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PROOF

Solubility of Atmospheric Nutrients over the Eastern Mediterranean: Comparison between Pure-Water and Sea-Water, Implications Regarding Marine Production

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Abstract

Aerosol filter samples were selected from sample library of Erdemli site; located on the coastline of the Eastern Mediterranean, in order to carry out solubility experiments. The nutrient (PO_4^{3-}, Si_{diss}, NO_3^- and NH_4^+) solubilities were investigated by using pure-water and sea-water. The arithmetic means of phosphate and dissolved silica indicated distinct difference (larger than 50 %) between pure-water and sea-water whereas; the calculated mean concentrations of nitrate and ammonium did not reveal substantial discrepancy for pure-water and sea-water extractions. The difference for phosphate and silicate might be attributed to pH and ionic strength of sea water, size distribution and association of phosphate/silicate particles with less soluble compounds such as calcium phosphate, kaolinite, opal, quartz and origin of the aerosol species. The difference between pure-water and sea-water extractions for nitrate and ammonium was estimated to be small, corresponding to 1 % to -3 %. This similarity can be ascribed to highly soluble chemical forms such as NH_4NO_3, $Ca(NO_3)_2$, $NaNO_3$ $(NH_4)_2SO_4$ and NH_4HSO_4. Calculations revealed that atmospheric P flux would sustain 0.4 % and 0.9 % of the primary production reported for coastal and offshore waters of Cilician Basin. Whereas, atmospheric nitrogen contribution on primary production would be as high as 3.7 % and 8.4 % in coastal and offshore waters, correspondingly. The impact of atmospheric input on the marine productivity became more important particularly during the stratified periods such as summer and autumn. During these period, atmospheric P input might sustain 80 % of the new production whereas, atmospheric N input might support 8 times higher new product than that detected for surface waters.

Keywords: Solubility, atmospheric nutrient input, marine production, Cilician Basin, Eastern Mediterranean

Doğu Akdeniz üzerindeki Atmosferik Besin Tuzlarının Çözünürlüğü: Saf-Su ve Deniz-Suyu Arasında Kıyaslama, Denizsel Üretim Konusunda Değerlendirme

Özet

Çözünürlük deneyleri gerçekleştirmek amacıyla Doğu Akdeniz'in kıyısında konuşlanmış Erdemli istasyonuna ait örnek kütüphanesinden aerosol filtre örnekleri seçilmiştir. Besin tuzu çözünürlükleri (PO_4^{3-}, Si_{diss}, $NO_3^-$and NH_4^+) saf-su ve deniz-suyu kullanılarak incelenmiştir. Fosfat ve silikat'ın aritmetik ortalamaları saf-su ve deniz-suyu arasında belirgin (% 50'den fazla) bir fark gösterirken nitrat ve amonyum için hesaplanan ortalamalar saf-su ve deniz-suyu ekstraksiyonlarında belirgin bir fark ortaya koymamıştır. Fosfat ve silikat için gözlenen fark pH, deniz suyu iyon şiddeti, parçacık boy dağılımı ve fosfat/silikat'ın kalsiyum fosfat, kaolinit, opal, kuvars gibi az çözünebilir parçacıklara eşlik etmesine ve aerosol türlerinin menşeine atfedilebilir. Nitrat ve amonyum için saf-su ve deniz-suyu ekstraksiyonlarındaki fark, sırasıyla % 1 ve % -3, olarak hesaplanmıştır. Bu benzerlik, yüksek çözünebilirlik gösteren NH_4NO_3, $Ca(NO_3)_2$, $NaNO_3$ $(NH_4)_2SO_4$ ve NH_4HSO_4 kimyasal forumlara atfedilebilir. Hesaplamalar atmosferik P akısının, Kilikya Baseni'nin kıyı ve açık suları için rapor edilen birincil üretimin % 0.4 ve % 0.9 destekleyebileceğini ortaya koymuştur. Diğer yandan, kıyı ve açık sulardaki birincil üretime atmosferik azot katkısı sırasıyla % 3.7 ve % 8.4 tespit edilmiştir. Atmosferik girdinin denizsel üretim üzerine etkisi özellikle tabakalaşmanın görüldüğü yaz ve sonbahar gibi dönemlerde daha önemli hale gelmektedir. Bu dönemlerde, atmosferik P girdisi birincil yeni üretimin % 80'ni karşılayabilirken atmosferik azot girdisi yüzey sularda belirlenen birincil yeni üretimin sekiz katını destekleyebilmektedir.

Anahtar Kelimeler: Çözünürlük, atmosferik besin tuzu girdisi, denizsel üretim, Kilikya Baseni, Doğu Akdeniz.

Introduction

During the last two decades aerosol research has been attracted by scientists who are interested in great variety of subjects including earth sciences, environmental engineering, oceanography, modeling and atmospheric chemistry. Atmospheric particles or aerosols play a central role in global processes (such as biogeochemistry, atmospheric chemistry and climate) and public health (Arimoto, 2001, Satheesh and Moorthy, 2005; Levin *et al.,* 2005; Huang *et al.,* 2006; Chen *et al.,* 2007; Herut *et al.,* 2005, Paytan *et al.,* 2009). From oceanographers point of view the atmospheric nutrient deposition has been considered as a vital source of the new primary production particularly for oligotrophic waters (Markaki *et al.,* 2003; Herut *et al.,* 2005, Paytan *et al.,* 2009). On the one hand, the atmospheric inputs supply essential macro and micro nutrients for marine primary production; on the other hand the nutrient content of the atmospheric deposition, considering the normal oceanic Redfield Ratio, may cause a dramatic change in phytoplankton population (Markaki *et al.,* 2010; Koçak *et al.,* 2010).

The Mediterranean Sea is characterized by its oligotrophic (deficit in macro nutrients) surface waters and low primary productivity, defining as low nutrient and low chlorophyll (LNLC) region. The oligotrophy of Mediterranean is primarily resulted by its anti-estuarine circulation and hence the nutrient deficiency in the basin increases from west to east along with decreasing primary productivity (Krom *et al.,* 2004, Pitta *et al.,* 2005). The molar N/P ratio in the Eastern Mediterranean (25-28) is found to be higher than those of observed for Western Mediterranean (22) and the normal oceanic Redfield ratio of 16. Taking into account aforementioned features, the limitation of the primary productivity in the Eastern Mediterranean is attributed to macro nutrient phosphorous (Yılmaz and Tuğrul, 1998).

A number of studies have been carried out to determine the levels of nutrients in aerosol, rainwater and assess the importance of atmospheric deposition onto the surface waters (Loye-Pilot *et al.,* 1993; Guerzoni *et al.,* 1999; Herut *et al.,* 1999, 2002; Kouvarakis *et al.,* 2001; Markaki *et al.,* 2003; 2010; Koçak *et al.,* 2010). However, only few studies have attempted to evaluate nutrient solubilities by using sea-water and pure-water as extraction medium. Markaki *et al.* (2003) used samples from Finokalia, Central Mediterranean whilst Chen *et al.* (2006) applied aerosol filters collected at Elat, Golf of Aqaba. Comparison between sea-water and pure-water from two studies revealed contradictory results for phosphate solubility. Former study did not demonstrate any statistical difference for the solubility of P in sea-water and pure-water (slope=0.99, R^2=0.80). On contrary, latter showed that the dissolution of PO_4^{3-} was 11 % lower in sea-water than that observed for pure-water. Thus, this study aims at assessing the sea-water and pure-water solubility of nutrients namely, PO_4^{3-}, Si_{diss}, NO_3^- and NH_4^+ by using aerosol samples from Erdemli site, Eastern Mediterranean. The assessment of the soulibilities of aforementioned mediums are of importance since the measured concentrations of macro-nutrients are used for calculating atmospheric inputs and thus exploring the possible influence of atmospheric deposition on the marine productivity. Atmospheric deposition of nutrients was also calculated in order o assess the possible impact of fluxes on the new primary production in the Eastern Mediterranean.

Materials and Methods

Sites Description and Sample Collection

Aerosol sampling campaign was carried out at a rural site located on the coastline of the Eastern Mediterranean, Erdemli, Turkey (36° 33′ 54″ N and 34° 15′ 18″E, Figure 1). High-volume sampler was

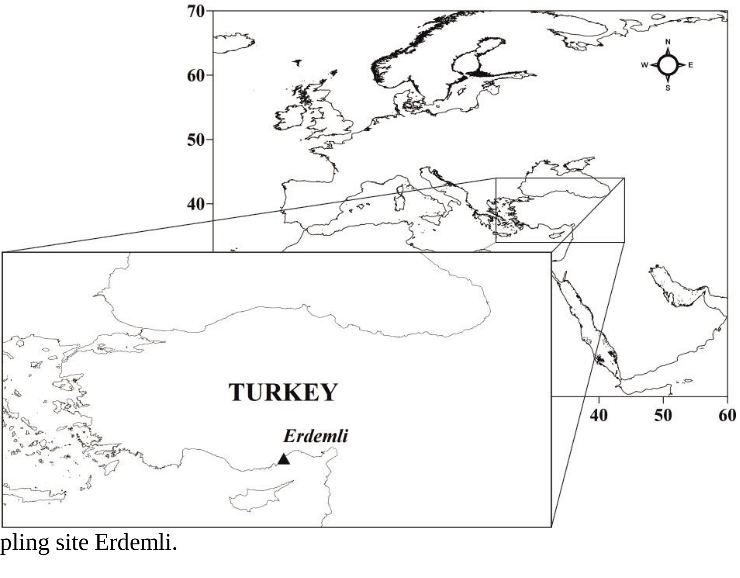

Figure 1. Location of sapling site Erdemli.

positioned on a sampling tower (at an altitude of ~22 m, ~10 m away from the sea) which is situated at the Institute of Marine Sciences, Middle East Technical University. From south, sampling tower looks out over Mediterranean Sea. From the north, it is surrounded by lemon trees and cultivated land. The sampling site is not under direct influence of any industrial activities (for more details see Kubilay and Saydam, 1995; Koçak *et al.,* 2004b).

A total of 1520 bulk aerosol (using a high volume sampler with flow rates of around 1 m^3 min^{-1} on Whatman-41 cellulose fiber filters) and 235 rainwater (applying automatic Wet/Dry sampler, Model ARS 1000, MTX Italy) samples were collected from January 1999 to December 2007 (for more details see Koçak *et al.,* 2010). From sample library, 34 aerosol filter samples were selected to carry out solubility experiments applying two different mediums namely: pure-water and sea-water.

Sample Analysis

The soluble nutrient measurements in samples were carried out by a Technicon Model, four-channel Autoanalyzer (for more details see Yılmaz and Tuğrul, 1998). The detection limits were 0.02, 0.10, 0.02 and 0.04 µM for phosphate, reactive silicate, nitrate and ammonium, respectively. The precision for each species was found to be better than 9 % (for more details see Koçak *et al.,* 2010).

The subsamples and blanks were extracted for 36 hrs in the dark at room temperature in precleaned centrifuge tubes containing 15 mLMilliQ (18.2 Ω) and 100 µL chloroform. In order to evaluate solubilities, the same extraction procedure was adopted using Northeastern Mediterranean surface sea-water (filtered with 0.2 µm, Herut *et al.,* 2002) as an extraction medium. Samples were immediately analyzed for nutrients after centrifuging at 3500 rpm for 15 min.

Calculation of Nutrient Fluxes and Air Masses Back Trajectories

The dry (Eqn. 1) and wet (Eqn. 2) atmospheric fluxes of nutrients were calculated according to the procedure explained in Herut *et al.* (1999, 2002). The dry deposition (F_d) of nutrients can be calculated as the product of atmospheric mean nutrient concentrations (C_d) and their settling velocities (V_d), where F_d is given in units of µmol m^{-2} d^{-1}, C_d in units of µmol m^{-3} and V_d in units of m d^{-1}. Atmospheric dry deposition fluxes were calculated applying measured pure-water soluble concentrations and relationship between pure-water and sea-water. Furthermore, the settling velocity values of 1.56, 1.59, 1.84 and 0.14 were used to estimate dry depositions of PO_4^{3-}, Si_{diss}, NO_3^- and NH_4^+ in the North Levantine Basin (Koçak *et al.,* 2010). The wet atmospheric deposition fluxes (F_w) were calculated from the annual amount of precipitation (P_{annual}) and the volume weighted mean concentration (C_w) of the substance of interest.

$$F_d = C_d x V_d \qquad [1]$$

$$F_w = C_w x P_{annual} \qquad [2]$$

Three-day backward trajectories arriving at 1 km, 2 km, 3 km and 4 km levels were computed by the HYSPLIT Dispersion Model for Erdemli sites (HybridSingle Particle Langrangian Integrated Trajectory; Draxler and Rolph, 2003) and demonstrated by one-hour endpoint locations in terms of latitude and longitude.

Results and Discussion

Seasonal Variations of the Pure-Water Soluble Nutrients

The monthly variations in the average concentrations of pure-water soluble nutrients along with standard deviations are illustrated in Figure 2. The monthly arithmetic mean and corresponding standard deviations between January 1999 and December 2007 were calculated from data reported by Koçak *et al.,* 2010. It is apparent that the concentrations of all nutrient species were significantly variable on a monthly time scale in agreement with previous studies carried out in the Mediterranean region (Bergametti *et al.,* 1989; Herrut *et al.,* 1999, 2002; Kubilay *et al.,* 2000; Markaki *et al.,* 2003, 2010; Koçak *et al.,* 2004a, 2010). The monthly mean concentrations and corresponding standard deviations of the nutrient species changed at least factor of 2 from month to month. Phosphate and silicate indicated their higher monthly means and standard deviations in transitional (particularly in March and October) period compared to those observed in winter and summer period. However, close investigation of the seasonal diagrams revealed that silicate had the highest mean (standard deviation) value during October and phosphate had the maximum mean (standard deviation) in March. Furthermore, silicate denoted substantial decrease in its mean concentrations from spring to summer than that detected for phosphate. Observed difference between phosphate and silicate in summer might be attributed to the contribution of sources other than soil on phosphate. In addition to mineral aerosol, combustion (such as coal combustion and biomass burning), biogenic and volcanic ash particles have been suggested as sources of phosphorous (Mahowald *et al.,* 2008). Since the sampling site is not under the influence of any volcanic activities, combustion (particularly biomass burning) and biogenic aerosol might also be suggested as potential sources of phosphate in summer period.

As reported in the literature (Kubilay and

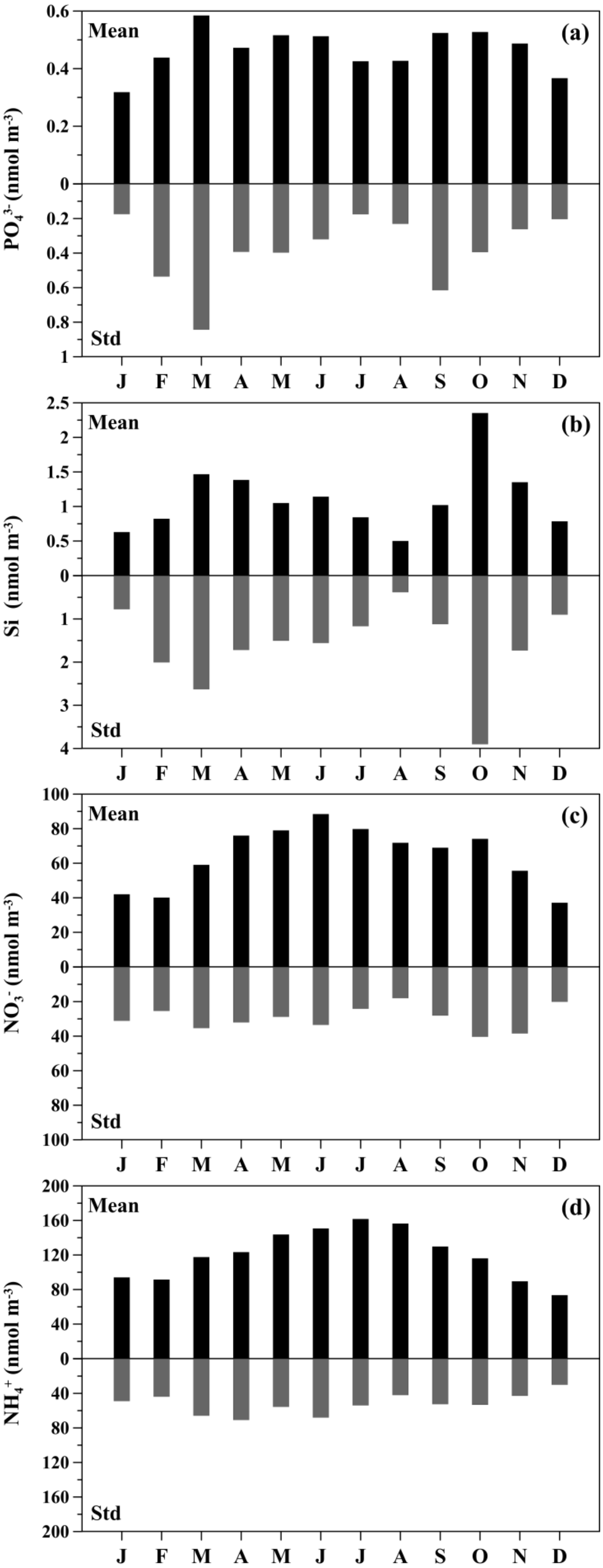

Figure 2. Seasonal varibility in the concentrations of pure-water soluble nutrients.(a) PO_4^{3-}, (b) Si_{diss}, (c) NO_3^- and (d) NH_4^+. Black and gray bars denote arithmetic means and corresponding standard deviations, respectively.

Saydam, 1995; Moulin *et al.*, 1998; Koçak *et al.*, 2004a) severe sporadic dust events occur over the Eastern Mediterranean during the spring and autumn seasons when the air mass trajectories originate principally from North Africa (as well as from the Middle East/Arabian Peninsula).It has been show that both species are essentially influenced by mineral dust episodes when air mass transport originates from Sahara and the Middle East Deserts (Bergametti *et al.*, 1989; Herut *et al.*, 1999; Markaki *et al.*, 2003; Koçak *et al.*, 2010). To illustrate influence of air mass transport originating from Sahara Desert and the Middle East Desert two examples will be used. The first example (Figure 3) was observed between 5 March and 13 March 2002 and it lasted 9 days, with mean phosphate and silicate values at about 0.60 and

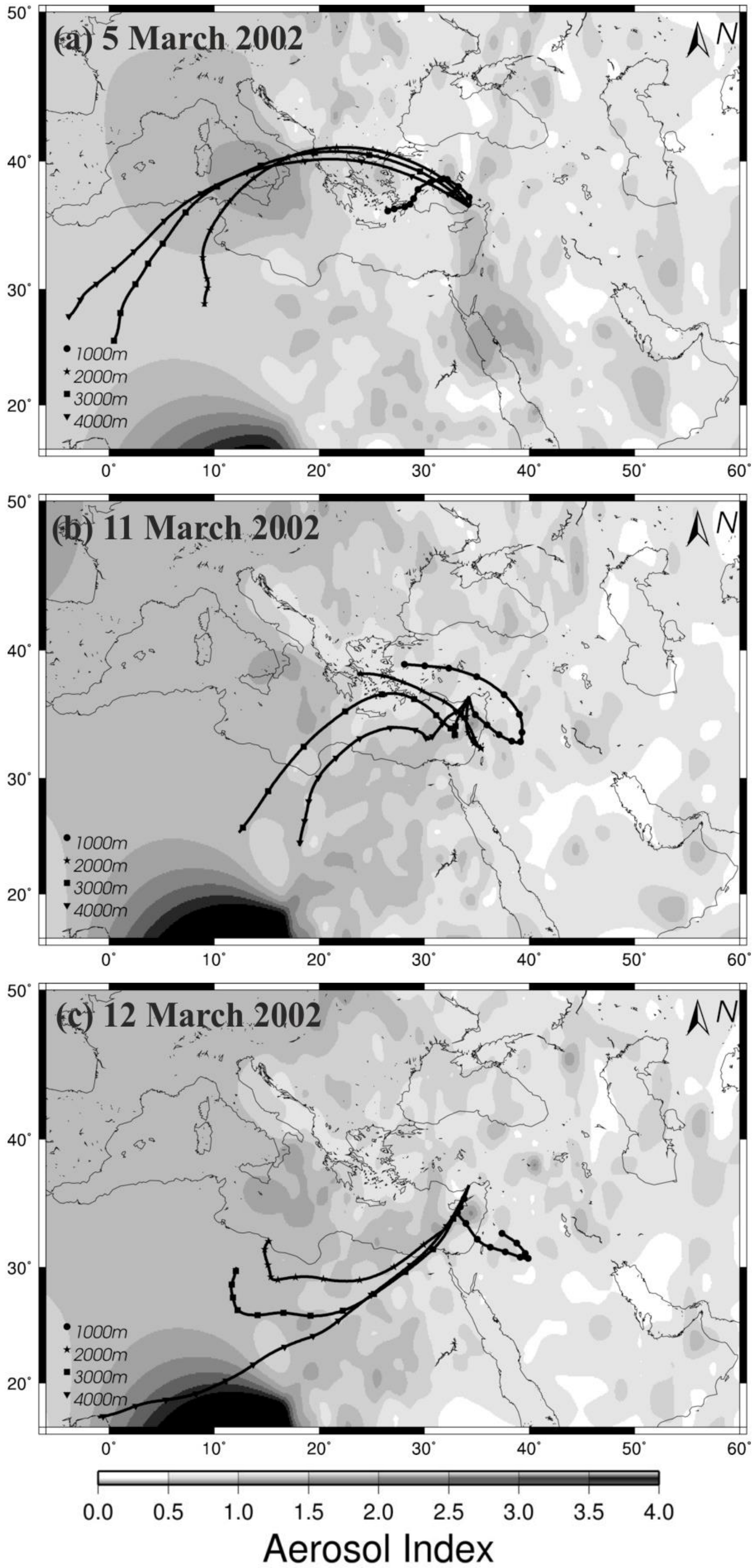

Figure 3. Air masses back trajectories and Total Ozone Mapping Spectrometer Aerosol Index for 05 March 2002 (a), 11 March 2002 (b) and 12 March 2002 (c). 1 km (Black Circle), 2 km (Black Star), 3 km (Black Square) and 4 km (Black Triangle).

2.3 nmol m^{-3}, respectively. The phosphate and silicate maximums for this event were detected on 11 March 2002, with corresponding values of 0.83 and 7.0 nmol m^{-3}. Overall, the back trajectories indicated air mass flow reaching Erdemli from North Africa. The TOMS (Total Ozone Mapping Spectrometer) Aerosol Index for this event also supported a dust cloud over the central and eastern Mediterranean region. The second example (Figure 4) was identified with mean phosphate and silicate concentrations of 1.75 and 15.2

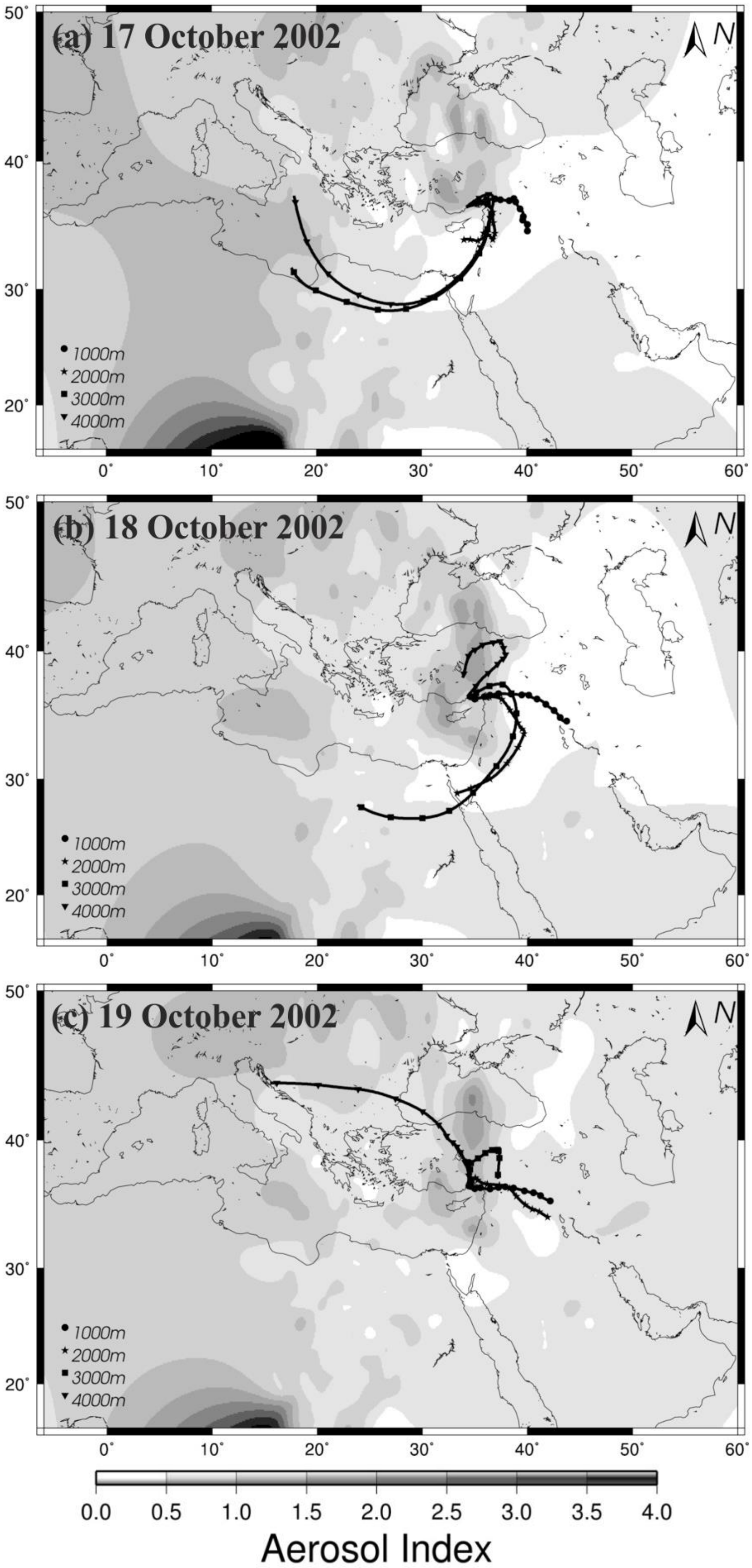

Figure 4. Air masses back trajectories and Total Ozone Mapping Spectrometer Aerosol Index for 17October 2002 (a), 18 October 2002 (b) and 19 October 2002 (c). 1 km (Black Circle), 2 km (Black Star), 3 km (Black Square) and 4 km (Black Triangle).

nmol m^{-3} from 17 October to 20 October 2002. The values of phosphate and silicate were found to be ranged between 0.59-2.60 and 2.6-26.6 nmol m^{-3} during the dust event, lasting 4 days. The highest concentrations for both species were observed on 19 October 2002 with values of 2.60 and 26.6 nmol m^{-3}, respectively. The air masses back trajectories demonstrated transport originating from the Middle East deserts (mainly from Iranian Desert) with TOMS Aerosol Index values ranging from 0.5 to 2.0.

Unlike phosphate and silicate, nitrate and ammonium had a seasonal cycle with a winter minimum and a summer maximum. During winter months (January, February and December) mean concentrations of nitrate and ammonium were found to be less than 50 and 90 nmol m^{-3}, respectively. From spring to summer, monthly mean concentrations of nitrate and ammonium gradually increased and reached their peak in summer with corresponding values of around 90 and 160 nmol m^{-3}. Lower values in winter season might be attributed to removal of particles by efficient wet scavenging and lower gas-to-particle conversion rates due to less solar influx. On the other hand, elevated mean concentrations during summer might be related to less efficient dry deposition and higher conversion rates of precursor gases to aerosol particles under the prevailing summer conditions (Mihalopoulos *et al.,* 1997; Bardouki *et al.,* 2003; Koçak *et al.,* 2004b).

Nutrient concentrations in Pure-Water and Sea-Water

Table 1 illustrates the arithmetic mean concentrations of macro-nutrients along with corresponding standard deviations and change between pure-water (PW) and sea-water (SW) for aerosol filter samples obtained from Erdemli sampling site. The pure-water soluble PO_4^{3-} and Si_{diss} concentrations in aerosol ranged between 0.03-1.30 and 0.5-18.1 nmol m^{-3} with arithmetic mean values and standard deviations of 0.31±0.25 and 3.5±3.1 nmol m^{-3}, respectively. The pure-water soluble NO_3^- and NH_4^+ concentrations in aerosol samples were found to be ranged between 12.0-154.8 and 35.3-239.0 nmol m^{-3} with mean values and standard deviations of 63.3±29.3 and 115.7±49.9 nmol m^{-3}, respectively. The sea-water soluble PO_4^{3-} and Si_{diss} mean concentrations and standard deviations were 0.15±0.11 and 1.2±0.6 nmol m^{-3} with values ranging from 0.03-0.52 and 0.2-3.4, correspondingly. The sea-water soluble NO_3^- and NH_4^+ concentrations varied between 10.6-145.2 and 35.3-239.0 nmol m^{-3} with mean values and standard deviations of 64.1±28.2 and 39.3-214.1 nmol m^{-3}, in turn.

The arithmetic means of phosphate and dissolved silica indicated distinct difference between pure-water and sea-water whereas; the calculated mean concentrations of nitrate and ammonium did not reveal substantial discrepancy for pure-water and sea-water extractions. The difference between pure-water and sea-water extractions was found to be larger than 50 % for phosphate and dissolved silica. The difference between pure-water and sea-water extractions for nitrate and ammonium was estimated to be small, corresponding to 1 % to -3 %, respectively.

Figure 5 demonstrates scatter plots along with residual correlation coefficients and regression equations for macro-nutrient (PO_4^{3-}, Si_{diss}, NO_3^- and NH_4^+) concentrations which were obtained from pure-water and sea-water (at the confidence level of 95 %). The slopes of regression lines for PO_4^{3-} and Si_{diss} were found to be drastically lower than unity, corresponding to 0.40 (intercept=0.03, R^2=0.77) and 0.16 (intercept=0.56, R^2=0.65), respectively. Results obtained from scatter plots for these species implied that pure-water and sea-water concentrations were distinctly different from each other. In sharp contrast to PO_4^{3-} and Si_{diss}, the slopes of the regressions lines for NO_3^- and NH_4^+ were found to be close to the unity with values of 0.97 (intercept=2.6, R^2=0.98) and 0.94 (intercept=2.7, R^2=0.99), respectively. Obtained slopes and intercepts suggested that NO_3^- and NH_4^+ concentrations were not considerably different for two extraction mediums.

Comparison between Sea-water and Pure-water solubility of Nutrients

PO_4^{3-} and Si_{diss}: Figure 6 (a, b) demonstrates concentrations of PO_4^{3-} and Si_{diss} in pure-water and sea-water according to sample day. It is apparent from the diagrams, PO_4^{3-} and Si_{diss} indicated substantial change in their concentrations, with the values of individual species varying up to order of magnitude from sample to sample. For instance, considering pure-water solubilities, from 19 to 21 March 2007, PO_4^{3-} and Si_{diss} concentrations were found to be fluctuating between 0.04-0.43 and 0.5-3.9 nmol m^{-3},

Table 1. Arithmetic mean concentrations of nutrients (in nmol m^{-3}) in pure-water and sea-water along with standard deviations and percentage change for aerosol samples collected at Erdemli

Nutrient Species	PW-extracted	SW-extracted	Equation	Change (%)
PO_4^{3-}	0.31±0.25 (0.03-1.30)	0.15±0.11 (0.03-0.52)	SW = PW*0.40+0.03	-52
Si_{diss}	3.5±3.1 (0.5-18.1)	1.2±0.6 (0.2-3.4)	SW = PW*0.16+0.6	-67
NO_3^-	63.3±29.3 (12.0-154.8)	64.0±28.2 (10.6-145.2)	SW = PW*0.97+2.6	+1
NH_4^+	115.7±49.9 (35.3-239.0)	111.9±47.1 (39.3-214.1)	SW = PW*0.94+3.4	-3

PW and SW refer to pure-water and sea-water, respectively.

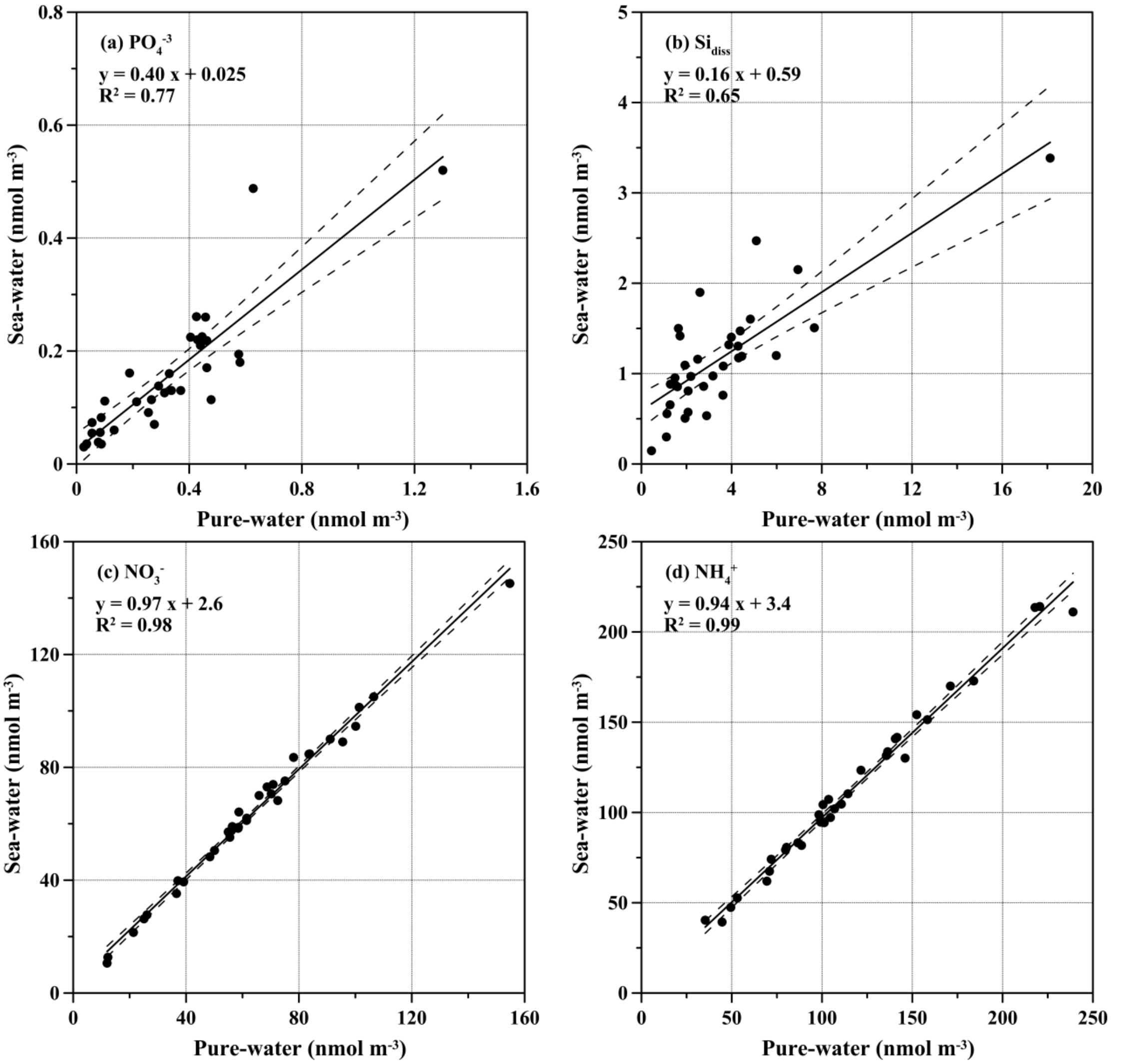

Figure 5. Scatter plot diagrams between pure-water and sea-water soluble nutrients. (a) PO_4^{3-}, (b) Si_{diss}, (c) NO_3^- and (d) NH_4^+.

respectively. The highest values for PO_4^{3-} and Si_{diss} were observed on 22 March 2007, with concentrations of 1.30 and 18.1 nmol m^{-3}, respectively. Short-term variability, as such, has been attributed to (a) changes in emission strength (b) local meteorology (particularly rain) and (c) changes in airflow or source region (Bergametti *et al.*, 1989; Kubilay and Saydam, 1995; Güllü *et al.*, 1998; Kubilay *et al.*, 2000).

In the Eastern Mediterranean region, elevated concentrations of phosphate and silicate were found to be associated mainly with air masses originating from Sahara Desert and the Middle East deserts (Koçak *et al.*, 2010). To illustrate, two different events observed under the southerly (22 March 2007) and northerly (16 March 2007) airflow will be used.

As stated above, the highest phosphate and silicate values were observed on 22 March 2007. Figure 7a presents air masses back trajectories and Ozone Mapping Spectrometer Aerosol Index for 22 March. Air masses back trajectories for 22 March showed at all levels airflow originating from south. Air mass trajectory at 1 km level demonstrated transport originating from the Middle East deserts whilst trajectories at 2 km and 3 km levels showed that air masses arriving at Erdemli from Saharan region. Furthermore, OMI-AI (Ozone Monitoring Spectrometer Aerosol Index) image for 22 March indicated the existence of the mineral dust over the Eastern Mediterranean. As can be noticed, OMI-AI image revealed a large dust cloud over the region, between the coordinates 22-40 N° and 25-47 E°. Corresponding phosphate and silicate concentrations for pure-water and sea-water were 1.30-18.1 nmol m^{-3} and 0.52-3.4 nmol m^{-3}, respectively. The distinct difference between pure-water and sea-water solubilities, more specifically change in phosphate (-60 %) and silicate (- 80 %) might be attributed to less soluble compounds (see below). In sharp contrast to previous event, on 16 March 2007, phosphate and silicate values were observed around 0.03-1.1 nmol m^{-3} and 0.03-0.6 nmol m^{-3} for pure-water and sea-water, respectively. Calculated changes for phosphate and silicate were almost zero and – 50 %, respectively. Air masses back trajectories for this event are illustrated in Figure 7b. During this event, the trajectories at all levels indicated airflow

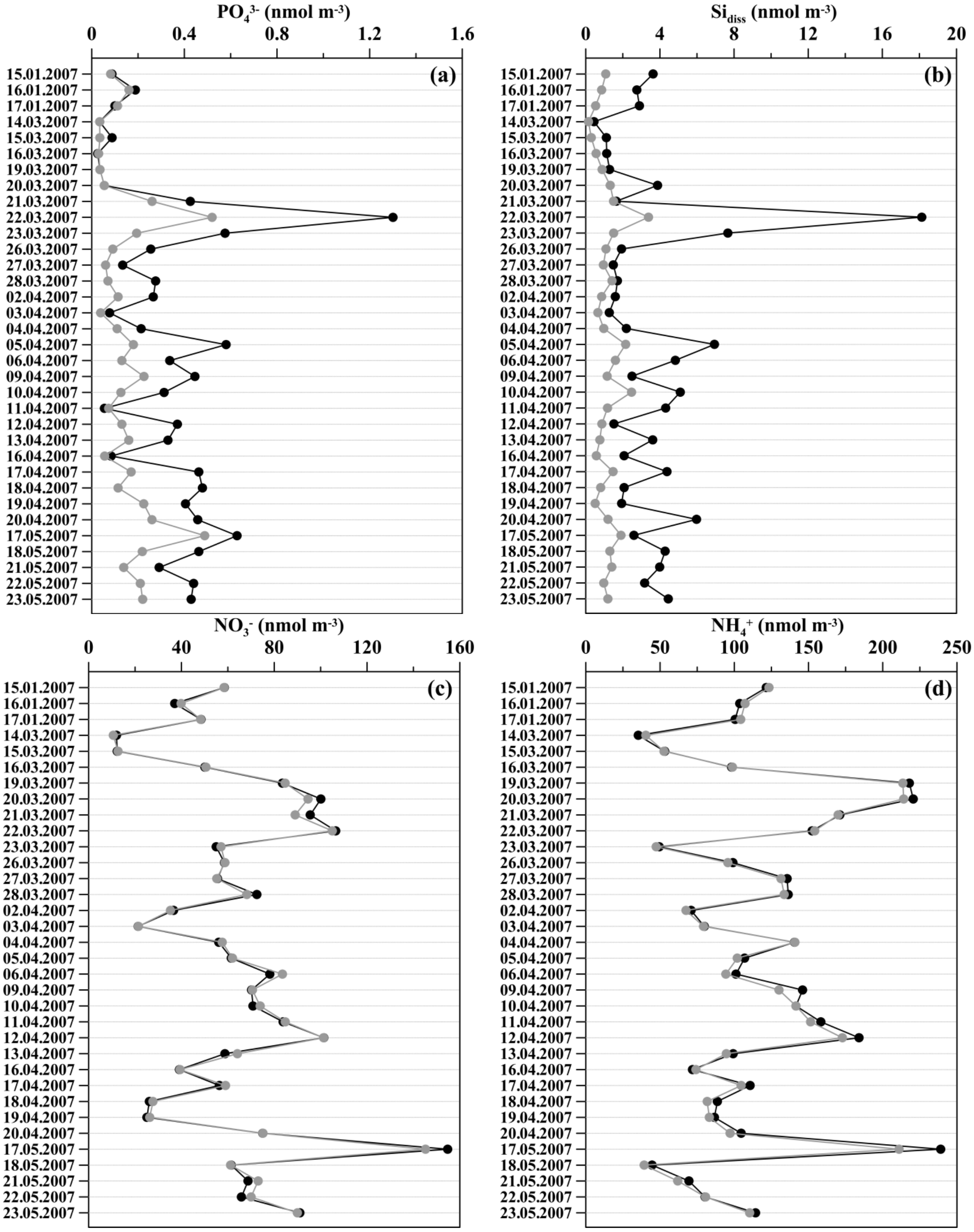

Figure 6. Nutrient concentrations extracted by pure-water (black lines and dots) and surface Eastern Mediterranean sea-water (grey lines and dots) from aerosol samples (n=34) collected from Erdemli, (a) PO_4^{3-},(b) Si_{diss},(c) NO_3^- and (d) NH_4^+.

originating from North-west specifically: Balkans and Western Europe. As it well documented, these source regions supply anthropogenic dominated aerosol particles into Eastern Mediterranean (Kubilay and Saydam, 1995; Mihalopoulos *et al.*, 1997; Güllü *et al.,* 1998; Koçak *et al.,* 2009). Therefore, the solubility difference between pure-water and sea-water might be related to crustal dominated aerosol population via low temperature weathering process and man-made aerosol population through high temperature/condensation reactions (Chester *et al.*, 1995).

Non-parametric Wilcoxon matched pairs test was applied to compare nutrient solubilities in sea-water and pure-water. The Wilcoxon test showed that there were statistical difference in the dissolutions of PO_4^{3-} and Si_{diss} in pure-water and sea-water. As stated above, the mean concentrations of sea-water PO_4^{3-} and Si_{diss} (0.15 and 1.2 nmol m^{-3}) were 52 % and 66 % lower than those for pure-water (0.31 and 3.5 nmol m^{-3}), respectively. This difference might be attributed to pH and ionic strength of sea water, size distribution and association of phosphate/silicate aerosols with less soluble compounds such as calcium phosphate, kaolinite, opal, quartz and origin of the aerosol species (Guieu *et al.,* 1997; Chen *et al.,* 2006; Koçak

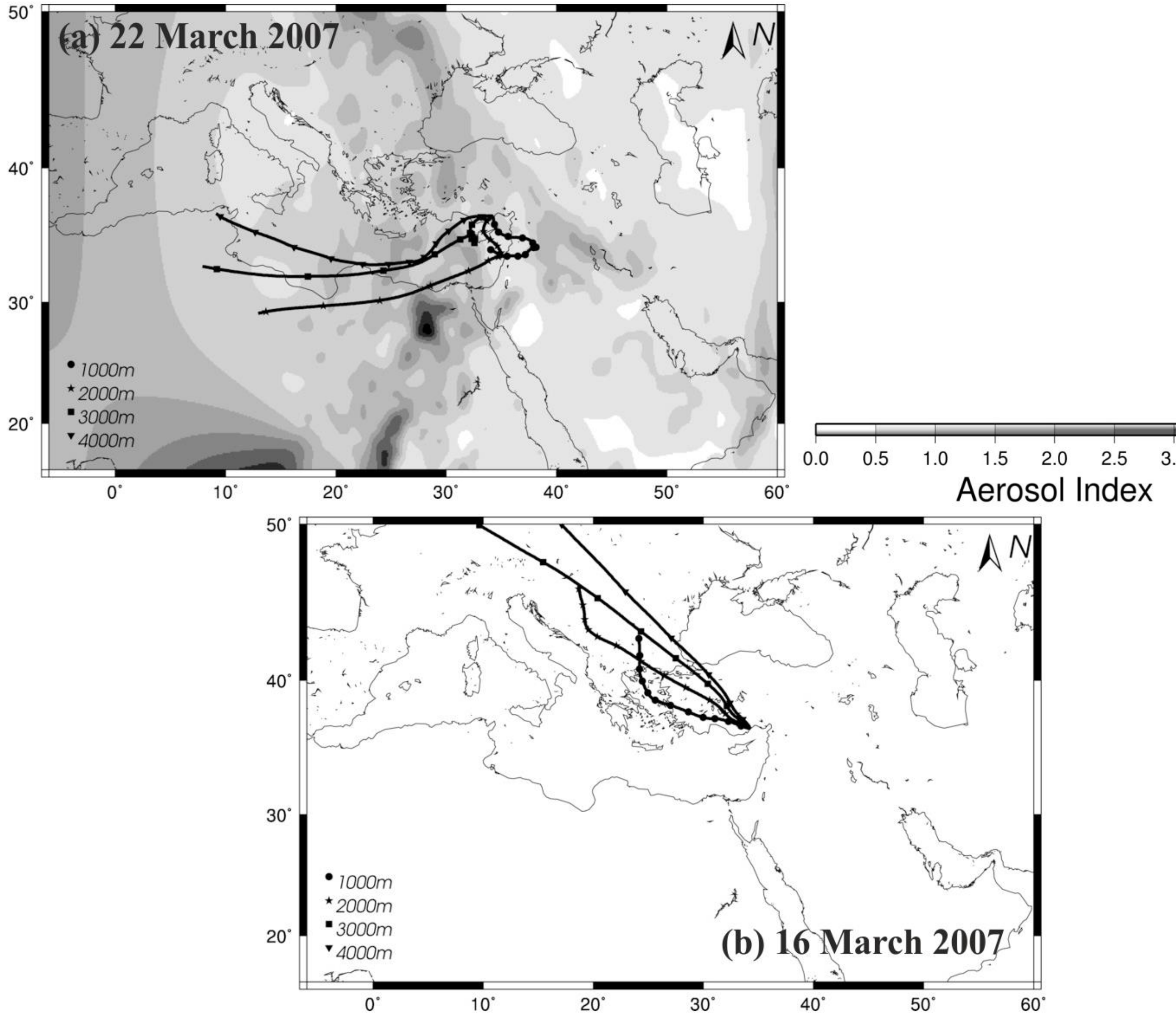

Figure 7. Air masses back trajectories and Ozone Mapping Spectrometer Aerosol Index for 22 March 2007 (a) and air masses 2007 (b). 1 km (Black Circle), 2 km (Black Star), 3 km (Black Square) and 4km(Black Triangle).

et al., 2007a; Baker *et al.,* 2007). There are few studies which have directly compared the dissolution of nutrients in sea-water and pure-water. For instance, Markaki *et al.* (2003) compared sea-water and pure-water solubility of P after extracting samples from Finokalia for 45 min. Results from this study did not reveal any statistical difference for solubility of P in sea-water and pure-water (slope=0.99, R^2=0.80). Similarly, Chen *et al.* (2006) studied the dissolution of PO_4^{3-} in sea-water and pure-water,. after extracting aerosol samples from Gulf of Aqaba for 30 min. Dissolution of PO_4^{3-} was found to be 11 % lower in sea-water than those observed for pure-water.

NO_3^- and NH_4^+: Figure 6 (c, d) exhibits concentrations of NO_3^- and NH_4^+ in pure and sea water. As highlighted above, the mean concentrations of NO_3^- and NH_4^+ (64.1 and 111.9 nmol m^{-3}) in sea-water were found to be similar to values obtained for pure-water (63.3 and 115.7 nmol m^{-3}). In sharp contrast to PO_4^{3-} and Si_{diss}, there were no statistical differences for nitrate and ammonium solubilities in pure and sea water. Therefore, obtained results for nitrate and ammonium implies that sea water does not influence the solubility of these nutrients considering high pH and ionic strength of sea water. This peculiarity suggests that aerosol nitrate and ammonium are almost exclusively associated with highly soluble chemical forms such as NH_4NO_3, $Ca(NO_3)_2$, $NaNO_3$ $(NH_4)_2SO_4$ and NH_4HSO_4 (Bardouki *et al.,* 2003, Koçak *et al.,* 2007b). Similar results have been documented by Chen *et al.* (2006) for the dissolution of NO_3^- and NH_4^+ in sea-water and pure-water.

Atmospheric Depositions of Nutrients and Implications Regarding Marine Production

The atmospheric dry and wet deposition fluxes of nutrients PO_4^{3-}, Si_{diss}, NO_3^- and NH_4^+ between January 1999 and December 2007 are demonstrated in Table 2. It is evident that the dry and wet deposition fluxes of phosphate and silicate were at least order of magnitude less than those calculated for nitrate and ammonium. The atmospheric depositions of phosphate (0.93 µmol m^{-2} d^{-1}), silicate (2.5 µmol m^{-2} d^{-1}) and ammonium (62 µmol m^{-2} d^{-1}) were dominated by wet deposition, elucidating 77 %, 63 % and 90 % of the total atmospheric fluxes. Whereas, the atmospheric flux of nitrate was equally influenced by dry (61 µmol m^{-2} d^{-1}) and wet (60 µmol m^{-2} d^{-1}) deposition modes. The molar N/P ratio for dry (243) deposition was found to be factor of two higher than that of observed for wet deposition (131), implying higher phosphate deficiency for dry mode. On the other hand, Si/N ratio (0.02) for both dry and wet depositions was almost identical. Atmospheric Si/N ratio, with a value of 0.02, was almost 50 times lower than that of Redfield ratio (Si/N ~ 0.94). It might be argued that atmospheric fluxes were severely deficient in silicate compare to nitrogen. Consequently, the atmospheric N/P and Si/N rations were found to be considerably deviated from reported Redfield ratios.

Taking into account the values presented in Table 2, 1.21 µmol m^{-2} d^{-1} P was calculated in the study area. If one assumes that all P and N are bioavailable to primary producers for primary production and if a Redfield C/P and N/C ratios of 106 and 106/16 are applied, it would be estimated that atmospheric P and N depositions can support new production of 1.6 and 15.1 mg C m^{-2} d^{-1}, respectively. Recent study has been shown that annual primary production for coastal and offshore waters of Cilician Basin were around 413 mg C m^{-2} d^{-1} and 179 mg C m^{-2} d^{-1} , respectively (Yücel, 2013). On average, atmospheric P flux can sustain 0.4 % and 0.9 % of the production reported for coastal and offshore waters. Whereas, nitrogen flux can sustain 3.7 % and 8.4 % of the primary production detected for coastal and offshore waters, respectively. On the one hand, the atmospheric contribution was found to be less than 9 %, on the other hand, it might constitute a considerable fraction of the new production. It has been noted that f- ratio, defined as ratio between new and total production, may vary from 0.05 to 0.16 in oligotrophic seas such as Mediterranean (Eastrada, 1996 and references therein). For instance, mean value of 0.16 was applied by Eastrada (1996) to assess the amount of new production in the Eastern Mediterranean. If the f-ratio of 0.16 is applied, the annual new production for coastal and off shore water of Cilician Basin would be 66 mg C m^{-2} d^{-1} and 29 mg C m^{-2} d^{-1}, respectively. Consequently, contribution of atmospheric P and N on the primary production would increase factor of 6, ranging from 2.5-5.6 % to 23-53 for P and N, respectively. The impact of atmospheric input on the marine productivity becomes more important particularly during the stratified periods such as summer and autumn. For instance, average new production from June to October period was found to be around 2 mg C m^{-2} d^{-1} (assuming f ratio of 0.16). Throughout this period, atmospheric P might sustain 80 % of the new production whereas, atmospheric N can support 8 times higher new production than that observed for surface waters.

Conclusion

The concentrations of all nutrient species were significantly variable on a monthly time scale. Phosphate and silicate denoted their higher monthly means and standard deviations in transitional (particularly in March and October). The seasonal cycle of these species was found to be influenced by dust intrusions from Sahara Desert and the Middle East Desert. Nitrate and ammonium had a seasonal cycle with a winter minimum and a summer

Table 2. Atmospheric dry and wet depositions of nutrients (in µmol m^{-2} d^{-1}) along with molar N/P and Si/N rations. Corrections in calculation were obtained by applying relationship between pure-water and sea-water solubilities

	Dry Deposition *[a]Without correction* (µmol m^{-2} d^{-1})	*Dry Deposition* *[b]With correction* (µmol m^{-2} d^{-1})	*Wet Deposition* (µmol m^{-2} d^{-1})	*Atmospheric Deposition* (µmol m^{-2} d^{-1})
$P\text{-}PO_4^{-3}$	0.63	0.28	0.93	1.21
Si_{diss}	4.2	1.5	2.5	4.0
$N\text{-}NO_3^-$	104	61	60	121
$N\text{-}NH_4^+$	14	7	62	69
DIN	128	68	122	190
N/P	203	243	131	157
Si/N	0.03	0.02	0.02	0.02

maximum. Elevated mean concentrations during summer was ascribed to less efficient dry deposition and higher conversion rates of precursor gases to aerosol particles under the prevailing summer conditions.

The arithmetic means of phosphate and dissolved silica indicated distinct difference between pure-water and sea-water whereas; the calculated mean concentrations of nitrate and ammonium did not reveal substantial discrepancy for pure-water and sea-water extractions. The difference between pure-water and sea-water extractions was found to be larger than 50 % for phosphate and dissolved silica. This difference might be attributed to pH and ionic strength of sea water, size distribution and association of phosphate/silicate aerosols with less soluble compounds such as calcium phosphate, kaolinite, opal and quartz and origin of the aerosol species. The difference between pure-water and sea-water extractions for nitrate and ammonium was estimated to be small, corresponding to 1 % to -3 %, respectively. This similarity can be ascribed to highly soluble chemical forms such as NH_4NO_3, $Ca(NO_3)_2$, $NaNO_3$ $(NH_4)_2SO_4$ and NH_4HSO_4.

Calculations revealed that atmospheric P fluxes would sustain 0.4 % and 0.9 % of the new production reported for coastal and offshore waters. Whereas, atmospheric nitrogen contribution on new production would be as high as 3.7 % and 8.4 % in coastal and offshore waters, correspondingly. Impact of atmospheric inputs on the marine productivity becomes more important particularly during the stratified periods such as summer and autumn. For example, average new production from June to October period was found to be around 2 mg C m^{-2} d^{-1} (assuming f ratio of 0.16). During this period, atmospheric P t might sustain 80 % of the new production whereas; atmospheric N might support 8 times higher new product than that detected for self waters.

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