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Variability of atmospheric deposition of dissolved nitrogen and phosphorus in the Mediterranean and possible link to the anomalous seawater N/P ratio

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ABSTRACT

Atmospheric deposition of Total Dissolved Nitrogen (TDN) and Phosphorus (TDP) was studied in bulk deposition samples simultaneously collected at several locations around the Mediterranean, during one year period (June 2001–May 2002). Dissolved Inorganic Phosphorus (DIP) and Nitrogen (DIN) atmospheric deposition fluxes ranged from 243 to 608 μmol $m^{-2}y^{-1}$ and from 18.1 to 47.7 mmol $m^{-2}y^{-1}$ respectively, presenting an important spatial variability within the basin.

Wet deposition was found to be the main factor controlling DIN deposition in the Mediterranean. The amount of DIN deposited during the wet period was 2–8 times higher than that deposited during the dry season. It was estimated that about 65% of the total DIP was deposited during the wet period. Dust events as well as regional biomass burning were also found to contribute significantly to the DIP deposition. A significant percentage of the TDN and TDP of the samples were in organic form with Dissolved Organic Phosphorus (DOP) and Nitrogen (DON) accounting for 38% and 32% of TDP and TDN respectively.

DIN/DIP molar ratio of the bulk deposition varied depending on the location of the sampling site in the Mediterranean basin, presenting an increasing trend from the Western (60) to the Eastern Mediterranean basin (105). This variation is similar to that observed in the seawater column, indicating an important link between atmospheric deposition and seawater productivity of the area.

1. Introduction

The Mediterranean Sea is known to be among the most oligotrophic areas in the world (Redfield et al., 1963; Sournia, 1973; Bethoux et al., 1998). Especially the Eastern basin is considered to be an ultra oligotrophic system as compared to the Western basin (Krom et al., 2003). Studies performed in the area proved that it is not only nutrient depleted but it is also highly deprived in P relative to N (Krom et al., 2005). An unexpectedly high N/P molar ratio has been observed in Mediterranean deep water (20:1–28:1), significantly higher than the normal oceanic Redfield ratio (16:1) (Mc Gill, 1965, 1969; Coste and Minas, 1967; Coste et al., 1988; Berland et al., 1980; Krom et al., 1991) and displaying an eastward increasing trend from about 20:1–24:1 in the Western to 28:1 in the Eastern Mediterranean.

The atmospheric deposition of nitrogen and to a lesser extent of phosphorus has been recognized as significant in the Mediterranean region. The atmospheric nitrogen flux to the whole Mediterranean Sea is equal to the riverine input (Martin et al., 1989; Loÿe-Pilot et al., 1990a,b; UNEP/WMO, 1997). Krom et al. (2004) presented a detailed nutrient budget for the Eastern Mediterranean where atmospheric inputs of DIN and DIP account for 61% and 28% of the total budget of N and P respectively.

As a consequence, the atmospheric deposition is expected to strongly influence the marine P and N cycles and the trophic status of the Mediterranean Sea (Migon et al., 1989; Loÿe-Pilot et al., 1990a,b; Bergametti et al., 1992; Guerzoni et al., 1999; Herut et al., 1999, 2002; Kouvarakis et al., 2001; Ridame and Guieu, 2002; Markaki et al., 2003). The atmospheric input to the Mediterranean Sea displays a high N/P ratio for dissolved or soluble inorganic forms (Migon et al., 1989; Herut and Krom, 1996; Ridame et al., 2003), which could be one possible reason of the high N/P ratio in deep sea waters (Guerzoni et al., 1999; Kouvarakis et al., 2001; Ridame et al., 2003; Krom et al., 2004). This high N/P ratio in the Eastern Mediterranean could be retained within the system by the absence of significant denitrification in either the sediments or intermediate water (Krom et al., 2004). The above observations emphasize the need for a better characterisation of the atmospheric deposition of nutrients such as N and P, in the marine Mediterranean ecosystem.

Despite the importance of atmospheric deposition in biogeochemical cycling of N and P in the Mediterranean, no simultaneous data from various locations around the Mediterranean have been collected so far. In addition, the potential role of organic forms of N and P has been not considered. Especially for DON (Dissolved Organic Nitrogen) recent estimates (Spokes et al., 2000; Cornell et al., 2003; Mace et al.,

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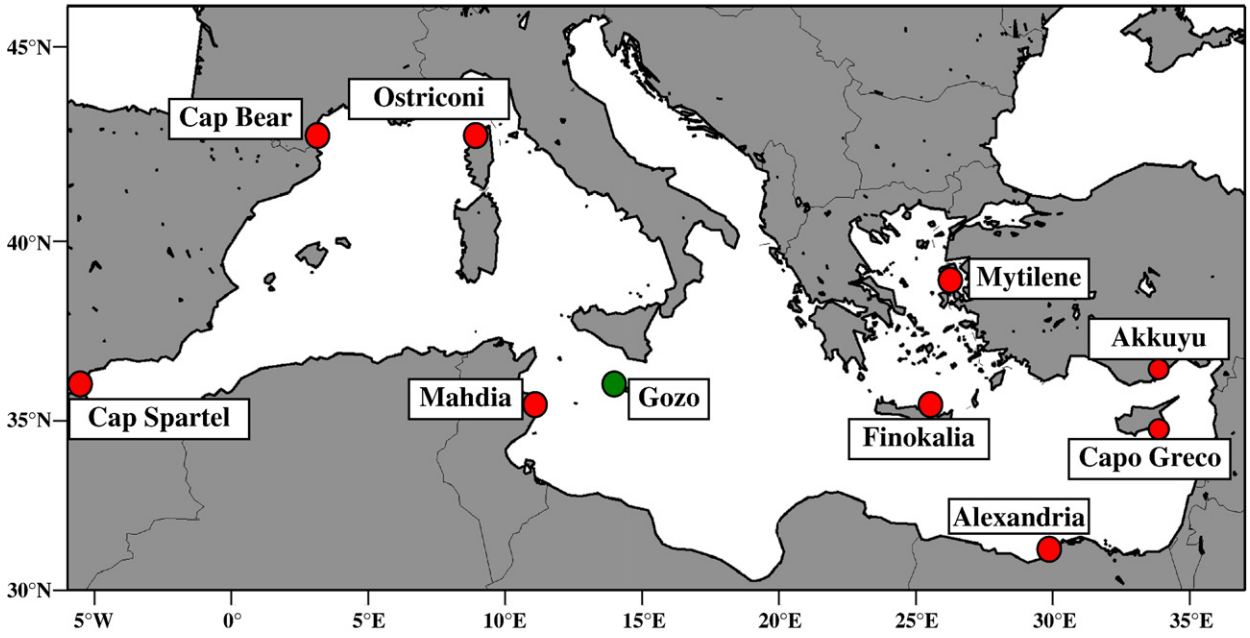

Fig. 1. Location of ADIOS sampling sites in the Mediterranean.

2003) reported that it can account for 20 to 60% of the total DIN flux. Finally no effort has been made to link the increasing seawater N/P ratio from the west to the east with the atmospheric deposition.

This work tries to fill these gaps by reporting results on the temporal and spatial variability of the atmospheric deposition of Total Dissolved Nitrogen (TDN) and Phosphorus (TDP) based on data simultaneously collected at several locations around the Mediterranean, during one year period.

2. Sampling and analysis

2.1. Sampling sites

Ten sampling stations were implemented in the frame of the ADIOS EU funded project along the northern and southern coasts of the Mediterranean Sea in order to take into account the main sources and deposition regimes over the Mediterranean basin (Fig. 1) (Guieu et al., 2010-this issue). The selected sites were chosen to

Table 1
Main characteristics of the ADIOS sampling sites.

	Station coordinates	Altitude	Geological substrate	Vegetation	Local soil conditions	Vicinity of human settlements	Distance to the sea
Morocco Cap Spartel	35°47N . 05°54 W	326 m	Silicic sandstones	Low shrubland	Soil covered by vegetation	5 km NW of the town of Tangier	1500 m
France Cap Bear	43°31N . 03°09 E	100 m	Gneiss	Low shrubland and bare rocks	Soil covered by vegetation and rocks	20 km from the town of Perpignan	500 m
France Corsica Ostriconi	42°40N . 09°04 E	60 m	Granite	Low shrubland and bare rocks	Soil covered by vegetation and rocks	A few houses, 500 m	800 m
Tunisia Mahdia	35°25N . 11°02 E	10 m	Sands and gravels	Olive plantations and low vegetation	Building terrace	2 km from the town of Mahdia	200 m
Malta Gozo	36°04N . 14°13 E	160 m	Limestone sand	Low shrubland and rocks	Soil covered by vegetation and rocks	Small villages to the South	400 m
Greece Crete Finokalia	35°20N . 25°40 E	130 m	Limestones and marls	Low shrubland	Soil covered by vegetation	Small village at 2 km	250 m
Greece Lesbos Mytilene	39°02N . 26°36 E	100 m	Serpentinites and peridotites	Low shrubland	Soil covered by vegetation	10 km from the town of Mytilene	1000 m
Egypt Alexandria	31°12N . 29°53 E	12 m	Sands and alluvial fans	No	Building terrace	Upwind of the town of Alexandria by N winds	100 m
Cyprus Cavo Greco	34°57N . 34°05 E	40 m	Limestones	Few vegetation	Hard rocks	Broadcast station at 200 m No village in the vicinity	800 m
Turkey Akkuyu	36°08N . 33°32 E	50 m	Limestones and marls	Shrubland	Soil covered by vegetation	A few houses at 1 km No village in the vicinity	300 m

be as far as possible from any local and regional influences, so that the results could be considered representative of long range transport and open sea deposition. The stations were located in the Eastern Mediterranean basin: Akkuyu (Turkey), Alexandria (Egypt), Mytilene (Lesvos-Greece), Finokalia (Crete, Greece), Cavo Greco (Cyprus), in the Central Mediterranean basin: Gozo (Malta), Mahdia (Tunisie) and in the Western Mediterranean basin: Ostriconi (Corsica), Cap Spartel (Tanger-Morocco) and Cap Bear (Perpignan-France). Details about the characteristics of the sampling sites are reported in Table 1. In order to check the representativity of the ADIOS year observations and the validity of the sampling methodology, extension of sampling for an additional year, as well as a complete survey of the different forms of atmospheric deposition have been conducted at two island stations located one in the Eastern Mediterranean (Crete) and the other one in the Western basin (Corsica). Both islands, Crete and Corsica, were chosen due to their central position in the Mediterranean basin, relatively far from Saharan and anthropogenic sources. Therefore, the data from these sites could be to some extent considered as representative of the open Mediterranean Sea.

2.2. Sample collection

The sampling device used to collect the bulk samples (wet and dry deposition simultaneously collected) was made of a 4 l Nalgene high density polyethylene (HDPE) bottle, with a polyethylene funnel (surface = 113 cm^2) attached on the top; a polyester mesh (mesh-opening of 33 μm) at the base of the funnel prevents from contamination of the sample by plant debris or insects. This type of sampler will be referred in the following as the ADIOS collector. All collectors were prepared and cleaned in the Unité Biogéochimie Marine/Ecole Normale Supérieure laboratory (UBM-ENS) in Montrouge before being sent to the field where they remained open for about a month. It is known that microbial processes in wet and dry deposition sampled for chemical analysis, but not preserved from biological action, cause transformation of significant fractions of available nutrients from inorganic into organic form (Ayers et al., 2003). Previous published work (Ayers et al., 1998, 2003) as well as tests performed with natural rainwater samples in our laboratory showed that addition of thymol (at least 0.6 g l^{-1}) prevents from losses of inorganic nutrients (namely N and P) in the deposition samples. Thymol solution (200 ml − 2.5 g l^{-1}) has been thus added to all collectors prior to deployment to prevent any biological activity and consumption of N and P.

At Finokalia a second bulk deposition collector with a collection surface covered by glass beads (Kouvarakis et al., 2001) has been used for comparison with the ADIOS collector deployed at the 10 sites.

The ADIOS sampling period covers one year, from June 2001 to May 2002, except for the site of Gozo (Malta) where the sampling took place from March 2002 to February 2003. At each site almost 12 monthly samples were collected during the sampling year, except for the Alexandria station where the sampling was discontinuous and the sampling station moved during the experimental year. Thus even though the data of Alexandria are reported, they have been excluded from the calculations of the mean deposition values of the Eastern Mediterranean basin.

2.3. Sample treatment and analysis

Immediately after collection all samples, (except for those from Crete) were sent back to the central ADIOS laboratory, (UBM/ENS, Montrouge) where they were filtrated through 0.4 μm Nuclepore© polycarbonate filters. One aliquot of the filtrate was used for pH determination, and another one was immediately sent to the Environmental Chemical Processes Laboratory in Crete (ECPL) for analysis of the main anions (chloride, nitrate, phosphate and sulfate) and cations (sodium, potassium, calcium, magnesium and ammonium). The samples were stored at 4 C until analysis (performed within a month). A Dionex AS4A-SC column with ASRS-ULTRA-II suppressor in autosuppression mode of operation was used for the analysis of anions. For cations a CS12 column was used with a CSRS-ULTRA suppressor. The reproducibility of the measurements defined as standard deviation of five consecutive analysis was better than 2%, and the detection limits defined as 3 times the standard deviation of the blank were 0.5 μM for NH_4^+, 0.7 μM for PO_4^{-3} and 0.15 μM for NO_3^-. Hereafter, the sum of dissolved nitrate and ammonium, and the dissolved inorganic phosphorus will be referred to as DIN and DIP respectively.

To obtain a lower detection limit Dissolved Inorganic Phosphorus (DIP) was also determined spectrophotometrically using the Ascorbic Acid Method, (APHA, AWWA, WEF, 2000, Standard Methods for the Examination of Water and Wastewater, 20th Edition). This specific method was chosen because among its main assets a blank can be measured for every sample, avoiding colour interferences (due to thymol addition). The detection limit defined as 3 times the standard deviation of the blank was 0.3 μM. The Ascorbic Acid method has been compared successfully to Ion Chromatography: slope $P_{IC}/P_{colorimetry} = 1.01$ ($r^2 = 0.97$, $n = 83$). Standard deviation of triplicate analysis for the Ascorbic Acid method was better than 3% and dissolved inorganic phosphorus recovery identified from standard addition tests on real samples ($n = 6$) was 100% ± 3% (1 SD).

In order to complete elemental analysis, total dissolved phosphorus (TDP) and total dissolved nitrogen (TDN) were also measured after the digestion of the samples according to the Persulfate Digestion Method (APHA, AWWA, WEF, 2000, Standard Methods for the Examination of Water and Wastewater, 20th Edition). Each sample was analysed for TDP in triplicate and the reproducibility was better than 10% (1SD). Standard addition tests were performed and the recovery for TDP was found to be 90% ± 7%. The dissolved organic phosphorus (DOP) was estimated indirectly by subtracting the dissolved inorganic phosphate from the total phosphate (DOP = TDP − DIP).

With the Persulfate Oxidation Method, all nitrogenous compounds are oxidized to nitrate ions under alkaline conditions at 100 C to 110 °C (APHA, AWWA, WEF, 2000, Standard Methods for the Examination of Water and Wastewater, 20th Edition). The samples are then passed through a Cu–Cd column where nitrate is reduced to nitrite, which is then diazotized with sulphanilamide and addition of N-(1-naphthyl)-ethylenediamine forming a high colored azo-complex determined spectrophotometrically at 543 nm (APHA, AWWA, WEF, 2000, Standard Methods for the Examination of Water and Wastewater, 20th Edition). The detection limit defined as 3 times the standard deviation of the blank was 1.7 μM. Each sample was analysed in triplicate and the reproducibility was better than 8% (1 SD). Recovery from standard addition tests on real samples ($n = 3$) was found to be 105% ± 6%. The dissolved organic nitrogen (DON) was determined by subtracting DIN from the TDN.

Table 2
Comparison between DIN and DIP annual fluxes determined using ADIOS and glass beads collectors with the fluxes associated with wet (rain) and dry deposition (aerosol and gases) at Finokalia during the ADIOS year.

Type of deposition	DIN mmol m^2 y^{-1}	DIP μmol m^2 y^{-1}
Wet	22.8	76
Dry (aerosols)	14.2	124
Dry (gases)	20.6	–
Wet + dry (aerosols)	37.0	200
Wet + dry (aerosols and gases)	57.6	200
Bulk ADIOS sampler	39.3	243
Bulk glass beads	62.7	251

(Chosen deposition velocities: for aerosols: IP, $NO_3 = 1.5$ cm s^{-1} and $NH_4^+ = 0.2$ cm s^{-1}; for gases: HNO_3, $NH_3 = 1$ cm s^{-1}).

Table 3
DIN and DIP annual fluxes at the ADIOS sampling sites.

	Sampling site	Sampling periods	Number of samples	DIN flux mmol $m^{-2}y^{-1}$	DIP μmol $m^{-2}y^{-1}$	DIN/DIP
Western Basin	Cap Spartel	06/2001–05/2002	12	28.2	608	46.3
	Cap Bear	06/2001–05/2002	12	45.9	574	80.0
	Ostriconi	06/2001–05/2002	12	25.4	464	54.7
Central Basin	Mahdia	06/2001–05/2002	10	18.1	371	48.7
	Gozo[a]	03/2002–02/2003	12	46.1	355	129.9
Eastern Basin	Finokalia[b]	06/2001–05/2002	11 + 1	39.3	243	161.6
	Mytilene	06/2001–05/2002	12	28.9	316	91.4
	Alexandria[c]	06/2001–05/2002	6	77.9	466	167.1
	Cavo Greco	06/2001–05/2002	12	47.7	469	101.8
	Akkuyu	06/2001–05/2002	12	30.6	480	63.8

[a] at Gozo, the sampling took place during one year, but started later than the ADIOS year.
[b] at Finokalia, the sample of March was lost due to a storm, thus March data was extrapolated using the glass beads collector.
[c] at Alexandria, the sampling covered only 6 months and the site was changed during the year: the data presented here are neither retained for calculations, nor for discussion.

All glassware and filters were pretreated and washed following the recommendations described in the APHA, AWWA, WEF, 2000, Standard Methods for the Examination of Water and Wastewater.

3. Results and discussion

3.1. Efficiency of dry deposition collectors

As bulk collectors could underestimate dry deposition collection, the efficiency of the ADIOS sampler to collect the dry deposition of DIN and DIP should be evaluated. At Finokalia in parallel to the sampling of bulk deposition with the ADIOS and the glass bead collectors, sampling of rain water (wet only collector), aerosols and gaseous species have been performed. Although these results will be presented in detail elsewhere, they enabled a direct evaluation of the capacity of ADIOS and glass-bead devices to collect dry deposition.

Table 2 reports the DIN and DIP fluxes determined using the ADIOS and glass bead collectors and compares them with the fluxes of wet (rain) and dry deposition of aerosols and, in the case of DIN species, to dry gaseous deposition.

Inorganic phosphorus (IP) exists mainly in aerosol phase and size segregation measurements showed that it is confined mainly in the coarse (>1 μm) mode (Markaki et al., 2003). Thus dry DIP deposition, due to coarse aerosols fallout, is expected to be well collected by bulk collectors. By adding the wet and dry aerosol DIP deposition a value of 200 μmol $m^{-2}y^{-1}$ is obtained (Table 2). Taking into account the uncertainties in the adopted dry deposition velocities, this estimation is in good agreement with the values obtained using the ADIOS and glass beads collectors being 243 μmol $m^{-2}y^{-1}$ and 251 mmol $m^{-2}y^{-1}$ respectively, which increases our confidence in the bulk deposition of DIP obtained using the ADIOS collectors.

For the estimation of the total DIN deposition, the situation is more complicated since DIN does exist not only in particulate but also in gaseous phase mainly as HNO_3 and NH_3. As these two gaseous compounds have quite high deposition velocities, the contribution of the gaseous species to the total DIN deposition values is expected to be significant (Kouvarakis et al., 2001). DIN fluxes obtained using the ADIOS collector are reported in Table 2. These fluxes are also compared to the individual fluxes of rain, aerosols and gaseous DIN species. The DIN annual flux obtained using the ADIOS collector – 39.3 mmol $m^{-2}y^{-1}$ – is lower than the sum of all individual DIN fluxes, but in rather good agreement with the sum of wet and aerosol DIN deposition indicating, as for DIP, the capacity of ADIOS device to quantitatively collect particulate species, even for DIN. But the ADIOS collector seems to be unable to collect gaseous DIN species.

The observed difference between the ADIOS (39.3 mmol $m^{-2}y^{-1}$, $n=12$) and the glass beads (62.3 mmol $m^{-2}y^{-1}$, $n=30$) collectors can be attributed to the gaseous DIN compounds deposition, mainly those of acidic character such as HNO_3 and NO_x which are efficiently trapped by the basic surfaces of glass beads. This is in agreement with the data presented in Table 2 and the observation by Kouvarakis et al. (2001).

Table 4
Annual deposition fluxes of nitrogen and phosphorus reported for the entire Mediterranean Basin during this study and comparison to literature values.

Sampling site		Type of sampling	References	DIN	TN	DIP	TP
				mmol $m^{-2}y^{-1}$		μmol $m^{-2}y^{-1}$	
Western Mediterranean							
Spain (SE)	Lanjaron	Bulk	a		33.9 / 45.3		390 / 636
Spain (NE)	Montseny	Bulk	b	40.2			
France (S)	Tour du Valat	Bulk	c	20.8 / 27.4			
France (SE)	Cap Ferrat	Wet	d	43.4 / 51.8			
		Wet	e			62	165 (TIP)
France (Corsica)	Bavella	Bulk	f	46.0 / 54.7			
	Ghisoni	Bulk	c	31.0 / 35.4			
	C. Cavallo	Bulk	g				1290
	Ostriconi	Bulk	h				547 / 1058
Italy (Sardinia)	C. Carbonara	Wet + dry	i	17.3			
	Torre Grande	Wet	j	16.5			
Eastern Mediterranean							
Greece (Crete)	Heraklion	Wet	k	22.0 / 27.0			
	Finokalia	Wet + dry	k, l	31.3 / 38.3		190	
Turkey (S)	Antalya	Wet	m	23.0			
Turkey (SE)	Erdemli	Wet + dry	l	60.1 (NO3 only)		168 (TRP)	
Israel	Ashod	Wet	n	26.0		290	
	Tel Shikmona	Wet	n	34.4		290	
	Israeli coast	Wet	n	20.0		258	
	Israeli coast	Wet + dry	n, o	26.4n / 76.6o			1290 (TIP)
Western Mediterranean		Bulk	This study	33.2		549	
Eastern Mediterranean		Bulk	This study	36.6		377	

TIP = total inorganic phosphorus; TRP = total reactive phosphorus
(a)Morales-Bacquero et al. (2006) – 2 years; bulk wet + bulk dry; mountainous site. (b) Avila and Roda (2002) – 17 years; mountainous site. (c) Loÿe-Pilot et al. (1990a) – 17 months : 2 annual fluxes retrieved. (d) Migon et al. (1989) – 2 years. (e) Migon and Sandroni (1999) – wet DIP and TIP – 1 year. (f) Loÿe-Pilot et al. (1990b) – 3 years; mountainous site. (g) Bergametti et al. (1992) – 2 years. (h) Ridame (2001) – 18 months: 2 annual fluxes retrieved. (i) Guerzoni et al. (1995) – 1 year. (j) Le Bolloch and Guerzoni (1995) – 2 years. (k) Kouvarakis et al. (2001) – 4 years. (l) Markaki et al. (2003) – Crete: 1 year – Erdemli: 11 months (in wet deposition: NO_3 only and total reactive phosphorus (TRP)). (m) Tuncel G. (2001). (n) Herut et al. (1999) – Ashod: 3 years – Tel Shikmona: DIP = 5 years, DIN = 4 years – Israeli coast = estimated values. (0) Herut et al. (2002) – estimated values.

Table 5
Interannual variability of DIN and DIP annual fluxes at 3 ADIOS locations.

Sampling site	# samples	Year	DIN mmol m^{-2} y^{-1}	DIP μmol m^{-2} y^{-1}
Ostriconi[a]	24	06/2001–05/2002	25.4	464
		06/2002–05/2003	26.9	430
Cap Bear[a]	24	06/2001–05/2002	45.9	574
		06/2002–05/2003	47.5	667
Finokalia[b]	59	06/2001–05/2002	62.7 / 39.3*	251 / 243*
		06/2002–05/2003	63.1	328

[a] Data for Ostriconi and Cap Bear are obtained from the ADIOS collector.
[b] Data for Finokalia are obtained from the glass beads collector, but the values from the ADIOS collector (*) are also given for the ADIOS year (06/2001–05/2002).

3.2. DIN and DIP deposition fluxes

Table 3 summarizes the measurements at the 10 sampling locations. Annual fluxes have been calculated from the monthly data by integration and extrapolated to 12 months in case of missing data.

DIP and DIN fluxes ranged from 243 to 608 μmol $m^{-2}y^{-1}$ and from 18.1 to 47.7 mmol $m^{-2}y^{-1}$ respectively. Despite the fact that DIP fluxes appear higher in the Western Mediterranean, they do not present important variation along the basin. On the other hand DIN fluxes in the Eastern Mediterranean are higher than those in the Western Mediterranean, as will be further discussed.

Only a few studies about bulk DIN and DIP deposition have been conducted in the Mediterranean basin and much less (mainly performed in the Eastern Mediterranean) examine simultaneously DIN and DIP deposition fluxes in bulk deposition samples (Table 4). Thus, especially for the Western Mediterranean, a direct comparison of the DIP values presented in this study with previous data sets is impossible as such data is missing. Regarding DIN, our values in the Western Mediterranean are in similar range with those reported by Morales-Baquero et al. (2006), Avila and Roda (2002), and Loye-Pilot et al. (1990b).

For the Finokalia station, in the Eastern basin, atmospheric fluxes of DIN and DIP were already available. Indeed, based on data from wet deposition and aerosol samples, for one year period (1999–2000), Markaki et al. (2003) reported DIP deposition at 193.4 μmol $m^{-2}y^{-1}$ and DIN deposition at 31.3 mmol $m^{-2}y^{-1}$. These estimates compare well with the present results for the Finokalia station: 243 μmol $m^{-2}y^{-1}$ (DIP) and 39.3 mmol $m^{-2}y^{-1}$ (DIN).

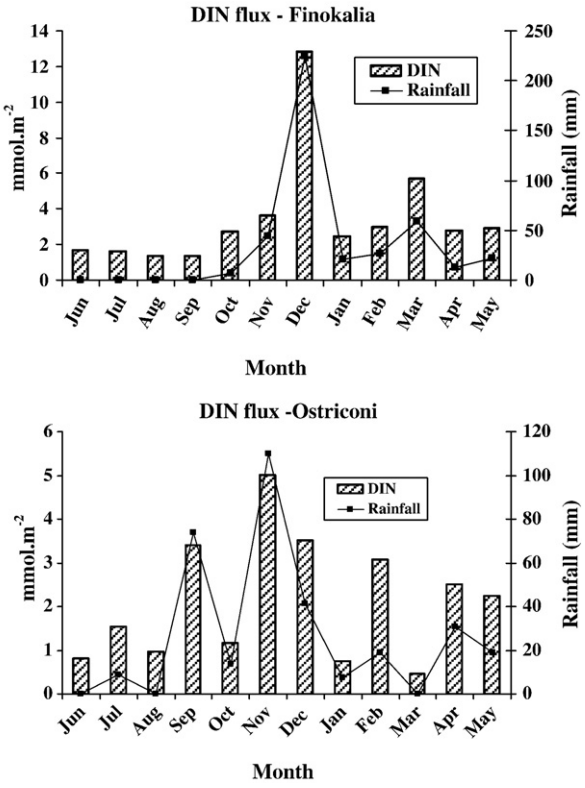

Fig. 2. Temporal variation of monthly DIN deposition (ADIOS collector) versus rainfall at the two main ADIOS stations in Western (Ostriconi) and Eastern (Finokalia) Mediterranean.

Table 6
Percent deposition of DIN and DIP fluxes during the wet and dry seasons for all the stations.

Location	Annual rainfall	% in dry season			% in wet season		
	mm	Rainfall	DIN	DIP	Rainfall	DIN	DIP
Cap Spartel	659	12	33	34	88	67	66
Cap Bear	654	32	42	35	68	58	65
Ostriconi	324	31	35	37	69	65	63
Mahdia	219	15	29	25	85	71	75
Gozo	673	7	24	42	93	76	58
Finokalia	399	0,6	22	40	99,4	78	60
Mytilene	664	0,4	16	22	99,6	84	78
Alexandria	12						
Capo Greco	421	0	21	21	100	79	79
Akkuyu	1004	5	11	33	95	89	67

Dry season: May to September.
Wet season: October to April.

3.3. Representativity of the ADIOS sampling year for annual DIN and DIP fluxes

To check whether the DIN and DIP fluxes determined during the ADIOS year are representative of the DIN and DIP deposition in the Mediterranean, the sampling at 3 locations (two in the Western basin and one in the Eastern) has been continued for a longer period (2 years at Cap Bear, Ostriconi and Finokalia). The results are reported in Table 5. DIN and DIP depositions measured at the 3 locations during the ADIOS year are comparable to the longer sampling indicating that the reported fluxes for the ADIOS period are typical for the Mediterranean.

3.4. Temporal and spatial variability of DIN and DIP

3.4.1. Temporal variation

Fig. 2 illustrates the temporal variability of DIN at Finokalia and at Ostriconi, the main stations in each basin. Maximum DIN deposition was observed for both Mediterranean basins during the winter period. Indeed all the major precipitation peaks coincide with high DIN fluxes highlighting the importance of rain as deposition pathway for N species. Thus wet deposition is expected to be an important factor controlling DIN deposition in the area.

To further examine this assumption the ADIOS year was divided in two periods, depending on the occurrence of rain: the dry (from May to September, i.e. 40% of the year) and the wet season (from October to April, i.e. 60% of the year). The amount of DIN deposited during the wet period was 2–8 times higher than that deposited during the dry season. More precisely the percentage of DIN which was deposited during the wet season ranged from 58% in Cap Bear to 89% in Akkuyu. In addition all over the basin and during both seasons the percentage of DIN deposition was significantly correlated to rainfall (data from Table 6, figure not shown) confirming the importance of wet deposition in controlling DIN fluxes around the basin.

On the other hand, no significant correlation with rainfall was observed for DIP indicating the additional role of other factors. Indeed, DIP deposition depends on various factors such as the amount of atmospheric Inorganic Phosphorus (IP), and its solubility, both depending on air-mass origins and the amount of rain among others (Ridame and Guieu, 2002). To examine the relative importance of these factors, the temporal variability of DIP at Finokalia and at Ostriconi was reported as a function of rainfall (Fig. 3). For both stations many of the DIP maxima seem to be linked to the rainfall. By distinguishing between wet and dry season as for DIN, it was estimated that about 65% of the total DIP was deposited during the wet period (Table 6).

Significant dust events (higher than 5 g m^{-2}), deduced from Al fluxes and denoted by a star in Fig. 3 were also found to contribute significantly to the DIP deposition. Finally, high DIP fluxes observed at Finokalia and, to a less extent in Corsica, during the dry period could be attributed to regional biomass burning events and the predominance of northern polluted air masses (Sciare et al., 2003). Indeed back-trajectory analysis revealed that the dry season in the Eastern Mediterranean is mainly characterized by air masses of North/North-East origins (Central and Eastern Europe and Balkans) and from July to September, 90% of the surface wind occurrences correspond to these directions (Mihalopoulos et al., 1997). These winds enhance long-range transport of pollution as indicated by the high levels of nss-SO_4^{2-} fluxes observed during this period (Fig. 3). Long-range transport from Eastern Europe and Balkans can also account for the levels of DIN observed at Finokalia during the dry period (Fig. 2). In Corsica DIP variability during the dry period was found to be better explained by biomass burning events, as indicated by the nss-K^+ variability (Fig. 3).

3.4.2. Spatial variation

DIP fluxes varied depending on the geographic location of the sampling sites: the annual fluxes appear to be higher in the Western Mediterranean basin (t-test, $p = 0.1$).

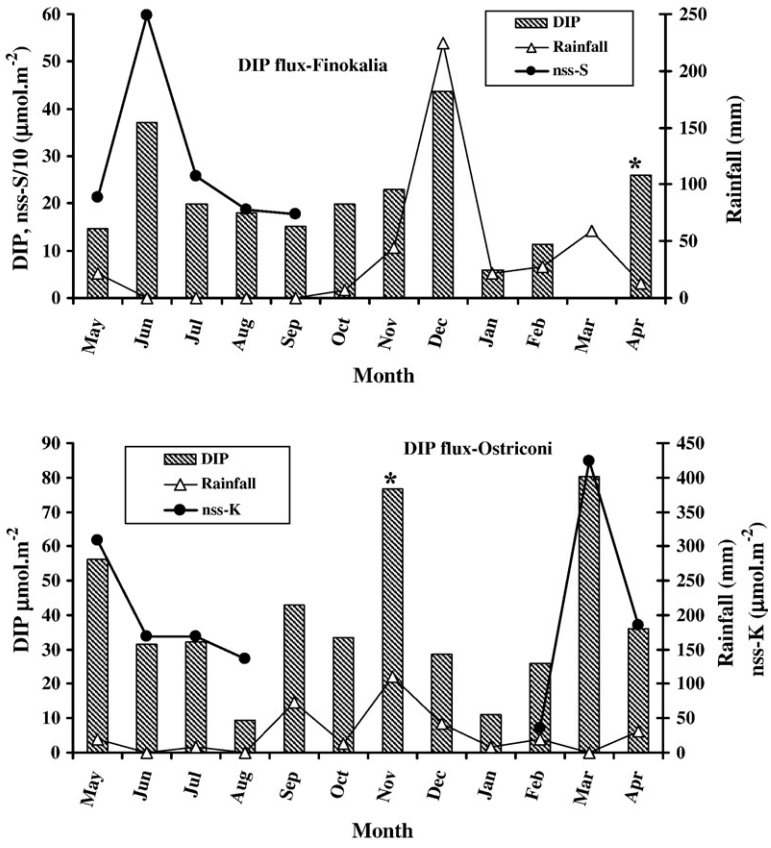

Fig. 3. Temporal variation of DIP monthly deposition versus rainfall, nss-S and nss-K fluxes at the two main ADIOS stations in Western (Ostriconi) and Eastern (Finokalia) Mediterranean. (*) indicates occurrence of high magnitude dust events (>5 g m^{-2}) during the month.

Lower values are observed in the Levantine basin and especially at sites far from the continents, such as Finokalia. Inorganic P deposition rate was by 20–30% lower at islands than coastal regions as continental areas are more affected by local / regional terrigenous and anthropogenic sources.

For DIN deposition, although no statistically significant difference is observed between Western and Eastern Mediterranean the lowest DIN values have been observed in the Western (Cap Spartel, Ostriconi) compared to the Eastern basin. This situation may be partly the result of the effort for anthropogenic emissions reduction in the western countries of Europe, but more probably due to the high and increasing emissions in the eastern European and western Asian countries (EMEP 2007) (EMEP, 2007). These hypothesis are supported by the similar spatial trend observed for the deposition of nss-SO_4^{-2} (mainly of anthropogenic origin) during the ADIOS period: 11.4 mmol S $m^{-2}.y^{-1}$ in the Western basin compared to 16.6 mmol S $m^{-2}.y^{-1}$ in the Eastern one, a difference which is statistically significant (*t*-test, $p=0.05$) and in agreement with the observations of Avila et al. (1996) and Avila and Roda (2002) for sulphur compounds.

Another possible explanation for the lower DIN fluxes in the Western Mediterranean is the difference in N speciation between the two basins. Thus although in the Eastern part $NaNO_3$ and $Ca(NO_3)_2$ are the main forms of nitrate in aerosols and consequently in deposition, NH_4NO_3, formation has been reported by several authors for the Western Mediterranean atmosphere (Loÿe-Pilot et al., 1993; Klein, 1998; Sellegri et al., 2001; Querol et al., 2004). It is well known that deposition velocities of NH_4NO_3 are a factor of 5–10 smaller than those of $NaNO_3$, and $Ca(NO_3)_2$, leading to smaller dry deposition fluxes in the Western than in the Eastern basin.

3.5. Organic nitrogen and phosphorus deposition

Inorganic forms of phosphorus and nitrogen are expected to be the main components of the total P and N content of the environmental samples but for a more complete and detailed approach the organic fraction must also be examined. It is known that organic P (OP) and organic N (ON) are very important components of the cells of various plants and animals (organisms). P and N are among the basic elements of DNA, RNA, ATP, ADP and phospholipids (Paytan and McLaughlin. 2007) and N is a specific constituent of proteins. Organic nitrogen in the atmosphere is encountered mainly as aminoacids, urea, amines, alkylonitrates and azarenes (Cornell et al., 2003).

Despite the importance of the subject, no studies examine thoroughly the deposition and the percentage of ON and OP species in the Mediterranean. This study tries to fill in this gap by estimating the percentage of these species in the TDN and TDP content of the atmospheric deposition bulk samples. Table 7 reports the percentage of DOP and DON determined during this study.

Approximately 38% of TDP is attributed to DOP and 32% of TDN to DON and thus a significant percentage of the dissolved N and P content of the samples was in the organic form. For DON this percentage is in good agreement with the findings of Cornell et al., (2003) and Chen et al., (2007) who suggested that, on average, 20–33% of the total atmospheric nitrogen occurs in the organic form. For DOP our results are also in very good agreement with the findings of Chen et al., (2007) who reported that, on average, 31% of the TDP in the Gulf of Aqaba aerosols occurred in the organic form.

No significant variation was observed in the contribution of the organic species to the total dissolved N and P, indicating a quite uniform distribution of the DON and DOP

Table 7
Spatial variability of the percentage contribution of DON in TDN and DOP in TDP.

	%DON	%DOP
Cap Bear	25.8 (n=20)	36.4 (n=6)
Ostriconi	30.3 (n=20)	31.3 (n=27)
Mahdia	38.4 (n=8)	49.4 (n=9)
Cap Spartel	32.5 (n=8)	31.6 (n=10)
Akkuyu	29.6 (n=7)	42.1 (n=6)
Alexandria	30.1 (n=5)	42.7 (n=6)
Finokalia	34.2 (n=113)	32.6 (n=102)

Table 8
Spatial variability of the DIN/DIP molar ratio.

Mediterranean Basin	Mean DIN/DIP	St. dev.
Western Mediterranean Basin	60.3	17.5
Central Mediterranean Basin	89.3	57.4
Eastern Mediterranean Basin	104.7[a]	41.2[a]
	117.2[b]	45.3[b]

[a] Alexandria data excluded.
[b] with Alexandria data.

over the entire Mediterranean. This suggests that the DON and DOP are somehow linked to the DIN and DIP concentrations and fluxes, most probably due to common sources.

However as the number of samples analyzed for DON and DOP had lower temporal coverage than for DIN and DIP no fluxes estimations are given.

3.6. Spatial variability of atmospheric deposition DIN/DIP ratio and its implications

Based on the results reported during the ADIOS period, DIN/DIP ratios in the atmospheric deposition were calculated for each station (Table 3). The annual mean values and their standard deviation for each sub-basin are presented in Table 8. The DIN/DIP ratios reported for ADIOS type samples in Tables 3 and 8 represent minimum values as DIN values do not include the contribution from gaseous DIN species (especially in the form of HNO_3 and NO_x). The contribution of the organic fraction of N and P was not taken into account due to uncertainties in DON and DOP bioavailability.

At both Eastern and Western basins, if only open sea island stations are considered (Table 3), the variability of DIN/DIP ratio in the atmospheric deposition is quite small. DIN/DIP ratio varies depending on the location. The lower values are encountered in the Western basin, while the DIN/DIP ratio increases steadily towards the east. Precisely, the mean values at the Western and Eastern basins were 60.3 and 104.7 respectively (Table 8). A statistical analysis (t-test, $p=0.05$) indicates that the mean values determined for both Western and Eastern basins are significantly different.

This observation is particularly important when examined in parallel with the similar trend found in the sea water DIN/DIP ratio. According to Krom et al. (1991, 1992), DIN/DIP ratio in the Mediterranean water column presents significant variation, as it increases from 22 in the Western basin to 24–29 in the Eastern one.

Our data confirm the existence of an unbalanced N/P ratio in the atmospheric deposition in the entire Mediterranean. Since this source contributes significantly to the N and P budget in both basins (Martin et al., 1989; Loÿe-Pilot et al., 1990a,b; Guerzoni et al., 1999; Krom et al., 2004; Ribera d' Alcala et al., 2003), it is expected that the unbalanced N/P in atmospheric deposition could be reflected in the seawater and contributes to the observed eastward increase in seawater N/P ratio.

4. Conclusion

The simultaneous measurements of DIN and DIP atmospheric deposition in the entire Mediterranean basin with good spatial coverage and a unified protocol allowed a better assessment of N and P deposition in the Mediterranean basin and their impact on marine biogeochemistry.

Dissolved Inorganic Phosphorus (DIP) and Nitrogen (DIN) atmospheric deposition fluxes ranged from 243 to 608 μmol $m^{-2}y^{-1}$ and from 18.1 to 77.9 mmol $m^{-2}y^{-1}$ respectively presenting an important spatial variability within the basin. The representativity of the DIN and DIP data reported here, are confirmed by extending the bulk deposition sampling at the two representative island stations (Ostriconi and Finokalia) for an additional year.

Wet deposition was found to be the main deposition mechanism for both DIN and DIP species all over the Mediterranean. DIP deposition was enhanced by dust storms, regional biomass burning events and polluted air masses from Europe and/or former Soviet Union countries.

The dissolved organic N and P content of the samples were also determined. It was found that both DON and DOP are important contributors of N and P deposition and represent almost one-third of the total dissolved atmospheric nitrogen and phosphorus load. This clearly indicates the importance of the organic forms of these nutrients and thus more detailed studies on their specific forms and origin are needed.

The DIN/DIP molar ratio was found to increase eastwards with mean values of 60.3 and 104.7 for the Western and Eastern basins, respectively. Given the importance of atmospheric deposition in the area and by taking into account that a similar trend has been observed for the N/P ratio in the Mediterranean deep water, it is expected that unbalanced N/P in the atmospheric deposition could be reflected in seawater and account, at least partly, for the eastward increase of the N/P ratio observed in the Mediterranean deep waters.

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