIA-II has been previously tested and was able to predict the equilibrium partitioning of ammonia and nitric acid to within measurement uncertainty (Nowak

et al., 2006; Fountoukis et al., 2009; Hennigan et al., 2015; Guo et al., 2015). Here, ISORROPIA-II was run in the “forward mode” assuming a metastable aerosol state. It should be noted that gas phase measurements of ammonia ($\text{NH}_{3(g)}$) were generally not available, so we expect the pH to be underpredicted by at most one unit (Guo et al., 2015). This also implies that the computed vapor pressure of $\text{NH}_{3(g)}$ will be underestimated, as the total ammonia/ammonium is not known to be introduced to the model. However, for the days that available data of $\text{NH}_{3(g)}$ do exist, measured concentrations and predictions by the model are in fairly good agreement: Gas phase measurements have an average concentration of $0.79 \pm 0.27 \mu\text{g m}^{-3}$ while predicted concentrations have an average of $0.65 \pm 0.32 \mu\text{g m}^{-3}$.

3 Results and discussion

3.1 PM_{10} chemical composition and $f(\text{RH})_{\text{water}}$

For the measurement period, the average values for the main aerosol constituents were 1.85 ± 0.94 , 2.31 ± 1.61 , 0.81 ± 0.58 and $0.52 \pm 0.22 \mu\text{g m}^{-3}$ for organics, sulfate, ammonium and BC, respectively. In terms of contribution to the PM_{10} mass concentration, the two most abundant components of the submicron range were sulfate and organics, with mass fractions of 39.6 and 33.8 % respectively, followed by ammonium (14.8 %), BC (9.3 %) and nitrate (2.1 %). Chloride has a negligible contribution to the total submicron mass concentration. The time series of the main aerosol constituents and their overall contribution, as measured by the ACSM, are portrayed in Fig. 1. More details about the ACSM measurements and performance can be found in Stavroulas et al. (2015).

The chemical composition is expected to influence the water content of aerosol, as well. Mean RH and T during the study period were $57 \pm 11 \%$ and $27.4 \pm 3.7^\circ\text{C}$. As described in the Sect. 2.3, $f(\text{RH})_{\text{water}}$ was calculated from the data from the two nephelometers. With the use of Eqs. (1) and (2), we calculated LWC from the neph-

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elometers for the whole measurement period. The average value of $f(\text{RH})_{\text{water}}$ was $2.19 \pm 1.75 \mu\text{g m}^{-3}$, which according to the dry mass measurements, can contribute on average, up to 33 % of the total submicron mass concentration. We also sought to establish a link between $f(\text{RH})$ and RH and taking into account all available scattering data ($n = 7044$) the following parameterization has been established:

$$f(\text{RH}) = 1.067(\pm 0.004) + 1.99(\pm 1.05) \times 10^{-7} \text{RH}^{3.547(\pm 0.035)} \quad (7)$$

Based on this, we reconstructed the time series of the hygroscopic growth factors, with a very good correlation between calculated and measured values ($y = 0.99x$, $R^2 = 0.85$) (also see Supplement). This parameterization does not appear to be influenced by changes in the chemical composition. Uncertainties in the RH measurement by the probe are in the order of 5 % while dry and wet aerosol light scattering coefficients measurement uncertainty is in the order of 20 %.

3.2 Inorganic and organic water predictions

3.2.1 Inorganic aerosol water

The thermodynamic model ISORROPIA-II (<http://isorrophia.eas.gatech.edu>; Fountoukis and Nenes, 2007) was used to predict the contribution of inorganic species to LWC. The water attributed to the inorganic component of the aerosol has an average value of $1.77 \pm 1.45 \mu\text{g m}^{-3}$. The lowest values are observed during August, probably because of the higher temperatures that enhance evaporation of water from the aerosol. The timeseries for aerosol water associated both with inorganic and organic aerosol components are shown in Fig. 2, where it can be seen that most of the time, the variability of the two water components follow each other closely, with water concentrations associated with organics being about 1 : 10 ($12 \pm 9\%$) of those associated with the inorganic aerosol components.

3.2.2 Organics: hygroscopicity and aerosol water

The contribution of the organic submicron fraction of the aerosol to the particle water was calculated from the combination of the CCN and chemical composition measurements, as described in Sect. 2.4. Assuming that the cumulative aerosol hygroscopicity can be represented as the sum of contribution of the inorganic (expressed mostly by ammonium sulfate) and organic fraction of the aerosol, the measured hygroscopicity can be calculated by the sum:

$$\kappa = \varepsilon_{\text{inorg}}\kappa_{\text{inorg}} + \varepsilon_{\text{org}}\kappa_{\text{org}}, \quad (8)$$

where ε_j and κ_j are the volume fraction and hygroscopicity of the inorganic and organic species. Once the aerosol species concentrations are determined, the corresponding volume fractions for ammonium sulfate and organics are calculated, and a set of hygroscopicity parameter equations is produced. As mentioned in the Sect. 2.2, hygroscopicity parameters for 60, 80, 100 and 120 nm particles are measured. In a former CCN study at the same site (Bougiatioti et al., 2011) it was shown that from many different particle sizes, the characteristic hygroscopicity parameter κ^* of the 100 nm particles was the closest one to the κ determined by PM_{10} filter measurements. Therefore we created two different sets of kappa equations along with the volume fractions to calculate the total κ^* , one for the 100 and another one for the 120 nm. With the subsequent application of multivariate regression analysis to the set of $n = 2429$ and 1801 equations (for 100 and 120 nm respectively), κ_{org} is determined to be 0.28 ± 0.01 based on the $\kappa_{100\text{nm}}$ and 0.24 ± 0.01 based on the $\kappa_{120\text{nm}}$. The average value of 0.26 is used in equation 5 to calculate the time series of W_{org} . The average value W_{org} was thus found to be $0.56 \pm 0.37 \mu\text{g m}^{-3}$, which constitutes on average $\sim 27.5\%$ of the calculated $f(\text{RH})_{\text{water}}$. The overall uncertainty of this calculation is estimated by Guo et al. (2015) to be around 30%. That study for south eastern United States of America, found a higher contribution of organic species (on average 35%) to the total water that

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can be explained by the dominance of organics in the submicron range aerosol, with an average mass fraction of 67 %.

3.2.3 Aerosol water

Aerosol water is the sum of $W_{\text{org}} + W_{\text{inorg}}$, determined as previously explained. This can be further compared with the time series of the $f(\text{RH})_{\text{water}}$ deduced from concurrent observations by the two nephelometers (Sect. 2.3), independent from the aerosol water calculated as here explained. The particle water predicted from the sum of the organic and inorganic contributions to the water agrees very well with the water measured by the nephelometers (Fig. 3). More specifically, the total predicted water is highly correlated and on average within 10 % of the measured water, with slope = 0.92 and $R^2 = 0.8$ for the whole measurement period ($n = 5201$ points).

The diurnal variability of the calculated water components, along with the total measured water, ambient T and RH is shown in Fig. 4. It must be noted at this point that the presented diurnal variability corresponds to the entire period of the study and this pattern seems to be independent of the geographical sector and/or source region. The diurnal variability of aerosols from different sources, further presented at Sect. 3.4, has been explicitly studied and found not to differ significantly, therefore the total diurnal variability was selected as being representative of the whole measurement period. Predicted and measured aerosol LWC diurnal variabilities are in very good agreement. As expected, the highest LWC values are observed during nighttime, when RH is also at its maximum, resulting in significant water uptake. W_{org} shows a significant diurnal variability with morning and afternoon average mass concentrations being 10–15 times lower than nighttime ones. Thus, during daytime W_{inorg} is the main component of particle water as the average values for the predicted water ($W_{\text{org}} + W_{\text{inorg}}$) are very close to the ones of the inorganic water alone. On the other hand, during nighttime, the two averages start to diverge and this could be attributed to the higher contribution of organic water during nighttime, when the photochemical activity and temperature are minimum and RH high.

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3.3 Aerosol pH

The predicted pH for the aerosols collected at Finokalia during the studied period was highly acidic with an average value of 1.25 ± 1.14 (median 1.51) and varying between -0.97 and 3.75 . pH varied by almost 1 unit throughout the day. This can be translated as an almost 10-fold increase of the $H_{\text{air}}^+ / \text{LWC}$ ratio from early morning to mid-day and to a lesser extent during early night. This significant variation in pH can be partially explained by the diurnal variation of H^+ and its increase which coincides temporally with the decrease in pH (Fig. 5) and by the reduction of aerosol water (LWC) during daytime compared to the higher LWC during nighttime (Fig. 4). This implies the diurnal variability of pH is mostly driven by the reduction of aerosol water during daytime compared to the higher aerosol water during nighttime.

When studying the diurnal variability of pH for the different sources/geographical sectors (Supplement) it occurs that pH differs depending on the source and origin of the air masses. Air masses from the northwestern, northeastern Europe and Turkey, as well as from Greek mainland, do not exhibit significant diurnal variability. When no distinction is made between source regions, the pattern of the overall pH variability with a drop in pH values during midday as presented in Fig. 5, is similar to the diurnal variability of pH for air masses influenced by mineral dust (coming from the SW) and by biomass burning, but with pH values from biomass burning being 1–1.5 units higher. Nevertheless, the mean pH values for each one of the source regions are very close to the overall pH mean value when no distinction of origin is made.

Furthermore, accounting only for the water associated with the inorganic aerosol component, particle water is underestimated by around 9%, thus resulting in a slightly lower pH (more acidic) by 0.07–0.38 units of pH (Fig. 6a). As seen in Sect. 3.2, W_{org} is on average 27.5% of the total water, as a result the pH increases by 0.14 units when the organic water is included (Fig. 6a). When the contribution of organic water is taken into account, the recalculation of pH gives an average value of 1.38 ± 1.11 (median 1.65). The pH calculated by ISORROPIA-II correlates very well with the pH

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corrected using Eq. (6) for inclusion of the organic water ($W_{\text{org}} + W_{\text{inorg}}$) ($R^2 = 0.98$, Fig. 6b). Subsequently, if organic mass and organic hygroscopicity data are not available, ISORROPIA-II solely based on inorganic composition data, will provide an adequate estimate of both H_{air}^+ and W_{inorg} and thus of pH.

3.4 Aerosol water and pH based on aerosol fraction and source region

Apart from the time-resolved aerosol water and pH calculations for the submicron aerosol fraction, aerosol water and pH were also calculated based on the daily PM_{10} filter chemical composition analysis. For comparison purposes the corresponding PM_1 measurements have also been averaged to daily values. Characteristic source regions/sources were subsequently selected based on back-trajectory analysis and chemical tracers. Furthermore, biomass burning events have been identified based on source apportionment of BC and Positive Matrix Factorization (PMF) analysis of the organic mass spectra obtained from the ACSM as detailed in Bougiatioti et al. (2014). Dust events were identified by containing large amounts of particulate matter and high concentrations of crustal ions, such as Ca^{2+} . The main measured and calculated parameters are presented in Table 1.

It can be seen that, in general, for anthropogenic-laden air masses (e.g. from Istanbul, Black Sea and Continental Europe) aerosol mass resides mainly (60–70 %) in the submicron aerosol and thus the submicron fraction seems also to drive the pH of PM_{10} , while most of the aerosol water (~70 %) is present in the coarse fraction. Biomass burning exhibits the highest values of pH in the submicron fraction and the lowest values in total water mass concentration. Interestingly enough, the value of 2.77 for biomass burning pH is well above the value of 2, which favors the partitioning of nitrate to the aerosol phase (e.g., Meskhidze et al., 2003) The correlation observed during fire events between biomass burning organic aerosol and particulate nitrates (e.g. Bougiatioti et al., 2014) may be explained by these higher pH levels, rather than just high levels of nitric acid and/or ammonia. Higher pH levels of biomass burning

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on the contrary, the grand majority of the aerosol water is present in the coarse mode. This may be due to the important contributions of the hygroscopic sea salt components in the coarse mode and of the less hygroscopic organics in the fine mode.

In terms of mass concentration, the air masses affected by the two natural sources, namely of marine and dust origin, contain the largest amounts of total submicron water. Even though total water exhibits the highest mass concentrations for the specific sources, the relative contribution of organic water to the submicron fraction is the lowest ($\sim 19\%$ for dust and $\sim 15.5\%$ for marine). For these two natural sources, the ratio between submicron pH and calculated pH for the PM_{10} fraction is the lowest observed, $30 \pm 17\%$ (median 25%) and $6 \pm 19\%$ (median 5%).

The low pH values observed during the studied period in the submicron mode and independently of air masses origin could have significant implications for nutrient availability and especially for P solubility which is the nutrient limiting sea water productivity of the eastern Mediterranean.

The Supplement related to this article is available online at doi:10.5194/acpd-15-29523-2015-supplement.

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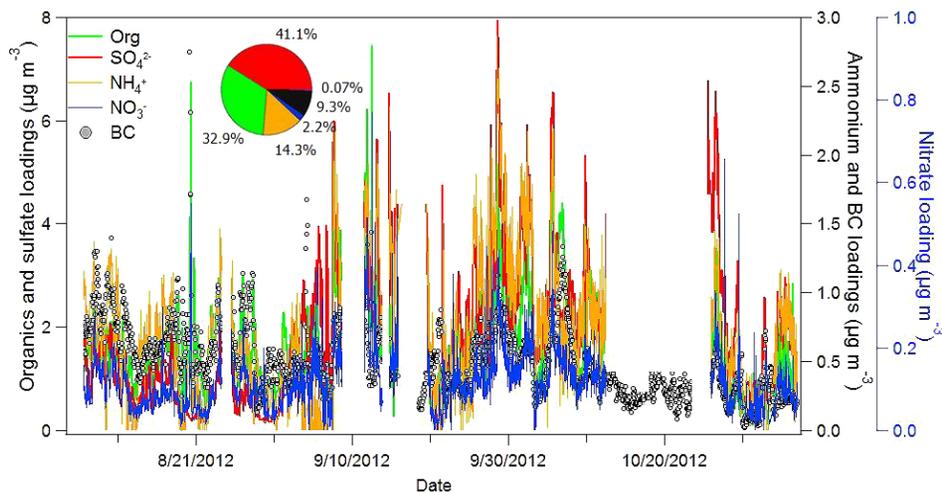


Figure 1. Time series of the main submicron aerosol components at Finokalia, Crete, during the measurement period in 2012.

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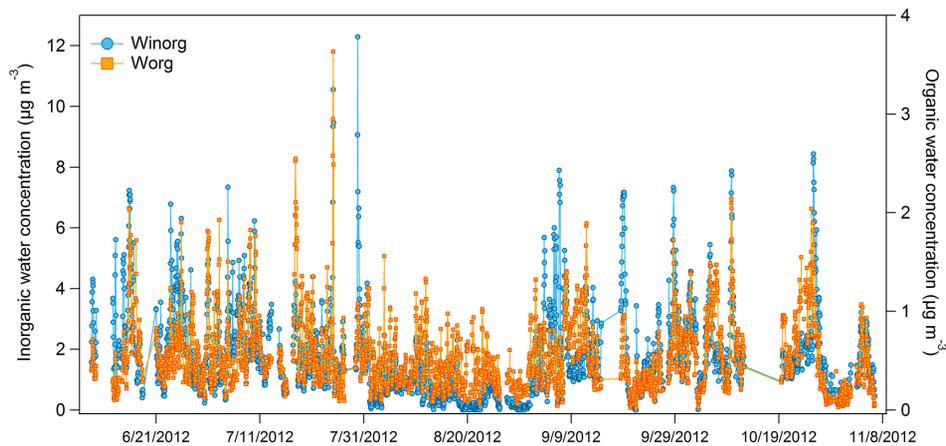
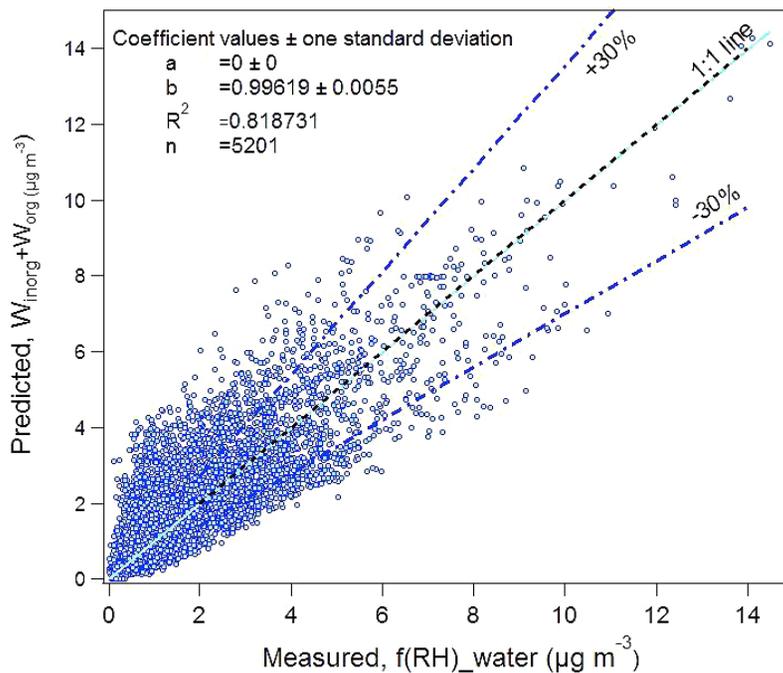
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Figure 2. Time series of the two calculated aerosol water components, the water associated with the inorganic (W_{inorg}) and the organic (W_{org}) aerosol components.

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**Figure 3.** Correlation between calculated and measured LWC of aerosol.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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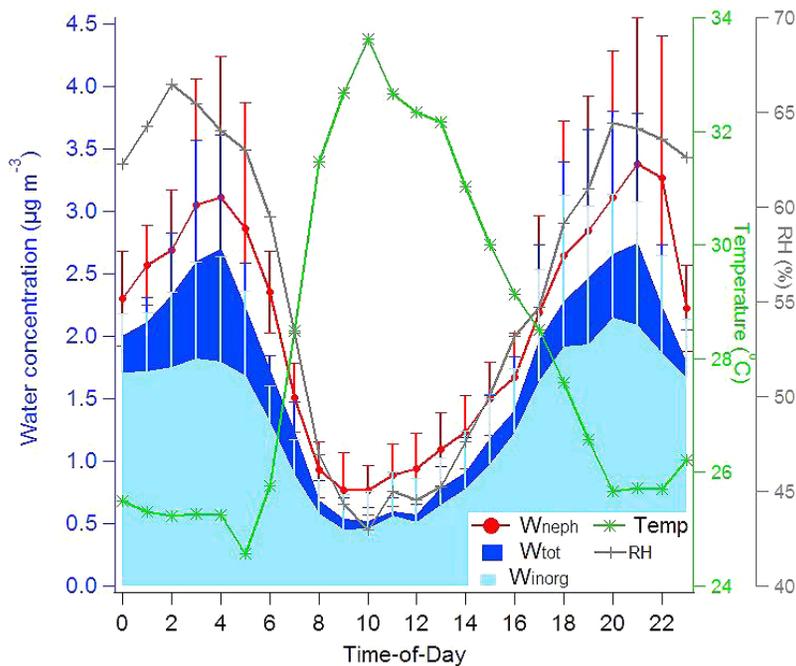


Figure 4. Diurnal profiles of predicted and measured water, along with measured RH and T . Average hourly averages and standard deviations plotted as error bars in local hour are shown.

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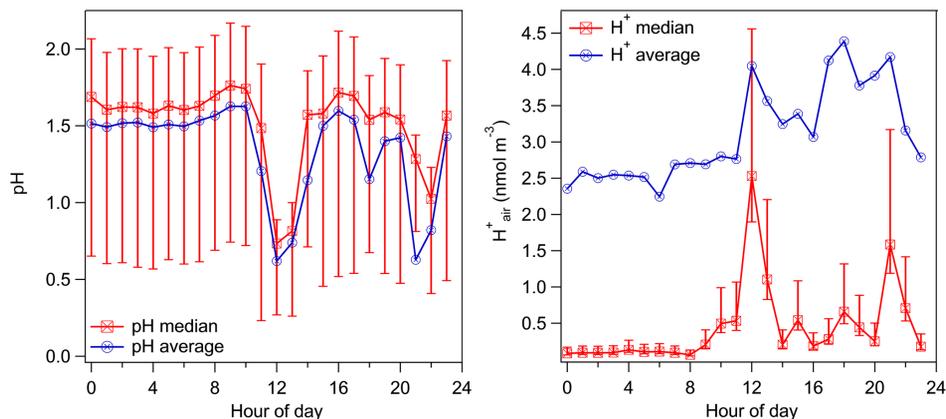


Figure 5. Diurnal profile of pH (a) and H^+ (b) calculated based on total predicted water and hydronium concentrations predicted by ISORROPIA-II. Average and median (with 25%, 75% quantiles) values are provided.

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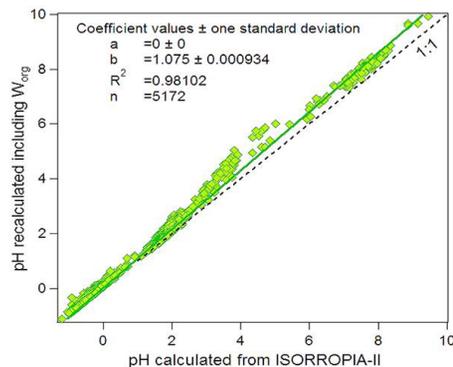
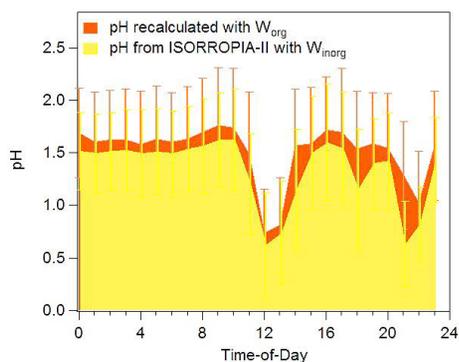


Figure 6. (a) Diurnal variability of pH based on total predicted water (orange using both W_{org} and W_{inorg}) and only the inorganic water (yellow using only W_{inorg}), respectively. Average hourly values and standard deviation in the form of error bars are provided, (b) Comparison between the pH predicted by ISORROPIA-II based on inorganic aerosol composition and that recalculated including also the organic component.