Dear Dr. Evangelos Gerasopoulos,

The authors would like to thank the two reviewers for their very helpful and informative comments. Please find below our responses to all the comments made by the two reviewers. We are confident that the modified manuscript as a result of our response to the reviewer's comments will be a clearer and more focused document.


Please find below our answers and response to comments.


Yours Faithfully,

Dr. Mustafa Koçak

**Reviewer 1**

Q1: There have been some recent reviews of WSON which the authors might reference (e.g. Cape et al., 2011 Atmos. Res 102,30-48) since they summaries much of the material and offer a somewhat wider perspectives and more recent information on the composition of WSON.
*A1: Cape et al., 2011 was also used for defining the composition of WSON, including vehicle exhaust, cooking, algal blooms and degraded proteins (see lines 48,49, 50 and 52).*

Q2: There is also now a global model of WSON (Kanakidou et al., 2012 Global Biogeochem. Cycl.26, doi10.1029/2011GB004277) which has contributed to an updated global nitrogen cycle revising the Duce et al 2008 paper cited (Jickells et al., 2017 Global Biogeochem. Cycl.31, doi10.1029/2016GB005586).
*A2: Jickells et al. 2017 was used to update change in reactive nitrogen and reactive anthropogenic organic nitrogen from mid 1800 to 2000s (see lines 68-70).*

Q3: Line 60, while amines will neutralise acids, it is not obvious the rest of WSON will.
*A: The sentence was changed as follow 'Similar to ammonium, 'some' organic nitrogen species such as urea and amines have acid-neutralizing capacities (Ge et al., 2011)'. Urea was kept in the text since it shows slightly alkaline character. Furthermore, amino-acids such as Lysine, Histidine and Arginine exhibit alkaline character (see line 58).*

Q4: Line 62 I don't think Twohy discusses WSON.
*A4: Twohy et al. (2005) has mentioned about organo-nitrogen compounds. To quote Twohy et al. 'Our analysis indicates that organic species do not have to be mixed with inorganic particles to act as CCN, and that organo-nitrogen compounds nucleate cloud droplets in the Indian Ocean. If these particles are present in other polluted areas, they could contribute substantially to the global indirect aerosol effect' (conclusion page 3, 12th paragraph). Therefore, if these organo-nitrogen compounds nucleate cloud droplets, they would be water-soluble.*

Q5: Line 80 and later on, there is really pretty clear Evidence that the Eastern Mediterranean is P limited. There is a vast body of work by Krom and colleagues that supports this (see most recently Pawley et al 2017Global Biogeochem.Cycl.31, 1010-1031 and the earlier summary in Krom et al 2010Prog. In Oceanography 85,236-244) and my reading of the Yücel 2017 paper does not actually contradict this view.

*A5: This issue was clarified as suggested (see lines from 76 to 87).*

Q6: Line81-2 It is mentioned a little bit later on, but not here, that Mace et al have reported WSON from exactly the same site as the study here. This should be noted here and also in section 3.1.

*A6: Reference was noted as advised (see lines 88-89 and 296-297).*

Q7: Note also the reference list lacks dates and while in the text the authors refer to Mace et al a,b and c, these are not identified in the references by these letters.

*A7: Correction was made considering Mace et al 2003a, b and c (see lines from 783 to 790).*

Q8: Analytical Methods. In general the results seem to be of good quality, although there is no mention of how blanks were determined (i.e. what procedures were used to create blank samples for analysis), what standards were used in analysis and whether any certified reference materials were used.

*A8: As stated before Operational blank filters for aerosol were processed in the same way as the collected samples with the exception that no air was passed through the filters. Information about blanks for rain was added to text: Operational blanks for rain samples were taken by using 100 mL of Milli-Q water after cleaning the HDPE buckets with phosphate free detergent, HCl (10 %) and Milli-Q water (see lines from 139 to 141).Details about standard, recovery analysis and quality assurance for WSTN was given in Materials and Methods section (see lines from 169 to 178).*

Q9: I do not really understand what the sentence line163-4 about blanks being <10 % means, Is this true for all ions?

*A9: Sentence was clarified by using 'for all' (see line 189-190)*

Q10: On line163 20 ppb is ambiguous, is it as ppb nitrogen and Why not use molar units as elsewhere in the paper?

*A10: Molar unit was used as suggested (see line 179).*

Q11: Section2.4 discusses the quite well known challenges of estimating WSON and its relatively low precision as a derived quantity (see Cape et al for instance). The precision of WSON depends a lot on the Relative concentrations of the three components of the total nitrogen analysis, so it is not possible really to quote a single number. The authors discussion e.g. lines170-174 and 175 (and lines 221-222) does not really explain what they actually estimate the precision to be.

*A11: Modification was made as suggested (see lines from 208 to 216).*

Q12: The use of PMF (which I am no expert on) here seems to require provision of precision estimates, but I do not understand how the arbitrary thresholds used here (line185-7) were arrived at or how sensitive there results are to these values.

*A12: Appendix was added in order to clarify uncertainty estimates (see lines from 602 to 633). As it is well known, it impossible to include negative values when one carries out multivariate statistics. Application of PMF without negative values, yielded worse slope than that of obtained by using threshold. For instance, the slope of the estimated WSON against measured WSON was 30 % less than unity. Furthermore, DISP error estimates showed that there were factor swaps and significant change in Q during DISP. In other words, PMF application without threshold exhibited that solutions were not robust.*

Q13: Section2.6 As I understand it PMF is a form of principal component analysis and hence is an appropriate tool for this kind of source apportionment. I would suggest the authors may be better putting an explanation of the principal of the method here and putting the highly technical discussion in to some sort of appendix, because I think many readers will not really be able to follow this section.

*A13: We agree with the comment. Consequently, appendix was added into the text (see lines from 602 to 6633).*

Q14: Section 3.1 and 3.2 I Wonder if these sections could be shortened a bit given that the results are broadly in line with other work in this region.

*A14: As can be seen from the Table 2, there are only two references in the region (Mace et al., 2003 and Violaki and Mihalopoulos, 2010). If one relies on these two references, the scientific discussion and comparison would be insufficient to enrich the findings/arguments about WSON. Thus, the 3.1 and 3.2 were preserved as is.*

Q15: Line 304-307 I do not disagree with the interpretation here, but it is worth noting that this does carry the implicit assumption that land based sources dominate the emission of WSON.

*A15: We agree with the comment. '(iii) small contributions from non-land based local emissions such as sea salt and algal blooms' was added as third reason.*

Q16: Section 3.3. this section is very general and the issue is approached in a more quantitative manner in 3.5 and 3.6, so I wonder if the section could be shortened.

*A17: We agree that more detail was given in 3.5 and 3.6, however, temporal variability (Section 3.3) includes both daily and seasonal variability and it is only one and a half page. It was kept as is.*

Q17: Section 3.4 Mace et al suggested that the Saharan Dust was a major source of WSON at this site and they did this I think by a correlation between $nssCa^{2+}$ and WSON. Here the association with dust seems to be weaker but the discussion does not really address this point, but simply notes there is an association with dust. This could be discussed further.

*A17: Regarding Mace et al., 2003a this summary may be made. The obtained samples only covers dust period. Indeed, there was a strong correlation between $nssCa^{2+}$ and WSON ($R^2$ =075). On the other hand, there was also a strong correlation between nitrate and WSON (R2 = 0.69) (Mace et al., 2003a, page 5-7, Table 3). Subsequently, even during the dust period (from March 22 to May 4) it seems that WSON was almost equally impacted by mineral dust (not sure only from Sahara, see below) and man-made nitrate. Moreover, I am not sure whether all dust events were originated from Sahara Desert. For example, Figure 2a (Mace et al., 2003a, page 5-3) shows that on 5 April 2000 the Erdemli site was under the influence of the Middle East (air masses arriving at 1000 and 900 hPa) and Sahara (air masses arriving at 700 and 500 hPa) Deserts at the same time. However, such an interpretation in the text would be impolite since the authors only considered Saharan Dust in spite of strong correlation between nitrate and WSON and air masses back trajectories.*

Q18: Section 3.5 In Table 5 the WSON and other parameters are classified into 5 groups, but in the text here the discussion splits the data in to two. It would be easier for the reader if the manuscript discussion and the tables did one or other of these, rather than mix them up in this way.

*A18: Modification in this section was made as advised (see lines from 472 to 478).*

Q19: Section 3.6 As noted earlier I am no expert PMF. The striking thing for me from Figure6 and the discussion, is that WSON does not resolve in any simple way in to any of the components identified, emphasizing the multiplicity of sources that it has, and this is particularly striking within such a large data set. I would also query the interpretation of what the associations mean (lines 469-474). The authors interpret the results in terms of formation mechanisms, but an alternative explanation might be emission sources.

*A19: We agree with the suggestion. Therefore, Factors 1, 2 and 5 were respectively attributed to ammonium-bisulfate (regional emissions), nitrate (combustion) and soil re-suspension (see lines 515-518 and 522-524).*

Q20: Section 3.7As noted earlier the Eastern Mediterranean appears to be phosphorus limited. If this is the case then the addition of nitrogen will not necessarily stimulate any

Additional primary production, but rather contribute to the high N/P ratio (see earlier) Krom and Pawley references) and so the hypothesis behind the calculation (line500-

509) is flawed and the conclusions about the impacts on new production are incorrect.

Section4. This is really a summary and not a conclusion and simply repeats the earlier material.

*A20: Please see A5. The last paragraph of section 3.7 was removed from the text as suggested by Reviewer 2. We agree that the section 3.4 is not a conclusion. Thus, the summary was used instead of conclusion (see line 560).*

**Reviewer 2**

Q1: Aerosol WSON concentrations exhibited large temporal variations mainly due to rain and the origin of air mass flow. Rain scavenges all compounds why preferably WSON?

*A1: I agree. Rain scavenges all compounds. Meteorology was used instead of rain (see page 1, line 21).*

Q2: NO$_3$ is a secondary aerosol?

*A2: NO$_3$ is a secondary aerosol (please see A10).*

Q3: 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. I suggest to remove this part or to be more cautious.

*A3: The sentence (the last paragraph of the section 3.7) was removed as suggested.*

Q4: Did the samples were uniformly distributed all over seasons?

*A4: Information about the seasonal observational coverage was added to the experimental section (see answer to question 8).*

Q5: Did the authors perform recovery experiments with well-known mixtures of organic and inorganic compounds?

*A5: Recovery experiments were carried out by using nitrate, ammonium, urea and mixture of all three species. Furthermore, the performance of our laboratory was studied by participating Quality Assurance of Information for Marine Environmental Monitoring in Europe (QUASIMEME) program. More information about recovery experiments was supplemented (see lines from 169 to 179).*

Q6: Please also report median in addition to average. Also how mean and median values changes if all data are considered (sensitivity test).

*A6: Median values were typed in Table 2. Number of samples were also included. Table 2 shows statistical summary for all samples (see line 287 and 288). Median values for WSON, NO$_3^-$, NH$_4^+$ and WSTN were respectively 10 %, 20 %, 40 % and 10 % lower than those that of arithmetic means.*

Q7: What is the seasonality of coarse/fine ratio of WSON? Also how this ratio varies as a function of air masses origin or better in dust vs non-dust samples?

*A7: Details about coarse/fine ratio of WSON for each season, air mass and dust/non-dust were given in Table 4 and 5 (also see lines 408-410, 458-460 and 477-480).*

Q8: At Table 4, the number of samples reported is only 216, whereas at line 120 they report analysis of 337 results. Why this difference? They correspond to samples with precision larger than 0,3? If yes what is the seasonal representativity of these 216 samples?

*A8: A total of 216 aerosols corresponded to samples with precision larger than 0.3. The observational coverage for winter, spring, summer and fall was respectively 60 %, 92 %, 81 % and 79 %. The seasonal observational coverage, after applying precision value of 0.3 (for more details see section 2.4 and Eq.4), was found to be comparable for winter (49 %), spring (53 %), summer (51 %) and fall (52 %) (see lines 129-132).*

Q9: In rain water how many values have been omitted with precision lower than 0,3? What is the temporal variability of the omitted data?

*A9: During the calculations of the dry and wet deposition, the values presented in Table 1 were utilized. Therefore, none of the aerosol and rain samples was omitted (see lines 208-209 and 221-222).*

Q10: Sources attribution (PMF). Using only IC data, source attribution of WSON is highly subjective. No ancillary data such as metals or OC/EC, Nox are available? Why no $NH_4$ is founding agricultural factor? Given the compounds associated with this factor better assign it to soil re-suspension. Also factor A should better attributed to long-range transport (regional sources) due to the presence of $NH_4$ and $SO_4$. Similarly factor B with the presence mainly of $NO_3$ could be better attributed to anthropogenic sources (combustion) Line 487, better replace water-soluble nitrogen by WSTN.

*A10: I agree that usage of ancillary data such metals and OC/EC during PMF would yield better results. Unfortunately there was no ancillary data such as metals, OC/EC and NOx. However, factor 1, 2, 3 and 4 were comparable to those obtained for Erdemli by using water-soluble ions and metals (Koçak et al., 2009). Factors 1, 2 and 5 were respectively attributed to ammonium-bisulfate (regional), nitrate (combustion) and soil re-suspension as suggested. Small amount of $NH_4$ (3.7 %) was associated with factor 5. As stated in section 3.1, 96 % of the $NH_4$ was originated from fine mode. Moreover, considering the first 20 % of the highest loadings in factor 5 (re-suspension), there was strong relationship between WSON and $NH_4$ (r = 0.64). Thus, it sees that $NH_4$ was reasonably associated with re-suspension. . Water-soluble nitrogen was replaced by WSTN (see 515-518, 522-524 and Figure 6).*

**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 $23.8 \pm 16.3$ 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 ==meteorology== 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 ($38.2\pm17.5$ nmol N m$^{-3}$) was 1.3 times higher than that of non-dust events ($29.4\pm13.9$ 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.

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

**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, 1905 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; Glibert 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, livestock and animal husbandry), cooking, high temperature fossil fuel combustion, vehicle exhaust, man-made biomass burning and industrial activities. In contrast natural sources of WSON include mineral dust, bacteria, algal blooms, degraded proteins, 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; Cape et al., 2011; 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, some 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 (Timperley et al., 1985; Peierls 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 3 and 5 fold, respectively, leading to a significantly modified global nitrogen cycle (Jickells et al., 2017). This in term has impacted upon the marine nitrogen biogeochemical cycling (Galloway et al., 2002, 2008; Duce et al., 2008; Jickells et al., 2017).

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). Generally, the primary productivity in the Eastern Mediterranean is phosphorous limited (Krom et al., 1991; Krom et al., 2010; Powley et al., 2017). Depending on season, the limitation by nitrogen or co-limitation by nitrogen and phosphorus in the Eastern Mediterranean have been reported (Yücel, 2013; Yücel, 2017 and references therein). Based on molar N/P ratios in the atmospheric input (order of magnitude higher than that of Redfield, Markaki et al., 2003, 2010 ; Koçak et al., 2010) and riverine fluxes (at least 1.8 times larger than that of Redfield,

Ludwig et al., 2009; Koçak et al., 2010) it has been suggested that the Eastern Mediterranean receives excessive amounts of dissolved inorganic nitrogen and this unbalanced inputs may result in even more phosphorus deficiency (Ludwig et al., 2009; Koçak et al., 2010) whilst the atmospheric deposition of reactive nitrogen may cause accumulation of nitrogen in water column (Jickells et al., 2017). Very little research has focused on the importance of water-soluble organic nitrogen inputs to marine productivity in the Eastern Mediterranean (Mace et al., 2003a; 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 $\sim$ 22 m, $\sim$ 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

4

108 fertilizer), the city of Mersin with a population of around 800.000 is located 45 km to the east

109 of the sampling site (Kubilay and Saydam, 1995; Koçak et al., 2012) and hence aerosol and

110 rainwater samples may have been influenced by aforementioned regional anthropogenic

111 activities when air mass transported from the east.

112

113 **2.2. Sample Collection and Preparation**

114 *Aerosol:* A Gent type stacked filter unit (SFU) was used to collect aerosol samples in two size

115 fraction (coarse: d = 10-2.5 μm and fine: d < 2.5 μm) (for more details see Hopke et al., 1997;

116 Koçak et al., 2007). Briefly, the first section of the filter holder was loaded with an 8 μm pore

117 size polycarbonate filter (Whatman Track Etched 111114, circle diameter: 47 mm), whilst the

118 second section was loaded with a 0.4 μm pore size polycarbonate filter (Whatman Track

119 Etched 111107, circle diameter: 47 mm). The cassette unit was then placed into the

120 cylindrical cassette holder, which is designed to prevent the intrusion of particles larger than

121 10 μm when the sampler is operated at a flow rate of 16.0-16.5 L/min. Daily (24 hours)

122 temporal sample resolution was carried out. Operational blank filters were processed in the

123 same way as the collected samples with the exception that no air was passed through the

124 filters. In order to minimize any possible contamination, the filter loading and unloading were

125 achieved in a laminar airflow cabinet.

126 The aerosol sampling campaign commenced in March 2014 and ended in April 2015.

127 During the sampling period, a total of 674 aerosol samples in two size fractions (coarse = 337;

128 fine = 337) were obtained. The observational coverage of the aerosol sampling period was 80

129 %. The observational coverage for winter, spring, summer and fall was respectively 60 %, 92

130 %, 81 % and 79 %. The seasonal observational coverage, after applying a precision value of

131 0.3 (for more details see section 2.4 and Eq.4), was found to be comparable for winter (49 %),

132 spring (53 %), summer (51 %) and fall (52 %). The sampling was terminated from time to

time due to technical malfunction of the SFU and/or cleaning procedure of the 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). Operational blanks for rain samples were taken by using 100 mL of Milli-Q water after cleaning the HDPE buckets with phosphate free detergent, HCl (10 %) and Milli-Q water (3 times).

*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 $^{o}$C) 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.

The standards were prepared from $KNO_3$ of high purity (> 99 %, Merck Extra Pure, CC551961). In order to evaluate accuracy of the WTSN measurements, nitrate, ammonium, urea and mixture of these species were detected by Torch Teledyne Tekmar instrument. Recovery for these substances was better than 92 %. In addition, the accuracy of the total nitrogen determination by the instrument was verified against intercalibration samples of QUASIMEME Program (Quality Assurance of Information for Marine Environmental Monitoring in European Laboratory Performance Studies). Correspondingly, recoveries for QNU277SW (IMS-METU = 4.67 μM, Mean = 5.17 μM), QNU278SW (IMS-METU = 10.41 μM, Mean = 11.30 μM) and QNU279SW (IMS-METU = 4.67 μM, Mean = 5.17 μM) 90 %, 92 % and 83 %. Blank values of WSTN for aerosol and rain samples were less than the limit of detection (3.6 nmol).

182   *Water soluble Inorganic and Ancillary Species:* In addition to $NO_3^-$ and $NH_4^+$, major water-

183   soluble ions concentrations were measured by using a Dionex ICS-5000 Ion Chromatography

184   instrument. Water-soluble anions ($Cl^-$, $SO_4^{2-}$, $NO_3^-$) were determined by applying AS11-HC

185   separation column, KOH (30 mM) eluent and AERS-500 (4 mm) suppressor whilst water-

186   soluble cations ($Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$) were detected electrochemically by using a CS12-A

187   separation column, MSA (20 mM) eluent and CSRS-300 (4 mm) suppressor (Product Manual

188   for Dionex IonPac AS11-HC-4m, IonPac CS12A Manual). ==The blank contributions for all==

189   ==water-soluble ions in aerosol samples were found to be less than 10 % and concentrations==

190   ==were corrected for blanks.==

191

## 2.4. Calculations

193       WSON concentrations (see Eq. 1) were determined from the difference between the

194   individual concentrations of WSTN and water-soluble inorganic nitrogen (WSIN) (see Eq. 2)

195   since there is no direct analytical method to detect the concentration of water-soluble organic

196   nitrogen. The precision for WSON was calculated via using the formula (see Eq. 3) suggested

197   by Hansell (1993). The precision (75 nmol N $m^{-3}$) was found to be almost three times higher

198   (see Eq. 4, R ~ 0.3) than that of the arithmetic mean of WSON in aerosols whilst it (90 µmol

199   N $L^{-1}$) was estimated to be approximately four times larger than that of volume weighted

200   mean of WSON in rain. Such high values are not unusual. For example, if the data presented

201   by Mace et al. (2003a) would be used, precisions would have been 5 and 8 times higher than

202   those of the concentrations of WSON in aerosol and rain, respectively. Table 1 shows the

203   number of negative WSON values and the positive WSON biases for coarse and fine modes.

204   Correspondingly, about 5 (n=18) and 15 % (n=52) of the values were negative in coarse and

205   fine particles. The substitution with zero yielded 2 and 14 % positive bias for coarse and fine

206   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 (see Table 1) whilst the values presented in Table 1 will be used for calculating dry and wet deposition. It has been stated that the uncertainty in WSON concentrations results from the additions of errors such as oxidation efficiency of method, sampling material, storage of samples and usage of preservative (Cape et al., 2011). These authors have particularly pointed out that low precision for samples with low concentrations of WSON and high levels of WSIN (see Eq. 2). Although, the calculation of precision for WSON is very difficult owing to aforementioned errors, Hansell (1993) has proposed estimation of precision for WSON exclusively relaying on measured WSTN and WSIN concentrations. Consequently, 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. A total of 216 aerosol samples were found to be higher than the value of 0.3.

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

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

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

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

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

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

9

231    The wet and dry atmospheric fluxes of nitrogen species were calculated according to

232    the procedure explained in Herut et al. (1999, 2002). The wet atmospheric deposition fluxes

233    ($F_w$) were calculated from the annual precipitation ($P_{annual}$) and the volume weighted mean

234    concentration ($C_w$) of the substance of interest.

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

236    The dry deposition ($F_d$) is calculated as the product of the atmospheric mean nutrient

237    concentrations ($C_d$) and their settling velocities ($V_d$), where $F_d$ is given in units of $\mu$mol m$^{-2}$

238    yr$^{-1}$, $C_d$ in units of $\mu$mol m$^{-3}$ and $V_d$ in units of m yr$^{-1}$.

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

240    The settling velocities ($V_d$, see Eq. 8) for each water-soluble nitrogen species were

241    calculated by using an approach adopted by Spokes et al. (2001). $C_c$ and $C_f$ refer to as the

242    relative contribution of coarse and fine modes and 2.0 and 0.1 cm s$^{-1}$ are deposition velocities

243    proposed by Duce et al. (1991) for coarse and fine particles, respectively.

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

245

246    **2.5. Air Masses Back Trajectories and Airflow Classification**

247    Three day back trajectories of air masses at the four altitude (1000, 2000, 3000 and

248    4000 meter) levels arriving at Erdemli station were computed by using the HYSPLIT

249    Dispersion Model (HybridSingle Particle Lagrangian Integrated Trajectory; Draxler and

250    Rolph, 2003). Three day back trajectories reaching at the altitude of 1000 m were classified

251    into six sectors: (i) Middle East, (ii) North Africa, (iii) Turkey, (iv) Eastern Europe, (v)

252    Western Europe and (vi) Mediterranean Sea in order to assess the influence of airflow on

253    WSON concentration in PM$_{10}$ (for more details see Koçak et al., 2012).

254

255

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

The receptor modeling tool *Positive Matrix Factorization* (U.S. Environmental Protection Agency PMF version 5.0, hereinafter referred to as 'PMF') was utilized to identify the sources of WSON in $PM_{10}$ at Erdemli. PMF has been proven to be a robust tool in characterizing the sources of aerosol (Paatero and Tapper, 1994; Huang et al., 1999; Lee et al., 1999; Viana et al., 2008; Koçak et al., 2009, for more details see Appendix A). EPA PMF 5.0 software mainly consists of Model Run and Rotational tools (see EPA/600/R-14/108; USEPA, 2014). Before application of the software, the user must supply two input files namely, concentration and uncertainly. The former contains concentrations of the aerosol species whilst the latter has corresponding uncertainty for each variable. Uncertainty was set to 5 % for each species with the exception of WSON (15 %) since WSON exclusively donated high uncertainty (for more details see Appendix A). The base run of PMF was achieved by setting the number of runs and random starting points (in other word seeds) to 250 and 50, respectively. Base Model Displacement (DISP), Bootstrap (BS) and Bootstrap 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-shape plots of Fpeak solutions were examined to determine convergence toward the axis or lower/zero contribution. Thus, Fpeak value 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

280     estimated WSON against measured WSON was 10 % less than unity with correlation

281     coefficient and intercept of 0.87 and 1.5 (nmol N m$^{-3}$), respectively.

282

**3. Results and Discussion**

**3.1. General Characteristics of the Data**

285     In this section the general characteristics of the Water-Soluble Organic Nitrogen

286     (WSON), Nitrate (NO$_3^-$), Ammonium (NH$_4^+$) and Water-Soluble Total Nitrogen (WSTN) in

287     aerosol and rain will be discussed.

288

289     *Aerosol:* The statistical summary for WSON, NO$_3^-$, NH$_4^+$ and WSTN in PM$_{10}$ aerosol

290     samples obtained from Erdemli between March 2014 and April 2015 is presented in Table 2.

291     Median values for WSON, NO$_3^-$, NH$_4^+$ and WSTN were respectively 10 %, 20 %, 40 % and

292     10 % lower than those of arithmetic means. Among the nitrogen species, WSON exhibited

293     the highest arithmetic mean, followed by ammonium and nitrate concentrations respectively.

294     The maximum concentration of WSON was estimated to be 79 nmol N m$^{-3}$ with a mean value

295     and standard deviation of 23.8 ± 16.3 nmol N m$^{-3}$. The observed arithmetic was comparable to

296     those reported by Mace et al. (2003a) for the same site. Approximately 66 % of the WSON

297     was associated with coarse particles, the remaining fraction (34 %) was present within the fine

298     mode. A number of studies have reported the relative size distribution of WSON for the

299     Eastern Mediterranean marine aerosol  (Finokalia, Violaki and Mihalopoulos, 2010) and those

300     observed at remote marine sites (Hawaii, Cornell et al., 2001; Tasmania, Mace et al., 2003b).

301     The aerosol WSON at Finokalia (68 %) and Hawaii were primarily found in the fine mode

302     whilst WSON in the south Pacific marine aerosol (Tasmania) was mainly associated with the

303     coarse fraction. It is likely that the WSON at Erdemli (a) is relatively less impacted by

304 anthropogenic sources and/or (b) is more influenced by mineral dust transport and re-

305 suspension of cultivated soil compared to that observed at Finokalia.

306       $NO_3^-$ and $NH_4^+$ aerosol concentrations ranged between 0.2-88.4and 0.5-164.4 nmol N

307 $m^{-3}$ with mean values (standard deviations) of 17.9 ($\pm$15.7) and 23.3 ($\pm$24.4) nmol N $m^{-3}$. As

308 expected, $NO_3^-$ was mainly associated with coarse particles, accounting for 87 % of the

309 observed mean value while $NH_4^+$ was dominant in the by fine mode, contributing 96 % to the

310 detected mean concentration. Similar results have been reported for Eastern Mediterranean

311 marine aerosol (Bardouki et al, 2003; Koçak et al., 2007). The predominance of $NO_3^-$ in the

312 coarse mode might be due to gaseous nitric acid or other nitrogen oxides reacting with

313 alkaline sea salts and mineral dust particles. In contrast, the occurrence of $NH_4^+$ in the fine

314 fraction is mainly as a result of the reaction between gaseous alkaline ammonia and acidic

315 sulfuric acid (Mihalopoulos et al., 2007).

316       WSTN concentrations in aerosols varied between 9.7 and 176.5 nmol N $m^{-3}$ with an

317 arithmetic mean value of 63.5$\pm$ 32.0 nmol N $m^{-3}$, respectively. The mean WSTN

318 concentration being almost equally influenced by coarse (51 %) and fine particles (49 %).

319 Table 2 demonstrates the relative contributions of WSON, $NO_3^-$ and $NH_4^+$ to the WSTN in

320 $PM_{10}$. As can be deduced from the table, the WSTN concentration was equally influenced by

321 WSON and $NH_4^+$, each species contributing 37% and 35 %, respectively. In contrast the

322 contribution of $NO_3^-$ to WSTN was found to be 28 %.

323

324 ***Rain:*** Volume-weighted-mean (VWM) concentrations of WSON, $NO_3^-$, $NH_4^+$ and WSTN in

325 rainwater are presented in Table 2, along with the minimum and maximum concentrations as

326 well as the relative contributions of WSON, $NO_3^-$ and $NH_4^+$ to WSTN. As can be deduced

327 from table, VWM concentrations of each species were comparable, $NH_4^+$ exhibited the highest

328 concentration with a value of 28.7 $\mu$mol N $L^{-1}$. The VWM concentration of WSON and $NO_3^-$

329    were 21.5 and 23.3 µmol N L$^{-1}$, respectively. Considering their relative contributions to

330    WSTN, WSON and NO$_3^-$ account 29 and 32 % of the WSTN whilst NH$_4^+$ represented 39 %

331    of the observed WSTN concentration in rainwater.

332

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

334    The concentrations of WSON in marine aerosols and rain samples collected from

335    different sites located around the Mediterranean, Atlantic and Pacific regions are illustrated in

336    Table 3. Comparing the current WSON values with those reported in the literature is

337    challenging due to (i) different applied sampling periods, sampling and measurement

338    techniques and (ii) the high uncertainty associated with the estimation of WSON Furthermore,

339    within the literature there is a lack of information defining the uncertainty of WSON though

340    there is a substantial statistical knowledge. Keene at al. (2002) in particular, have highlighted

341    the tendency in the literature to neglect negative values or substitute such values with zero

342    instead when calculating the WSON from the difference between WSTN and WSIN. As these

343    authors have highlighted the omission or substitution of such values inevitably would result in

344    a positive bias in the WSON concentrations.

345    In general, the lowest concentrations in aerosols were found in those derived from

346    remote or pristine marine environments. The WSON concentrations in the atmosphere over

347    the Indian (Amsterdam Island: 1.0 nmol N m$^{-3}$, Violaki et al., 2015), Atlantic (Barbados: 1.3

348    nmol N m$^{-3}$, Zamora et al., 2011) and Pacific Ocean (Hawaii, Oahu: 4.1 nmol N m$^{-3}$, Cornell

349    et al., 2001, Tasmania: 5.3 nmol N m$^{-3}$, Mace et al., 2003b) were at least 4 times less than

350    those observed for Eastern Mediterranean (Erdemli: 23.8 nmol N m$^{-3}$, this study; Finokalia:

351    17.1 nmol N m$^{-3}$, Violaki and Mihalopoulos, 2010). These lower values might be attributed to

352    (i) the absence of the strong anthropogenic sources in the vicinity of the sampling sites, (ii)

353    the dilution of the WSON originating from long range transport via both dry and wet

354 deposition and/or (iii) small contributions from non-land based local emissions such as sea

355 salt and algal blooms. The highest WSON concentrations emerged particularly over China

356 (Ho et al., 2015) concentration of WSON measured in $PM_{2.5}$ and Taiwan (Chen et al., 2010)

357 with values above 70 nmol N m$^{-3}$. As stated in Chen et al. (2010) WSON concentrations at

358 these sampling sites were markedly influenced by anthropogenic activities such as fossil fuel

359 combustion and man induced biomass burning. Concentrations over the Amazon (Mace et al.,

360 2003c) in the dry season (61 nmol N m$^{-3}$) have also been noted. Such high values were

361 ascribed to natural fires (Mace et al., 2003c). The mean WSON concentration at Erdemli

362 (23.8 nmol N m$^{-3}$) was comparable to that reported previously for the same site (29 nmol N m$^{-3}$

363 , Mace et al., 2003a). In contrast, the present WSON concentration was almost 1.5 times

364 higher than that observed at Finokalia (Violaki and Mihalopoulos, 2010).

365      The reported WSON values for rain also exhibited the lowest concentrations in those

366 derived from remote or pristine marine environments, such as Hawaii (2.8 μmol N L$^{-1}$,

367 Cornell et al., 2001). The highest WSON concentrations were observed in China (North China

368 Plain: 103 μmol N L$^{-1}$, Zhang et al., 2008) and Norwich, UK (33 μmol N L$^{-1}$, Cornell et al.,

369 1998), respectively. These high values were again attributed to the anthropogenic sources.

370

371 **3.3. Temporal Variability of Water-Soluble Nitrogen Species in Aerosol Erdemli**

372      Fig.1 illustrates daily variation of the water-soluble nitrogen species in aerosol

373 samples together with the daily rainfall from March 2014 to April 2015. The same figure also

374 presents the concentrations in rainwater samples collected between October 2014 and April

375 2015. It is clear that WSON concentrations exhibited large variations from one day to another

376 day. The daily variability in the concentration of WSON may be an order of magnitude. Such

377 variability has also been reported in the Atlantic (Zamora et al., 2011), Pacific (Chen et al.,

378 2010) and Eastern Mediterranean marine aerosols (Violaki and Mihalopoulos, 2010). These

379  studies demonstrated that the daily change in the concentrations of WSON arises from a

380  combination of (a) meteorological parameters (such as rain, temperature and wind

381  speed/direction), (b) chemical reactions, (c) history of air masses back trajectories and (d)

382  source emission strength.

383      In general, lower concentrations of WSON were found to be associated with rainy

384  days. To serve as an illustration, one of the lowest WSON concentrations was observed on

385  19th of October 2014, after two consecutive days of rainfall, with a value of 6 nmol N m$^{-3}$. In

386  contrast, one of the highest observed WSON concentrations (66.1 nmol N m$^{-3}$) was detected

387  on 2nd of March 2014 when the air mass back trajectories were associated with south/south

388  westerly airflow (for more details see section 3.4). Another high concentration of WSON was

389  observed on 5th of July 2014, with a value of 66 nmol N m$^{-3}$.  94% of the WSON was present

390  in the coarse mode, however, during this event there was no intense dust intrusion either from

391  the Sahara or from the Middle Eastern deserts. Corresponding OMI-AI index and nssCa$^{2+}$ (33

392  nmol m$^{-3}$) also supports this observation (see Fig.2). Lower layer air mass back trajectories

393  (1000 and 2000 m) demonstrated that Erdemli was under the influence of north/north westerly

394  airflow from Turkey after passing over Turkey's largest cultivated plain, Konya. Thus, this

395  high value might be attributed to re-suspension of the soil affected by intense agricultural

396  activities. On 20th of January 2015 the WSON concentration was 60 nmol N m$^{-3}$, 72 % being

397  present in the fine mode. For this event, the NH$_4^+$ concentration was 20 nmol N m$^{-3}$, two

398  times higher than the observed arithmetic mean in winter. Corresponding trajectories, AOD

399  (Aerosol Optical Depth) and AC (Angstrom Component) images are presented in Fig.3.

400  Airflow at 1 km showed air mass flow arriving at the sampling site from Turkey. AOD values

401  over the sampling site and coastline of Northeastern Mediterranean ranged from 0.2 to 0.5

402  whilst AC values demonstrated that the region was dominated by fine particles. Based on

403  above indicators, it may be concluded that anthropogenic sources were dominant.

404    A summary of the statistical analyses of the seasonal dataset of aerosol associated

405    WSON, $NO_3^-$ and $NH_4^+$ are shown in Table 4. The Mann-Whitney U test indicated that there

406    was a statistically significant difference among seasons, such that Summer > Spring ≈ Winter

407    > Fall. The arithmetic mean value of WSON in the summer was found to be 1.3 and 2.0 times

408    greater those observed for Spring/Winter and Fall, respectively. Percent WSON contributions

409    of coarse mode for winter (50 %), spring (50 %) and fall (55 %) were comparable. However,

410    WSON was chiefly associated with coarse particles in summer, amounting to 83 %. This high

411    value in summer might be due to the absence of rainfall (see Fig.1) and enhanced re-

412    suspension of cultivated soil in the region. In summer, the mean concentration of $NH_4^+$ was

413    almost 2.4 times larger than all other seasons. The mean water-soluble $NO_3^-$ in summer was

414    1.4 higher than that of spring. High $NH_4^+$ and $NO_3^-$ concentrations in summer might be

415    attributed again to the absence of rainfall and increase in incoming radiation. Similar results

416    have been reported for the Eastern Mediterranean (Bardouki et al., 2003).

417

418    **3.4. Influence of Mineral Dust Episodes on WSON aerosol concentrations**

419    As it is well documented, the Eastern Mediterranean Sea is heavily impacted by

420    mineral dust episodes originating from Sahara and the Middle East deserts (Kubilay and

421    Saydam, 1995; Kubilay et al., 2000, Koçak et al., 2004a, b and 2012).

422    For the current study between March 2014 and April 2015, water-soluble non-sea salt

423    calcium concentrations higher than 50 nmol m$^{-3}$ (2000 ng m$^{-3}$, as a threshold value) were

424    defined as mineral "dust events". These events were additionally confirmed using air mass

425    back trajectories and OMI-AI. However, it is worth mentioning that for samples containing

426    concentrations of nssCa$^{2+}$ less than 50 nmol m$^{-3}$, mineral dust transport from Sahara and the

427    Middle East deserts to sampling site may not be excluded, peculiarly in winter. Yet, the

428   application of such an arbitrary value is inevitable since it provides simplicity to explore if

429   there is any influence of mineral dust intrusion on WSON.

430   For example, one of the highest WSON concentrations (66.1 nmol N m$^{-3}$) was

431   observed on 2$^{nd}$ of March 2014 when the air mass back trajectories was associated with

432   south/south westerly airflow. During this event, nssCa$^{2+}$ and NO$_3^-$ showed a dramatic increase

433   in their concentrations compared to those observed during the previous day, reaching up to

434   429 and 60 nmol m$^{-3}$, respectively.  OMI (Ozone Mapping Instrument) Aerosol Index (AI)

435   and three-day backward trajectory (1, 2, 3 and 4 km altitudes) air masses arriving at the

436   Erdemli sampling site on 2$^{nd}$ of March 2014 is shown in Fig.4. As can be seen from the figure,

437   all air masses (except at 1 km altitude) originated from North Africa whereas the back

438   trajectory for 1 km altitude exhibited airflow from the Middle East. Hence, suggesting that the

439   sampling site was under the influence of mineral dust transport originating from desert

440   regions located at the Middle East and North Africa. In support, the OMI-AI diagram clearly

441   indicates a large dust plume over the Eastern Mediterranean between coordinates 20-45 ˚N

442   and 15-40 ˚E. The Aerosol Index was found to be very high over the Northeastern

443   Mediterranean, ranging from 2.0 to 4.5.  During this dust episode, 85% of the WSON was

444   associated with the coarse fraction, which further supports mineral dust being a main source

445   of water-soluble organic nitrogen.

446   Arithmetic mean concentrations together with corresponding standard deviations of

447   WSON, NO$_3^-$, NH$_4^+$ and nssCa$^{2+}$ for dust and non-dust events are presented in Fig.5. As can

448   be deduced from diagram (except for NH$_4^+$), WSON, NO$_3^-$ and nssCa$^{2+}$ indicated distinct

449   difference between dust and non-dust events. Indeed, the application of the non-parametric

450   Mann Whitney U test indicated statistically significant differences between dust and non-dust

451   events for WSON (p <0.03), NO$_3^-$ (p < 0.00002) and nssCa$^{2+}$ (p < 0.000001) whereas no

452   statistically significant difference were observed for NH$_4^+$,(p=0.56). The crustally derived

453  nssCa$^{2+}$ and anthropically derived NO$_3^-$ for dust events had arithmetic mean of 95.8 nmol m$^{-3}$

454  and 26.1 nmol N m$^{-3}$ which were almost four and two times higher than those of observed for

455  non-dust events, respectively. Such an increase in concentrations during dust events for these

456  species has been previously reported in the Eastern Mediterranean (Koçak et al., 2004b).

457  Similarly, the arithmetic mean of WSON (38.2 nmol m$^{-3}$) during dust events was 1.3 times

458  higher compared to the value observed during non-dust events (29.4 nmol m$^{-3}$). Percent

459  contributions of coarse WSON for dust and non-dust events were almost identical, being 58 %

460  and 60 %, respectively.  A similar enrichment of WSON during dust events has been reported

461  for Erdemli (Mace et al., 2003a; Yellow Sea (Shi et al., 210) and Finokalia (Violaki and

462  Mihalopoulos, 2010). In addition, Griffin et al. (2007) have demonstrated a significant

463  difference between dust and non-dust events for bacterial and fungal colony forming units at

464  Erdemli, the former being much greater. Thus, it might be speculated that this enhancement

465  during dust events can be due to (a) mineral dust borne microorganisms, (b) interaction (e.g.

466  adsorption, acid-base reaction) and/or between mineral dust and organic nitrogen compounds.

467

468

469  **3.5. Impact of Airflow on WSON**

470  Arithmetic mean concentrations together with corresponding standard deviations for

471  water-soluble nitrogen species and nssCa$^{2+}$ in aerosol samples according to categorized air

472  mass sectors (at 1 km) are presented in Table 5. WSON concentrations for Middle East, North

473  Africa and Turkey were comparable and arithmetic mean values were respectively 33, 36 and

474  32 nmol m$^{-3}$. Correspondingly, mean WSON concentrations for Eastern Europe, Western

475  Europe and Mediterranean Sea were 26, 26 and 22 nmol m$^{-3}$, being at least 1.2 times lower

476  than those observed for Middle East, North Africa and Turkey (Mann-Whitney U test, p <

477  0.05). Coarse mode contributions of WSON for air flow from Middle East (61 %), North

478    Africa (58 %) and Turkey (63 %) ranged from 58 to 63 %. However, lower coarse mode

479    contributions were observed when air flow originated from Eastern Europe (49 %), Western

480    Europe (48 %) and Mediterranean Sea (27 %). The highest $NO_3^-$ concentrations were

481    associated with airflow from North Africa and Turkey with a value of 18 and 15 nmol N m$^{-3}$,

482    respectively, and there was a statistically significant difference compared to the remaining air

483    mass sectors ($p > 0.05$). The mean concentrations of $NO_3^-$ for air masses derived from North

484    Africa and Turkey was at least 1.3 times larger than those calculated for the Middle East,

485    Eastern Europe, Western Europe and Mediterranean Sea air sectors ($p > 0.05$). $NH_4^+$ had the

486    highest concentration under the influence of airflow derived from Turkey. For this airflow,

487    detected concentration was 1.5-2.4 times greater than those calculated for other air masses

488    sectors. The Mann-Whitney test showed that there was a statistically significant difference in

489    the $nssCa^{2+}$ concentrations. Arithmetic mean concentrations of $nssCa^{2+}$ in the Middle East and

490    North Africa were approximately 2 times higher compared to the remaining air masses. As

491    expected, these two airflows were primarily influenced by crustal material due to sporadic

492    dust events originating from deserts located in North Africa and the Middle East.

493

494    **3.6. Source Apportionment for WSON in Aerosol**

495        A number of studies have discussed the possible sources of WSON in aerosol material

496    by applying either simple correlation analyses (Mace et al., 2003a; Violaki and Mihapoulos,

497    2010; Ho et al., 2015) or multivariate factor analyses (Chen and Chen, 2010), including PMF

498    (Chen et al., 2010). Usage of correlation analyses is useful when the number in sample-

499    populations are limited however; large datasets are required in order to carry out PMF and

500    FA. Direct and indirect emissions of WSON from the sea surface have been demonstrated

501    (Miyakazi et al., 2011; Altieri et al., 2016). Previous studies in the Eastern Mediterranean

502    have observed WSON to be associated with mineral dust (Mace et al., 2003a; Violaki and

503　Mihalopoulos, 2010). As stated by Mace et al. (2003a), WSON might either have originated

504　from mineral dust or carried by dust events owing to adsorption of gaseous organic nitrogen

505　compounds onto pre-existing particles. In addition, Violaki and Mihalapoulos (2010) have

506　shown fossil fuel and biomass burning as sources of WSON to the Eastern Mediterranean

507　atmosphere.

508　　　Fig.6 describes the potential sources of WSON by applying PMF 5.0. The

509　predominant two factors were chiefly found to be related with WSTN. The first factor had a

510　high-loading for $NH_4^+$ with a value of 0.81 and a moderate loading of $SO_4^{2-}$ (0.45). As

511　expected, the factor contribution plot (not shown) indicated summer maximum, demonstrating

512　accumulation of these particles due to the absence of rain and enhanced gas-to-particle

513　formation under the prevailing conditions (high temperature and solar radiation). The

514　equivalent ratio of $NH_4^+$ and $SO_4^{2-}$ for this factor was 0.79, indicating $(NH_4)HSO_4$ formation

515　(Koçak et al., 2007). 60 % of the air mass trajectories was found to be originated from Turkey

516　when the first highest 20 % of the factor loading were considered. Consequently, this factor

517　might principally be ascribed to regional sources such as urban agglomerations (Ankara,

518　İzmir, and İstanbul) and industrial activities (particularly Marmara Region). The second factor

519　explained 77 % of the $NO_3^-$ variation and described 17 and 10 % of the $SO_4^{2-}$ and $NH_4^+$,

520　variation, respectively. This group was also associated with cations such as $Na^+$ (11 %), $K^+$ (7

521　%), $Mg^{2+}$ (22 %) and $Ca^{2+}$ (29 %), implying reactions mainly between acidic nitrate and

522　alkaline species. It has been shown that emissions of $Cl^-$ and $NO_3^-$ resulting from motor

523　vehicles (Lim at al., 2010). Taking into account the absence of $Cl^-$, this factor may be

524　attributed to combustion. The first and second factors accounted for 20 and 22 % of the

525　variability in WSON, respectively. It might, therefore be argued that the variability of  WSON

526　in the first group resulted from the reaction between volatile organic N and ammonium sulfate

527　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 (n = 337; 21.3 mmol N $m^{-2}$ $yr^{-1}$) and wet (n = 23; 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 total nitrogen (57.8 mmol 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. The atmospheric deposition of the dissolved inorganic nitrogen (DIN = 37.3 mmol N $m^{-2}$ $yr^{-1}$) was found to decrease about 45 % compared to the value reported by Koçak et al. (2010, DIN = 70 mmol N $m^{-2}$ $yr^{-1}$). The reason of this decrease is out the scope of this article; nonetheless, there is a need to understand how DIN flux changed from the beginning of 2000s to 2015.

## 4. Summary

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.

577     3) Influence of mineral dust transport on aerosol WSON concentrations was assessed.

578     The crustally derived $nssCa^{2+}$ and anthropogenic $NO_3^-$ for dust events had arithmetic mean of

579     95.8 nmol $m^{-3}$ and 26.1 nmol N $m^{-3}$ which were almost four and two times higher than those

580     of observed for non-dust events. The arithmetic mean of WSON (38.2 nmol $m^{-3}$) for dust

581     events was 1.3 times higher compared to that observed for non-dust events (29.4 nmol $m^{-3}$).

582         4) Source apportionment suggested that aerosol WSON was mainly originated from

583     anthropogenic sources including agricultural (43 %), secondary aerosols (20 %) and nitrate

584     (22%), whereas, the two natural sources crustal material (10 %) and sea salts (5%) contributed

585     15 % to the WSON.

586         5) The total atmospheric deposition of water-soluble nitrogen (57.8 mmol N $m^{-2}$ $yr^{-1}$

587     ) was mainly via wet deposition (36.7 mmol N $m^{-2}$ $yr^{-1}$). In contrast the atmospheric fluxes of

588     WSON and $NO_3^-$ were equally influenced by the dry and wet deposition modes. On average,

589     WSON accounted for 36 % of the total atmospheric deposition of WSTN. From the beginning

590     of 2000s to 2015, the atmospheric deposition of the dissolved inorganic nitrogen declined

591     about 45 %, as a consequence there is a need to understand how DIN flux changed.

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**Appendix A**

In this section, the authors briefly summarize the main features of the positive matrix factorization (PMF).

PMF receptor model was described in detail by Paatero and Tapper (1994), Paatero (2007) and EPA PMF 5.0 User Guide. The details of the algorithm are also provided by Paatero (2007). This multivariate tool decomposes data matrix (X: n rows in other words number of samples and m columns: number of species) into two matrices: (i) source contributions $(G = n \ x \ p)$ and (ii) source profiles $(F = p \ x \ m)$. This can be given as follow

$$X = GF + E$$

where E and p denote the residual part and the number of factors extracted, respectively.

In order to run PMF, two input files are needed: (i) concentration and (ii) uncertainty. The first file includes concentrations whilst the second files contains uncertainty for each species. Uncertainty for PMF application can be calculated by different approaches such as ad hoc formula (Antilla et al., 1995), fixed fraction of the concentration (Paatero et al., 2014) or more complicated way as proposed by Polissar et al. (1998). No matter how it is calculated, if uncertainty is too high for one parameter, species will be categorized as bad by the PMF. For example, the precision of WSON for this study was found to be almost 3 times than that of arithmetic mean. If one uses the Eq.3 to calculate uncertainty of WSON for each data point, then it will be omitted by PMF owing to very high uncertainty values. Consequently, there will be no source apportionment for WSON. In order to obtain reasonable factor profiles for WSON, two step procedure was proposed. First, the usage of Eq.3 to eliminate WSON samples when their corresponding precisions are lower than mean R value of 0.3 (see Eq.4). Second, set the uncertainty to higher value for WSON (15 %) compared to the remaining species (5 %) since WSON inevitably exhibits very low precision (see Eq.1 and Eq.3).

626    After base run one has to estimate the quality of the obtained results from PMF (for

627    more details see EPA PMF 5.0 user guide and Paatero et al., 2014). Base Model Displacement

628    (DISP), Bootstrap (BS) and Bootstrap Displacement (BS-DISP) methods are the main tools to

629    assess quality. It has been exhibited that three methods complement each other (for more

630    details see Paatero et al., 2014). EFA PMF 5.0 provides aerosol data obtained from Baltimore

631    and guides the applicant step by step to robustly use the source apportionment program of

632    EPA PM 5.0. More details are given by EFA 5.0 user guide and it is accessible to the

633    scientific community.

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635    The authors declare that they have no conflict of interest.

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650    M. Koçak developed the concept and designed the study. M. Nehir and M. Koçak performed
651    the experiments, analyzed the data and prepared the manuscript.
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**Figure Captions**

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

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

**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 20$^{th}$ of January 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 dark red.

**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 2$^{nd}$ of March 2014 for Erdemli. Aerosol Index (AI) from OMI (Ozone Mapping Instrument) distribution also illustrated with a color bar from grey to dark red.

**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. Orange and blue 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.


**Table Captions**

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

**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.

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

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

**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

**Table 6.** Atmospheric dry (337 samples) and wet (23 samples) 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.

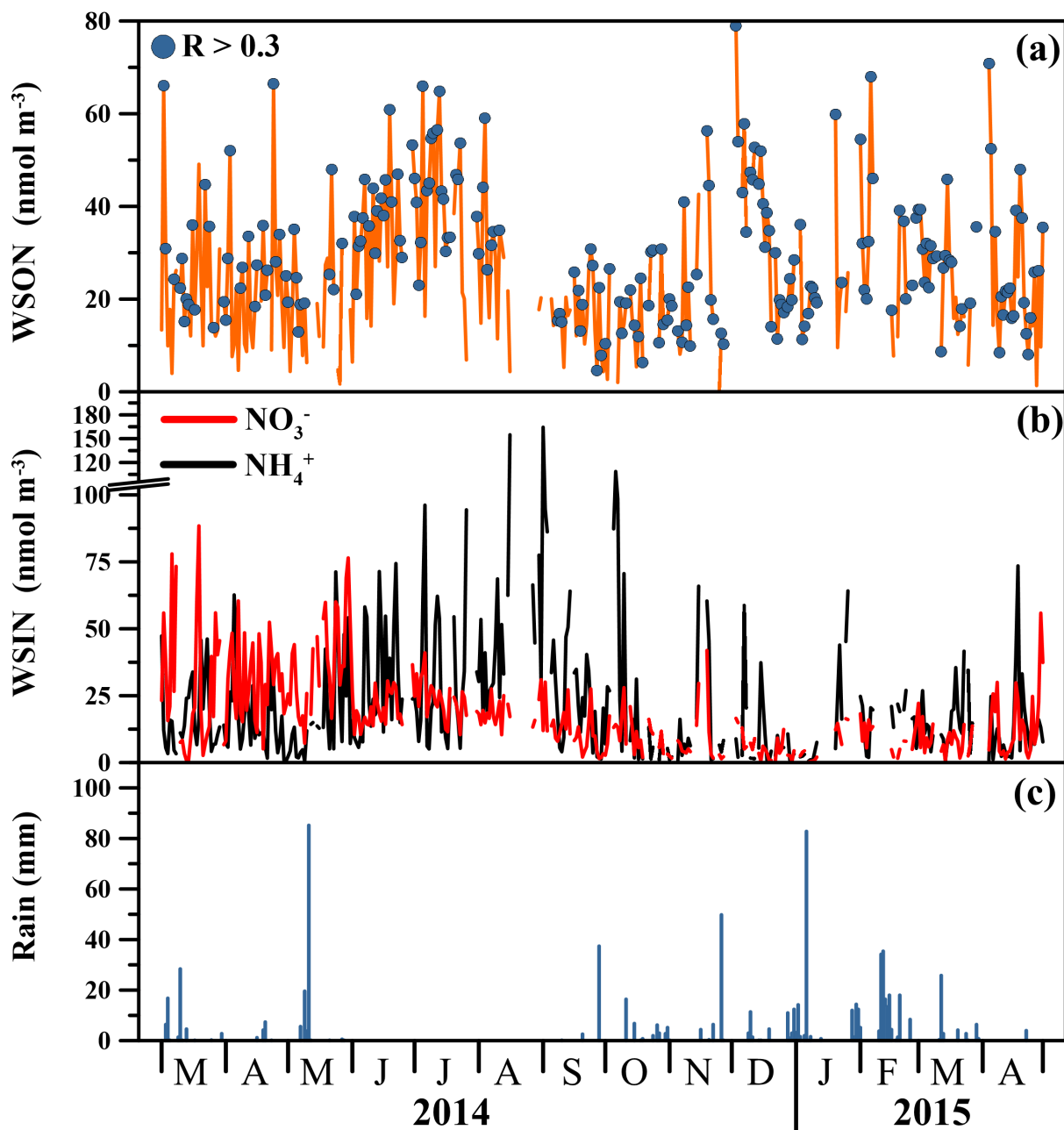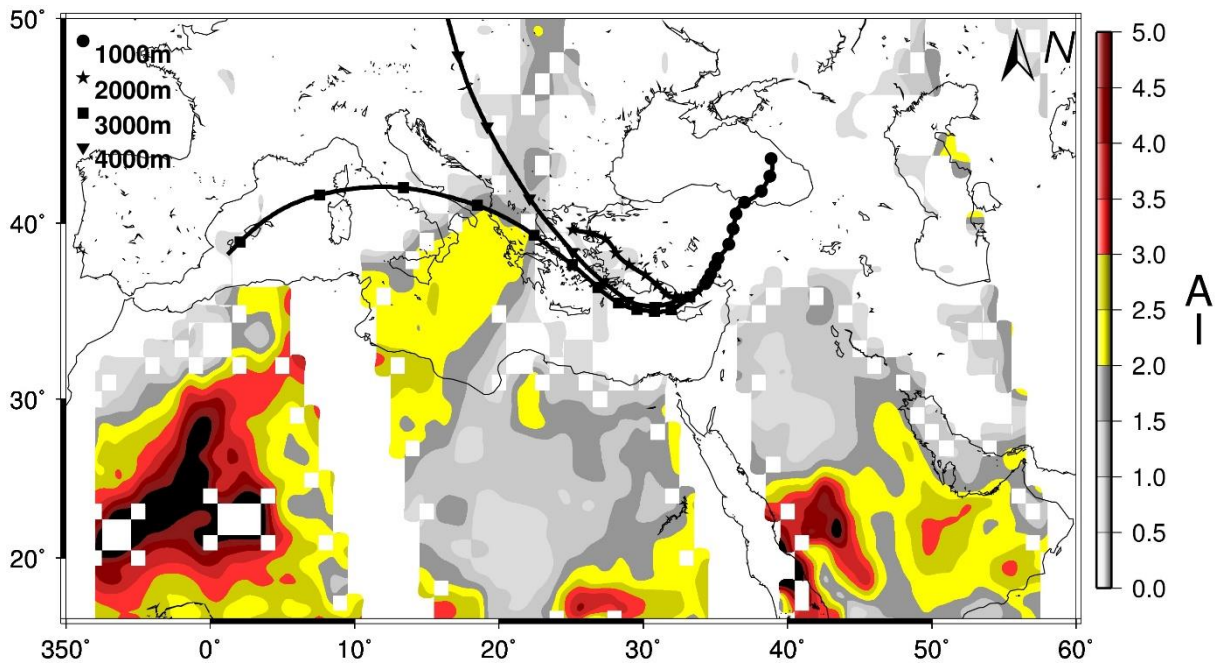**Figure 1.** The daily variations in the concentrations of (a) WSON, (b) $NO_3^-$ and (c) $NH_4^+$ (nmol N m$^{-3}$) together with rain amount (mm) from March 2014 and April 2015 for $PM_{10}$.
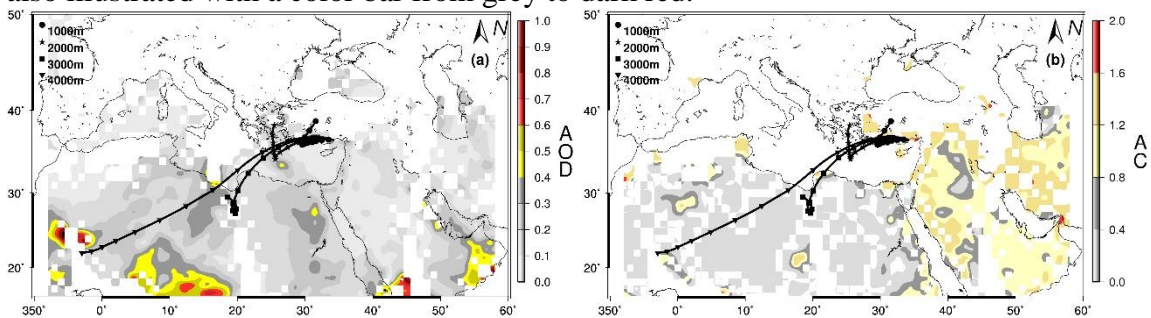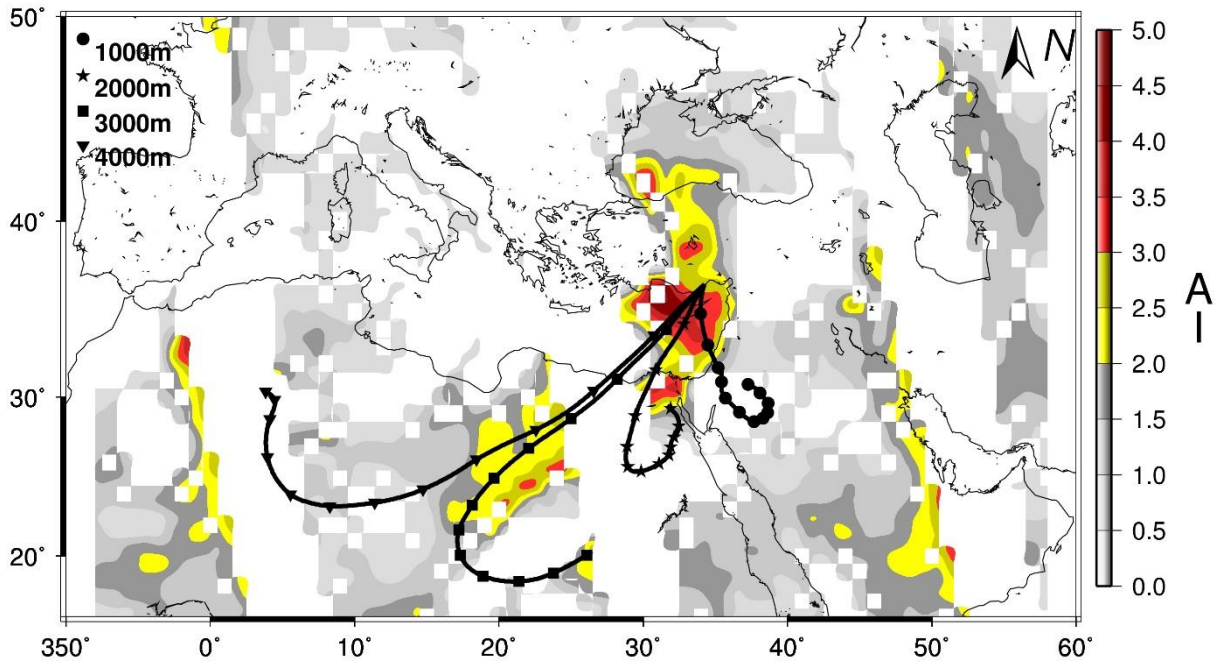
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**Figure 2.** Three day back trajectories showing the transport of air masses 1000m (black circle), 2000m (black star), 3000m (black square) and 4000m (black triangle) on 5$^{th}$ of July 2014 for Erdemli. Aerosol Index (AI) from OMI (Ozone Mapping Instrument) distribution also illustrated with a color bar from grey to dark red.



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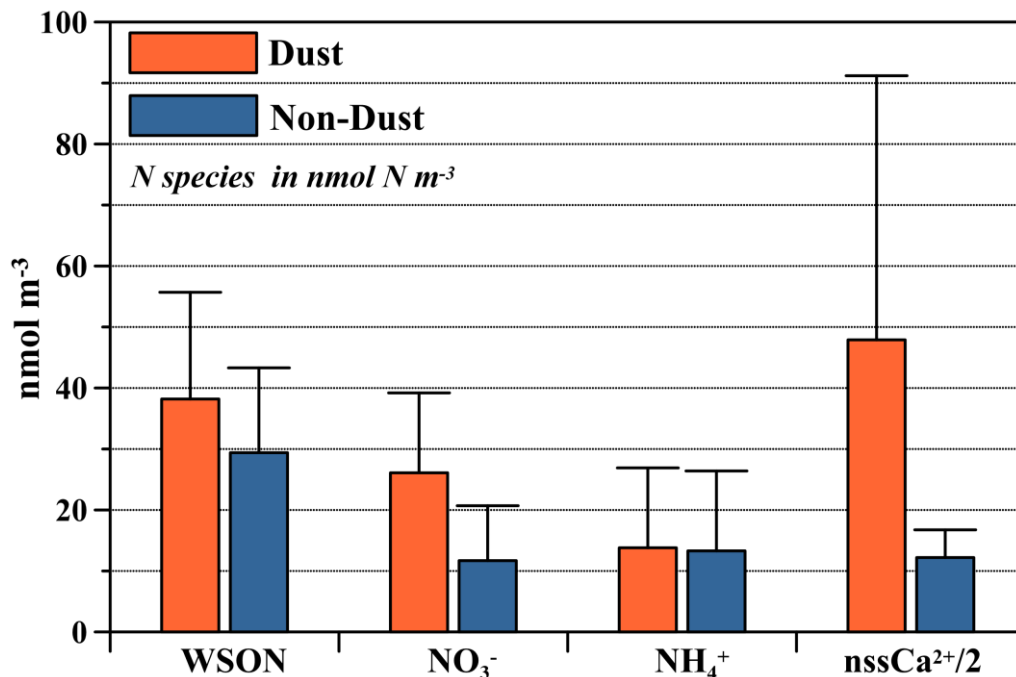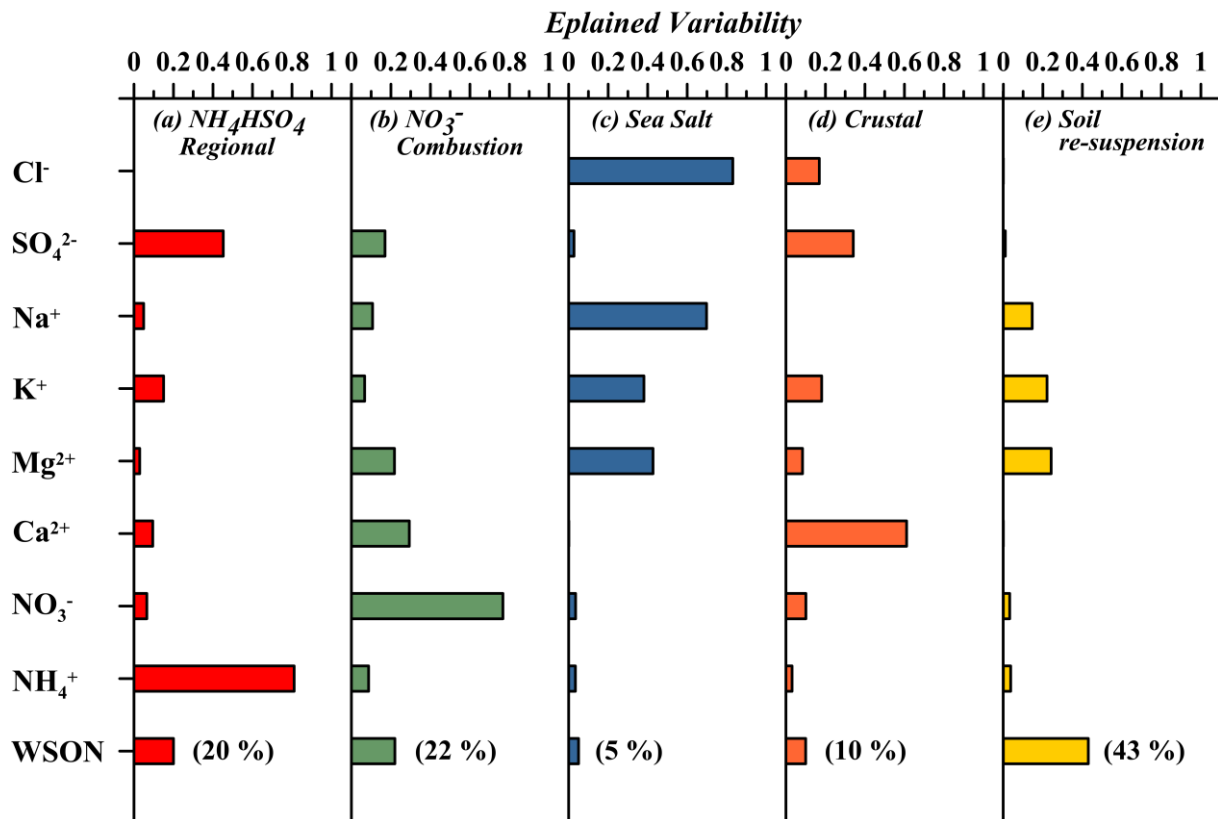
**Figure 3.** Three day back trajectories showing the transport of air masses 1000m (black circle), 2000m (black star), 3000m (black square) and 4000m (black triangle) on 20$^{th}$ of January 2015 for Erdemli. Aerosol Optical Depth (AOD, a) and Angstrom Component (AC, b) from MODIS (Moderate Resolution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

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**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 2$^{nd}$ of March 2014 for Erdemli. Aerosol Index (AI) from OMI (Ozone Mapping Instrument) distribution also illustrated with a color bar from grey to dark red.



**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. Orange and blue 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.

984

**Tables**

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**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 for arithmetic mean, respectively.*

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**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 $m^{-3}$) Number of samples: 337* | | | | |
|---|---|---|---|---|
|  | *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 |
| Median | 57.7 | 21.4 | 14.3 | 14.3 |
| 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 $m^{-3}$) Number of samples : 23* | | | | |
| 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

994

**Table 3.** Comparison of WSON concentrations in aerosol (nmol N m$^{-3}$) and rain (μmol N L$^{-1}$) 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] |

*RC, NS and SP refer to relative contribution of WSON to WSTN, number of samples and sampling period, respectively.*

**Table 4.** Seasonal statistical summary of the WSON, $NO_3^-$, $NH_4^+$, WSTN (nmol N $m^{-3}$) and nss$Ca^{2+}$ (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 |
| Coarse/$PM_{10}$ (%) | 50 | 50 | 83 | 55 |
| $NO_3^-$ | 7±5 | 15±12 | 21±7 | 9±8 |
| $NH_4^+$ | 10±12 | 11±9 | 24±16 | 10±13 |
| nss$Ca^{2+}$ | 28±13 | 28±13 | 28±13 | 41±11 |
| Number of Samples | 47 | 79 | 46 | 44 |
| Meteorology Parameter | Winter | Spring | Summer | Fall |
| T ($^o$C) | 11±3 | 16±3 | 27±12 | 20±15 |
| Rain (mm) | 78 | 118 | 0.5 | 132 |
| Number of Rain Events | 16 | 16 | 2 | 15 |

**Table 5.** Arithmetic means along with standard deviations of WSON, $NO_3^-$, $NH_4^+$ (nmol N $m^{-3}$) and nss$Ca^{2+}$ (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 | Coarse/$PM_{10}$ (%) | $NO_3^-$ | $NH_4^+$ | nss$Ca^{2+}$ |
|---|---|---|---|---|---|
| Middle East | 33±12 | 61 | 12±12 | 13±15 | 48±71 |
| North Africa | 36±16 | 58 | 18±11 | 12±14 | 46±38 |
| Turkey | 32±13 | 63 | 15±10 | 19±15 | 23±9 |
| Eastern Europe | 26±14 | 49 | 10±9 | 10±8 | 21±9 |
| Western Europe | 26±14 | 48 | 10±8 | 11±9 | 20±7 |
| Mediterranean Sea | 22±10 | 27 | 10±8 | 8±6 | 19±8 |

**Table 6.** Atmospheric dry (337 samples) and wet (23 samples) 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 | |