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Atmospheric Chemistry and Physics Discussions

Atmospheric Water-Soluble Organic Nitrogen (WSON) in the Eastern Mediterranean: Origin and Ramifications Regarding Marine Productivity

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Abstract

Two-sized aerosol and rain sampling were carried out at a rural site located on the coast of the Eastern Mediterranean, Erdemli, Turkey (36° 33′ 54″ N and 34° 15′ 18″ E). A total of 674 aerosol samples in two size fraction (coarse = 337; fine = 337) and 23 rain samples were collected between March 2014 and April 2015. Samples were analyzed for NO_3^-, NH_4^+ and ancillary water-soluble ions by Ion Chromatography and water-soluble total nitrogen (WSTN) by applying a High Temperature Combustion Method. The mean aerosol WSON was 23.8 ± 16.3 nmol N m^{-3}, reaching a maximum of 79 nmol N m^{-3}, with about 66 % being associated with coarse particles. The volume weighted mean (VWM) concentration of WSON in rain was 21.5 µmol N L^{-1}. The WSON contributed 37 % and 29 % to the WSTN in aerosol and rainwater, respectively. Aerosol WSON concentrations exhibited large temporal variations mainly due to rain and the origin of air mass flow. The highest mean aerosol WSON concentration was observed in the summer and was attributed to the absence of rain and re-suspension of cultivated soil in the region. The mean concentration of WSON during dust events (38.2±17.5 nmol N m^{-3}) was 1.3 times higher than that of non-dust events (29.4±13.9 nmol N m^{-3}). Source apportionment analysis demonstrated that WSON was originated from agricultural activities (43 %), secondary aerosol (20 %), nitrate (22 %), crustal (10 %) and sea-salt (5 %). The dry and wet depositions of WSON were equivalent and amounted to 36 % of the total atmospheric WTSN flux. Considering the Cilician Basin, the atmospheric water-soluble nitrogen flux would sustain 33 % and 76 % of the new production in the associated coastal and open waters, respectively.

Keywords: Atmospheric water-soluble organic nitrogen, mineral dust, source apportionment, atmospheric deposition and marine productivity, Eastern Mediterranean

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1. Introduction

Research assessing the atmospheric deposition of nitrogen (with a focus on inorganic N in rainwater i.e. ammonium and nitrate) can be traced back to the mid-1800s (Miller, 1995 and references therein) as it was accepted to be a vital plant nutrient. Miller (1905) mentioned about organic nitrogen in rain samples as well. To quote Miller: '*With regard to the amount of organic nitrogen in the rainwater, the only available analyses relating to Rothamsted are those of Frankland who found from 0.03 to 0.66 per million in 69 samples*'. Cornell et al., (1995) highlighted the importance of organic nitrogen in rain and snow accounting for almost half of the total atmospheric dissolved nitrogen deposition. Since then, research defining the quantitative importance of soluble organic nitrogen in the atmospheric transport of nitrogen has greatly expanded (Neff et al, 2002; Cornell et al., 2003; Mace et al., 2003a, b, c; Gilbert et al., 2005; Sorooshian et al., 2008; Violaki and Mihalopoulos, 2010; Violaki et al., 2010; Altieri et al., 2016).

WSON arises from a variety of sources including both natural and anthropogenic. Anthropogenic sources include agricultural activities (including fertilizer application, animal husbandry), high temperature fossil fuel combustion, man-made biomass burning and industrial activities. In contrast natural sources of WSON include mineral dust, bacteria, sea salt, organic debris, natural biomass burning (Neff et al, 2002; Cornell et al., 2003; Mace et al., 2003a, b, c; Gilbert et al., 2005; Sorooshian et al., 2008; Altieri et al., 2016). Atmospheric organic nitrogen can also be formed through chemical reactions. For example, reactions between volatile organic compounds, NO_x and ammonium sulfate aerosols may lead to the formation of nitrogen-containing compounds (Surratt et al., 2008; Galloway et al., 2009; De Haan et al., 2011; Yu et al., 2011). Furthermore, atmospheric organic nitrogen plays an essential role in many global processes which may impact on the chemistry of the atmosphere as well as climate and biogeochemical cycles. Similar to ammonium, organic nitrogen species

such as urea and amines have acid-neutralizing capacities (Ge et al., 2011). It has been shown that nitrogen containing organic compounds nucleate cloud droplets and may contribute considerably to the indirect aerosol effect (Twohy et al., 2005). Phytoplankton and bacteria production in aquatic environments has been found to be stimulated by the addition of water-soluble organic nitrogen (Timperly et al., 1985; Peierlt and Paerl, 1997; Seitzinger and Sanders, 1999). The laboratory experiments performed by Seitzinger and Sanders (1999) demonstrated production of coastal marine bacteria and phytoplankton which are stimulated by the addition of water-soluble organic nitrogen, 45-75 % being Bioavailable. From the mid 1800s to 2000, as a result of anthropogenic activities, reactive nitrogen and reactive anthropogenic organic nitrogen have increased by almost 10 and 4 fold, respectively, leading to a significantly modified global nitrogen cycle. This in term has impacted upon the marine nitrogen biogeochemical cycling (Galloway et al., 2002, 2008; Duce et al., 2008).

The Mediterranean Sea is characterized by oligotrophic surface waters with Low Nutrient Low Chlorophyll (LNLC) regions. This has been attributed to mainly anti-estuarine (reverse thermohaline) circulation (Hamad et al., 2005). The Eastern Mediterranean (25) has higher molar N/P ratios than those observed in the Western Mediterranean (22) and the Redfield ratio (Krom et al., 2004; Yılmaz and Tuğrul, et al., 1998). It has been proposed that the primary productivity in the Eastern Mediterranean is phosphorous limited (Thingstad et al., 2005). However it has also been suggested that the primary productivity and bacterial activity in the Eastern Mediterranean is limited by nitrogen or co-limited by nitrogen and phosphorous (Yücel, 2013; Yücel, 2017). Very little research has focused on the importance of water-soluble organic nitrogen inputs to marine productivity in the Eastern Mediterranean (Violaki and Mihalopoulos, 2010; Violaki et al., 2010). Hence, the unique contributions of the current study will be to (i) define the temporal variability of atmospheric water-soluble organic nitrogen, (ii) assign the origin of the water-soluble organic nitrogen, (iii) assess the influence

of mineral dust on water-soluble organic nitrogen and (iv) enhance our knowledge of the quantitative dry and wet deposition for water-soluble organic nitrogen and its possible influence on marine productivity in the North Eastern Mediterranean.

These will be achieved by using the acquired data from the analyses for water soluble inorganic and organic nitrogen species of a series of size fractionated aerosol (coarse and fine) and rain samples collected from March 2014 to April 2015 from the northern coast (Erdemli, Turkey) of the Levantine Basin, Eastern Mediterranean.

2. Material and Methods

2.1. Sampling Site Description

Aerosol and rain sampling were carried out at a rural site located on the coast of the Eastern Mediterranean, Erdemli, Turkey (36° 33′ 54″ N and 34° 15′ 18″ E). The sampling tower (above sea level ~ 22 m, ~ 10 m away from the sea) is situated at the Institute of Marine Sciences, Middle East Technical University (IMS-METU). Its immediate vicinity is surrounded by cultivated land to the north and to the south of the Northern Levantine Basin. Although the site is not under the direct influence of any industrial activities (soda and fertilizer), the city of Mersin with a population of 800.000 is located 45 km to the east of the sampling site (Kubilay and Saydam, 1995; Koçak et al., 2012) and hence aerosol and rainwater samples influenced by air mass transport from the east may have been influenced by these regional anthropogenic activities.

2.2. Sample Collection and Preparation

Aerosol: A Gent type stacked filter unit (SFU) was used to collect aerosol samples in two size fraction (coarse: d = 10-2.5 μm and fine: d < 2.5 μm) (for more details see Hopke et al., 1997; Koçak et al., 2007). Briefly, the first section of the filter holder was loaded with an 8 μm pore

size polycarbonate filter (Whatman Track Etched 111114, circle diameter: 47 mm), whilst the second section was loaded with a 0.4 µm pore size polycarbonate filter (Whatman Track Etched 111107, circle diameter: 47 mm). The cassette unit was then placed into the cylindrical cassette holder, which is designed to prevent the intrusion of particles larger than 10 µm when the sampler is operated at a flow rate of 16.0-16.5 L/min. Daily (24 hours) temporal sample resolution was carried out. Operational blank filters were processed in the same way as the collected samples with the exception that no air was passed through the filters. In order to minimize any possible contamination, the filter loading and unloading were achieved in a laminar airflow cabinet.

The aerosol sampling campaign commenced in March 2014 and ended in April 2015. During the sampling period, a total of 674 aerosol samples in two size fractions (coarse = 337; fine = 337) were obtained. The observational coverage of the aerosol sampling period was 80 %. The sampling was terminated from time to time due to technical malfunction of the SFU and/or cleaning procedure of sampling apparatus.

Rain: Rainwater samples were collected using an automatic Wet/Dry sampler (Model ARS 1000, MTX Italy). A total of 23 rain samples were collected during the sampling period. After each rain event, the rainwater samples were immediately transferred to the laboratory for filtration (0.4 µm Whatman, polycarbonate filters).

Storage of Samples: Aerosol and rainwater samples were stored frozen (-20 ˚C) immediately after collection until analyses (not more than a month). Cape et al. (2001) have been shown that there were no significant losses for inorganic and organic nitrogen during the storage (freezing for 3 months) of rain samples with an added biocide.

Sample Preparation: In order to determine the concentrations of water-soluble nitrogen species (WSTN, NO_3^- and NH_4^+) and major water-soluble ions (Cl^-, SO_4^{2-}, Na^+, K^+, Mg^{2+}, Ca^{2+}) in an aerosol sample, one quarter of the filter was extracted for 60 minutes in 20 mL of ultra-pure water (18.2 Ωm) by mechanic shaking. About 100 µL chloroform (Merc 2444, 99.8 %) was added as a preservative to prevent biological activity after removing the filter (Bardouki et al., 2003, Koçak et al., 2007). Before measuring the water-soluble species, extracts were filtered with 0.4 µm pore size polycarbonate filters.

2.3. Chemical Analysis

Water Soluble Total Nitrogen: High Temperature catalytic oxidation (Torch Teledyne Tekmar TOC/TN) was applied to determine the WSTN concentrations in the aerosol and rainwater samples. The liquid aliquot of the sample is injected into the combustion furnace (750 ^oC) and the N in the sample was then converted to NO gas. The carrier gas (high purity dry air) sweeps the sample into nondispersive infrared detector. From here, the sample is carried to the nitrogen module. In this unit NO is mixed with O_3 since the chemiluminescent detection of NO is based on the reaction between NO and O_3. After the formation of excited nitrogen dioxide (NO_2^*), the extra energy is given of as light when NO_2^* relaxes to its ground state. The light signal to an electronic signal for quantification is then measured by a chemiluminescence detector with a photomultiplier tube.

Water soluble Inorganic and Ancillary Species: In addition to NO_3^- and NH_4^+, major water-soluble ions concentrations were measured by using a Dionex ICS-5000 Ion Chromatography instrument. Water-soluble anions (Cl^-, SO_4^{2-}, NO_3^-) were determined by applying AS11-HC separation column, KOH (30 mM) eluent and AERS-500 (4 mm) suppressor whilst water-soluble cations (Na^+, K^+, Mg^{2+}, Ca^{2+})were detected electrochemically by using a CS12-A

separation column, MSA (20 mM) eluent and CSRS-300 (4 mm) suppressor (Product Manual for Dionex IonPac AS11-HC-4m, IonPac CS12A Manual).

Blank values of WSTN for aerosol and rain samples were less than limit of detection (20 ppb). The blank contributions of water-soluble ions in aerosol samples were found to be less than 10 % and concentrations were corrected for blanks.

2.4. Calculations

WSON concentrations (see Eq. 1) were determined from the difference between the individual concentrations of WSTN and water-soluble inorganic nitrogen (WSIN) (see Eq. 2) since there is no direct analytical method to detect the concentration of water-soluble organic nitrogen. The precision for WSON was calculated via using the formula (see Eq. 3) suggested by Hansell (1993). The precision (75 nmol N m^{-3}) was found to be almost three times higher (see Eq. 4, R ~ 0.3) thanthat of the arithmetic mean of WSON in aerosols whilst it (90 µmol N L^{-1}) was estimated to be approximately four times larger than that of volume weighted mean of WSON in rain. Such high values are not unusual. For example, if the data presented by Mace et al. (2003a) would be used, precisions would have been 5 and 8 times higher thanthose of the concentrations of WSON in aerosol and rain, respectively. Table 1 shows the number of negative WSON values and the positive WSON biases for coarse and fine modes. Correspondingly, about 5 (n=18) and 15 % (n=52) of the values were negative in coarse and fine particles. The substitution with zero yielded 2 and 14 % positive bias for coarse and fine mode whereas; the omission of zero resulted in 8 and 34 % positive bias in coarse and fine WSON mean concentrations. Consequently, the presentation of the general characteristics of the data includes all negative concentrations. In order to evaluate the variability in the aerosol WSON and apply PMF, however, different approach was adopted. To this end, arbitrary thresholds have been defined as the ratio between WSON mean concentration and the

calculated precision (see Eq. 4). Thus, during assessing the variability in aerosol WSON and the application of PMF, WSON concentrations having R values larger than 0.3 will be considered since the arbitrary threshold simply reduces the uncertainty.

$$WSON = WSTN - WSIN \quad (1)$$

$$WSIN = NO_3^- + NH_4^+ \quad (2)$$

$$S_{WSON} = (s_{WSTN}^2 + s_{WSIN}^2)^{1/2} \quad (3)$$

$$R = \frac{WSON_{MEAN}}{S_{WSON}} \quad (4)$$

The rain volume weighted average concentration (C_w) of nitrogen species can be calculated as follow:

$$C_W = \frac{\sum_{i=1}^{n} C_i x Q_i}{\sum_{i=1}^{n} Q_i} \quad (5)$$

The wet and dry atmospheric fluxes of nitrogen species were calculated according to the procedure explained in Herut et al. (1999, 2002). The wet atmospheric deposition fluxes (F_w) were calculated from the annual precipitation (P_{annual}) and the volume weighted mean concentration (C_w) of the substance of interest.

$$F_W = C_W \times P_{annual} \quad (6)$$

The dry deposition (F_d) is calculated as the product of the atmospheric mean nutrient concentrations (C_d) and their settling velocities (V_d), where F_d is given in units of μmol m^{-2} yr^{-1}, C_d in units of μmol m^{-3} and V_d in units of m yr^{-1}.

$$F_d = C_d \times V_d \quad (7)$$

The settling velocities (V_d, see Eq. 8) for each water-soluble nitrogen species were calculated by using an approach adopted by Spokes et al. (2001). C_c and C_f refer to as the relative contribution of coarse and fine modes and 2.0 and 0.1 cm s^{-1} are deposition velocities proposed by Duce et al. (1991) for coarse and fine particles respectively.

$$V_d = C_c \times 2.0 + C_f \times 0.1 \quad (8)$$

202

203 **2.5. Air Masses Back Trajectories and Airflow Classification**

204 Three day back trajectories of air masses at the four altitudes (1000, 2000, 3000 and
205 4000 meter) levels arriving at Erdemli station were computed by using the HYSPLIT
206 Dispersion Model (HybridSingle Particle Lagrangian Integrated Trajectory; Draxler and
207 Rolph, 2003). Three day back trajectories reaching at the altitude of 1000 m were classified
208 into six sectors: (i) Middle East, (ii) North Africa, (iii) Turkey, (iv) Eastern Europe, (v)
209 Western Europe and (vi) Mediterranean Sea in order to assess the influence of airflow on
210 WSON concentration in PM_{10} (for more details see Koçak et al., 2012).

211

212 **2.6. Positive Matrix Factorization (PMF) for Source Apportionment of WSON**

213 The receptor modeling tool *Positive Matrix Factorization* (U.S. Environmental
214 Protection Agency PMF version 5.0, hereinafter referred to as 'PMF') was utilized to identify
215 the sources of WSON in PM_{10} at Erdemli. PMF has been proven to be a robust tool in
216 characterizing the sources of aerosol (Paatero and Tapper, 1994; Huang et al., 1999; Lee et
217 al., 1999; Viana et al., 2008; Koçak et al., 2009). EPA PMF 5.0 software mainly consists of
218 Model Run and Rotational tools (see EPA/600/R-14/108; USEPA, 2014). Before application
219 of the software, the user must supply two input files namely, concentration and uncertainly.
220 The former contains concentrations of the aerosol species whilst the later has corresponding
221 uncertainty for each variable. Uncertainty was set to 5 % for each species with the exception
222 of WSON (15 %) since WSON exclusively donated high uncertainty. The base run of PMF
223 was achieved by setting the number of runs and random starting points (in other word seeds)
224 to 250 and 50, respectively. Base Model Displacement (DISP), Bootstrap (BS) and Bootstrap
225 Displacement (BS-DISP) methods were sequentially used after base run. The DISP accesses

the rotational ambiguity. DISP error estimates showed that there were no factor swaps and significant decrease in Q during DISP, being 0 and 0.00, respectively. Therefore, DISP results did not reveal rotational ambiguity, implying the solutions to be robust. Except in one case, results from BS and BS-DISP (n=50) did not indicate any asymmetry and rotational ambiguity for 5 factors. To evaluate the rotational ambiguity, different Fpeak values were applied, considering changes in dQ to be less than 5 %. Furthermore, G-sape plots of Fpeak solutions were examined to determine convergence toward the axis or lower/zero contribution. Thus, Fpeak values of -0.7 was used and five factors were identified by using PMF 5.0. BS of Fpeak at -0.7 did not reveal any swaps for five factors. The slope of the estimated WSON against measured WSON was 10 % less than unity with correlation coefficient and intercept of 0.87 and 1.5 (nmol N m^{-3}), respectively.

3. Results and Discussion

3.1. General Characteristics of the Data

In this section the general characteristics of the Water-Soluble Organic Nitrogen (WSON), Nitrate (NO_3^-), Ammonium (NH_4^+) and Water-Soluble Total Nitrogen (WSTN) in aerosol and rain will be discussed.

Aerosol*:* The statistical summary for WSON, NO_3^-, NH_4^+ and WSTN in PM_{10} aerosol samples obtained from Erdemli between March 2014 and April 2015 is presented in Table 2. Among the nitrogen species, WSON exhibited the highest arithmetic mean, followed by ammonium and nitrate concentrations respectively. The maximum concentration of WSON was estimated to be 79 nmol N m^{-3} with a mean value and standard deviation of 23.8 ± 16.3 nmol N m^{-3}. Approximately 66 % of the WSON was associated with coarse particles, the remaining fraction (34 %) was present within the fine mode. A number of studies have

reported the relative size distribution of WSON for the Eastern Mediterranean marine aerosol (Finokalia, Violaki and Mihalopoulos, 2010) and those observed at remote marine sites (Hawaii, Cornell et al., 2001; Tasmania, Mace et al., 2003a). The aerosol WSON at Finokalia (68 %) and Hawaii were primarily found in the fine mode whilst WSON in the south Pacific marine aerosol (Tasmania) it was mainly associated with the coarse fraction. It is likely that the WSON at Erdemli (a) is relatively less impacted by anthropogenic sources and/or (b) is more influenced by mineral dust transport and resuspension of cultivated soil compared to that observed at Finokalia.

NO_3^- and NH_4^+aerosol concentrations ranged between 0.2-88.4and 0.5-164.4 nmol N m^{-3} with mean values (standard deviations) of 17.9 (±15.7) and 23.3 (±24.4) nmol N m^{-3}. As expected, NO_3^- was mainly associated with coarse particles, accounting for 87 % of the observed mean value whilst NH_4^+ was dominant in the by fine mode, contributing 96 % to the detected mean concentration. Similar results have been reported for Eastern Mediterranean marine aerosol (Bardouki et al, 2003; Koçak et al., 2007). The predominance of NO_3^- in the coarse mode might be due to gaseous nitric acid or other nitrogen oxides reacting with alkaline sea salts and mineral dust particles. In contrast the occurrence of NH_4^+ in the fine fraction is mainly as a result of the reaction between gaseous alkaline ammonia and acidic sulfuric acid (Mihalopoulos et al., 2007).

WSTN concentrations in aerosols varied between 9.7 and 176.5 nmol N m^{-3} with anarithmeticmean value of 63.5± 32.0 nmol N m^{-3}, respectively. The mean WSTN concentration being almost equally influenced by coarse (51 %) and fine particles (49 %).Table 2 demonstrates the relative contributions of WSON, NO_3^- and $NH_4^+$to the WSTN in PM_{10}. As can be deduced from the table, the WSTN concentration was equally influenced by WSON and NH_4^+, each species contributing 37% and 35 %, respectively. In contrast the contribution of NO_3^- to WSTN was found to be 28 %.

276

277 ***Rain:*** Volume-weighted-mean (VWM) concentrations of WSON, NO_3^-, NH_4^+ and WSTN in
278 rainwater are presented in Table 2, along with the minimum and maximum concentrations as
279 well as the relative contributions of WSON, NO_3^- and NH_4^+ to WSTN. As can be deduced
280 from table, VWM concentrations of each species were comparable, NH_4^+exhibited the highest
281 concentration with a value of 28.7 µmol N L^{-1}. The VWM concentration of WSON and NO_3^-
282 were 21.5 and 23.3 µmol N L^{-1}, respectively. Considering their relative contributions to
283 WSTN, WSON and NO_3^- account 29 and 32 % of the WSTN whilst NH_4^+represented 39 % of
284 the observed WSTN concentration in rainwater.

285

286 **3.2. Comparison of WSON in Aerosol and Rain with data from the Literature**

287 The concentrations of WSON in marine aerosols and rain samples collected from
288 different sites located around the Mediterranean, Atlantic and Pacific regions are illustrated in
289 Table 3. Comparing the current WSON values with those reported in the literature is
290 challenging due to (i) different applied sampling periods, sampling and measurement
291 techniques and (ii) the high uncertainty associated with the estimation of WSON.
292 Furthermore, within the literature there is a lack of information defining the uncertainty of
293 WSON though there is a substantial statistical knowledge. Keene at al. (2002) in particular,
294 have highlighted the tendency in the literature to neglect negative values or substitute such
295 values with zero instead when calculating the WSON from the difference between WSTN
296 and WSIN. As these authors have highlighted the omission or substitution of such values
297 inevitably would result in a positive bias in the WSON concentrations.

298 In general the lowest concentrations in aerosols were found in those derived from
299 remote or pristine marine environments. The WSON concentrations in the atmosphere over
300 the Indian (Amsterdam Island: 1.0 nmol N m^{-3}, Violaki et al., 2015), Atlantic (Barbados: 1.3

nmol N m^{-3}, Zamora et al., 2011) and Pacific Ocean (Hawaii, Oahu: 4.1 nmol N m^{-3}, Cornell et al., 2001, Tasmania: 5.3 nmol N m^{-3}, Mace et al., 2003b) were at least 4 times less than those observed for Eastern Mediterranean (Erdemli: 23.8 nmol N m^{-3}, this study; Finokalia: 17.1 nmol N m^{-3}, Violaki and Mihalopoulos, 2010). These lower values might be attributed to (i) the absence of the strong anthropogenic sources in the vicinity of the sampling sites and/or (ii) the dilution of the WSON originating from long range transport via both dry and wet deposition. The highest WSON concentrations emerged particularly over China (Ho et al., 2015, concentration of WSON measured in $PM_{2.5}$) and Taiwan (Chen et al., 2010) with values above 70 nmol N m^{-3}As stated in Chen et al. (2010) WSON concentrations at these sampling sites were markedly influenced by anthropogenic activities such as fossil fuel combustion and man induced biomass burning. Concentrations over the Amazon (Mace et al., 2003c) in the dry season (61 nmol N m^{-3}) have also been noted. Such high values were ascribed to natural fires (Mace et al., 2003c). The mean WSON concentration at Erdemli (23.8 nmol N m^{-3}) was comparable to that reported previously for the same site (29 nmol N m^{-3}, Mace et al., 2003a). In contrast, the present WSON concentration was almost 1.5 times higher than that observed at Finokalia (Violaki and Mihalopoulos, 2010).

The reported WSON values for rain also exhibited the lowest concentrations in those derived from remote or pristine marine environments, such as Hawaii (2.8 μmol N L^{-1}, Cornell et al., 2001). The highest WSON concentrations were observed in China (North China Plain: 103 μmol N L^{-1}, Zhang et al., 2008) and Norwich, UK (33 μmol N L^{-1}, Cornell et al., 1998), respectively. These high values were again attributed to the anthropogenic sources.

3.3. Temporal Variability of Water-Soluble Nitrogen Species in Aerosol Erdemli

Fig.1 illustrates daily variation of the water-soluble nitrogen species in aerosol samples together with the daily rainfall from March 2014 to April 2015. The same figure also

presents the concentrations in rainwater samples collected between October 2014 and April 2015. It is clear that WSON concentrations exhibited large variations from one day to another day. The daily variability in the concentration of WSON may be an order of magnitude. Such variability has also been reported in the Atlantic (Zamora et al., 2011), Pacific (Chen et al., 2010) and Eastern Mediterranean marine aerosols (Violaki and Mihalopoulos, 2010). These studies demonstrated that the daily change in the concentrations of WSON arises from a combination of (a) meteorological parameters (such as rain, temperature and wind speed/direction), (b) chemical reactions, (c) history of air masses back trajectories and (d) source emission strength.

In general, lower concentrations of WSON were found to be associated with rainy days. To serve as an illustration, one of the lowest WSON concentrations was observed on 19th of October 2014, after two consecutive days of rainfall, with a value of 6 nmol N m^{-3}. In contrast, one of the highest observed WSON concentrations (66.1 nmol N m^{-3}) was detected on 2nd of March 2014 when the air mass back trajectories were associated with south/south westerly airflow (for more details see section 3.4). Another high concentration of WSON was observed on 5th of July 2014, with a value 66 nmol N m^{-3}. 94% of the WSON was present in the coarse mode, however, during this event there was no intense dust intrusion either from the Sahara or from the Middle Eastern deserts. Corresponding OMI-AI index and nssCa^{2+} (33 nmol m^{-3}) also supports this observation (see Fig.2). Lower layer air mass back trajectories (1000 and 2000 m) demonstrated that Erdemli was under the influence of north/north westerly airflow from Turkey after passing over Turkey's largest cultivated plain, Konya. Thus, this high value might be attributed to re-suspension of the soil affected by intense agricultural activities. On 20th of January 2016 the WSON concentration was 60 nmol N m^{-3}, 72 % being present in the fine mode. For this event, the NH_4^+ concentration was 20 nmol N m^{-3}, two times higher than the observed arithmetic mean in winter. Corresponding trajectories, AOD

(Aerosol Optical Depth) and AC (Angstrom Component) images are presented in Fig.3. Airflow at 1 km showed air mass flow arriving at the sampling site from Turkey. AOD values over the sampling site and coastline of Northeastern Mediterranean ranged from 0.2 to 0.5 whilst AC values demonstrated that the region was dominated by fine particles. Based on above indicators, it may be concluded that anthropogenic sources were dominant.

A summary of the statistical analyses of the seasonal dataset of aerosol associated WSON, NO_3^- and $NH_4^+$are shown in Table 4. The Mann-Whitney U test indicated that there was a statistically significant difference among seasons, such that Summer > Spring ≈ Winter > Fall. The arithmetic mean value of WSON in the summer was found to be 1.3 and 2.0 times greater those observed for Spring/Winter and Fall, respectively. Furthermore, WSON was chiefly associated with coarse particles in summer, amounting to in excess of 80%. This high value in summer might be due to the absence of rainfall (see Fig.1) and enhanced re-suspension of cultivated soil in the region. In summer, the mean concentration of NH_4^+ was almost 2.4 times larger than all other seasons. The mean water-soluble NO_3^-in summer was 1.4 high than that of spring. High NH_4^+ and NO_3^- concentrations in summer might be attributed again to the absence of rainfall and increase in incoming radiation. Similar results have been reported for the Eastern Mediterranean (Bardouki et al., 2003).

3.4. Influence of Mineral Dust Episodes on WSON aerosol concentrations

As it is well documented, the Eastern Mediterranean Sea is heavily impacted by mineral dust episodes originating from Sahara and the Middle East deserts (Kubilay and Saydam, 1995; Kubilay et al., 2000, Koçak et al., 2004a, b and 2012).

For the current study between March 2014 and April 2015, water-soluble non-sea salt calcium concentrations higher than 50 nmol m^{-3} (2000 ng m^{-3}, as a threshold value) were defined as

mineral "dust events". These events were additionally confirmed using air mass back trajectories and OMI-AI. However, itt is worth mentioning that for samples containing concentrations of $nssCa^{2+}$ less than 50 nmol m^{-3} mineral dust transport from Sahara and the Middle East deserts to sampling site may not be excluded, peculiarly in winter. Yet, the application of such an arbitrary value is inevitable since it provides simplicity to explore if there is any influence of mineral dust intrusion on WSON.

For example, one of the highest WSON concentrations (66.1 nmol N m^{-3}) was observed on 2nd of March 2014 when the air mass back trajectories was associated with south/south westerly airflow. During this event, $nssCa^{2+}$ and NO_3^- showed a dramatic increase in their concentrations compared to those observed during the previous day, reaching up to 429 and 60 nmol m^{-3}, respectively. OMI (Ozone Mapping Instrument) Aerosol Index (AI) and three-day backward trajectory (1, 2, 3 and 4 km altitudes) air masses arriving at the Erdemli sampling site on 2nd of March 2014 is shown in Fig.4. As can be seen from the figure, all air masses (except at 1 km altitude) originated from North Africa whereas the back trajectory for 1 km altitude exhibited airflow from the Middle East. Hence, suggesting that the sampling site was under the influence of mineral dust transport originating from deserts regions located at the Middle East and North Africa.. In support, the OMI-AI diagram clearly indicates a large dust plume over the Eastern Mediterranean between coordinates 20-45 ˚N and 15-40 ˚E. The Aerosol Index was found to be very high over the Northeastern Mediterranean, ranging from 2.0 to 4.5. During this dust episode, 85% of the WSON was associated with the coarse fraction, which further supports mineral dust being a main source of water-soluble organic nitrogen.

Arithmetic mean concentrations together with corresponding standard deviations of WSON, NO_3^-, NH_4^+ and $nssCa^{2+}$ for dust and non-dust events are presented in Fig.5. As can be deduced from diagram, (except for NH_4^+,), WSON, NO_3^- and $nssCa^{2+}$ indicated distinct

401 difference between dust and non-dust events. Indeed, the application of the non-parametric
402 Mann Whitney U test indicated statistically significant differences between dust and non-dust
403 events for WSON ($p < 0.03$), NO_3^- ($p < 0.00002$) and $nssCa^{2+}$ ($p < 0.000001$) whereas no
404 statistically significant difference were observed for NH_4^+,($p=0.56$). The crustally derived
405 $nssCa^{2+}$ and anthropically derived NO_3^- for dust events had arithmetic mean of 95.8 nmol m^{-3}
406 and 26.1 nmol N m^{-3} which were almost four and two times higher than those of observed for
407 non-dust events, respectively. Such an increase in concentrations during dust events for these
408 species has been previously reported in the Eastern Mediterranean (Koçak et al., 2004b).
409 Similarly, the arithmetic mean of WSON (38.2 nmol m^{-3}) during dust events was 1.3 times
410 higher compared to the value observed during non-dust events (29.4 nmol m^{-3}). A similar
411 enrichment of WSON during dust events has been reported for Erdemli (Mace et al., 2003a;
412 Yellow Sea (Shi et al., 210) and Finokalia (Violaki and Mihalopoulos, 2010). In addition,
413 Griffin et al. (2007) have demonstrated a significant difference between dust and non-dust
414 events for bacterial and fungal colony forming units at Erdemli, the former being much
415 greater.. Thus, it might be speculated that this enhancement during dust events can be due to
416 (a) mineral dust borne microorganisms and/or (b) interaction (e.g. adsorption, acid-base
417 reaction) between mineral dust and organic nitrogen compounds.
418
419 **3.5. Impact of Airflow on WSON**
420 Arithmetic mean concentrations together with corresponding standard deviations for water-
421 soluble nitrogen species and $nssCa^{2+}$ in aerosol samples according to categorized air mass
422 sectors (at 1 km) are presented in Table 5 WSON concentrations can be broadly categorized
423 in two classes namely (a) Middle East, North Africa, Turkey and (b) Eastern Europe, Western
424 Europe and Mediterranean Sea. WSON concentrations in the first group were found to be at
425 least 1.2 higher than those observed for the second group. The application of the Mann-

Whitney U test indicated that there was a statistically significant difference in the concentrations of WSON between the following air mass categories: North Africa/Turkey/Middle East > Eastern Europe/Western Europe/ Mediterranean Sea ($p < 0.05$) The highest NO_3^- concentrations were associated with airflow from North Africa and Turkey with value of 18 and 15 nmol N m^{-3}, respectively, and there was a statistically significant difference compared to the remaining air mass sectors ($p > 0.05$). The mean concentrations of NO_3^- for air masses derived from North Africa and Turkey was at least 1.3 times larger than those calculated for the Middle East, Eastern Europe, Western Europe and Mediterranean Sea air sectors ($p > 0.05$). NH_4^+ had the highest concentration under the influence of airflow derived from Turkey. For this airflow, detected concentration was 1.5-2.4 times greater than those calculated for other air masses sectors. The Mann-Whitney test showed that there was a statistically significant difference in the $nssCa^{2+}$ concentrations. Arithmetic mean concentrations of $nssCa^{2+}$ in the Middle East and North Africa were approximately 2 times higher compared to the remaining air masses. As expected, these two airflows were primarily influenced by crustal material due to sporadic dust events originating from deserts located in North Africa and the Middle East.

3.6. Source Apportionment for WSON in Aerosol

A number of studies have discussed the possible sources of WSON in aerosol material by applying either simple correlation analyses (Mace et al., 2003c; Violaki and Mihapoulos, 2010; Ho et al., 2015) or multivariate factor analysis (Chen and Chen, 2010), including PMF (Chen et al., 2010). Usage of correlation analyses is useful when the number in sample-populationsare limited however; large datasets are required in order to carry out PMF and FA. Direct and indirect emissions of WSON from the sea surface have been demonstrated (Miyakazi et al., 2011; Altieri et al., 2016). Previous studies in the Eastern Mediterranean,

have observed WSON to be associated with mineral dust (Mace et al., 2003a; Violaki and Mihalopoulos, 2010). As stated by Mace et al. (2003a), WSON might either have originated from mineral dust or carried by dust events owing to adsorption of gaseous organic nitrogen compounds onto pre-existing particles. In addition, Violaki and Mihalapoulos (2010) have shown fossil fuel and biomass burning as sources of WSON to the Eastern Mediterranean atmosphere.

Fig.6 describes the potential sources of WSON by applying PMF 5.0. The predominant two factors were chiefly found to be related with water-soluble inorganic nitrogen species. The first factor had a high-loading for NH_4^+ with a value of 0.81and a moderate loading of SO_4^{2-} (0.45). These species, would suggest the formation of secondary aerosols. As expected, the factor contribution plot (not shown) indicated summer maximum, demonstrating accumulation of these particles due to the absence of rain and enhanced gas-to-particle formation under the prevailing conditions (high temperature and solar radiation). The equivalent ratio of NH_4^+ and SO_4^{2-} for this factor was 0.79, indicating $(NH_4)HSO_4$ formation(Koçak et al., 2007). The second factor explained 77 % of the NO_3^-variation and described 17 and 10 % of the SO_4^{2-} and NH_4^+, variation, respectively. This group was also associated with cations such as Na^+ (11 %), K^+ (7 %), Mg^{2+} (22 %) and Ca^{2+} (29 %), implying reactions mainly between acidic nitrate and alkaline species. The first and second factors accounted for 20 and 22 % of the variability in WSON, respectively. It might, therefore be argued that the variability of WSON in the first group resulted from the reaction between volatile organic N and ammonium sulfate aerosols whilst the variability of WSON explained by the second factor was as a result of the reaction between volatile organic compounds and NO_x and/or neutralization of acidic nitrate by alkaline nitrogen-containing compounds such as urea and amine The third factor was heavily influenced by Cl^- (0.8) and Na^+ (0.70) while moderately impacted by Mg^{2+} and K^+. This factor is likely due to sea salt formation.. The

forth factor was predominantly impacted by Ca^{2+} and hence may be attributed to crustal material. Crustal sources explained 10 % of the WSON variability. The final defined factor had a moderate loading of WSON (EV = 0.43, explained 43 %) while it was affiliated with Na^+ (0.15), K^+ (0.22) and Mg^{2+} (0.24). The factor contribution diagram denoted highest values in summer (not shown) and hence it can be attributed to re-suspension of the soil particularly affected by intense agricultural activities.

3.7. Atmospheric Depositions of N-Species and Implications Regarding Marine Production

The atmospheric dry (21.3 mmol N m^{-2} yr^{-1}) and wet (36.7 mmol N m^{-2} yr^{-1})deposition fluxes of WSON, NO_3^- and NH_4^+ and WSTN from March 2014 and April 2015 are demonstrated in Table 6. The atmospheric deposition of water-soluble nitrogen (57.8mmol N m^{-2} yr^{-1})was chiefly originated from wet deposition (36.7 mmol N m^{-2} yr^{-1}), amounting to 63 % of the total atmospheric deposition. This difference might be attributed to the water-soluble ammonium, for instance, the atmospheric depositions of NH_4^+ (15.6 mmol N m^{-2} yr^{-1}) was dominated by wet deposition, contributing 92 % of the total ammonium atmospheric flux. Whereas, the atmospheric flux of WSON and NO_3^- were more or less equally influenced by both deposition modes. Corresponding WSON (9.8 mmol N m^{-2} yr^{-1}) and NO_3^-(10.0 mmol N m^{-2} yr^{-1}) contributions to dry deposition were found to be 46 % and 48 % respectively. In contrast, NH_4^+(1.3 mmol N m^{-2} yr^{-1})was only estimated to contribute 6 % of the total deposition. Wet deposition of nitrogen was impacted by WSON (10.8 mmol N m^{-2} yr^{-1}), NO_3^- (11.7 mmol N m^{-2} yr^{-1}), and NH_4^+ (14.3 mmol N m^{-2} yr^{-1})in the increasing order 29 % < 32 % < 39 %. On average, WSON accounted for 36 % of the total atmospheric deposition of WSTN.

If one assumes that all N species are bioavailable to primary producers for primary production and if a Redfield N/C ratio of 106/16 is applied, it would be estimated that atmospheric N depositions can support new production 7.95 g C yr^{-1}. It has been shown that annual primary production for coastal and open waters of Cilician Basin were around 413 mg C m^{-2} d^{-1} and 179 mg C m^{-2} d^{-1}, respectively (Yücel, 2013). It has been noted that f- ratio (ratio between new and total production) may ranged between 0.05 and 0.16 in oligotropic seas such as Mediterranean (Estrada, 1996 and references therein). If the f-ratio of 0.16 is applied, the annual new production for coastal and open waters of Cilician Basin would be 24.15 g C yr^{-1} and 10.5 g C yr^{-1} respectively. Consequently, the atmospheric water-soluble nitrogen flux was found to sustain 33 % of the new production in coastal and 76 % of it in open waters.

4. Conclusion

In the current study, water-soluble organic nitrogen in aerosol and rain samples obtained over the Eastern Mediterranean has been investigated. From this investigation the following summary may be made:

1) Of the nitrogen species, aerosol WSON (23.8 ± 16.3 nmol N m^{-3}) exhibited the highest arithmetic mean, followed by ammonium (23.3 ± 14.4 nmol N m^{-3}) and then nitrate (17.9 ± 15.7 nmol N m^{-3}). Aerosol WSON was mainly associated with coarse particles (66 %). The WSTN was equally influenced by WSON and NH_4^+, each contributing 37 and 35 %, respectively, whereas the contribution to WSTN of $NO_3^-$was 28 %. In rainwater, the VWM concentrations of water-soluble nitrogen species were comparable. WSON and NO_3^- accounted for 29 and 32 % of the WSTN whilst NH_4^+ elucidated 39 % of the WSTN.

2) Aerosol WSON concentrations exhibited large variations from one day to another day. Generally, lower concentrations were observed during rainy days. Higher concentrations

of aerosol WSON were associated with different airflow. The three highest concentrations were related to (i) mineral dust transport from Sahara and the Middle East deserts, (ii) north/north westerly airflow from Turkey's largest cultivated plain, Konya and (iii) mid-range pollution transport from the Turkish coast. 3) Influence of mineral dust transport on aerosol WSON concentrations was assessed. The crustally derived $nssCa^{2+}$ and anthropogenic NO_3^- for dust events had arithmetic mean of 95.8 nmol m^{-3} and 26.1 nmol N m^{-3} which were almost four and two times higher than those of observed for non-dust events. The arithmetic mean of WSON (38.2 nmol m^{-3}) for dust events was 1.3 times higher compared to that observed for non-dust events (29.4 nmol m^{-3}).

4) Source apportionment suggested that aerosol WSON was mainly originated from anthropogenic sources including agricultural (43 %), secondary aerosols (20 %) and nitrate (22%), whereas, the two natural sources crustal material (10 %) and sea salts (5%) contributed 15 % to the WSON.

5) The total atmospheric deposition of water-soluble nitrogen (57.8 mmol N m^{-2} yr^{-1}) was mainly via wet deposition (36.7 mmol N m^{-2} yr^{-1}). In contrast the atmospheric fluxes of WSON and NO_3^- were equally influenced by the dry and wet deposition modes. On average, WSON accounted for 36 % of the total atmospheric deposition of WSTN. The annual new production for coastal and open waters of Cilician Basin was estimated to be 24.15 g C yr^{-1} and 10.5 g C yr^{-1}, respectively. Using these estimates the atmospheric water-soluble nitrogen flux could sustain 33 % of the new production in coastal and 76 % of it in open waters.

The authors declare that they have no conflict of interest.

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M. Koçak developed the concept and designed the study. M. Nehir and M. Koçak performed the experiments, analyzed the data and prepared the manuscript.

References

Altieri, K., Fawcett, S., Peters, A., Sigman, D., Hastings, M.: Marine biogenic source of atmospheric organic nitrogen in the subtropical North Atlantic. P. Natl. Acad. Sci., *113 (4),* 925-930, 2016.

Bardouki, H., Liakakou, H., Economou, C., Sciare, J., Smolik, J., Zdimal, V., Eleftheriadis, K., Lazaridis, M., Dye, C., Mihalopoulos, N.: Chemical composition of size resolved atmospheric aerosols in the eastern Mediterranean during summer and winter. *Atmos. Environ., 37,* 195–208, 2003.

Cape, J. N., Kirika, A., Rowland, A. P., Wilson, D. R., Jickells, T. D., Cornell, S: Organic nitrogen in precipitation: real problem or sampling artefact? *The Scientific World, 1,* 230–237, 2001.

Chen, H. and Chen, L:. Occurrence of water soluble organic nitrogen in aerosols at a coastal area. *J. Atmos. Chem., 65,* 49–71, 2010, doi: 10.1007/s10874-010-9181-y.

Chen, H., Chen, L., Chiang, Z., Hung, C., Lin, F., Chou, W., Gong, G., Wen, L.: Size fractionation and molecular composition of water-soluble inorganic and organic nitrogen in aerosols of a coastal environment. *J. Geophys. Res., 115, D22*, 2010, doi:10.1029/2010JD014157.

Cornell, S., Rendell, A. Jickells, T.: Atmospheric inputs of dissolved organic nitrogen to the oceans, *Nature, 376,* 243– 246, 1995.

Cornell, S., Jickells T., Thornton C.: Urea in rainwater and atmospheric aerosol, *Atmos. Environ., 32,* 1903-1910, 1998.

Cornell, S., Mace, K., Coeppicus, S., Duce, R., Huebert, B., Jickells, T., Zhuang, L.Z.: Organic nitrogen in Hawaiian rain and aerosols. *J. Geophys. Res. 106,* 7973–7983, 2001.

Cornell, S. E., Jickells, T. D., Cape, J. N., Rowland, A. P., Duce, R.A.: Organic nitrogen deposition on land and coastal environments: a review of methods and data, *Atmos. Environ., 37,* 2173–2191, 2003.

De Haan, D.O., Hawkins, L.N., Kononenko, J.A., Turley, J.J., Corrigan, A.L., Tolbert, M.A., Jimenez, J.L.: Formation of Nitrogen-Containing Oligomers by Methylglyoxal and Amines in Simulated Evaporating Cloud Droplets, *Environ. Sci. Technol., 45,* 948-991, 2011.

Draxler, R.R., Rolph, G.D., 2003. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory), Model Access via NOAA ARL READY Website. NOAA Air Resources Laboratory, Silver Spring, MD. http://www.arl.noaa.gov/ready/ hysplit4.html.

Duce, R.A., Liss, P.S., Merrill, J.T., Atlas, E.L., Buat-Menard, P.: The atmospheric input of trace species to the world ocean. *Glob. Biogeochem. Cycles, 5*, 193–259, 1991.

Duce, R. A., LaRoche, J., Altieri, K., Arrigo, K. R., Baker, A. R., Capone, D. G., Cornell, S., Dentener, F., Galloway, J., Ganeshram, R. S., Geider, R. J., Jickells, T., Kuypers, M. M., Langlois, R., Liss, P. S., Liu, S. M., Middelburg, J. J., Moore, C. M., Nickovic, S., Oschlies, A., Pedersen, T., Prospero, J., Schlitzer, R., Seitzinger, S., Sorensen, L. L.,

605 Uematsu, M., Ulloa, O., Voss, M., Ward, B., Zamora, L.: Impacts of atmospheric
606 anthropogenic nitrogen on the open ocean. *Science, 320,* 893–897, 2008.

607 Estrada, M.: Primary production in the northwestern Mediterranean. *Sci. Mar., 60 (2),*
608 55-64, 1996.

609 Galloway, J., Cowling, E.: Reactive nitrogen and the world: 200 years of change.
610 Ambio 31, 64-71, 2002.

611 Galloway, J. N., Townsend, A. R., Erisman, J.W., Bekunda, M., Cai, Z. C., Freney, J.
612 R., Martinelli, L. A., Seitzinger, S. P., Sutton, M. A.: Transformation of the nitrogen cycle:
613 Recent trends, questions, and potential solutions, *Science, 320,* 889-892, 2008.

614 Galloway, M. M., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Flagan, R. C.,
615 Seinfeld, J. H., Keutsch, F. N.: Glyoxal uptake on ammonium sulphate seed aerosol: reaction
616 products and reversibility of uptake under dark and irradiated conditions. *Atmos. Chem. Phys.,*
617 *9*, 3331-3345, 2009. doi:10.5194/acp-9-3331-2009.

618 Ge, X., Wexler, A., Clegg, S., 2011. Atmospheric amines e part I. A review. *Atmos.*
619 *Environ. 45,* 524-546.

620 Glibert PM, Trice TM, Michael B, Lane L.: Urea in the tributaries of the Chesapeake
621 and coastal bays of Maryland. *Water Air Soil Poll. 43*, 160-229, 2005.

622 Griffin, D.W., Kubilay, N., Koçak, M., Gray, M.A., Borden, T.C., Shinn, E: Airborne
623 desert dust and aeromicrobiology over the Turkish Mediterranean coastline. *Atmos. Environ.,*
624 *41,* 4050–4062, 2007.

625 Hamad, N., Millot, C., Taupier-Letage, I.: A new hypothesis about the surface
626 circulation in the eastern basin of the Mediterranean Sea. *Prog. Oceanogr., 66,* 287–298,
627 2005.

628 Hansell, D.: Results and observations from the measurement of DOC and DON in
629 seawater using a high-temperature catalytic oxidation technique. *Mar. Chem., 41,* 195-202,
630 1993.

631 Herut, B., Krom, M.D., Pan, G., Mortimer, R.: Atmospheric input of nitrogen and
632 phosphorus to the Southeast Mediterranean: sources, fluxes, and possible impact. *Limnol.*
633 *Oceanorg., 44,* 1683–1692, 1999.

634 Herut, B., Collier, R., Krom, M. D.: The role of dust in supplying nitrogen and
635 phosphorus to the Southeast Mediterranean. *Limnol. Oceanorg., 47,* 870–878, 2002.

636 Ho, K., Ho, S. S., Huang, R., Liu, S., Cao, J., Zhang, T., Chuang H., Chan C.S., Hu D.,
637 Tian, L.: Characteristics of water-soluble organic nitrogen in fine particulate matter in the
638 continental area of China. *Atmos. Environ., 106,* 252-261, 2014.

639

640 Hopke, P. K., Xie, Y., Raunemaa, T., Biegalski, S., Landsberger, S., Maenhaut, W.,
641 Artaxo, P., Cohen, D.: Characterization of the Gent Stacked Filter Unit PM_{10} Sampler.
642 *Aerosol Sci. Tech., 27,* 726-735, 1997.

643 Huang, S., Rahn, K.A., Arimoto, R.: Testing and optimizing two factor analysis
644 techniques on aerosol at Narragansett, Rhode Island. *Atmos. Environ., 33,* 2169–2185, 1999.

645 Keene, W., Montag, J., Maben, J., Southwell, M., Leonard, J., Church, T., Moody, J.,
646 Galloway, J.: Organic nitrogen in precipitation over Eastern North America. *Atmos. Environ.,*
647 *36(28),* 4529-4540, 2002.

648 Koçak M., Nimmo, M., Kubilay, N., Herut, B.: Spatio-temporal aerosol trace metal
649 concentrations and sources in the Levantine Basin of the Eastern Mediterranean. *Atmos.*
650 *Environ., 38,* 2133-2144, 2004a.

651 Koçak, M., Kubilay, N., Mihalopoulos, N.:. Ionic composition of lower tropospheric
652 aerosols at a Northeastern Mediterranean site: implications regarding sources and long-range
653 transport. *Atmos. Environ., 38,* 2067-2077, 2004b.

654 Koçak, M., Mihalopoulos, N., Kubilay, N.: Chemical composition of the fine and
655 coarse fraction of aerosols in the Northeastern Mediterranean. *Atmos. Environ., 41,* 7351-
656 7368, 2007.

657 Koçak, M., Mihalopoulos, N., Kubilay, N.: Source regions of PM10 in the Eastern
658 Mediterranean atmosphere. *Atmos. Res., 92,* 464-474, 2009.

659 Koçak, M., Theodosi, C., Zarmpas, P., Seguret, M.J.M., Herut, B., Kallos, G.,
660 Mihalopoulos, N., Kubilay, N., Nimmo, M.: Influence of mineral dust transport on the
661 chemical composition and physical properties of the Eastern Mediterranean aerosol. *Atmos.*
662 *Environ. 57,* 266-277, 2012.

663 Krom, M.D., Herut, B., Mantoura, R.F.C.: Nutrient budget for the Eastern
664 Mediterranean: implications for P limitation. *Limnol. Oceanorg., 49,* 1582–1592, 2004.

665 Kubilay, N. and Saydam, C.: Trace elements in atmospheric particulates over the
666 Eastern Mediterranean: concentration, sources and temporal variability. *Atmos. Environ., 29,*
667 2289-2300, 1995.

668 Kubilay N., Nickovic S., Moulin C., Dulac F.: An illustration of the transport and
669 deposition of mineral dust onto the eastern Mediterranean. *Atmos. Environ., 34,* 1293-1303,
670 2000.

671 Lee, E., Chan, C.K., Paatero, P.: Application of positive matrix factorization in source
672 apportionment of particulate pollutants in Hong Kong. *Atmos. Environ., 33,* 3201–3212, 1999.

673 Mace, K.A., Kubilay, N. , Duce, R.A.: Organic nitrogen in rain and aerosol in the
674 eastern Mediterranean atmosphere: An association with atmospheric dust. *J. Geophys. Res.,*
675 *108, D10,* 4320, 2003a, doi:10.1029/2002JD002997.

676 Mace KA, Duce RA, Tindale NW.: Organic nitrogen in rain and aerosol at Cape Grim,
677 Tasmania Australia. *J. Geophys Res., 108*, 4338, 2003b.

678 Mace, K., Artaxo, P., Duce, R.: Water-soluble organic nitrogen in Amazon Basin
679 aerosols during the dry (biomass burning) and wet seasons. *J. Geophys. Res. 108*, 4512,
680 2003c. http://dx.doi.org/10.1029/2003JD003557.

681 Mihalopoulos, N., Kerminen, V., M., Kanakidou, M., Berresheim, H., Sciare, J.:

682 Formation of particulate sulfur species (sulfate and methanesulfonate) during summer over
683 the Eastern Mediterranean: a modelling approach. *Atmos. Environ. 41,* 6860-6871, 2007.

684 Miller, J.: The nitrogen content of rain falling at Rothamsted. *J. Agricul. Sci., 1,* 280-
685 303, 1905.

686 Miyazaki, Y., Kawamura, K., Jung, J., Furutani, H., Uematsu, M.: Latitudinal
687 distributions of organic nitrogen and organic carbon in marine aerosols over the western
688 North Pacific, *Atmos. Chem. Phys., 11,* 3037–3049, 2011. doi:10.5194/acp-11-3037-2011.

689 Neff, J. C., Holland, E. A., Dentener, F. J., McDowell, W. H., and Russell, K. M.: The
690 origin, composition and rates of organic nitrogen deposition: A missing piece of the nitrogen
691 cycle. *Biogeochemistry, 57*, 99–136, 2002.

692 Paatero, P., Tapper, U.: Positive matrix factorization: a non-negative factor model with
693 optimal utilization of error estimates of data value. *Environmetrics, 5,* 111–126, 1994.

694 Peierls, B. L. and Paerl, H. W.: Bioavailability of atmospheric organic nitrogen
695 deposition to coastal phytoplankton. *Limnol. Oceanogr., 42,* 1819–1823, 1997.

696 Seitzinger, S. P. and Sanders, R. W.: Atmospheric inputs of dissolved organic nitrogen
697 stimulate estuarine bacteria and phytoplankton. *Limnol. Oceanogr., 44,* 721–730, 1999.

698 Shi, J.H., Gao, H.W., Qi, J.H., Zhang, J., Yao, X.H.: Sources, compositions, and
699 distributions of water-soluble organic nitrogen in aerosols over the China Sea. *J. Geophys.*
700 *Res. 115, 2010.*

701 Sorooshian, A., Murphy, S. M., Hersey, S., Gates, H., Padro, L. T., Nenes, A.,
702 Brechtel, F. J., Jonsson, H., Flagan, R. C,. Seinfeld, J. H.: Comprehensive airborne
703 characterization of aerosol from a major bovine source. *Atmos. Chem. Phys, 8 (17).* 5489-
704 5520, 2008.

705 Spokes, L.J., Jickells, T. D., Jarvis, K.: Atmospheric inputs of trace metals to the
706 northeast Atlantic Ocean: the importance of south-easterly flow. *Mar. Chem., 76,* 319-330,
707 2001.

708 Surratt, J.D., Gómez-González, Y., Chan, A.W.H., Vermeylen, R., Shahgholi, M.,
709 Kleindienst, T.E., Edney, E.O., Offenberg, J.H., Lewandowski, M., Jaoui, M., Maenhaut,
710 Claeys, W.M., Flagan, R.C. and Seinfeld, J.H.: Organosulfate Formation in Biogenic
711 Secondary Organic Aerosol. *J. Phys. Chem. A, 112 (36),* 8345–8378, 2008.

712 Twohy, C. H., Petters, M. D., Snider, J. R., Stevens, B., Tahnk, W., Wetzel, M.,
713 Russell, L., Burnet, F.: Evaluation of the aerosol indirect effect in marine stratocumulus
714 clouds: Droplet number, size, liquid water path, and radiative impact. *J. Geophys. Res., 110,*
715 D08203, 2005. doi:10.1029/2004JD005116.

716

717 Thingstad, T. F., Krom, M. D., Mantoura, R. F. C., Flaten, G. A. F., Groom, S., Herut,
718 B., Kress, N., Law, C. S., Pasternak, A., Pitta, P., Psarra, S., Rassoulzadegan, F., Tanaka, T.,
719 Tselepides, A., Wassmann, P., Woodward, E. M. S., Riser, C. Wexels, Zodiatis, G., Zohary,
720 T.: Nature of Phosphorus Limitation in the Ultraoligotrophic Eastern Mediterranean. *Science,*

721 *309,* 1068-1071, 2005.

722 Timperley MH, Vigor-Brown RJ, Kawashima M, Ishigami M.: Organic nitrogen
723 compounds in atmospheric precipitation: their chemistry and availability to phytoplankton.
724 *Canadian J. Fish Aquat. Sci., 42,* 1171–1177, 1985.

725 Viana, M., Pandolfi, M., Minguillon, M.C., Querol, X., Alastuey, A., Monfort, E.,
726 Celades, I.: Inter-comparison of receptor models for PM sources apportionment: case study in
727 an industrial area. *Atmos. Environ. 42,* 3820–3832, 2008.

728 Violaki, K. and Mihalopoulos, N.: Water-soluble organic nitrogen (WSON) in size-
729 segregated atmospheric particles over the Eastern Mediterranean. *Atmos. Environ., 44,* 4339-
730 4345, 2010.

731 Violaki, K., Zarbas, P., Mihalopoulos, N.: Long-term measurements of dissolved
732 organic nitrogen (DON) in atmospheric deposition in the Eastern Mediterranean: fluxes,
733 origin and biogeochemical implications. *Mar. Chem. 120,* 179-186, 2010.

734 Violaki, K., Sciare, J., Williams, J., Baker, A.R., Martino, M., Mihalopoulos, N.:
735 Atmospheric Water-Soluble Organic Nitrogen (WSON) over marine environments: A global
736 perspective. *Biogeosciences, 12,* 3131-3140, 2015.

737 Yılmaz, A. and Tuğrul, S.: The effect of cold- and warm-core eddies on the
738 distribution and stoichiometry of dissolved nutrients in the northeastern Mediterranean. *J.*
739 *Mar. Sys., 16,* 253–268, 1998.

740 Yu, G., Bayer, A. R., Galloway, M. M., Korshavn, K. J., Fry, C. G., Keutsch, F. N.:
741 Glyoxal in Aqueous Ammonium Sulfate Solutions: Products, Kinetics and Hydration Effects.
742 *Environ. Sci. Tech., 45*, 6336–6342, 2011. doi:10.1021/es200989n.

743 Yücel, N.: Monthly changes in primary and bacterial productivity in the north-eastern
744 Mediterranean shelf waters. *Ph.D. thesis*, Middle East Technical University, Institute of
745 Marine Sciences, Erdemli, Turkey, 2013.

746 Yücel, N.: Seasonal and spatial variation of bacterial production and abundance in the
747 northern Levantine Sea. *Mediterr. Mar. Sci., 18,* 97-106, 2017.

748 Zamora, L. M., Prospero, J. M., Hansell, D. A.: Organic nitrogen in aerosols and
749 precipitation at Barbados and Miami: Implications regarding sources, transport and deposition
750 to the western subtropical North Atlantic. *J. Geophys. Res., 116, D20, 2011.*

751 Zhang, Y., Zheng, L., Liu, X., Jickells, T., Cape, N., Goulding, K., Fangmeier, A. and
752 Zhang, F.: Evidence for organic N deposition and its anthropogenic sources in China. *Atmos.*
753 *Environ., 42,* 1035-1041, 2008.

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759 **Figure Captions**

760 **Figure 1.** The daily variations in the concentrations of (a) WSON, (b) NO_3^- and (c) NH_4^+
761 (nmol N m^{-3}) together with rain amount (mm) from March 2014 and April 2015 for PM10.

762 **Figure 2.** Three day back trajectories showing the transport of air masses 1000m (black
763 circle), 2000m (black star), 3000m (black square) and 4000m (black triangle) on 5th of July
764 2014 for Erdemli. Aerosol Index (AI) from OMI (Ozone Mapping Instrument) distribution
765 also illustrated with a color bar from grey to black.

766 **Figure 3.** Three day back trajectories showing the transport of air masses 1000m (black
767 circle), 2000m (black star), 3000m (black square) and 4000m (black triangle) on 20th of
768 February 2015 for Erdemli. Aerosol Optical Depth (AOD, a) and Angstrom Component (AC,
769 b) from MODIS (Moderate Resolution Imaging Spectroradiometer) distribution also
770 demonstrated with a color bar from grey to black.

771 **Figure 4.** Three day back trajectories indicating the transport of air masses 1000m (black
772 circle), 2000m (black star), 3000m (black square) and 4000m (black triangle) on 2nd of
773 March 2014 for Erdemli. Aerosol Index (AI) from OMI (Ozone Mapping Instrument)
774 distribution also illustrated with a color bar from grey to black.

775 **Figure 5.** Arithmetic means together with corresponding Standard deviations of WSON, NO_3^-
776 , NH_4^+ and $nssCa^{2+}$ for dust and non-dust events at Erdemli site. Dark and light grey bars
777 denote arithmetic mean for dust and non-dust, respectively. Black vertical line shows standard
778 deviation.

779 **Figure 6.** Source apportionment of WSON from Positive Matrix Factorization for PM10 at
780 Erdemli.

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782 **Table Captions**

783 **Table 1.**The number of negative WSON values and positive biases in coarse and fine particles
784 at Erdemli.

785 **Table 2.** The statistical summary of the WSON, NO_3^-, NH_4^+ and WSTN for aerosol (nmol N
786 m^{-3}) and rain (µmol N L^{-1}) samples collected at Erdemli from March 2014 to April 2015.

787 **Table 3.** Comparison of WSON concentrations in aerosol (nmol N m^{-3}) and rain (µmol N L^{-1})
788 samples for different sites of the World.

789 **Table 4.** Seasonal statistical summary of the WSON, NO_3^-, NH_4^+, WSTN (nmol N m^{-3}) and
790 $nssCa^{2+}$ (nmol m^{-3}) in aerosol samples collected at Erdemli from March 2014 to April 2015.

791 **Table 5.** Arithmetic means along with standard deviations of WSON, NO_3^-, NH_4^+ (nmol N
792 m^{-3}) and $nssCa^{2+}$ (nmol m^{-3}) in aerosol samples as a function of the classified airflow
793 corresponding to three day air mass back trajectories reaching at Erdemli.

794 **Table 6.** Atmospheric dry and wet deposition of WSON, NO_3^-, NH_4^+ and WSTN together
795 with their relative contributions at Erdemli during the period of March 2014 and April 2015.

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Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-601
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799 **Figures**
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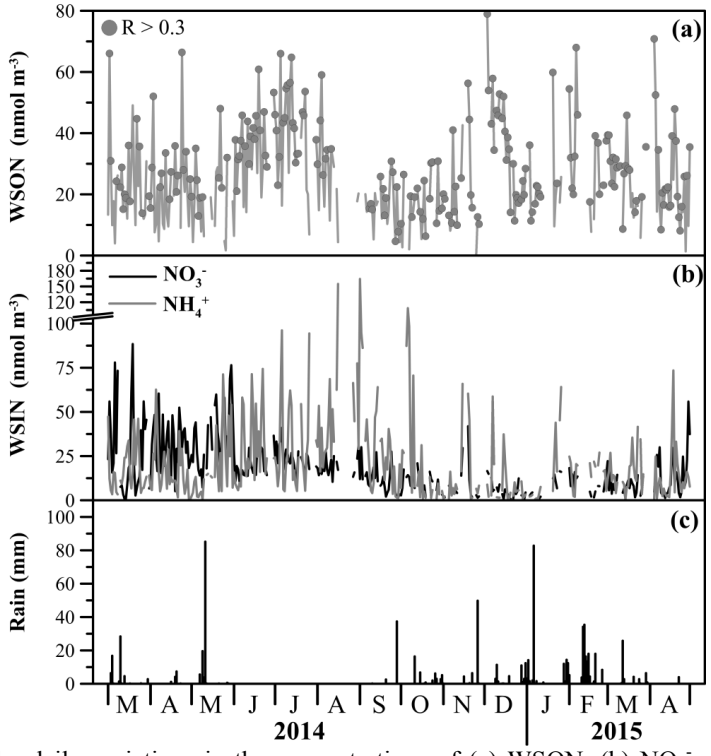

802
803 **Figure 1.** The daily variations in the concentrations of (a) WSON, (b) NO_3^- and (c) NH_4^+
804 (nmol N m^{-3}) together with rain amount (mm) from March 2014 and April 2015 for PM_{10}.
805
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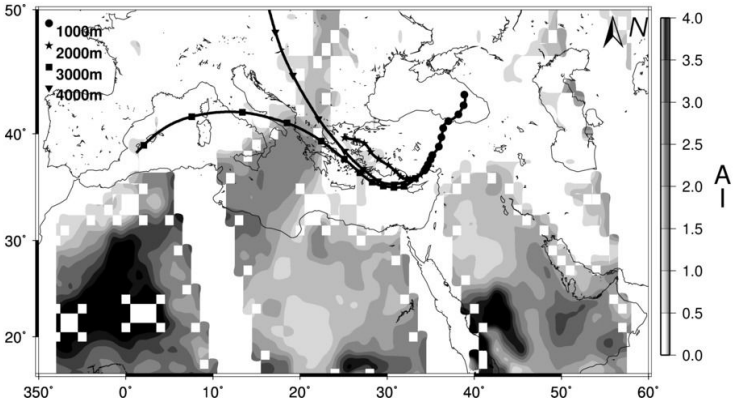

807
808 **Figure 2.** Three day back trajectories showing the transport of air masses 1000m (black
809 circle), 2000m (black star), 3000m (black square) and 4000m (black triangle) on 5th of July
810 2014 for Erdemli. Aerosol Index (AI) from OMI (Ozone Mapping Instrument) distribution
811 also illustrated with a color bar from grey to black.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-601
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 24 August 2017

Atmospheric Chemistry and Physics Discussions

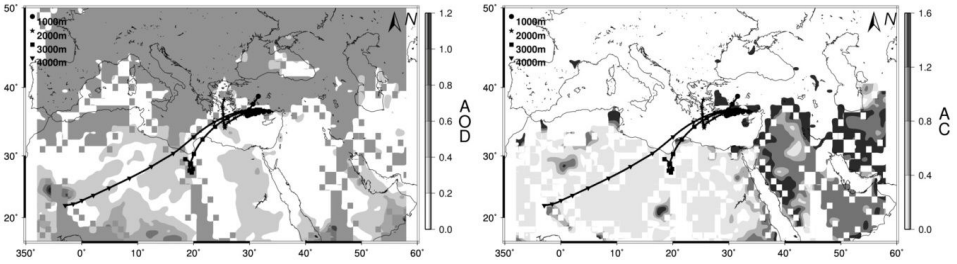

Figure 3. Three day back trajectories showing the transport of air masses 1000m (black circle), 2000m (black star), 3000m (black square) and 4000m (black triangle) on 20th of February 2015 for Erdemli. Aerosol Optical Depth (AOD, a) and Angstrom Component (AC, b) from MODIS (Moderate Resolution Imaging Spectroradiometer) distribution also demonstrated with a color bar from grey to black.

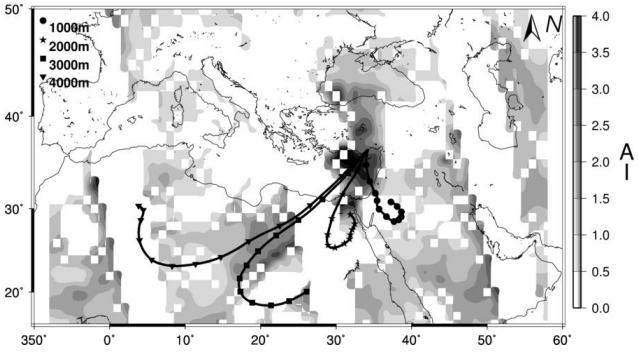

Figure 4. Three day back trajectories indicating the transport of air masses 1000m (black circle), 2000m (black star), 3000m (black square) and 4000m (black triangle) on 2nd of March 2014 for Erdemli. Aerosol Index (AI) from OMI (Ozone Mapping Instrument) distribution also illustrated with a color bar from grey to black.

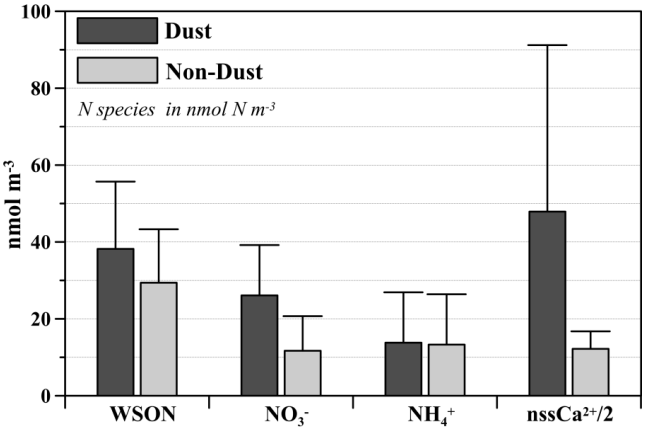

Figure 5. Arithmetic means together with corresponding standard deviations of WSON, NO_3^-, NH_4^+ and $nssCa^{2+}$ for dust and non-dust events at Erdemli site. Dark and light grey bars denote arithmetic mean for dust and non-dust, respectively. Black vertical line shows standard deviation.

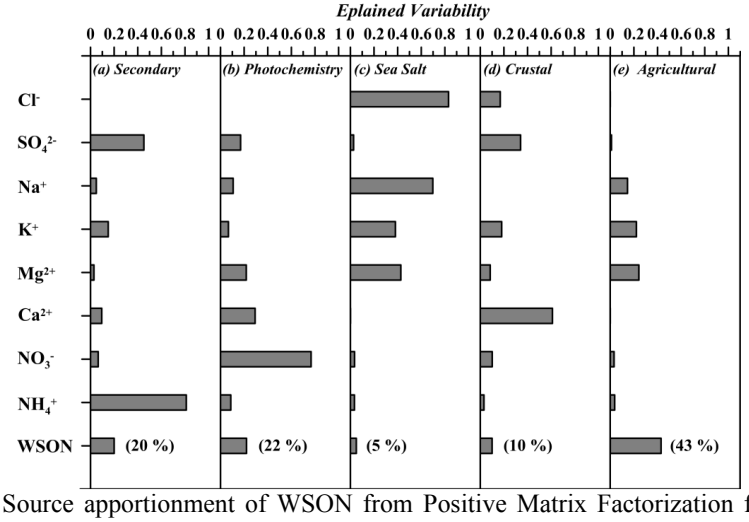

Figure 6. Source apportionment of WSON from Positive Matrix Factorization for PM_{10} at Erdemli.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-601
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 24 August 2017

Atmospheric Chemistry and Physics Discussions

Tables

Table 1. The number of negative WSON values and positive biases in coarse and fine particles at Erdemli.

	Coarse	**Fine**
Number of Samples	337	337
Number of Negatives	18	52
SZ[1]-Positive Bias (%)	2	14
PZ[2]-Positive Bias (%)	8	34

1 and 2 refer to as the Substitution with Zero and the Omission of Zero, respectively.

Table 2. The statistical summary of the WSON, NO_3^-, NH_4^+ and WSTN for aerosol (nmol N m^{-3}) and rain (µmol N L^{-1}) samples collected at Erdemli from March 2014 to April 2015.

AEROSOL (nmol N m^{-3})				
	WSTN	***WSON***	***NO_3^-***	***NH_4^+***
Arithmetic Mean	63.5	23.8	17.8	21.9
Standard Deviation	32.0	16.3	15.2	23.8
Minimum	9.7	-27.9	0.2	0.5
Maximum	176.5	79.0	88.4	164.4
Coarse/PM_{10} (%)	51	66	87	4
Relative Contribution to WSTS (%)		*37*	*28*	*35*
RAIN (µmol N m^{-3})				
VWM*	73.5	21.5	23.3	28.7
Minimum	24.3	-2.9	0.2	9.1
Maximum	356.2	257.2	74.6	122.6
Relative Contribution to WSTS (%)		*29*	*32*	*39*

*VWM refers to Volume Weighted Mean

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-601
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Discussion started: 24 August 2017

Atmospheric Chemistry and Physics Discussions

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858 **Table 3.** Comparison of WSON concentrations in aerosol (nmol N m^{-3}) and rain (µmol N L^{-1})
859 samples for different sites of the World.

Aerosol (nmol N m^{-3})	**WSON**	**NS**	**SP**	**Reference**
Mediterranean Sea				
Erdemli, Turkey	23.8	674	2014-2015	This Study
Erdemli, Turkey	29	39	2000	Mace et al. [2003a]
Finokalia, Crete	17.1	65	2005-2006	Violaki and Mihalopoulos [2010]
Pacific Ocean				
Hawaii	4.1	16	1998	Cornell et al. [2001]
Tasmania	5.3	24	2000	Mace et al. [2003b]
Taiwan	75.9	77	2006	Chen et. al. [2010]
Xi'an, China ($PM_{2.5}$)	300	65	2008-2009	Ho et. al. [2015]
Atlantic Ocean				
Barbados	1.3	57	2007-2008	Zamora et al. [2011]
Amazon, dry season	61	37	1999	Mace et al. [2003c]
Amazon, wet season	3.5	27	1999	Mace et al. [2003c]
Indian Ocean				
Amsterdam Island	1	42	2005	Violaki et al. [2015]
Rainwater (µmol N L^{-1})	**WSON**	**NS**	**SP**	**Reference**
Mediterranean Sea				
Erdemli, Turkey	21.5	23	2014-2015	This Study
Erdemli, Turkey	15	18	2000	Mace et al. [2003a]
Finokalia, Crete	18	18	2003-2006	Violaki et al. [2010]
Pacific Ocean				
*Tahiti**	4.8	8		Cornell et al. [1998]
Hawaii	2.8	17	1998	Cornell et al. [2001]
Tasmania	7.2	6		Mace et al. [2003b]
North China Plain, China	103	15	2003-2005	Zhang et al. [2008]
Kilauea, Hawaii	6.5	20	1998	Cornell et al. [2001]
Atlantic Ocean				
Bermuda	5.6	5	1994	Cornell et al. [1998]
Mace Head	3.3	7		Cornell et al. [1998]
Norwich, UK	33	12		Cornell et al. [1998]
Virginia, US	3.1	83	1996-1999	Keene et al. [2002]
Delaware, US	4.2	50	1997-1999	Keene et al. [2002]
New Hampshire, US	0.6	12	1997	Keene et al. [2002]

860 *RC, NS and SP refer to relative contribution of WSON to WSTN, number of samples and sampling period,*
861 *respectively.*
862
863
864 **Table 4.** Seasonal statistical summary of the WSON, NO_3^-, NH_4^+, WSTN (nmol N m^{-3}) and
865 $nssCa^{2+}$ (nmol m^{-3}) in aerosol samples collected at Erdemli from March 2014 to April 2015.

Aerosol *Species*	**Winter**	**Spring**	**Summer**	**Fall**
WSON	33±16	28±13	41±11	20±10
NO_3^-	7±5	15±12	21±7	9±8
NH_4^+	10±12	11±9	24±16	10±13
$nssCa^{2+}$	28±13	28±13	28±13	41±11
Number of Samples	47	79	46	44
Meteorology *Parameter*	**Winter**	**Spring**	**Summer**	**Fall**
T (°C)	11±3	16±3	27±12	20±15
Rain (mm)	78	118	0.5	132
Number of Rain Events	16	16	2	15

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-601
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Discussion started: 24 August 2017

Atmospheric Chemistry and Physics Discussions

Table 5. Arithmetic means along with standard deviations of WSON, NO_3^-, NH_4^+ (nmol N m^{-3}) and $nssCa^{2+}$ (nmol m^{-3}) in aerosol samples as a function of the classified airflow corresponding to three day air mass back trajectories reaching at Erdemli

Airflow	**WSON**	**NO_3^-**	**NH_4^+**	**$nssCa^{2+}$**
Middle East	33±12	12±12	13±15	48±71
North Africa	36±16	18±11	12±14	46±38
Turkey	32±13	15±10	19±15	23±9
Eastern Europe	26±14	10±9	10±8	21±9
Western Europe	26±14	10±8	11±9	20±7
Mediterranean Sea	22±10	10±8	8±6	19±8

Table 6. Atmospheric dry and wet deposition of WSON, NO_3^-, NH_4^+ and WSTN together with their relative contributions at Erdemli during the period of March 2014 and April 2015.

Species	**F_d (mmol N m^{-2} yr^{-1})**	**Relative Contribution**
WSON	9.8	46
NO_3^-	10.0	48
NH_4^+	1.3	6
WSTN	21.1	
Species	**F_w (mmol N m^{-2} yr^{-1})**	**Relative Contribution**
WSON	10.7	29
NO_3^-	11.7	32
NH_4^+	14.3	39
WSTN	36.7	