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Atmospheric input of inorganic nitrogen to the Western Mediterranean

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Abstract. Bulk inorganic nitrogen deposition was monitored over a period of 3 years at the Bavella Pass (Corsica, France). Annual fluxes range between 126 and 150 μmol.m^{-2}.d^{-1}, increasing slightly with annual rainfall. Natural background average concentrations of rain water and associated fluxes were estimated from a classification of rain events into 'natural' (Oceanic and Saharan), polluted and composite. Long range transport of incoming polluted air masses increases the atmospheric wet nitrogen input by at least a factor of 1.6 in this Mediterranean area. Extrapolation of atmospheric dissolved inorganic nitrogen input to the Western Mediterranean leads to fluxes of 80 to 100 μmol.m^{-2}.d^{-1}. This atmospheric input is in the same order of magnitude as the inorganic nitrogen riverine input. As a consequence, the nitrogen budget for the Mediterranean has had to be reassessed. Atmospheric wet inorganic nitrogen input is of noticeable importance to marine Mediterranean ecosystems, representing on average 10 to 25% of new production in the Western Basin, with values of up to 60% in oligotrophic zones.

Introduction

The increase of airborne, man-made nitrogen compounds in the Northern hemisphere and their influence on atmospheric deposition is now well-documented (Brimblecombe & Stedman 1982; Beilke 1983; Neftel et al. 1985). Inorganic nitrogen contributes significantly to the ionic strength and acidity of rain water (Rohde & Rood 1986; Legrand et al. 1984) and consequently to ecological damage to ecosystems such as lakes and forests (Drablos & Tollan 1980; Schindler 1986). The consequences of atmospheric deposition on marine ecosystems have not as yet been thoroughly investigated, unlike terrestrial ecosystems (Boring et al. 1988), because of the negligible effect of rain acidity on buffered sea water. However, the impact of atmospheric nitrogen as a nutrient for marine ecosystems is an important matter for scientific debate.

Knap et al. (1986) have claimed that atmospheric nitrogen deposition has no direct bearing on the sustentation of new production in the Sargasso Sea

and by extension in all oligotrophic ocean areas. However, Paerl, (1985) whose assumption is based on bioassays, believes that the inorganic nitrogen content of acid rain may actually increase primary production in coastal waters, and Fanning, (1989) shows that nitrogen limitation is more prevalent than phosphorus limitation in the surface ocean. Moreover, nitrogen deposition has been thought to be partly responsible for some of the recent harmful algal blooms which have been observed in the estuarine and coastal waters of Eastern North America (Oppenheimer et al. 1988, quoted in International Herald Tribune of 4-28-88 and Time of 5-9-1988).

We consider here the significance of the atmospheric input of nitrogen to the Mediterranean Basin, where a budget of this element is partly available (UNEP 1984, Bethoux & Copin-Montégut 1986) and where the primary marine production pattern is relatively well-known (Sournia 1973; Minas & Bonin 1988; Minas et al. 1988). The aim of this paper is:

— to establish the wet atmospheric depositional flux of inorganic nitrogen;
— to assess its variability according to the origins of incoming air masses scavenged by precipitation;
— to evaluate the increase of atmospheric deposition due to anthropogenic influences;
— to compare the atmospheric depositional input of nitrogen to the Western Mediterranean sea with that of other land-based sources, mostly riverine discharge;
— to discuss the impact of nitrogen deposition at the sea surface on marine Mediterranean ecosystems.

Sampling and analytical procedures

Data were collected in South Corsica, in the North Western Mediterranean Basin, from a sampling station located near the Bavella Pass (41°50N, 9°10E), at 1200 m above sea level in an uninhabited area (Fig. 1). Figure 1 also demonstrates the main marine regions which have previously been considered in the MEDPOL inventory of pollutant discharges to the Mediterranean, in the frame of the United Nations Environmental Programme (UNEP 1984).

Systematic collection of precipitation was carried out using an open plastic gauge of 400 cm^2 aperture. Sampling was on an event basis, except during winter snowfall when the site was less accessible; sampling times ranged from several hours to one week. Samples are generally supposed to

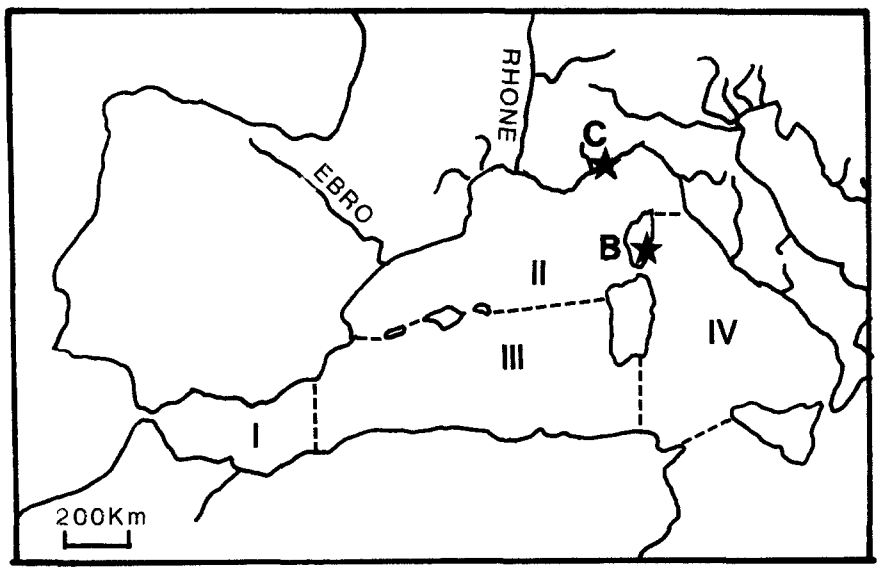

Fig. 1. Location of the Bavella (B) atmospheric sampling station and limits of the marine areas I to IV considered in the UNEP inventory of pollutants discharge from land-based sources to Mediterranean (C): Cap Ferrat sampling station (Migon et al. 1988).

correspond to bulk deposition (wet + dry), although some of those collected during periods of rain represent only wet deposition. However, the weak, dry deposition efficiency of the gauge means that most samples are only representative of wet deposition. The gauge was carefully cleaned with deionized water before sampling. The precipitation samples, including those resulting from melted snow, were filtered indoors close to the sampling site on 0.4 μm Nuclepore filters and were stored in darkness at 4°C in polyethylene bottles. Their ionic content was measured after several weeks. To investigate storage procedures reliability (loss by adsorption and/or biological uptake, or contamination) we tested different types of vessel (glass or polyethylene), different conservative methods (filtration: 0.4 μ, paper or glass fibre filters or no filtration. 4°C dark storage $\pm$ $HCCl_3$ or deep freezing $\pm$ $HCCl_3$) and we monitored the evolution of the samples with increasing storage time (immediate analysis versus delayed analysis: 1 day to 12 weeks). We did not observe any significant change for the 0.4 μ filtered samples, the observed differences falling within the analysis uncertainty. It appears that at the observed concentration levels, neither significant adsorption on recipient walls nor significant contamination occurs and that filtration prevents biological modification of the measured species. The suitability of dark storage for rain samples (Galloway & Likens 1978) was confirmed in this case. Chemical analysis was performed by classical methods, using

spectrocolorimetry for NO_3 (Na salicylate method – Rodier 1976) and NH_4 (indophenol blue method – Solorzano 1969). The detection limits were of 0.3 and 0.5 μmol.l^{-1} respectively for NO_3 and NH_4 with relative standard deviations of 2 and 3% respectively at the 15 μmol.l^{-1} level, and 7 and 2% at the 2 μmol.l^{-1} level. Routine analysis of NO_2 was not undertaken, tests having shown that this ion accounts for less than 1% of total DIN concentration.

Results and discussion

Some results of chemical composition of precipitation at the Bavella Pass, South Corsica have previously been interpreted. Antagonistic influences of natural and man-made emissions with neutralizing effects of acid rain by Saharan dust were strongly implicated (Loÿe-Pilot et al. 1986, 1987, 1988). In order to compare atmospheric deposition with the input from land-based sources of nitrogen inventoried by UNEP (1984), the authors consider dissolved inorganic nitrogen (DIN) to be the total contribution of NO_3^- and NH_4^+ ions.

Annual DIN deposition was computed from event data for the three year period 1984 to 1986. Table 1 gives the annual rainfall, inorganic nitrogen wet deposition fluxes with the respective contribution of nitrate and ammonium, DIN weighted mean concentrations for each year and averages for the whole period. These fluxes are higher for humid years (150 μmol.N.m^{-2}.d^{-1} in 1984 and 1986) than for the year with lower rainfall (126 μmol.N.m^{-2}.d^{-1} in 1985). However, annual nitrogen deposition is much less changing than annual rainfall; this is due to the general increase of concentrations when pluviometry decreases: about 30 μmol.l^{-1} in 1984 and 1986 and 40 μmol.l^{-1} in 1985, that is an increase of 30% of the concentrations for a decrease of 40% of the pluviometry (Table 1). The situation is more complex when each individual rain event is considered.

In fact, changes in the origin of air masses reaching the sampling zone appear to be the major cause of temporal fluctuations in the inorganic nitrogen concentrations in the rain water. This observation is supported by analysis of air mass trajectories, a tool which has proved very useful in previous atmospheric geochemical studies (Jickells et al. 1982; Morelli et al. 1983; Loÿe-Pilot et al. 1986; Dulac et al. 1987).

By considering air masses origins and associated primary sources of atmospheric material, ionic composition and particulate matter content of the precipitation, rain events may be classified as Oceanic, Saharan or Polluted (Table 2) or as a composite. This classification is based on the

Table 1. Annual rainfall, annual dissolved inorganic nitrogen deposition fluxes and annual weighted average dissolved inorganic nitrogen concentrations in rain water at the Bavella Pass sampling station during the years 1984, 1985 and 1986 and three years average annual values. The computed annual natural background deposition fluxes in inorganic nitrogen and the ratios between the actually measured and the natural background fluxes are also given.

Year	1984	1985	1986	Weighted average 3 years
Rainfall (mm)	1815	1146	1815	1599
DIN Flux $\mu mol.m^{-2}.d^{-1}$	149	126	150	143
$N.NO_3/N$ Tot. %	41	44	42	42
DIN Average concentration $\mu mol.l^{-1}$	29.6	40.2	30.1	32.3
Background DIN Flux $\mu mol.m^{-2}.d^{-1}$	90	56	90	79
Increasing factor due to the impact of human activity	1.6	2.2	1.7	1.8

three-dimensional back-trajectories of air masses reaching the sampling zone as established by the French 'Météorologie Nationale' for each individual rain episode. From the 164 precipitation samples collected from 1984 to 1986 at the Bavella Pass and representing 99.8% of total rainfall, 14, 15 and 47 events of typical Oceanic, Saharan and Polluted characteristics respectively were distinguished. The selected events in each class correspond to similar origins and pathways for air masses arriving at two pressure levels (700 and 850 hPa), and coherent geochemical characteristics of precipitation. The other rain episodes reflect mixing of air masses.

Three examples of clearly distinct events of each class are given in Table 3 and Fig. 2. Table 3 gives the rainfall intensity, pH values, NO_3, NH_4 and total DIN rain water concentrations and DIN deposition. Figure 2 represents the associated four days air mass back-trajectories finishing at 700 hPa pressure level. These episodes correspond to the arrival of relatively clean oceanic air (trajectories O_1, O_2, O_3), of Saharan dust (trajectories S_1, S_2, S_3) and of pollutants from Northern Europe and Italy (trajectories P_1, P_2, P_3).

Oceanic and Saharan rains are the most 'natural' of those collected. Average DIN concentration of the 14 Oceanic and 15 Saharan typical rain

Table 2. Characteristics of rain water collected at the Bavella Pass sampling station related to changes in the origins of incoming air masses.

Typical class of rain event	Oceanic	Saharan	Polluted
Incoming air mass characteristics			
Origins	West	South	North and East
Number of typical episodes observed during the three year period	14	15	47
Characteristics of rain water: solid phase			
Particulate matter content	Undetectable	Red and yellow dust	Black soot organic material
Characteristics of rain water: dissolved phase			
pH Value	4.8–5.8	5.4–7.1	3.9–4.8
DIN concentration range (μmol.N.l^{-1})	5–28	10–58	16–135
Average DIN concentration for the typical episodes listed above (μmol.l^{-1})	14.5	24.1	46.6

samples are 14.5 μmol.N.l^{-1} and 24.1 μmol.N.l^{-1} respectively. The weighted mean concentration of all these 'natural' events is 18.6 μmol.N.l^{-1}. This value is higher than those measured in rain water over very clean remote marine areas in the Pacific and South Indian Ocean – 1/5 μmol.N.l^{-1} (Duce 1983; Galloway & Gaudry 1984) – and in Bermuda – 7 μmol.N.l^{-1} (Knap et al. 1986) –. Taking into account the geographic configuration of the Mediterranean Basin, this difference may partly reflect the influence of neighbouring natural continental and coastal sources of atmospheric inorganic nitrogen (Söderlund & Svensson 1976; Logan 1983). Moreover, some of the 'natural' selected events may also have been slightly influenced by anthropic sources; oceanic air masses transported over Spain and France, and Saharan air masses passing over North African coastal regions, may indeed pick up polluted components from industrial and intensive agricultural areas. So a natural background DIN concentration of 18 μmol.l^{-1} for the Western Mediterranean is still an overestimation.

The average DIN concentration of the 47 polluted rain samples is 46.6 μmol.N.l^{-1}. This value is more than 3 times higher than that of rain of oceanic origin, twice that of Saharan rain, and about 2.5 times higher than

Table 3. Rainfall intensity, pH values, rain water concentrations in inorganic nitrogen and associated fluxes for typical episodes of incoming air masses considered in Fig. 2.

No. trajectory	Time of arrival of incoming air masses	Rainfall mm	pH	NO_3 $\mu mol.l^{-1}$	NH_4 $\mu mol.l^{-1}$	DIN $\mu mol.l^{-1}$	DIN Flux $\mu mol.m^{-2}$
Oceanic air masses							
O_1	01-23-84, 12 h	59.5	4.93	5.8	2.6	8.4	498
O_2	02-10-85, 6 h	33.5	5.01	10.2	6.2	16.4	549
O_3	01-12-86, 12 h	11.2	5.14	6.6	8.1	14.7	165
African air masses							
S_1	05-10-84, 6 h	68.0	6.89	14.2	7.6	21.7	1479
S_2	05-12-85, 18 h	15.0	7.14	22.3	0.9	33.2	497
S_3	03-06-86, 12 h	19.0	5.74	7.4	6.7	14.1	268
Polluted air masses							
P_1	03-08-84, 18 h	28.7	4.16	46.6	62.2	108.8	3124
P_2	02-22-85, 12 h	22.6	4.27	33.5	37.8	71.3	1612
P_3	06-20-86, 12 h	52.0	4.27	15.3	43.0	58.3	3033

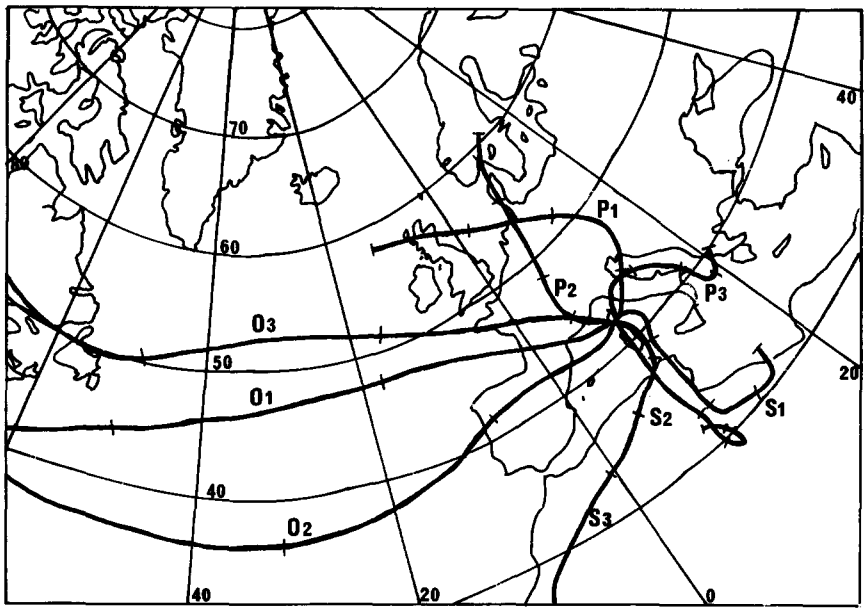

Fig. 2. Four days three-dimensional air masses back trajectories finishing at 700 hPa level over the Bavella Pass atmospheric sampling station for typical rainfall episodes considered in Table 2.

the Mediterranean natural background value referred to previously. Values reaching 260 μmol.N.l^{-1} have been measured. Such ranges in concentration in polluted samples, of up to 15 times the estimated natural background level, are in good agreement with the DIN rain water concentrations observed over various regions of the European continent (Wallen 1981; Beilke 1983; Nodop 1987). They are mainly explained by man-made activities: industrial emissions, domestic activities and agricultural practices.

Assuming an average background water concentration of 18 μmol.N.l^{-1}, the annual DIN wet deposition fluxes at the Bavella Pass can be estimated (Table 1) and compared to the actual fluxes; this comparison shows that the impact of anthropogenic sources increase the background DIN fluxes by a minimum factor of 1.6, 2.2, and 1.7 for the years 1984, 1985 and 1986, respectively, and 1.8 over the three year period (Table 1).

The extrapolation of the Bavella DIN nitrogen deposition fluxes to the Western Mediterranean Sea, where the rainfall is very much lower, is difficult. From a pluriannual rainfall monitoring at the Cousteau Buoy Laboratory (42°47N, 7°30E), an average annual value of about 350 mm has been measured, which agrees fairly well with the value of 330 mm computed by Bethoux (1979). Recent data on atmospheric deposition collected at the Cap Ferrat coastal sampling station, located on the French Riviera, (Migon

Table 4. Comparison of annual dissolved inorganic nitrogen deposition fluxes and average concentrations in rain water at the Bavella Pass and at the Cap Ferrat for dry and humid years.

Sampling site	Year	Rainfall mm	DIN Flux $\mu mol.m^{-2}.d^{-1}$	DIN Average concentration $\mu mol.l^{-1}$
Bavella Pass	Dry 1985	1146	126	40.2
Cap Ferrat[1]	Years 1986	549	119	79.4
Bavella Pass	Humid 1984	1835	149	29.6
Bavella Pass	Years 1986	1815	150	30.1
Cap Ferrat[1]	1987	947	142	54.8

[1] Data from Migon et al. 1988.

et al. 1988) will now be considered. At Cap Ferrat, the average annual rainfall of ca. 750 mm is 2.4 times lower than at the Bavella Pass i.e. 1800 mm for an 8 year period and twice the pluviometry over the open sea. But a comparison between the two sampling sites shows that the annual DIN deposition fluxes are very similar and vary little from dry to humid years (Table 4 and Fig. 3). These similarities, despite a factor of 2 between the annual rainfalls at the two locations, must be related to: (1) the inverse relationship between DIN concentrations and pluviometry, (2) the fact that at sea level, rains wash out the lowest and most contaminated layer of the atmosphere, (3) the geographical location of the site of Cap Ferrat which is nearer to local anthropogenic sources than Bavella.

The similarities in the data can be compared with the results of Pearson & Fisher (1971). From data obtained from several sampling stations surveyed over a one to three year period they found that annual DIN input in the Northern United States was virtually constant irrespective of rainfall. If such a hypothesis as applied to our limited data from Bavella and Cap Ferrat, it would result in an annual DIN input range of 120–150 $\mu mol.m^{-2}.d^{-1}$ for this part of the Mediterranean area.

The long-term series of observations performed at the Hubbard Brook Experimental Watershed, North Eastern USA (Likens et al. 1971 and Likens et al. 1977) partly confirms the Pearson & Fisher (1971) findings i.e. the lack of correlation between annual DIN deposition and annual rainfall, (the very low rainfall point excepted) (Fig. 3). Thus it seems reasonable to hypothesize that the main factor determining annual DIN input is the distance from sources of pollution. This assumption is validated by the long-term series measurement carried out at Pallanza, close to pollution sources of Northern Italy, where the annual DIN input ranging from 350 to 710 $\mu mol.N.m^{-2}.d^{-1}$, is more than three times higher than at Bavella (Mosello et al. 1985, and Mosello 1986) Fig. 3. Unfortunately, to the best

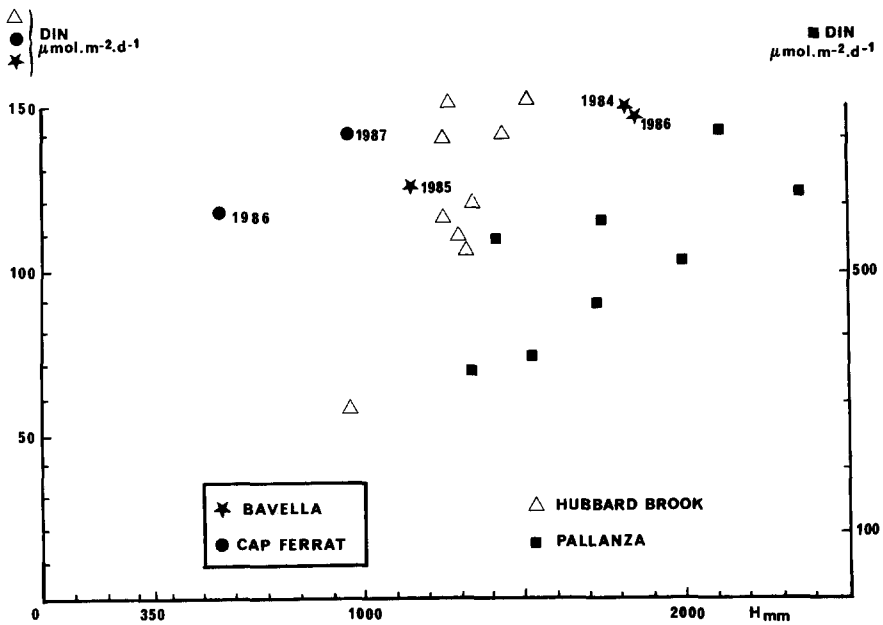

Fig. 3. Annual DIN input at Bavella and Cap Ferrat Mediterranean sites. Comparison with the annual DIN input data of the Hubbard Brook Experimental Watershed – remote site in the North Eastern USA (from Likens et al. 1971 and Likens et al. 1977) and of Pallanza – urban site near to industrial zones in Northern Italy – (from Mosello et al. 1985 and Mosello 1986). Pallanza data: right Y-scale.

of our knowledge, there is no other published data on the Western Mediterranean to constrain the variation of the DIN input in the Southern and Central Mediterranean located further from pollution sources.

The limited data available for Bavella and Cap Ferrat stations including extreme rainfall situations allow us to hypothesize an average DIN flux of about 130 μmol.N.m^{-2}d^{-1} for this part of the North Western Mediterranean.

Considering the lower pluviometry over the open Mediterranean Sea and the greater distance from coastal pollution sources, we must lower this value for the whole North Western Mediterranean. Therefore, an average atmospheric DIN depositional flux of about 100 µmol.N.m^{-2}.d^{-1} over the North Western Basin, surrounded by pollution sources, seems to be a realistic assessment. This flux to the UNEP zone II (see Fig. 1) – 250 000 km^2 –, corresponds to a DIN input of 130.10^3 T.y^{-1} (Table 5). The same flux may be reasonably extrapolated to the Tyrrhenian Sea (Zone IV), which is very close to the anthropic sources of the Italian peninsula and Sardinia. Zone I and III are also bordered by coastal regions with a

Table 5. Dissolved inorganic nitrogen input to Western Mediterranean. Comparison between the land to sea input and the atmospheric depositional input.

Marine Mediterranean Region	UNEP Zone II	UNEP Zones I to IV
Present estimation of DIN atmospheric deposition		
Average flux (μmol.m^{-2}.d^{-1})	100	80
Atmospheric input (10^3 T.y^{-1})	130	350
DIN input from land-based sources		
Land to sea total input (10^3 T.y^{-1})	387[a]	502[a]
Total riverine input (10^3 T.y^{-1})	340[a] 115*	403[a] 135*
Ebro input (10^3 T.y^{-1})	14[a]	14[a]
Rhône input (10^3 T.y^{-1})	227[a] 86[b] 72[c]	227[a] 86[b] 72[c]

[a] UNEP, 1974 [b]from Denant & Saliot 1985 [c]El Habr & Golterman, 1987
*reassessed total riverine input with a corrective factor of 1/3 calculated from the different Rhône input data: UNEP value (a); recent values (b, c).

reasonably high level of human activity, but the relative influence of anthropic emissions compared to atmospheric input from natural Saharan and oceanic sources is probably less in these areas. Assuming an average anual DIN flux of only 50 µmol.N.m^{-2}.d^{-1} for zones I and III, the average DIN depositional flux to the whole Western Mediterranean Basin may be estimated at 80 µmol.N.m^{-2}.d^{-1}. This flux over a surface area of 360 000 km^2 is equivalent to a DIN input of 350.10^3.t.y^{-1} for marine regions I to IV (Table 5).

The UNEP inventory (1974) gives a total inorganic nitrogen input from land-based sources to zone II and the four zones I to IV of 387.10^3 t.y^{-1} and 502.10^3 t.y^{-1},respectively. Riverine inputs are 340.10^3 and 403.10^3 t.y^{-1}, including 227.10^3 t.y^{-1} from the Rhône and 14.10^3 t.y^{-1} from the Ebro. These two major rivers contribute respectively 63% and 20% of the water discharge to zone II, and 51% and 16% to zones I to IV. UNEP data are not completely accurate though, and recent reassessment suggests values of inorganic nitrogen discharge by the Rhône of 86.10^3 t.y^{-1} (from Denant 1985) and 72.10^3 t.y^{-1} (El Habr & Golterman 1987), Table 5. In spite of ambiguities in the data, it appears that the dissolved inorganic nitrogen

Table 6. Reassessment of the atmospheric contribution to the Mediterranean Sea nitrogen balance, in comparison with the previous budget established by Bethoux and Copin-Montegut 1986.

Mediterranean Sea nitrogen budget from Bethoux and Copin-Montegut, 1986			
Hypothesis	1	2	3
Nitrogen deficit resulting from the exchanges at the Gibraltar Strait	25	19.7	14.4
Inorganic nitrogen terrestrial discharge (from UNEP, 1974)	7.4	7.4	7.4
Estimated organic nitrogen terrestrial discharge	3.9	3.9	3.9
Atmospheric input by rainfall	1.3	1.3	1.3
Resulting atmospheric N_2 fixation	12.4	7.1	2.1
Present estimation of the atmospheric contribution			
Atmospheric input by rainfall	4.6/7.3	4.6/7.3	4.6/7.3
Resulting atmospheric N_2 fixation	9.1/6.4	3.8/1.1	N_2 loss

Data in 10^{10} mol.y^{-1}.
The three hypotheses considered by these authors correspond to various estimations of the organic nitrogen content of waters entering the Mediterranean through the Gibraltar Strait.

atmospheric input is of the same order of magnitude as the riverine input for the North Western Mediterranean (zone II) and the Western Mediterranean – zones I to IV – (Table 5). If all UNEP data are overestimated to the same degree as the Rhône data, then the atmospheric input would be superior to the riverine input for the Western Mediterranean Sea as a whole (Table 5). The importance of the atmospheric inorganic nitrogen input is therefore clearly indicated, and must be taken into account when assessing the Mediterranean nitrogen budget.

The last N budget of the Mediterranean by Bethoux and Copin-Montegut (1986) minimizes the atmospheric dissolved input; taking a value of 17 μmol.l^{-1} for the mean concentration in rain, they obtained an annual flux of dissolved inorganic nitrogen of 14 μmol.m^{-2}.d^{-1}, that is $1.3.10^{10}$ mol.y^{-1} for the whole Mediterranean (Table 6). With such a value they had to hypothesize a significant direct biological fixation of N2 to balance their budget. Obviously, their mean rain DIN concentration of 17 μmol.l^{-1} is an underestimation. More recent data, collected by the same staff, lead to a weighted mean value of 65 μmol.l^{-1} for the 2 years 1986 and 1987 (Migon et al. 1988). Other data on Mediterranean coastal zones range from 47 μmol.l^{-1} for Western Sardinia (Cossu et al. 1987), $\simeq$ 50 μmol.l^{-1} for the Israeli Coast (Mamane 1987), to 72 μmol.l^{-1} for the Greek coast (Glavas

1988). Moreover, these last values, which do not take into account the very low, more concentrated rainfall events, are probably underestimated.

From our data, we can try to estimate the wet, inorganic N input to the whole Mediterranean. A value of 50 μmol.m^{-2}d^{-1} can be considered to be the lower hypothesis; since the Eastern Mediterranean is further from the strong pollution sources of Northwestern Europe than the Western Mediterranean, we can take 80 μmol.m^{-2}.y^{-1} to be an upper limit. Data from the Israeli Coast with DIN fluxes between 55 and 85 μmol.m^{-2}.d^{-1} (Mamane 1987 and Mamane et al. 1987) confirm the validity of this flux range.

Dissolved inorganic N input from rainfall to the whole Mediterranean must therefore be reassessed at higher values of 4.6 to 7.3.10^{10} mol.y^{-1}, which are still of the same order of magnitude as the terrestrial discharge. The contribution of direct biological fixation of N2 must consequently be lowered (Table 6); in the third hypothesis of Béthoux and Copin-Montégut, relative to the amount of organic nitrogen delivered at Gibraltar (Table 6), this contribution would be replaced by a loss of nitrogen from the sea to the atmosphere.

Finally, the ecological significance of the atmospheric input of dissolved inorganic nitrogen has to be considered. Atmospheric inputs contribute to new production (Dugdale & Goering 1967; Eppley & Paterson 1979; Duce 1987), where it comprises part of primary production due to the input into the photic zone of new nutrients (from land sources, deep waters or atmosphere – wet and dry deposition and biological fixation –). The remainder of primary production, regenerated production, is due to recycled nutrients from decaying biomass in surface water. In the Western Mediterranean, the ^{14}C primary production is from 50 to 100 g.C m^{-2}.y^{-1} (Sournia 1973; Minas & Bonin 1988; Minas et al. 1988). Although new production appears to be difficult to measure, and follows a very irregular pattern in the Mediterranean area (Minas et al. 1988) its contribution may be evaluated at 25% of the ^{14}C primary production (Minas et al. 1988), that is 12 to 25 g.C.m^{-2}.y^{-1}. In the oligotrophic zones of the Central Western Mediterranean, a primary production of about 50 g.C.m^{-2}.y^{-1} and a new production as low as 10% (5 g.C.m^{-2}.y^{-1}) are more probable (H.J. Minas pers. comm.).

Dissolved inorganic nitrogen input by rain may be accounted for by about 3 g.C.m^{-2}.y^{-1} in zone II and about 2.5 g.C.m^{-2}.y^{-1} in the whole Western Basin, using C/N Redfield ratios of 106/16 (Redfield et al. 1963). So, atmospheric inorganic nitrogen wet deposition may be accounted for by 10 to 25% of new production on a global scale, but in oligotrophic zones its contribution may go up to 60%. It appears therefore that this is not negligible, in contrast to the findings of Knap et al. (1986) for the Sargasso Sea.

Moreover, when taking into account dry, soluble inorganic and wet, dissolved organic nitrogen deposition this result would be more significant. Data on these two types of nitrogen deposition on coastal and open sea areas are scarce. In relatively remote marine areas, such as the Sargasso Sea, the dry input is from 16 to 95% of the wet input, with more probable values being between 28 and 54% (Duce 1987). An approximate value of 30% may be used as a low hypothesis. Data are even more scarce for dissolved organic nitrogen (DON) in rain, especially in marine areas. Williams (1967) found DON to be 33 and 40% of the total dissolved nitrogen for two periods of rain, that is 50 and 70% of the DIN. On the basis of a literature review, Meybeck (1982) found DON to be 35% of the total dissolved nitrogen, i.e. about 55% of the DIN. Knap et al. (1986) estimated DON to be approximately equal to DIN input in the Sargasso Sea.

Taking DON to be 70% of DIN, and dry deposition to be 30% of DIN, a rough estimate of total dissolved or soluble nitrogen input would be twice the dissolved inorganic input, that is $160\,\mu mol.m^{-2}.d^{-1}$ for the Western Basin as a whole and $200\,\mu mol.m^{-2}.d^{-1}$ for the North Western Basin. Dry, soluble inorganic nitrogen can be used directly for primary production; if dissolved inorganic nitrogen is also usable by photoplancton, as has been hypothesized (Knap et al. 1982), then the atmospheric input of total dissolved nitrogen would be quite significant, being responsible for 20 to 50% of new production, on average, for the Western Mediterranean Sea.

These values only represent order of magnitude estimates on a global scale. In fact, the Western Mediterranean Sea displays a very complex pattern relative to primary production (Sournia 1973; Minas et al. 1988). In addition to a complex spatial distribution, Mediterranean primary production displays a seasonal pattern; in summer the photic zone above the thermocline is depleted of nutrients, and very concentrated rains (supplying up to $3000\,\mu mol.N.m^{-2}$ in a few hours) are expected to have a local but significant impact on phytoplankton growth, as demonstrated by Paerl (1985).

Atmospheric nitrogen input to the Western Mediterranean Sea is therefore particularly significant, especially in oligotrophic zones. The increase in atmospheric nitrogen deposition, probably at least doubled by long distance transport of pollutants, is expected to have an ecological impact in oligotrophic areas and also, perhaps, in coastal areas if they are nitrogen (as opposed to phosphorus) depleted.

Conclusions

The present study has provided basic information on pluriannual atmospheric deposition of dissolved inorganic nitrogen at a location in South Corsica. When individual rain events were assessed, they showed marked fluctuations in their inorganic nitrogen concentrations and associated fluxes, the lower values being observed in situations of oceanic or Saharan influences (Western and Southern sectors). A significant increase in this natural background level was observed when incoming air masses shifted to Northern and Eastern sectors; this increase is related to intensive human activity in various regions of the European continent.

Despite uncertainties about atmospheric deposition and riverine discharge of dissolved inorganic nitrogen, it appears that these estimated inputs to the Western Mediterranean Basin are very similar. The previous nitrogen budgets in this marine region then have to be reconsidered, suggesting a higher contribution for atmospheric deposition and consequently, a lower contribution for biological fixation of atmospheric N_2.

Atmospheric dissolved inorganic nitrogen input is of noticeable ecological importance, representing 10 to 25% of new production on average, and 25 to 60% in oligotrophic zones. Taking into account dry, inorganic and wet, organic nitrogen deposition would approximately double the atmospheric input, and partly increase the impact on primary production. This conclusion is consistent with the findings of Paerl (1986) and Fanning (1989), but contradicts those of Knap et al. (1986). Better knowledge of the complex primary production pattern in the Western Mediterranean should lead to improved understanding of the impact of atmospheric nitrogen input.

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