Atmospheric Deposition of Macronutrients (Dissolved Inorganic Nitrogen and Phosphorous) onto the Black Sea and Implications on Marine Productivity*

M. KOÇAK

Institute of Marine Sciences, Middle East Technical University, Erdemli-Mersin, Turkey

N. MIHALOPOULOS

Department of Chemistry, University of Crete, Heraklion, and National Observatory of Athens, IERSD, Athens, Greece

E. TUTSAK

Institute of Marine Sciences, Middle East Technical University, Erdemli-Mersin, Turkey

K. VIOLAKI, C. THEODOSI, AND P. ZARMPAS

Department of Chemistry, University of Crete, Heraklion, Greece

P. KALEGERI

Institute of Marine Sciences, Middle East Technical University, Erdemli-Mersin, Turkey

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ABSTRACT

Two-sized aerosol samples were obtained from a rural site located close to Sinop on the south coastline of the Black Sea. In addition, bulk deposition samples were collected at Varna, located on the west coastline of the Black Sea. Both aerosol and deposition samples were analyzed for the main macronutrients, NO_3^-, NH_4^+, and PO_4^{3-}. The mean aerosol nitrate and ammonium concentrations were 7.1 ± 5.5 and 22.8 ± 17.8 nmol m^{-3}, respectively. The mean aerosol phosphate concentration was 0.69 ± 0.31 nmol m^{-3}, ranging from 0.21 to 2.36 nmol m^{-3}. Interestingly, phosphate concentration over Sinop was substantially higher than those of most Mediterranean sites. Comparison of the atmospheric and riverine inputs for the Black Sea revealed that atmospheric dissolved inorganic nitrogen (DIN) only ranged between 4% and 13%, while the atmospheric dissolved inorganic phosphorus (DIP) fluxes had significantly higher contributions with values ranging from 12% to 37%. The molar N:P ratios in atmospheric deposition for Sinop and Varna were 13 and 14, respectively, both of which were lower than the Redfield ratio (16). The atmospheric molar N:P ratios over the Black Sea were considerably lower than those reported for riverine fluxes (41) and the Mediterranean region (more than 200). The atmospheric P flux can sustain 0.5%–5.2% of the primary production, whereas the N flux can sustain 0.4%–4.8% of the primary production. The contribution of the atmospheric flux may enhance by 2.6 when the new production is considered.

1. Introduction

The Black Sea is an almost enclosed basin having limited interaction with the Mediterranean Sea through the Turkish Strait system. Its strong density stratification inhibits vertical mixing (Tuğrul et al. 1992; Özsoy and Ünlüata 1997). The Black Sea, being a dilution basin with a positive water balance because of excessive precipitation and riverine runoff compared to evaporation,

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Corresponding author address: M. Koçak, Institute of Marine Sciences, Middle East Technical University, P.O. Box 28, 33731 Erdemli-Mersin, Turkey.
E-mail: mkocak@ims.metu.edu.tr

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is the largest enclosed sea in the world [Tuncer et al. (1998) and references therein]. The euphotic zone in the Black Sea extends to a depth of 30 m and during stratified conditions (late spring, summer, and autumn) nitrate concentrations are found to be very low, with values less than 0.1 μM. The euphotic zone has a uniquely low N:P molar ratio of around 3, compared to the normal oceanic Redfield ratio of 16, suggesting that the primary productivity is nitrogen limited (Baştürk et al. 1997). These findings are also supported by nutrient enrichment experiments, with an increase in primary production after addition of nitrate and ammonium was observed (Yılmaz et al. 2006).

The annual discharges of nitrates to the Black Sea increased from 155 000 to 340 000 tons between the 1950s and early 1980s (Zaitsev and Mamaev 1997) leading to eutrophication and drastic change in the phytoplankton composition (Bodeanu 2002). The signs of recovery of Black Sea have been observed in the 2000s. For instance, pycnocline nitrogen concentration was around 5 μM in the preeutrophic period (1969–83). Afterward, it reached 7 μM with an increase of 40% in the eutrophic period (1984–95). Subsequently, its concentration dropped considerably and reached the value of about 5 μM in the posteutrophic period (1996–2008; Mikaelyan et al. 2013). Although a recovery of Black Sea ecosystem has been observed, it has been suggested that it cannot be considered as a major improvement of restoration of the ecosystem (Oğuz and Velikova 2010). The Black Sea (BS) is bordered by industrialized and semi-industrialized countries that act as a continuous source of manmade aerosols (Kubilay et al. 1995; Karakaş et al. 2004). The higher concentrations of manmade aerosols (such as sulfate, nitrate, Zn, and V) were found to be associated with the airflow from the European continent due to the industrialized nations (Hacısalihoğlu et al. 1992). On the other hand, the influence of the mineral dust transport from North Africa on the aerosol chemical composition has been shown, with significant increase in the crust-originated elements (such as Al and Fe) and decrease in the anthropic elements (Kubilay et al. 1995). The "diagnostic report" regarding improvements to the regular reporting process on the state of the Black Sea environment (Black Sea Commission 2010) states that nutrients and pollutants loads from diffuse sources including atmosphere is a priority issue to be attended. Furthermore, the role of the atmospheric inputs is expected to be a more important comparative to river since there is a decrease in nutrient loads (20% and 30% nitrogen and phosphorous decline, respectively, from 1988 to 1998; Ludwig et al. 2009) from rivers upon implementation of nutrients reduction measures by the Black Sea countries. However, the role of the atmosphere as an external source of nutrients to the BS still remains an open issue and only a couple of studies assessed atmospheric deposition of the macronutrients' nitrogen and/or phosphorus over the western Black Sea (Medinets and Medinets 2012; Varenik et al. 2015). The present study provides new long-term data of N and P from two different rural sites on the south and west coastline of the Black Sea, compares atmospheric with riverine inputs for the BS, and examines the variability of N:P ratio of atmospheric deposition with those of riverine inputs of the BS and atmospheric inputs in the eastern Mediterranean.

2. Materials and methods

a. Climatology of the Black Sea

The climatology of the Black Sea region is related to the large-scale atmospheric systems over Eurasia and the North Atlantic (Kosarev et al. 2008) that generally dominate the small-scale atmospheric phenomena (Oğuz et al. 2006). The climate in the western and the eastern Black Sea is different in terms of temperature and moisture. The dominant wind directions in the region are northerly, northeasterly, or northwesterly while southerly, southwesterly, or southeasterly winds occur less frequently. Wind conditions over the region show variability during the wintertime while more-uniform air flows are observed in the summer (Kosarev et al. 2008). Based on data collected from 1971 to 2000, Şensoy et al. (2008) reported that the Black Sea coast of Turkey received average rain ranging from 625 to 2200 mm yr^{-1} with a strong seasonal cycle. Todorova (2013) reported that the annual average precipitation for the 1961–90 climatic periods varied from 420 to 700 mm along the Bulgarian Black Sea coast. Although the majority of precipitation is observed in winter and autumn, substantial amounts of rain in spring and summer are also found. The temperature in the Black Sea region also shows a seasonal cycle with a uniform spatial distribution in summer and strong north–south gradient in winter (Özsoy and Ünlüata 1997). Moreover, winter in the eastern part of the Black Sea is warmer than in the western part (see supplementary Fig. S1 for Sinop).

b. Site description and sample collection

Two-sized aerosol (coarse: $10 > D_a > 2.5\,\mu$m; fine: $D_a < 2.5\,\mu$m, where D_a indicates aerosol diameter) and bulk (wet plus dry) deposition samples were collected from two different rural sites located on the south and west coastline of the Black Sea: (i) Sinop (two-sized aerosol samples; 42.02°N, 35.09°E) and (ii) Varna (atmospheric bulk samples; 43.18°N, 27.91°E), respectively

(Fig. 1). Aerosol samples were obtained from Sinop while bulk deposition samples were collected at Varna. Low-volume dichotomous stacked filter units (SFUs) were placed at Sinop University, Fisheries Faculty (at an altitude of ~13 m, ~200 m away from the sea). The sampling site directly looks out over the Black Sea from its north-southeast. The immediate vicinity of the sampling site is surrounded by forest trees and small villages. Sinop is a small city with a population of 100 000.

A Gent-type SFU sampler was utilized to collect atmospheric aerosol particles in two size classes, namely, coarse (polycarbonate filter, diameter: 47 mm, pore size: 8.0 μm) and fine (polycarbonate filter, diameter: 47 mm, pore size: 0.4 μm). The Gent-type SFU comprises a two-stage filter holder, cylindrical cassette holder with a 10-μm cut of point, protective shield, gas meter, and diaphragm pump. SFU acts as a two-stage sampler when sampler operates at a flow rate of 16–16.5 L min^{-1} (Hopke et al. 1997).

Bulk deposition samples were collected at Varna by using 4-L high-density polyethylene (HDPE) bottles. The bulk deposition bottles were placed on the roof of the Institute of Oceanology in Varna (300 m away from sea shore). Although there is no industrial activity around the sampling site, it is located close to a main road.

A polyethylene funnel (surface area = 113 cm^2) was attached to the top of the sampling bottles and a polyester mesh of 33 μm was used at the base of the funnel to prevent any possible contamination by plant debris or insects. A thymol solution [2.5 g $(200\,mL)^{-1}$] was added as biocide to bulk deposition collectors before commencing the sampling to prevent any biological activity. For more details on collections and sampling locations, see Koçak et al. (2015) and Theodosi et al. (2013).

The sampling at Sinop commenced in April 2009 and was completed in July 2010, whereas the sampling at Varna was started in May 2012 and ended in January 2014. Over the sampling periods, a total of 404 daily aerosol samples (coarse = 404; fine = 404) and 20 monthly bulk (wet plus dry) deposition samples were collected at Sinop and Varna, respectively.

c. *Analysis of samples*

For the determination of NO_3^-, PO_4^{3-}, and NH_4^+, one-quarter of the filter was extracted for 45 min in 10 mL of ultrapure water (18.2 Ωm) by sonic shaker and about 100 μL chloroform was added as a preservative to prevent biological activity after removing the filter. After collection, bulk deposition samples were immediately filtered through polycarbonate filters (Millipore, Isopore membrane, diameter: 47 mm, pore size: 0.4 μm). NO_3^- and PO_4^{3-} concentrations in samples were determined by applying a Dionex AS4A-SC separation column, sodium hydroxide eluent, and ASRS-I suppressor while NH_4^+ values were measured with a Dionex CS12-SC separation column, methane sulfonic acid eluent, and CSRS-I suppressor [for more details, see Bardouki et al. (2003)]. Our experiments showed that nitrite contributions were less than 3% of NO_3^- for aerosol samples.

The non-sea-salt contributions (nss) for Ca^{2+}, SO_4^{2-}, and K^+ were calculated from Na^+ concentration assuming a pure marine origin for Na^+ (Turekian 1976).

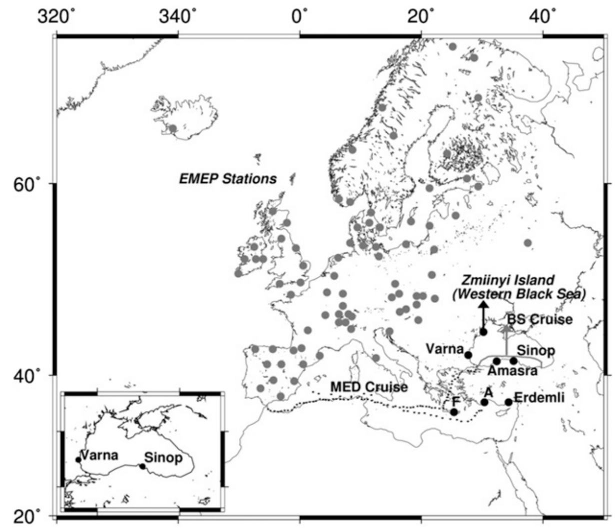

FIG. 1. Locations of sampling sites in the Black Sea, the eastern Mediterranean, and Europe. Gray dots show EMEP stations. Gray dashed line represents shipboard sampling in the Mediterranean (MED Cruise; Medinets 1996). Black dots represent other recording stations, including Antalya (labeled A; Güllü et al. 1998), Erdemli (Koçak et al. 2010), Finokalia (labled F; Kouvarakis et al. 2001), Amasra (Karakaş et al. 2004), and Zmiinyi Island (western Black Sea; Medinets and Medinets 2012); Sinop (daily aerosol sampling) and Varna (monthly bulk deposition sampling) are rural sites in the current study. The solid gray line denotes shipboard sampling in the Black Sea (BS Cruise; Kubilay et al. 1995).

3. Results and discussion

a. *Water-soluble nutrient concentrations in atmospheric samples*

1) WATER-SOLUBLE NUTRIENT CONCENTRATIONS IN AEROSOLS

Figures 2a–c illustrate the daily variability in the concentrations of the NO_3^-, nss-Ca^{2+}, NH_4^+, nss-SO_4^{2-}, PO_4^{3-}, and nss-K^+ between April 2009 and July 2010. The water-soluble nitrate, ammonium, and phosphate showed an order of magnitude change in their concentrations from day to day, resulting in high standard deviations (see Table 1). These water-soluble ions did not

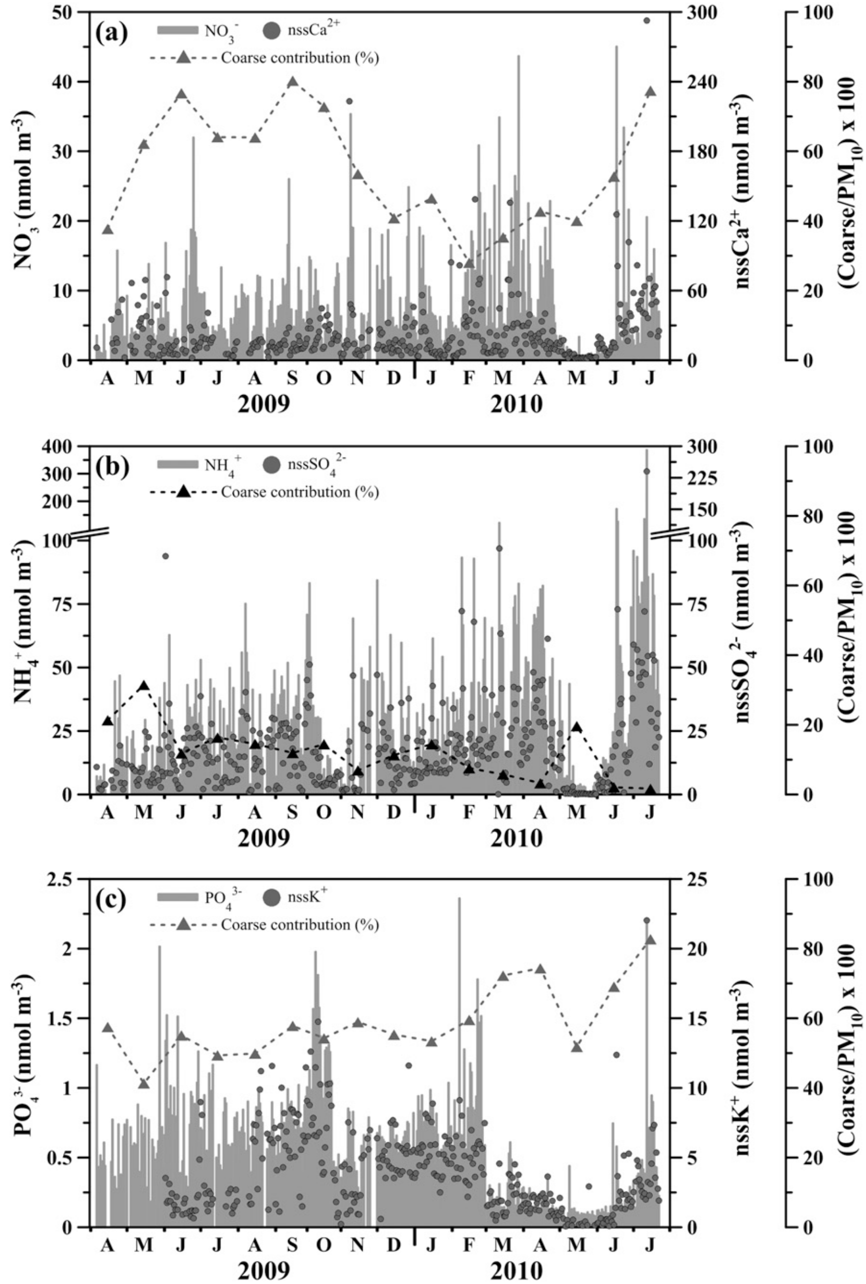

FIG. 2. Daily variability in the concentrations of (a) nitrate and nss-Ca^{2+}, (b) ammonium and nss-SO_4^{2-}, and (c) phosphate and nss-K^+ for PM_{10} between April 2009 and July 2010 along with monthly percentage coarse contribution.

denote a clear seasonality while they demonstrated complex temporal variability. The lowest concentrations of these species were found in May 2010. Recently, Koçak et al. (2015) have identified the distinct difference between May 2009 and 2010 by applying airmass trajectories, rain amount, and aerosol optical thickness (AOT). This noticeable difference has been ascribed to change in airflow (dominant flow from northwest short and northeast short sectors) and the amount of rain in the whole Black Sea, Mediterranean, and Europe. As it is well documented, the precipitation is the most efficient way to remove aerosols from the atmospheric compartment (Galloway et al. 1993; Güllü et al. 1998; Markaki et al. 2003; Koçak et al. 2010). It is most likely that the remarkable increase in the amount of the rain in the whole Black Sea, Mediterranean, and Europe lead to

TABLE 1. Statistical summary for (top) water-soluble aerosol nitrate, ammonium, and phosphate detected in aerosol samples obtained from Sinop between April 2009 and July 2010 and (bottom) seasonal variability in nitrate, ammonium, and phosphate measured in bulk samples for Varna from May 2012 to January 2014. The numbers in parentheses for bulk samples indicate the amount of rain.

	NO_3^-	NH_4^+	PO_4^{3-}
Aerosol (nmol m^{-3}) for Sinop			
Mean	7.1	22.8	0.69
Standard deviation	5.5	17.8	0.31
Minimum	0.5	0.6	0.21
Maximum	35.3	93.3	2.3
Seasonal bulk (mmol m^{-2}) for Varna			
Winter (242 mm)	4.0	2.3	0.62
Spring (387 mm)	5.8	1.3	0.48
Summer (87 mm)	4.0	1.6	0.43
Autumn (270 mm)	5.5	1.3	0.53

dramatic decrease in both anthropogenic and natural aerosols originated from these regions. On the other hand, comparing May 2009 and 2010, the transport from north not only decreased from 78% to 45% but they were associated with short fetch and mostly confined to the Black Sea in 2010. The low values observed in May 2010 also supported by low AOT (around 0.1) over the whole Black Sea region [for more details, see Koçak et al. (2015)]. In addition to May 2010, phosphate illustrated relatively lower values in March, April, and June (until 15 June). As can be clearly seen from Figs. 2a and 2c, phosphate concentrations covered with nss-Ca^{2+} (Fig. 2a) and nss-K^+. Water-soluble phosphate may arise from both natural and anthropogenic sources such as mineral dust, sea salt, primary biogenic particles, and combustion [Mahowald et al. (2009) and references therein]. In the eastern Mediterranean, for example, phosphate was found to be mainly associated with crustal material (Markaki et al. 2003). However, our study in Sinop has shown that phosphate was associated with biomass burning (nss-K^+), primary carbonaceous (EC), and crustal sources (nss-Ca^{2+}) (Koçak et al. 2015). For example, a strong correlation coefficient (r = 0.77) between PO_4^{3-} and nss-K^+ was found in autumn, suggesting their common origin (see Figs. S2 and S3). EC and nss-Ca^{2+} showed moderate correlation coefficients with PO_4^{3-} in winter and spring, respectively, denoting influence of primary carbonaceous and crustal particles on the observed levels of phosphate.

Although the winter in BS is characterized by low photochemistry and efficient removal of particles by wet scavenging, nitrate denoted elevated concentrations during this season. This might be ascribed to long-range transport and local anthropogenic activities such as residential heating and vehicular traffic (Tecer et al. 2008; Koçak et al. 2015). Elevated nitrate concentrations were found to be associated with airflow originating from continental Europe, central Anatolia (power generation through coal), Spain, Italy, Greece, and the industrialized Marmara region [see Koçak et al. (2015) for detailed discussion and trajectory analysis]. Ammonium is a crucial ion to neutralize the atmospheric acidic species through reaction between alkaline ammonia and nitric and sulfuric acids. Regression analysis showed that there was a statistically significant correlation between ammonium (nmol m^{-3}) and non-sea-salt sulfate (nmol m^{-3}) ($r = 0.95$, ammonium $= 0.8 \times$ sulfate $+ 0.3$). The correlation coefficient suggested that ammonium was mainly associated with non-sea-salt sulfate. Indeed, the slope of the regression denoted that ammonium was not sufficient to neutralize non-sea-salt sulfate completely leading to formation of NH_4HSO_4. In contrast to nitrate, the lowest values of nss-SO_4^{2-} were associated with airflow from Europe and this might be attributed to the reduction of sulfur emissions over Europe [Koçak et al. (2015) and references therein].

On average, nitrate and phosphate at Sinop were mainly associated with coarse fractions (~54% and 59%, respectively) while ammonium was dominated by fine aerosols (~90%). Coarse and fine contributions to the abovementioned nutrients denoted large variability from month to month. Coarse-mode contribution to nitrate (ammonium) ranged between 28% and 80% (between 2% and 38%). The fine-mode nitrate is thermally unstable and its abundance is determined by ammonium nitrate and gaseous nitric acid and ammonia, depending on temperature and relative humidity. Fine-mode nitrate abundance is also influenced by the ionic strength of the aerosol aqueous phase and the presence of alkaline particles such as sodium, potassium, and calcium (Metzger et al. 2006; Bian et al. 2014). The change in the relative contribution of coarse fraction for nitrate might be ascribed to reactions between alkaline sea-salt/crustal particles and nitrogen species such as HNO_3 and N_2O_5 (Mamane and Gottlieb 1992; Aymoz et al. 2004; Bardouki et al. 2003; Putaud et al. 2004). Indeed, 68% of the nitrate was found to be associated with sea-salt-originated sodium while the remaining nitrate might be attributed to forms such as $Ca(NO_3)_2$ and $Mg(NO_3)_2$ (Contini et al. 2014; Koçak et al. 2015).

Monthly contributions of coarse fraction for phosphate varied between 41% and 83%. As stated above, phosphate concentrations were influenced by both anthropogenic and natural (crustal) sources. To highlight the influence of the source onto phosphate distribution, two distinct events will be presented: (i) mineral dust dominated and (ii) pollution dominated. The mineral dust event (see Fig. S4) occurred on 12 July 2010 and characterized by nss-Ca^{2+} and nss-K^+ concentrations of 293 and 22 nmol m^{-3}, respectively. For this event, 78% of the observed PM_{10} mass (~135 $\mu g\,m^{-3}$) was found to be originated from crustal material. As expected, the corresponding PO_4^{3-} concentration reached the value of 2.18 nmol m^{-3} (the second highest in these data) and the contribution of the coarse fraction was 80%. The pollution dominated event (Fig. S5) occurred on 7 February 2010 with sea-salt and crustal contributions of 20% and 14%, respectively, denoting the anthropogenic nature of the event. The highest PO_4^{3-} concentration was found during this event with a value of 2.36 nmol m^{-3} with 89% of its concentration to be associated with fine particles.

The top half of Table 1a shows the statistical summary for water-soluble nitrate, ammonium, and phosphate detected in aerosol samples obtained in Sinop between April 2009 and July 2010 while the bottom half of Table 1b demonstrates the seasonal variability in nitrate, ammonium, and phosphate measured in bulk samples for Varna from May 2012 to January 2014. The water-soluble aerosol nitrate and ammonium ranged between 0.5 and 35.3 and between 0.6 and 93.3 nmol m^{-3} with arithmetic means and standard deviations of 7.1 ± 5.5 and 22.8 ± 17.8 nmol m^{-3}, respectively. The mean aerosol phosphate concentration was found to be 0.69 nmol m^{-3} with a standard deviation of 0.31 nmol m^{-3}, ranging from 0.21 to 2.36 nmol m^{-3}.

2) Water-soluble nutrient concentrations in bulk deposition

In bulk deposition samples, although the amount of rain (86 mm) in summer was at least 3 times less than those recorded during the remaining seasons, nitrate (4 mmol m^{-2}), ammonium (1.57 mmol m^{-2}), and phosphate (0.43 mmol m^{-2}) showed substantial bulk deposition in summer. For instance, 9% of the rain amount was observed in summer; however, the contribution of nitrate, ammonium, and phosphate to bulk fluxes was about 20%. The importance of dry deposition pathway for these species in conjunction with the very concentrated storm precipitations in summer could account for that behavior but, unfortunately, daily precipitation pattern is not available.

3) Spatial and temporal variability of water-soluble nutrients concentrations (aerosols and bulk deposition) in the Mediterranean and the Black Sea

Although the datasets from the literature cover different time periods and applied different sampling and analytical methodologies, comparisons between the sampling locations may present a good opportunity to explore the possible spatial variability. Aerosol nitrate and ammonium concentrations for different sampling sites are demonstrated in Figs. 3a and 3b. In general, observed nitrate values over the Mediterranean (Medinets 1996; Güllü et al. 1998; Kouvarakis et al. 2001) region were found to be higher than those detected over the Black Sea (Kubilay et al. 1995; Karakaş et al. 2004; Medinets and Medinets 2012) and continental Europe (EMEP stations). Broadly speaking, average nitrate concentration over Sinop (southern Black Sea; 7.1 nmol m^{-3}) was comparable to those reported for eastern Europe and Scandinavian countries, whereas

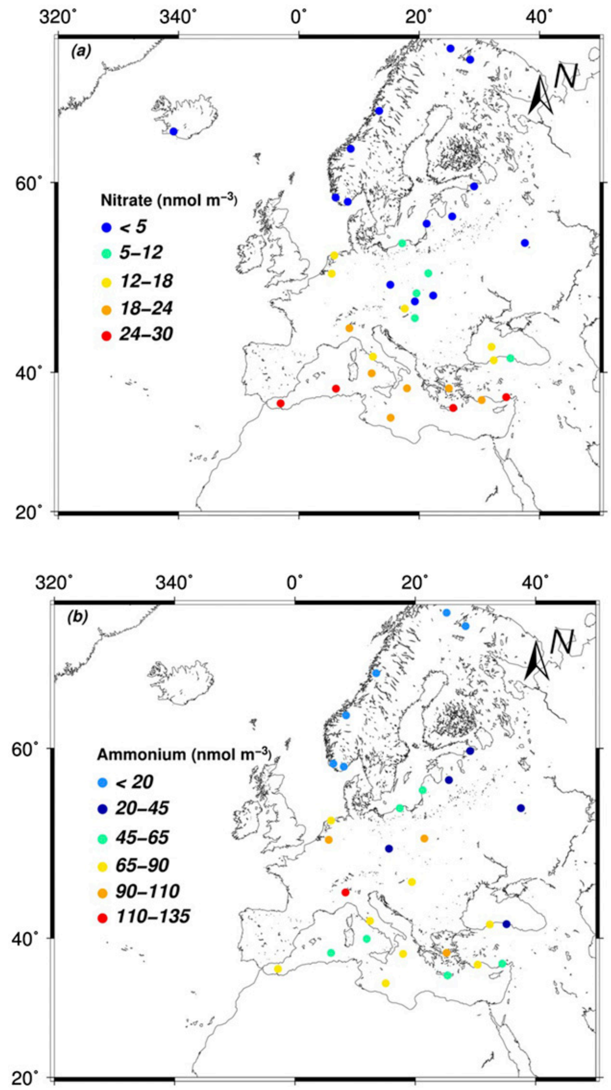

FIG. 3 . Spatial variation of mean water-soluble (a) nitrate and (b) ammonium aerosol (nmol m^{-3}). Measurements have been carried out at EMEP sites, near the Black Sea (Sinop), via shipboard measurements (Medinets 1996), in the eastern Mediterranean (Finokalia, Kouvarakis et al. 2001; Erdemli, Koçak et al. 2007; Antalya, Güllü et al. 1998), and in the North Atlantic Ocean (Barbados, Bermuda, and Tenerife; Savoie et al. 2002).

it was at least 2 times lower than those observed for Mediterranean sites. Average ammonium concentrations over the southern Black Sea (Sinop; 22.8 nmol m^{-3}) and northeastern Europe were found to be about 2–4 times smaller than those observed over the Mediterranean region. However, values over the Mediterranean were comparable with concentrations determined over western Europe. Aforementioned differences between the Black Sea and the Mediterranean might be attributed to the prevailing meteorological conditions, the latter being more dry and having more solar influx compared to the former region (Mihalopoulos et al. 1997). Nitrate and ammonium concentrations at Sinop were at least 2 times lower than those reported for Amasra ($NO_3^- \approx$ 14 nmol m^{-3}, $NH_4^+ \approx$ 78 nmol m^{-3}; Karakaş et al. 2004) and for shipboard measurements on the Black Sea ($NO_3^- + NO_2^- \approx$ 16 nmol m^{-3}; Kubilay et al. 1995). This dramatic decrease from the 1990s to the 2010s might mainly be attributed to reduction in fertilizer usage and NO_x reduction. The Black Sea Commission (2010) stated that the reduction was mainly due to the implementation of the Nitrate Directive. Not only the reduction in fertilizer usage but also the abatement in NO_x emissions in the region (EMEP 2013) may also contribute to the considerable decline from 1990 to 2010.

Figure 4 demonstrates the phosphate (PO_4^{3-}) values in aerosols observed at different sites situated at the Mediterranean and the southern Black Sea (Sinop). Interestingly, the mean phosphate concentration at Sinop (0.69 nmol m^{-3}) was comparable to those at Tel Shikmona (0.80 nmol m^{-3}; Herut et al. 2002; 0.72 nmol m^{-3}; Carbo et al. 2005). The observed concentration was 1.5 and 1.9 times larger than those reported for Erdemli and Eilat, respectively, while it was 7.4 times higher than the value detected at Finokalia. Based on phosphate-level comparisons and the previous discussion on phosphorus origin, biomass burning sources in the area around BS could account for the relatively high phosphate values over the Black Sea region, although it receives somewhat more precipitation than that of the Mediterranean. Indeed, Sciare et al. (2008) clearly highlighted the importance of biomass burning in the BS area all year long with peaks in spring and summer.

b. *Water-soluble nutrient deposition over the Black Sea*

1) DRY DEPOSITION OF NUTRIENT SPECIES

The settling velocities for the nutrient species were calculated by using an approach adopted by Spokes et al. (2001), after Ottley and Harrison (1993). Thereby, the settling velocities for each species can be estimated as follows: $V_d = (C_c \times 2.0) + (C_f \times 0.1)$, where C_c and C_f are the relative contribution of coarse and fine modes and 2.0 and 0.1 cm s^{-1} are deposition velocities suggested by Duce et al. (1991) for coarse and fine aerosols, respectively. For instance, for phosphate a mean settling velocity of 1.22 cm s^{-1} was calculated using the above equation [$(0.59 \times 2.0) + (0.41 \times 0.1)$].

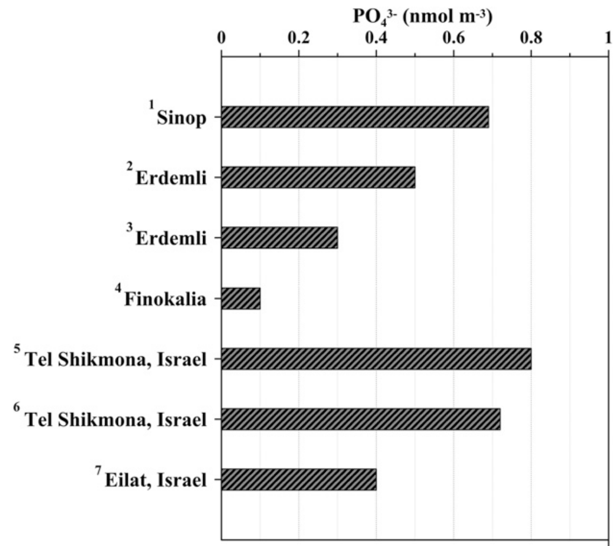

FIG. 4. Spatial variation of phosphate aerosol (nmol m^{-3}) from 1) the current study, 2) Koçak et al. (2010), 3) Markaki et al. (2003), 4) Markaki et al. (2003), 5) Herut et al. (2002), 6) Carbo et al. (2005), and 7) Chen et al. (2007).

On average, the settling velocities of 1.22, 1.14, and 0.19 cm s^{-1} were thus calculated for phosphate, nitrate, and ammonium, respectively. However, it should be noted that monthly settling velocities for these nutrient species might demonstrate important variability driven by the occurrence of pollution or mineral dust events which in turn influence their coarse-to-fine ratio (see section 3a). Monthly settling velocities for nitrate (phosphate) ranged between 0.63 and 1.62 (0.88 and 1.67) cm s^{-1}. Relatively larger variability was observed for ammonium, with settling velocities varying from 0.13 to 0.70 cm s^{-1}. Based on our knowledge, there are no reported V_d values for these nutrient species in the literature for the Black Sea. The mean setting velocities of phosphate, nitrate, and ammonium in the eastern Mediterranean and the present study are illustrated in Fig. 5. Settling velocities for phosphate, nitrate, and ammonium indicate small variability from region to region with values in the ranges of 1.2–2, 1–2, and 0.1–0.6 cm s^{-1} respectively. On the contrary, the settling velocities of phosphate can be dramatically influenced by pollution or mineral dust events. For example, on 7 February and 12 July 2010 (see section 3a), coarse contributions were 80% and 11%. Corresponding settling velocities were 0.31 and 1.62 cm s^{-1}, denoting the variability of the settling velocities in terms of pollution- and mineral dust–dominated events. As can be deduced from the Fig. 5, the settling velocity of phosphate at Sinop was at least 1.4 times lower than those applied in the eastern Mediterranean (Herut et al. 2002; Markaki et al. 2003; Carbo et al. 2005; Chen et al. 2007; Koçak et al. 2010). Nitrate settling velocity at Sinop was comparable to those observed for Tel Shikmona (Herut et al. 2002) and Eilat (Chen et al. 2007), whereas it was about 1.6 times smaller than those of Erdemli (Koçak et al. 2010) and Finokalia (Markaki et al. 2003). Except for Tel Shikmona (0.6 was applied without using experimental data), the settling velocity of ammonium was comparable to those reported for the eastern Mediterranean.

2) Estimated wet deposition of nutrient species

The scavenging ratios are useful tools to assess the amount of wet deposition from dry deposition in the absence of precipitation data (Galloway et al. 1993). This approach was successfully applied by Duce et al. (1991) to estimate the amount of atmospheric inputs of substances—such as nitrogen, phosphorous, and iron—onto the surface waters of the world's oceans. Therefore, the scavenging ratios were used for calculating the wet deposition of macronutrients. Since the scientific information about the concentrations of nitrate, ammonium, and phosphate in precipitation and aerosol over the Black Sea is sparse, the approximate values were chosen by using the scavenging ratios obtained from Erdemli (Koçak et al. 2010) and Finokalia (Markaki et al. 2003) sites. The scavenging ratios of 1170 (both Erdemli and Finokalia = 1170), 1000 (Erdemli ≈ 700, Finokalia = 1300), and 600 (Erdemli ≈ 400, Finokalia = 800) were applied by taking mean scavenging ratios from Erdemli and Finokalia to calculate the wet depositions of phosphate, nitrate, and ammonium for Sinop, respectively.

3) Bulk deposition of nutrient species

Table 2 illustrates dry, wet, and total atmospheric depositions (mmol m^{-2} yr^{-1}) of nutrients for different sites in the Black Sea and the eastern Mediterranean. As can be clearly deduced from the table, the dry deposition of NO_3^-, NH_4^+ [NO_3^- + NH_4^+ = dissolved inorganic nitrogen (DIN)], and PO_4^{3-} [dissolved inorganic phosphorous (DIP)] were found to be 2.6, 1.4, and 0.27 mmol m^{-2} yr^{-1}, respectively. Considering bulk deposition fluxes of nitrate, ammonium, and phosphate, the difference between 2012 and 2013 was found to be comparable, the previous year being almost 20% higher than the later year. The lowest atmospheric dry DIN deposition was found at Sinop (southern Black Sea). For instance, the observed deposition was 3 times lower than that reported for Finokalia while it was 6.3 and 7.8 times less than those observed at Erdemli and Tel Shikmona.

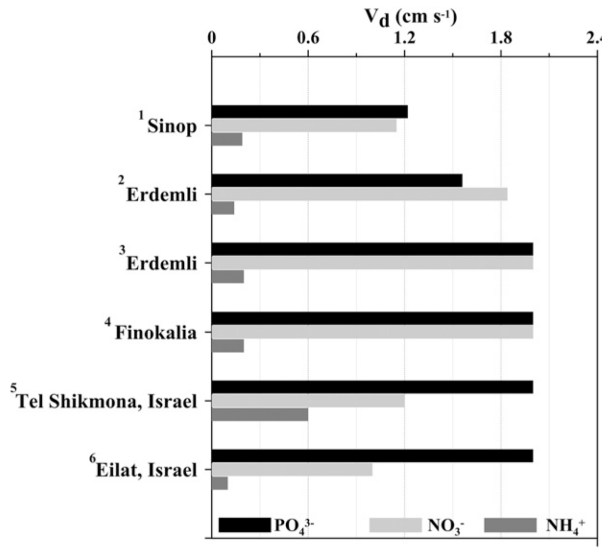

FIG. 5. Dry deposition velocities (cm s^{-1}) of the water-soluble nitrate, ammonium, and phosphate from the Sinop dataset and the literature for different Mediterranean regions: 1) current study, 2) Koçak et al. (2010), 3) Markaki et al. (2003), 4) Markaki et al. (2003), 5) Herut et al. (2002), and 6) Chen et al. (2007).

4) Spatial variation of atmospheric deposition of water-soluble nutrients in the Mediterranean and the Black Sea

Except for the western Black Sea (Zmiinyi Island), atmospheric DIN deposition in BS was lower than those reported for the eastern Mediterranean. Calculated DIN depositions for Varna and Sinop were respectively 1.3 and 4.6 times lower than values observed at Finokalia and 2.6–9.3 times lower compared to Erdemli and Tel Shikmona. The majority of the DIN over eastern Mediterranean sites was associated with NO_3^-, accounting at least 60%. Similarly, DIN mainly originated from nitrate (65%) at Sinop and Varna. On the contrary, DIN was dominated by NH_4^+ (65%) in the western Black Sea (Zmiinyi Island).

On the other hand, the atmospheric deposition of phosphate over the Black Sea was found to be relatively higher than those observed in the eastern Mediterranean. The atmospheric DIP depositions for Sinop and Varna were at least a factor of 4 higher than that of Finokalia. On the one hand, atmospheric DIP deposition at Sinop was about a factor of 2 lower than

TABLE 2. Atmospheric depositions for NH_4^+, NO_3^-, DIP, and DIN for the present study and the literature for the Black Sea and eastern Mediterranean.

	NH_4^+	NO_3^-	DIP^-	DIN	Reference
Dry deposition (mmol m^{-2} yr^{-1})					
Sinop (2009/10)	1.4	2.6	0.27	4.0	This study
Wet deposition (mmol m^{-2} yr^{-1})					
Sinop	0.7[a]	2.2[a]	0.27[a]	2.9[a]	This study
Western Black Sea (2004–10)	13.0	10.2	0.97	23.2	Medinets and Medinets (2012)
Atmospheric deposition (mmol m^{-2} yr^{-1})					
Sinop (2009/10)[b]	2.1	4.8	0.54	6.9	This study
Varna (2012/13)[c]	7.8	16.5	1.66	24.3	This study
Varna (2012)[c]	9.2	17.2	2.02	26.4	This study
Varna (2013)[c]	6.6	14.8	1.36	21.4	This study
Western Black Sea (2004–10)	31.9	17.5	3.13	49.4	Medinets and Medinets (2012)
Black Sea (mmol m^{-2} yr^{-1})					
Riverine	—	—	4.5	183	Ludwig et al. (2009)
Eastern Mediterranean					
Dry deposition (mmol m^{-2} yr^{-1})					
Erdemli (1999–2007)	3	22	0.22	25	Koçak et al. (2010)
Finokalia (1999–2000)	2	10	0.08	12	Markaki et al. (2003)
Tel Shikmona (1996–99)	11	20	0.51	31	Herut et al. (2002)
Wet deposition (mmol m^{-2} yr^{-1})					
Erdemli (1999–2007)	23	22	0.92	45	Koçak et al. (2010)
Heraklion (1999–2000)	11	9	0.07	20	Markaki et al. (2003)
Tel Shikmona (1996–98)	13	20	0.30	33	Herut et al. (1999)
Atmospheric deposition (mmol m^{-2} yr^{-1})					
Erdemli	26	44	1.14	70	Koçak et al. (2010)
Finokalia	13	19	0.15	32	Markaki et al. (2003)
Tel Shikmona	24	40	0.81	64	Herut et al. (1999, 2002)

[a] Wet deposition calculated from scavenging ratios and aerosol nutrient concentrations.
[b] Estimated deposition (from calculated dry and wet deposition).
[c] Bulk deposition.

depositions reported for Erdemli and Tel Shikmona; on the other hand, the DIP deposition over Varna was almost 2 times higher than those of two eastern Mediterranean sites. DIN and DIP deposition over the Black Sea atmosphere denotes important spatial variability. DIN and DIP depositions at Sinop were found to be at least 3 times less than those observed for Varna, while DIN and DIP depositions for Varna were found almost 2 times lower than those of Zmiinyi Island.

Comparison of the atmospheric and riverine inputs for the Black Sea suggested that DIN fluxes to the Black Sea were dominated by the riverine runoff with a mean flux around of 183 mmol m^{-2} yr^{-1}. If we consider the western Black Sea (Zmiinyi Island), the atmospheric contribution would be 27% of the riverine runoff, while DIN contributions from the current study (Sinop and Varna) would only be around 4% and 13% of the riverine runoff, respectively. On the contrary, the atmospheric phosphorus fluxes over Sinop and Varna had sizeable contributions with values ranging from 12% to 37% of the riverine runoff, respectively; that is, up to 10 times more important, in terms of percentage, compared to DIN fluxes.

c. Implications of the deposition of water-soluble nutrients for the Black Sea

The molar atmospheric DIN:DIP ratios from the present study and the literature for the Black Sea (riverine: Ludwig et al. 2009; western Black Sea, Zmiinyi Island: Medinets and Medinets 2012) and the Mediterranean (Markaki et al. 2010) are demonstrated in Fig. 6. The molar DIN:DIP ratios over the Mediterranean ranged from 49 to 286, suggesting severe P deficiency relative to nitrogen in atmospheric deposition. On the other hand, the atmospheric molar ratios of dissolved inorganic nitrogen to dissolved inorganic phosphorous did not reveal substantial variability over the Black Sea. The observed ratios ranged from 13 to 16. The lowest ratios were determined at Sinop (molar DIN:DIP ≈ 13) and Varna (molar DIN:DIP ≈ 14) while the highest ratio was calculated from the values reported by Medinets and Medinets (2012) for the western Black Sea

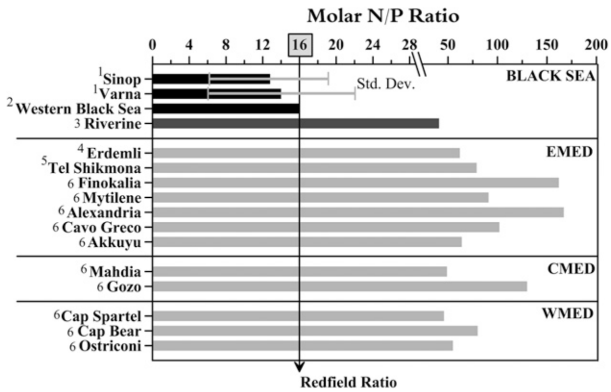

FIG. 6. DIN:DIP molar ratios for the present study and from the literature for the Black Sea: 1) current study, 2) Medinets and Medinets (2012), and 3) Ludwig et al. (2009); and for the Mediterranean Sea: 4) Koçak et al. (2010), 5) Herut et al. (1999, 2002), and 6) Markaki et al. (2010).

(Zmiinyi Island, molar DIN:DIP ~ 16). The latter ratio was found to be identical to the value of normal oceanic Redfield ratio (16), whereas the first two ratios were found to be lower than that of the Redfield ratio. The atmospheric DIN:DIP ratios over the Black Sea were found to be significantly lower (3–20 times) than those reported for the Mediterranean region. Furthermore, these atmospheric DIN:DIP ratios were also considerably smaller than that of riverine DIN:DIP ratio (~41) derived from Ludwig et al. (2009). Therefore, it may be argued that the riverine input was deficient in phosphorus (enhanced in nitrogen). In contrast to riverine runoff, the atmospheric deposition of dissolved inorganic nutrients, with the exception of Zmiinyi Island, appeared to be deficient in nitrogen. Although the excess amount of nitrogen is supplied to the Black Sea by riverine runoff, its euphotic zone has an exclusively low molar DIN:DIP ratio (~3), denoting that the primary production is nitrogen limited (Baştürk et al. 1997). Taking into account the values presented in Table 2 (for Sinop and Varna), 1.5–4.5 μmol m^{-2} day^{-1} of DIP and 18.9–66.6 μmol m^{-2} day^{-1} of DIN were calculated in the study area. If one assumes that all DIP and DIN are bioavailable to primary producers for new production and if the Redfield C:P and C:N ratios of 106/1 and 106/16 are applied, it would be estimated that atmospheric P and N depositions can support new production from 1.9 to 5.7 and from 1.5 to 5.4 mg C m^{-2} day^{-1}, respectively. Primary production in the western Black Sea, the central western gyre, the northwestern and southern shelves/shelf break regions, and the Sakarya Canyon region were found to be around 112–355, 112–145, 258–335, and 603 mg C m^{-2} day^{-1}, respectively (Yılmaz et al. 1997, 2006). The northwestern and southern shelves/shelf break regions (Danube, Dnestr, and Dnper Rivers) and the Sakarya Canyon (Sakarya River) region are considerably influenced by riverine inputs. Considering the regions influenced by riverine inputs, the atmospheric P and N fluxes can sustain less than 1% of the primary production. On the other hand, P and N fluxes can sustain up to 5% of the primary production reported for open waters (central western gyre). It has been noted that the *f* ratio, defined as ratio between new and total production, may vary from 0.25 to 0.46 in the Black Sea, with a mean of 0.38 (McCarthy et al. 2007). If the *f* ratio of 0.38 is applied, the contribution of the atmospheric fluxes to the new production would increase by a factor of about 2.6 compared to the contribution of total primary production.

4. Conclusions and recommendations

The present study provided the first comprehensive information on the importance of atmospheric deposition of DIN and DIP in the BS. Average aerosol nitrate and ammonium concentrations over the Sinop were found to be at least 2 times lower than those observed for Mediterranean region, likely owing to the prevailing meteorological conditions and especially rain. Interestingly, phosphate concentration at Sinop was substantially higher than those of the Mediterranean sites (except Tel Shikmona), highlighting the important role of biomass burning in the BS region.

NO_3^- deposition derived from Sinop and Varna accounted for ~65% of DIN. Compared to riverine runoff, the atmospheric DIN contributions derived from the current study for Sinop and Varna would only be around 4% and 13%, respectively, whereas the atmospheric DIP fluxes over Sinop and Varna had sizeable contributions with values ranging from 12% to 37%, respectively.

The atmospheric molar DIN:DIP ratios (ranging from 13 to 16) over the Black Sea were also found to be distinctively lower than those reported for riverine fluxes (~41 for Black Sea) and the Mediterranean region (more than 200). Taking into consideration the atmospheric molar N:P ratio, it is proposed that unbalanced nitrogen and phosphorus input may result in even more nitrogen deficiency in the Black Sea, particularly in open waters, in the future. Atmospheric N and P deposition can sustain up to 5% of the primary production reported for open BS waters and when an *f* ratio of 0.38 is applied for the BS, the contribution of the atmospheric fluxes to the new production of the BS would reach up to 13%.

Given the importance of atmospheric deposition in the Black Sea, apart from the long-term continuation to examine for possible trends, there is a clear need to (i) assess the importance of atmospheric deposition of the macronutrients nitrogen and phosphorous, including their inorganic and organic forms, and (ii) determine the soluble fractions of micronutrients and trace elements such as Fe, Mn, Zn, Cu, Cd, and Pb taking into account their antagonistic behaviors.

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