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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$_4$NO$_3$, Ca(NO$_3$)$_2$, NaNO$_3$, (NH$_4$)$_2$SO$_4$ and NH$_4$HSO$_4$. 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

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Çözünürlük deneyleri gerçekleştirilerek amacıyla Doğu Akdeniz’in kıyısında konuşlanmış Erdemli istasyonuna ait örnek kütüphanesinden aerosol filtre örnekleri seçilmiştir. Besin tuzu çözünürlükleri (PO$_4^{3-}$, Si$_{diss}$, NO$_3^-$ ve NH$_4^+$) saf-su ve deniz-suuyu kullanılarak incelemiştir. Fosfat ve silikat için gözlenen fark pH, deniz suyu iyon şiddetini, parçacık boy dağılımı ve fosfat/silikat’ın kalsiyum fosfat, kaolinit, opal, kuvars gibi az çözünebilir parçacıklara eşlik etmesine ve aerosol türlerinin menaceine atfedilebilir. Nitrat ve amonyum için saf-su ve deniz-suuyu ekstraksyonlarındaki fark, sırasıyla %1 ve %3'ten oldukça hassaplanmıştır. Bu benzerlik, yüksek çözünabilirlik gösteren NH$_4$NO$_3$, Ca(NO$_3$)$_2$, NaNO$_3$, (NH$_4$)$_2$SO$_4$ ve NH$_4$HSO$_4$ kimyasal formlarında atfedilebilir. Hidrojena atmosferik P aksını, Kilikya Basen’ini çevreleyen kıyı ve açık sulanın için rapor edilen birincil üretim %0.4 ve %0.9 destekleyebileceğini ortaya koymıştır. Diğer yandan, kıyı ve açık sulardaki birincil üretim atmosferik azot katkısı sırasıyla %3.7 ve %8.4 tespit edilmiştir. Atmosferik girdinin denizsel üretim üzerine etkisi özellikle tabakalaşmanın görülmesi, ve sondahar gibi dönemde daha önemli hale gelmektedir. Bu dönemde, atmosferik P girdisi birincil yetenin %80’ti karşılayabilen atmosferik azot girdisi yüzey sularda belirlenen birincil yetenin %80’i karşılayabilen atmosferik azot girdisi yüzey sularda belirlenen birincil yetenin %80’i karşılayabilir. Atmosferik P girdisi birincil yetenin %80’ti karşılayabilen atmosferik azot girdisi yüzey sularda belirlenen birincil yetenin %80’ti karşılayabilir.
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, R²=0.80). On contrary, latter showed that the dissolution of PO₄³⁻ 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, PO₄³⁻, Si₃, NO₃⁻ and NH₄⁺ by using aerosol samples from Erdemli site, Eastern Mediterranean. The assessment of the solubilities 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 to 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
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 mL MilliQ (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**

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$_{silic}$, 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.

$$F_d = C_d \times V_d$$  
$$F_w = C_w \times P_{annual}$$

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 Rolfh, 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
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

![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).](image-url)
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 nmol m$^{-3}$.

**Figure 4.** Air masses back trajectories and Total Ozone Mapping Spectrometer Aerosol Index for 17 October 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).
from 0.03-0.52 and 0.2-3.4, correspondingly. The sea-water soluble NO\textsubscript{3} and NH\textsubscript{4} concentrations varied between 10.6-145.2 and 35.3-239.0 nmol m\textsuperscript{-3} with mean values and standard deviations of 64.1±28.2 and 39.3±214.1 nmol m\textsuperscript{-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\textsubscript{4}\textsuperscript{3-}, Si\textsubscript{diss}, NO\textsubscript{3} and NH\textsubscript{4}) concentrations which were obtained from pure-water and sea-water (at the confidence level of 95%). The slopes of regression lines for PO\textsubscript{4}\textsuperscript{3-} and Si\textsubscript{diss} were found to be drastically lower than unity, corresponding to 0.40 (intercept=0.03, R\textsuperscript{2}=0.77) and 0.16 (intercept=-0.56, R\textsuperscript{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\textsubscript{4}\textsuperscript{3-} and Si\textsubscript{diss}, the slopes of the regressions lines for NO\textsubscript{3} and NH\textsubscript{4} were found to be close to the unity with values of 0.97 (intercept=2.6, R\textsuperscript{2}=0.98) and 0.94 (intercept=2.7, R\textsuperscript{2}=0.99), respectively. Obtained slopes and intercepts suggested that NO\textsubscript{3} and NH\textsubscript{4} concentrations were not considerably different for two extraction mediums. **Comparison between Sea-water and Pure-water solubility of Nutrients**

**PO\textsubscript{4}\textsuperscript{3-} and Si\textsubscript{diss}**: Figure 6 (a, b) demonstrates concentrations of PO\textsubscript{4}\textsuperscript{3-} and Si\textsubscript{diss} in pure-water and sea-water according to sample day. It is apparent from the diagrams, PO\textsubscript{4}\textsuperscript{3-} and Si\textsubscript{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\textsubscript{4}\textsuperscript{3-} and Si\textsubscript{diss} concentrations were found to be fluctuating between 0.04-0.43 and 0.5-3.9 nmol m\textsuperscript{-3}, respectively.
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 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
originating from North-west specifically: Balkans and Western Europe. As it well documented, these source regions supply anthropogenic dominant 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 et al., 2009).

**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$_4^+$.
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 \( \text{PO}_4^{3-} \) in sea-water and pure-water, after extracting aerosol samples from Gulf of Aqaba for 30 min. Dissolution of \( \text{PO}_4^{3-} \) was found to be 11% lower in sea-water than those observed for pure-water.

\[ \text{NO}_3^- \text{ and } \text{NH}_4^+ \]: Figure 6 (c, d) exhibits concentrations of \( \text{NO}_3^- \) and \( \text{NH}_4^+ \) in pure and sea water. As highlighted above, the mean concentrations of \( \text{NO}_3^- \) and \( \text{NH}_4^+ \) (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 \( \text{PO}_4^{3-} \) and \( \text{Si}^{4+} \), 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$_4$\textsubscript{3}NO$_3$, Ca(NO$_3$)$_2$, NaNO$_3$, (NH$_4$)$_2$SO$_4$, and NH$_4$HSO$_4$ (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$_4$\textsubscript{3-}, Si$_{diss}$, NO$_3$ and NH$_4$\textsuperscript{+} 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 depositional fluxes 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**              | **Dry Deposition**              | **Wet Deposition**              | **Atmospheric** |
| **Without correction**          | **With correction**             | **Without correction**          | **Deposition**                 |
| (µmol m$^{-2}$ d$^{-1}$)         | (µmol m$^{-2}$ d$^{-1}$)        | (µmol m$^{-2}$ d$^{-1}$)        | (µmol m$^{-2}$ d$^{-1}$)       |
| P-PO$_4$\textsuperscript{3-}    | 0.63                            | 0.28                            | 0.93                            | 1.21                            |
| Si$_{diss}$                      | 4.2                             | 1.5                             | 2.5                             | 4.0                             |
| N-NO$_3$                        | 104                             | 61                              | 60                              | 121                             |
| N-NH$_4$\textsuperscript{+}     | 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 \( \text{NH}_4\text{NO}_3 \), \( \text{Ca(NO}_3\text{)}_2 \), \( \text{NaNO}_3 \), \( \text{(NH}_4\text{)}_2\text{SO}_4 \) and \( \text{NH}_4\text{HSO}_4 \).

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 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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