

**The Nitrogen Cycle of the Eastern Mediterranean Sea from a Stable
Isotope Perspective**

Dissertation

Zur Erlangung des Doktorgrades der Naturwissenschaften im Department
Geowissenschaften der Universität Hamburg

vorgelegt von

Paraskevi Mara

aus

Athen, Griechenland

Hamburg

2011

Als Dissertation angenommen vom Department Geowissenschaften der
Universität Hamburg

auf Grund der Gutachten von

Prof. Dr. Kay-Christian Emeis

und

Prof. Dr. Nikolaos Mihalopoulos

Hamburg den, 12. April 2011

Prof. Dr. Jürgen Oßenbrügge

Leiter des Department Geowissenschaften

Abstract

The Eastern Mediterranean Sea (EMS) is a nutrient-poor ocean with unusually high nitrate to phosphate ratio (up to 28: 1) and relatively depleted $^{15}\text{N}/^{14}\text{N}$ ratios (expressed as $\delta^{15}\text{N}$) in deep-water nitrate and sediments, compared to other oceanic settings.

Up to now the principal hypothesis for the depleted $\delta^{15}\text{N}$ values observed in the region was the biological nitrogen fixation. The nutrient budgets and the surveys that were conducted in the EMS favoured the idea of nitrogen fixation since there was no direct and measurable evidence for the isotopic fingerprint of the atmospheric NO_x as there was the case in other oceanic environments. Furthermore other possible procedures in the marine environment that could reasonably explain the low $\delta^{15}\text{N}$ values were perhaps underestimated because of this hypothesis.

In order to elucidate the possible reasons and to provide new information on the biogeochemical nitrogen cycling in the EMS, this thesis uses stable isotopic ratios ($\delta^{15}\text{N}\text{-NO}_3$, $\delta^{18}\text{O}\text{-NO}_3$) to investigate sources and processes that could provide a comprehensive data set for the N-cycling in the region. For this reason atmospheric samples (rain and dry deposition as well as aerosol samples) were collected as part of a one-year field programme and analysed for their $\delta^{15}\text{N}$ composition. Furthermore, samples of dissolved total reduced nitrogen ($\text{DON}+\text{NH}_4$), inorganic nitrogen (DIN in nitrate), the suspended particulate (N_{susp}) as well as the sinking particulate N (intercepted by sediment traps, SPN), were isolated from multiple depths of the water column at 17 stations, in a sampling cruise conducted on January 2007 across the EMS with R/V METEOR (M71-3 cruise).

N isotope data in both dry and wet deposition samples showed constantly negative $\delta^{15}\text{N}$ values compared to air N_2 , implying a strongly depleted atmospheric source calculated to be -3.1 ‰. The low $\delta^{15}\text{N}$ of wet deposition is in agreement with data from other environments, but the consistently depleted nature of dry deposition is unusual and supports the formation of atmospheric NO_3^- compounds with dust and sea-salt particles.

In the water column of the EMS, ongoing nitrate assimilation showed depleted nitrate concentrations in the mixed layer, causing an enrichment in both $\delta^{15}\text{N}\text{-NO}_3$ (average $3.1\text{‰} \pm 2.0\text{‰}$) and $\delta^{18}\text{O}\text{-NO}_3$ (average $6.0\text{‰} \pm 2.4\text{‰}$) of residual nitrate over the deep-water nitrate pool ($\delta^{15}\text{N}\text{-NO}_3$ average $2.1\text{‰} \pm 0.3\text{‰}$; $\delta^{18}\text{O}\text{-NO}_3$ average

4.0‰ ±1.3 ‰). Products of assimilation (PN_{susp} and dissolved organic nitrogen, DON) were more abundant in the mixed layer than below the thermocline (below 200 m), and $\delta^{15}\text{N}_{\text{susp}}$ of suspended matter (average 2.3‰ ±2.3 ‰) and $\delta^{15}(\text{DON}+\text{NH}_4)$ (average 1.6‰ ±2.2 ‰), were isotopically more depleted in the mixed layer than in deeper water ($\delta^{15}\text{PN}$ average 7.3‰ ±0.8 ‰; $\delta^{15}(\text{DON}+\text{NH}_4)$ average 5.1‰ ±4.0 ‰). SPN intercepted by sediment traps at two depths (1600 m and 2700 m) at one station (deployed during the cruise and recovered 216 days later) had an average $\delta^{15}\text{SPN}$ of 0.9‰ ±0.8‰ in the shallow trap and 0.8‰ ± 1.0‰ in the deep trap.

Altogether the obtained data will provide additional insights and will present a different prospect for the depleted $\delta^{15}\text{N}$ values reported in the nitrogen cycling of EMS. In addition they underline the importance of continuing to make measurements in order to evaluate a) the eventual fate of anthropogenic nitrogen entrained to the EMS and b) the contribution of the deep water mass to the $\delta^{15}\text{N}$ of the region.

Contents

Chapter 1. Introduction and overview	1
1.1 General introduction	1
1.2 Nitrogen cycle	2
1.3 Nitrogen Isotopic fingerprints.....	4
1.4 Background on isotope composition of atmospheric nitrogen species and marine deposition.....	5
1.5 Describing the marine environment of the EMS	7
1.6 On the importance of the atmospheric inputs in EMS ecosystem	10
1.7. Is the atmospheric environment of EMS capable of providing strong evidence for the atmospheric deposition hypothesis?.....	12
Chapter 2. Outline and experimental design of the thesis	14
2.1 Thesis outline	14
2.2 Experimental design.....	15
2.2.1 Study Area.....	16
A) <i>Atmospheric deposition</i>	16
B) <i>Marine samples</i>	17
2.2.2 Applied Methods.....	18
Chapter 3. Establishing the nitrate isotopic signature in the atmosphere of Crete (eastern Mediterranean Sea)	20
3.1 Brief Introduction.....	20
3.2. Materials and Methods.....	21
3.2.1. Sampling	21
A) <i>Wet deposition</i>	22
B) <i>Bulk deposition</i>	22
C) <i>Aerosol samples</i>	23
3.2.2 Analytical methods	23
A) <i>Nitrogen isotopic composition in NO₃⁻</i>	23
B) <i>Atmospheric nutrients</i>	24
3.3. Results	25
3.3.1. NO ₃ ⁻ concentrations and isotopic composition in rain water	25
3.3.2. Isotopic composition in bulk deposition	27

3.4. Discussion	28
3.4.1. Factors controlling isotopic composition in wet and dry deposition	28
3.4.2. Isotope fingerprints and sources of dry deposited material	30
3.5. Implications for the N-cycle in the Eastern Mediterranean Sea	32

Chapter 4. The isotopic ratios of nitrate, dissolved and particulate nitrogen in the Eastern Mediterranean Sea (EMS): An attempt to provide a comprehensive data set of $\delta^{15}\text{N}$ in N-pools of the water column and to explain the processes causing the unusual isotopic ratios in the deep water of EMS .. 38

4.1 Overview	38
4.2 Materials and Methods.....	40
4.2.1. Analytical methods	42
A) Nitrogen ($\delta^{15}\text{N}$) and oxygen (^{18}O) analysis in nitrate (NO_3^-) and total reduced dissolved nitrogen (TDN).....	42
B) $\delta^{15}\text{N}$ analysis of particulate nitrogen in suspended solids (PN_{susp}).....	44
4.3 Results	44
4.3.1 Concentrations of nitrogen compounds	44
4.3.2 Isotopic composition of nitrogen compounds.....	48
4.4 Discussion	51
4.4.1 Isotopic composition of reactive nitrogen in sub-nitracline and deep water masses	52
4.4.2. Nitrate in the surface layer: Testing the model of incomplete nitrate utilisation.....	56
4.4.3 Constraints from differences in $\delta^{15}\text{NO}_3$ and $\delta^{18}\text{NO}_3$	57
5. Nitrification of fixed N or recycled N.....	60
6. Input of atmospheric NO_x	61

Chapter 5. Conclusions and outlook 66

Acknowledgments	71
References	73
Figure Captions	90
Table Captions.....	92
List of abbreviations	93
Data Appendix.....	94

Curriculum Vitae 119

Chapter 1. Introduction and overview

1.1 General introduction

For more than a century, scientists around the world have carried out intensive research in order to reveal all the processes, and therefore to understand, the global significance of biogeochemical cycles. Biogeochemical cycles always involve equilibrium states, a term that refers to the balance in the cycling of the element between compartments (Fig. 1.1).

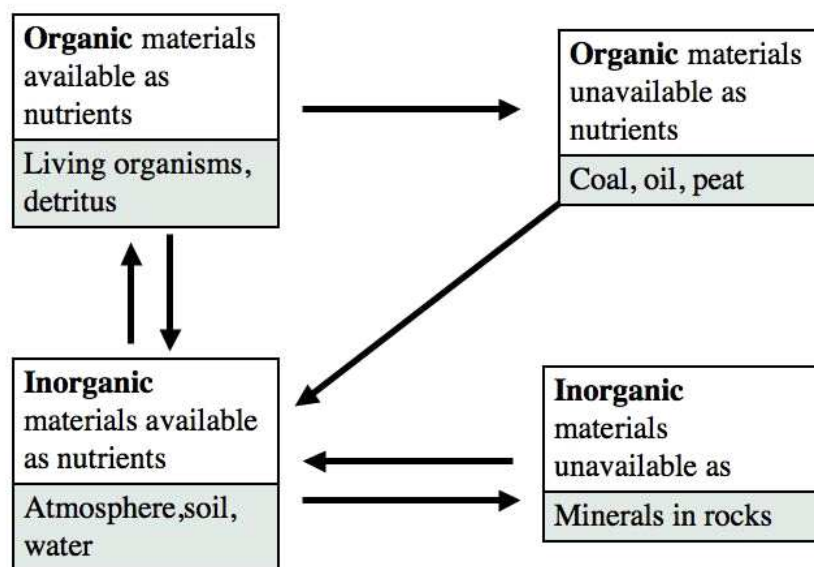


Fig. 1.1. Generalized diagram of a biogeochemical cycle within ecosystems

As a biogeochemical cycle describes the movements of substances over the entire globe, the study of a cycle is inherently multi-disciplinary. For example, the carbon cycle may be primarily related to research in ecology and atmospheric sciences, but biogeochemical dynamics is also related to other fields, such as geology and soil studies. In ecology and earth science, a biogeochemical cycle or a nutrient cycle is a pathway by which a chemical element or molecule moves through the biotic (biosphere) and abiotic (lithosphere, atmosphere, and hydrosphere) compartments of Earth. In effect, the element is recycled, although in some cycles there may be places (reservoirs) where the element is accumulated or held for a long period of time. By means of this procedure, elements, chemical compounds, and other forms of matter

are passed from one organism to another and from one part of the biosphere to another.

1.2 Nitrogen cycle

As nature's most effluent element, nitrogen gas (N_2) comprises 78.3% of the earth's atmosphere by volume (75.5% by mass). Compared to the atmosphere, the hydrosphere and the biosphere contain relatively little nitrogen (N) with the main difference that N, in the biosphere in particular, is highly reactive and is rapidly cycled.

The most important nitrogen forms in water include dissolved nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+); dissolved organic-nitrogen, and particulate organic and inorganic nitrogen (Delwiche, 1970; Stevenson, 1972b; Sprent, 1987). The major biogeochemical processes in N cycling (Fig. 1.2), include N_2 -fixation, ammonification, nitrification, uptake or assimilation, respiratory nitrate reduction, and denitrification.

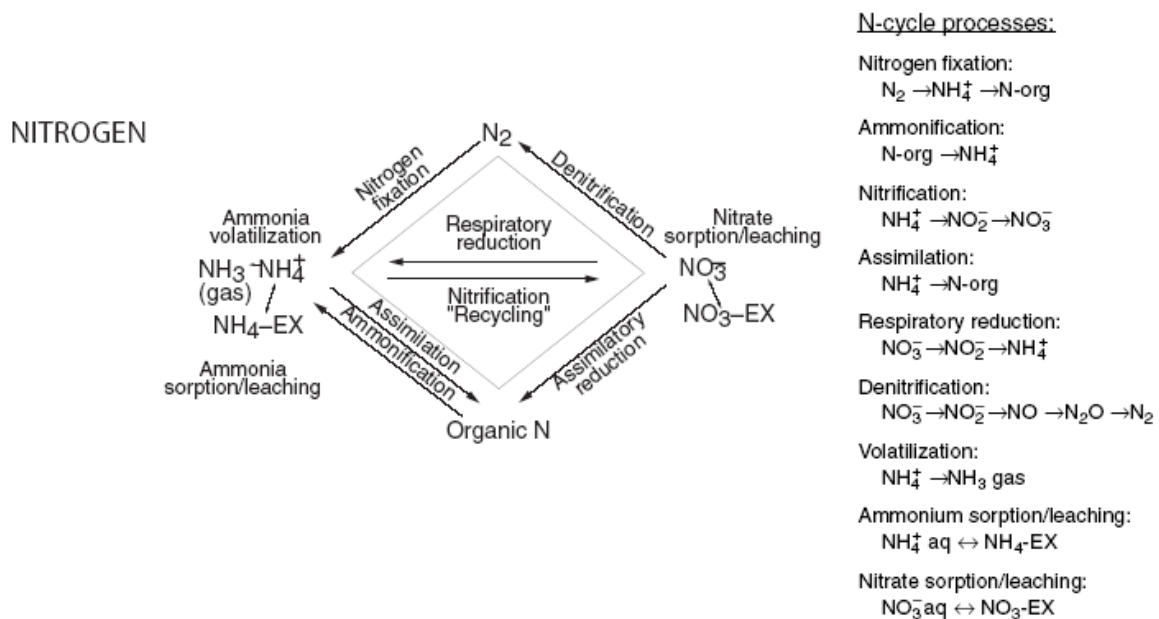


Fig. 1.2. Biochemical cycle of nitrogen

With the exception of ammonium assimilation, each biochemical transformation involves a change in the redox state of N, and a change in the pH (Sprent, 1987).

Determining nitrogen sources in the water bodies is important and complex. Nitrogen in seawater comes from watersheds, soils and sediments of the receiving water bodies, from direct deposition of nitrogen from the atmosphere, and from

nitrogen fixation in the water body itself (Burt et al., 1993). Some of the challenges in conducting nitrogen mass balance studies are to determine a) the unmeasured amounts of nitrogen removed from the water and stored in aquatic organisms and sediments, and b) the amounts of nitrogen added to the water from resuspension, erosion, and dissolution processes (Dingman, 1994). For example, N-NO_3 in surface waters can diffuse into underlying anoxic water layers or underlying anoxic sediments. In such environments biological activity assimilates some of the N-NO_3 and denitrifies the rest into nitrogen gases. Some of the nitrogen gases participate in nitrogen fixation and the remainder is emitted to the atmospheric boundary layer as long as the partial pressure remains above the equilibrium values given by Henry's Law.

The atmosphere has large horizontal transport speeds and can deposit trace nitrogen into other environments at distances of tens, or hundreds of kilometers from where it was originally injected. Once injected into the lower troposphere, trace nitrogen gases are acted on by the following processes: horizontal transport (by winds), mixing vertically and laterally by turbulence, chemical and physical transformation, and deposition from the atmosphere (Graedel and Grutzen, 1993). Atmospheric transport and mixing bring specific source emissions of various trace nitrogen gases into close proximity with trace gas emissions from hundreds of other sources to allow the complex chemical and physical transformations to occur. For example NH_3 from livestock sources can become comingled with automobile and industrial source emissions of sulphur (S) and nitrogen oxides to produce ammonium sulphate particles that are a major component of aerosols which produce regional haze events (Seinfeld and Pandis 1997; Ferm, 1998).

Atmospheric nitrogen is not useful to most organisms until it is converted ("fixed") to a bioavailable form (e.g. NO_3^-), that can be utilized. Natural and anthropogenic processes convert nitrogen to nitrogen oxides that are in turn converted in the atmosphere to nitrates and then are ultimately deposited on the Earth's surface. The growing use of the Haber-Bosch process in the creation of chemical nitrogen fertilizers for agricultural use, as well as other anthropogenic processes, has doubled the annual transfer of nitrogen into biologically available forms (Vitousek et al., 1997). In addition, there is a significant contribution to the transfer of nitrogen trace gases from Earth to the atmosphere, and from the land to the aquatic systems. One estimation (IPCC,1995) for the global sources of NO^- and NO_2^- (in units of millions of metric tons/yr of N) gives a total value of 52.6 and the top four sources are: fossil

fuel combustion, soil release, biomass burning and lightning. Concerning ammonia (NH₃), which can act as an important aerosol pollutant, the concentration in the atmosphere has tripled as a result of human activities.

1.3 Nitrogen Isotopic fingerprints

The use of nitrogen isotopes to identify nitrogen sources is based on the concept that nitrogen is interrelated in the biogeochemical cycle in many forms, and that measurable differences in the isotopic composition of nitrogen-source materials will persist as nitrogen-containing compounds transported from the source (Stumm and Morgan, 1981; Bolin and Cook, 1983; Peterson and Fry, 1987).

Nitrogen (N) has two naturally occurring stable isotopes, one with a relative atomic mass of 14 and the other of 15, referred to as ¹⁴N and ¹⁵N, respectively. The most common, ¹⁴N, has an abundance in N₂ gas of 99.63% (Junk and Svec, 1958; Mariotti, 1983) and is considered to be globally uniform. With the exception of adsorption reactions, the N-cycle processes tend to cause depletion of the heavier isotope in the products relative to the reactants (Kreitler, 1975; Letolle, 1980; Hubner, 1986).

Nitrogen isotope ratios are measured on the δ¹⁵N scale and expressed as *per mil* based on the equation:

$$\delta^{15}\text{N (per mil)} = \left[\frac{\left[\frac{^{15}\text{N}}{^{14}\text{N}} \right]_{\text{sample}}}{\left[\frac{^{15}\text{N}}{^{14}\text{N}} \right]_{\text{reference}}} - 1 \right] \times 1000$$

The composition of the sample is expressed with respect to the reference gas which by definition has a δ¹⁵N value of 0 ‰ (Heaton, 1986). The two isotopes of nitrogen exhibit different properties with regard to their reaction kinetics and thus, depending upon the nature of their respective formation processes and that of their precursors, the isotopic composition of particular species is different (Yeatman et al., 2001).

Particulates generally are less reactive compared to most dissolved nitrogen species. Ideally, suspended particulates in the water should consist of fragments of the original N-source material and should have an isotopic composition similar to the

source. Interpretation of isotopic composition of particulates can be complicated, however, because biological processes can add particulates to the suspended load. Algae, plankton, and bacteria can make up a substantial part of the particulate load (Berg and Staaf, 1981; Fairchild, 1983), especially during summer and autumn.

1.4 Background on and isotope composition of atmospheric nitrogen species and marine deposition

Fluxes of atmospheric nitrogen can enter the water column by direct (dry) deposition of aerosol particles or solvation of gaseous species (e.g. HNO₃, NH₃) and through rain-out (wet deposition) (Wankel et al., 2009).

Dry deposition is a procedure which helps in the removal of aerosols and gases from the atmosphere (Mihalopoulos et al., 1997). Aerosols, which mainly refer to solid and liquid phase particles suspended in air, are produced by a myriad of natural processes and human activities and are assigned to two main categories: fine particles (<1 μm diameter) and coarse particles (>1 μm diameter). They can be injected either directly into the atmosphere (examples of *primary* production), or formed from precursor gases that condense in the troposphere or stratosphere (examples of *secondary* production), presenting different chemical and physical features.

Depending on the size diameter of the aerosol, dry deposition can be determined by Brown's diffusion, inertial impaction or even by gravity. Concerning the dry deposition of gases, the model that is used extensively in the literature for the deposition velocity (Hicks and Liss, 1976), depends linearly on the wind speed and on the α_i factor, which is different for each compound (Table 1).

Compounds	α_i
HNO ₃	0.13
NH ₃	0.14
SO ₂	0.122

Table 1. α_i values for different compounds

Wet deposition is the other procedure that also removes particles and gases from the atmosphere. In the *in-cloud* wet deposition, there is incorporation of

particules into hydrometeors or into cloud droplets and fog droplets that either settle very slowly or are deposited by inertial impaction. During the *below-cloud* wet deposition, raindrops wash out particles from the atmosphere, when they are settling down.

The residence time of nitrogen molecules being measured in the wet and dry deposition ranges from minutes to weeks. Operationally wet deposition is measured by collecting precipitation (rain, snow, hail, etc.), which occurs during only a small percentage of the hours of a year but is still a very important removal process for chemical analysis. Dry deposition is much more difficult to monitor than wet, since it occurs all the time, but it can be the most crucial atmospheric nutrient procedure especially in oligotrophic environments (Fanning, 1989; Owens et al., 1992).

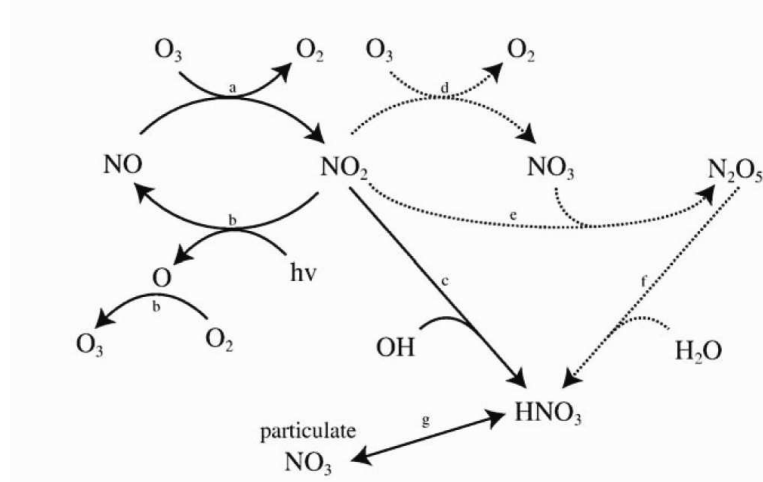


Fig.1.3. Depiction of NO_x cycling pathways leading to the formation of aerosol HNO₃ (or NO₃⁻). Solid lines represent reactions that occur during day time, while dashed lines correspond to the reactions performed at night.

Atmospheric nitrogen nutrients may occur in many forms including nitrate (as aerosol NO₃⁻ or HNO₃ vapor), organic nitrogen, and ammonium (NH₄⁺). In especially arid regions of the world, such as the EMS, dry deposition, in the form of aerosols, can represent the most dominant form of atmospheric nitrogen deposition (Kouvarakis et al., 2001). Studies of aerosol deposition to the ocean have been made in the open Atlantic and Pacific oceans (e.g., Arimoto et al., 1995; Baker et al., 2003, 2007; Chen and Siefert, 2004) as well as more regional seas including the Mediterranean Sea (Guieu et al., 1997; Migon et al., 1997; Ridame et al., 1999; Herut et al., 2001; Koçak et al., 2005; Bonnet and Guieu, 2006). Nitrate (including both particulate aerosol NO₃⁻ and gase HNO₃) represents the primary sink of atmospheric NO_x (NO + NO₂) which originates from both natural and anthropogenic sources (Fig. 1.3).

For many years, the only nitrogen isotope data known for ammonium and nitrate in rain water had been the measurements of Hoering (Hoering, 1957). Since then, studies of atmospheric nitrogen isotopes are still limited (e.g. Heaton, 1987; Freyer, 1991; Cornell et al., 1995; Russell et al., 1998; Kelly et al., 2005), compared to those reported for other ecosystems (Mulvaney et al., 1994; Slawk and Raimbault, 1995; Knapp et al., 2008a; Wankel et al., 2009). Reported values of $\delta^{15}\text{N}$ of atmospherically derived NO_3^- , from both wet and dry deposition, range widely (Heaton, 1987; Kendall, 1998; Russell et al., 1998; Yeatman et al., 2001; Hastings et al., 2003, 2004; Heaton et al., 2004; Elliott et al., 2007). Russell et al. (1998) have summarised the obtained isotopic values which were typically found to lie between -15 and +30‰ with considerable overlap between data from different sources. In large part this can be explained by variations in the $\delta^{15}\text{N}$ values for both natural and anthropogenic NO_x sources. For example, $\delta^{15}\text{N}$ of NO_x from coal power plants tend to have higher $\delta^{15}\text{N}$ values (+6 to +13‰; (Heaton,1987)), while vehicle exhaust has been shown to have lower $\delta^{15}\text{N}$ values (-13 to +6‰; (Moore, 1977; Heaton, 1987; Amman et al., 1999)). It is important however to note that Elliott et al. (2007) demonstrated a strong correlation between wet deposition's $\delta^{15}\text{N}$ - NO_3 and stationary source NO_x emissions in the northeastern US. Higher $\delta^{15}\text{N}$ values (up to +3.2‰) were obtained mainly in the areas that were impacted by higher NO_x emissions.

1.5 Describing the marine environment of the EMS

The Eastern Mediterranean Sea (EMS) has specific characteristics among the world's seas. It has been characterized by Azov (1991) as a ‘‘marine desert’’, a concept based on the impoverished phytoplankton biomass and productivity levels mainly due to phosphorus deficiency (Berland et al., 1980; Krom et al., 1991). Because of this deficiency, EMS is highly oligotrophic (Antoine et al., 1995) and the export production of organic carbon from the pelagic zone is exceedingly low (6-12 g C m⁻² a⁻¹) (B  thoux, 1989). Investigations conducted in the Mediterranean Sea (Dolan, 2000; Christaki et al., 2001; Pitta et al., 2001; van Wambeke et al., 2002) demonstrated a distinct longitudinal gradient of increasing oligotrophy from west to east in terms of the biomass.

The cause of the oligotrophy of the EMS is attributed to the general water mass circulation observed in the Mediterranean Sea. The circulation of the Mediterranean Sea is driven by an excess of evaporation over precipitation. The general circulation is an anti-estuarine thermohaline cycle open to the Atlantic, consisting of two closed sub-cycles in the western and eastern basin, respectively (Lascaratos et al., 1999). The communication between the two basins is constricted by the shallow trench between Sicily and Africa. The net water transport across this trench into the EMS is approximately 1 to 1.5 Sv (Moretti et al., 1993). The circulation starts at the Straits of Gibraltar when North Atlantic surface waters flow into the Western Mediterranean basin and move towards the Eastern basin. At this point it is important to note that the circulation in the upper 100–300 m of the Western Mediterranean Sea is dominated by Atlantic water that separates Mediterranean and frontal waters (Priour and Sournia, 1994). Persistent density fronts resulting from the interaction of saline Mediterranean and fresher Atlantic waters are associated with higher primary production rates than in surrounding waters (Lohrenz et al., 1988) and in the eastern basin (Azov, 1991), explaining the recorded longitudinal gradient of oligotrophy (Ignatiades et al., 2005).

Once the water circulation enters the Eastern basin, surface water density increases as intense evaporation increases surface salinity, transforming the Atlantic Surface Water (ASW) into the Levantine Intermediate Water (LIW). More specifically, the increasingly warm and dense water mass sinks in the area of the Rhodes Basin and feeds the LIW. This high temperature and high salinity water mass at depths between 200 and 500 m constitute the return flow of the general circulation when leaving the EMS as a westward current at depth in the Sicily Strait. A resultant outflow of nutrient-enriched subsurface water at the Strait of Sicily balances the inflow of Atlantic water (Miller, 1983). This physical circulation describes an unusual anti-estuarine flow that, as already mentioned, exports nutrients from the EMS making the ecosystem an impoverished system. Because of this situation, EMS can be characterized as an example of those pelagic ecosystems which depend on regenerated nutrients, with dissolved organic nutrients (such as dissolved organic nitrogen-DON) or particulate suspended matter being important substrates, while there is an effective recycling of new nutrients through the microbial loop (Zohary and Robarts, 1998; Thingstad et al., 2005).

EMS is also a unique ecosystem among other oligotrophic oceans because it is phosphorus limited (Krom et al. 1991), instead of nitrogen limited. The molar ratio of nitrate to phosphate (Redfield ratio: N: P; Redfield, 1958) appear to be in the vast majority of all its water masses higher than 20 while in the deep water it is ~ 28 : 1 (Krom et al. 1991; Kress and Herut 2001; Kress et al. 2003) (Table 2).

	Basin (>300 m)	Levante	Aegean	Adriatic	Ionian
Median Nitrate ($\mu\text{mol dm}^{-3}$)		4.70	2.11	5.07	4.47
Median Phosphate ($\mu\text{mol dm}^{-3}$)		0.13	0.09	0.21	0.12
Sum Nitrate/Sum Phosphate		24.8	18.2	23.4	28.7
number of data points		251	384	373	520

Table 2. Median concentrations of nitrate and phosphate in water masses below 300m depth (Schlitzer, 2004).

Evidence for P limitation of the surface waters of the Eastern Mediterranean has been obtained from: a) observations of phytoplankton and bacterial activity (Zohary and Robarts 1998), b) the determination of the $\delta^{15}\text{N}$ content of nitrate after phytoplankton bloom, which revealed a significantly enriched heavy N isotope characteristic of an ecosystem where primary production is terminated before completion such as by P limitation, (Struck et al. 2001) and c) by P addition experiments showing that although the ecosystem response to P addition is complex, the system exhibits a severe lack of phosphate.

The high N: P ratio is retained within the system because there is no significant denitrification in either the sediments or intermediate water (Krom et al., 2004). Support for this conclusion is provided by the observation that the only area of the Eastern Mediterranean where the N: P ratio in deeper water is ~ 16 : 1 is the northern Adriatic Sea, which is also the only area with significant denitrification (Krom et al., 2004). Furthermore, it is interesting that the $\delta^{15}\text{N}$ ratios of nitrate, suspended matter, and surface sediments in the EMS are significantly lower than those of other oligotrophic oceans (Struck et al., 2001; Pantoja et al., 2002; Çoban-Yildiz et al., 2006).

1.6 On the importance of the atmospheric inputs in EMS ecosystem

Up to now, three plausible hypotheses have been formulated in an attempt to explain the anomalous Redfield ratio, the excess reactive nitrogen concentrations, and the unusually depleted N-isotope ratios in the nitrate of EMS intermediate and deep waters.

In the first hypothesis, Krom et al. (1991) suggested that the high nitrate to phosphate ratio (and thus the nutrient limitation) occurred because phosphate has been removed from the Levantine Deep Water (LDW) by the adsorption of Saharan dust. However, when detailed adsorption experiments were carried out using Saharan dust and Mediterranean seawater spiked with phosphate, insignificant amounts of phosphate were adsorbed (Herut et al., 1999; Pan et al., 2002; Ridame et al., 2003; Krom et al., 2004).

The second hypothesis that was put forward in the literature gave the explanation of the unusual nutrient limitation based on the extensive N₂ fixation in the EMS system, either by sea grasses (macrophytes) or by N-fixing phytoplankton including as yet unidentified diazotrophic bacteria (Béthoux and Copin-Montegut, 1986; Béthoux et al., 1998; Pantoja et al., 2002). Evidence for extensive N₂ fixation has been suggested by Sachs and Repeta (1999), by Pantoja et al. (2002) and by Rees et al., (2006). Rees et al. (2006) focused mainly on a single location in the Cyprus eddy, while in general very low rates have been recorded at a series of stations adjacent to the Israeli coast (Berman-Frank et al., 2007) and in a transect across the EMS basin (Ibello et al., 2010).

Pantoja et al., (2002) attributed the low $\delta^{15}\text{N-NO}_3$ values found in the intermediate waters to the N₂ fixation. Based on calculations, Pantoja et al., (2002) estimated that ~ 90% of the nitrate present in the Eastern basin was formed by the same process. Indeed the east-west survey of the $\delta^{15}\text{N}$ distribution in the Mediterranean Sea made by the authors, revealed a decrease in surface $\delta^{15}\text{N}$ suspended PON ($2.7 \pm 1.2\text{‰}$ to $-0.2 \pm 0.7 \text{‰}$), $\delta^{15}\text{N}$ chlorins ($2.6 \pm 2.3 \text{‰}$ to $-7.1 \pm 1.3 \text{‰}$) and deep-water nitrate ($3.4 \pm 0.5 \text{‰}$ to $2.5 \pm 0.1 \text{‰}$), implying an eastward increase in the possible contribution of N₂ fixation to the water column nitrogen budget. Based on a two-end member source model, Pantoja et al., (2002) estimated that N₂ fixation could account for 20 - 90% of the N supply to the western and eastern Mediterranean, respectively, exceeding previous estimates (7 - 41%) based on nutrient

budgets (Béthoux et al., 1986). Koppelman et al., (2003) similarly suggested that light $\delta^{15}\text{N}$ -PON in mesozooplankton was due to consumption of phytoplankton, including a high proportion of N fixers.

The approach of N_2 fixation as an explanation for the unusual N: P ratio raises certain issues. The lack of a) direct evidence for substantial populations of N_2 -fixing algae in the Mediterranean Sea (Pantoja et al., 2002) and b) direct measurements of N_2 fixation rates, pose some questions about the occurrence of N_2 fixation in the EMS. It is still unclear why the process of N_2 -fixation should occur in a phosphate limited system which also belongs to the highly oligotrophic systems of the world.

The third hypothesis that could also explain the puzzling features of the nutrient cycles in the EMS is based on the atmospheric deposition of inorganic nitrogen (DIN). This process in the ocean can represent a potentially important new source of nitrogen, supporting primary production particularly in the oligotrophic regions of the world (Wankel et al., 2009).

The advantage of the atmospheric deposition hypothesis is that it can explain a number of observations considered as indications of occurrence of N_2 fixation. Based on previous evidence concerning the atmospheric input in the EMS, after a 3 year-period of measurement, Kouvarakis et al., (2001) suggested that atmospheric deposition of DIN could account for up to 370% of the measured PON in the sediment traps in the EMS, indicating that the atmospheric pathway alone can sufficiently account for the measured new nitrogen production. Some years later, Krom et al., (2004) presented a detailed nutrient budget of inputs to the EMS basin, showing that there is a high N: P ratio (~ 16: 1) in all the input sources, and particularly from the atmospheric source, where the N: P ratio is 117: 1. Furthermore Krom et al., (2004) based on detailed measurements of the atmospheric inputs of both N and P into the Eastern Mediterranean, (Mihalopoulos et al., 1997; Herut et al., 1999, 2002; Markaki et al., 2003), suggested that this new source could provide as much as 50% of bioavailable reactive nitrogen.

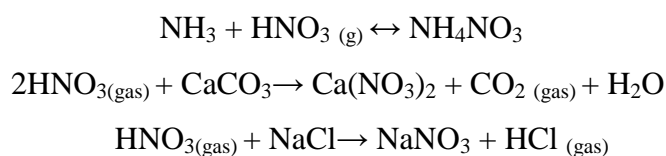
Krom's approach was different from other budgets that were carried out earlier (Sarmiento et al., 1988; Béthoux et al., 1998). These budget studies performed in the EMS assumed steady state conditions, calculating, due to the lack of atmospheric measurements, the atmospheric and terrestrial inputs into the eastern basin by the difference. Since the atmospheric loads of reactive nitrogen have increased

dramatically over the last decades (Kouvarakis et al., 2001) the approach of atmospheric deposition could explain neatly the anomalous N: P that is recorded in the region. Furthermore, the aeolian inputs of trace elements can be an effective external source in the EMS, since riverine inflow has declined over the years as a result of the construction of the Aswan dam on the Nile and from changes in irrigation (Martin et al., 1989; Guerzoni et al., 1999).

1.7. Is the atmospheric environment of EMS capable of providing strong evidence for the atmospheric deposition hypothesis?

Studying the atmospheric environment of EMS, Kouvarakis et al. (2001) observed a clear seasonality in the concentrations of nitric acid (HNO₃). Nitric acid is a major nitrogen source in the atmosphere over Crete, presenting the highest concentrations during the dry period (from May to September). Because the mechanism of HNO₃ formation is the same worldwide, there is an implication that the δ¹⁵N values of HNO₃ that are measured in other places in Europe (Fryer, 1991)¹ could reasonably be applied to the region of EMS.

This is not the case for particulate NO₃⁻ which can exist in the forms of a) ammonium nitrate (NH₄NO₃) and b) sodium (NaNO₃) and calcium nitrate Ca(NO₃)₂, which are mainly soil and sea salt-based aerosols (Metzger et al., 2006). The reactions that cause the formation of the three different compounds are given below:



In polluted air the dominant form of particulate NO₃⁻ is present in its fine-mode (< 1µm diameter), which corresponds to NH₄NO₃. Measurements performed in several locations in the EMS (Kouvarakis et al., 2001; Danalatos et al., 1995; Koçak et al., 2004) found no NH₄NO₃ during the dry period. The main reasons for the absence of ammonium nitrate in the area are attributed to the elevated temperatures, as well as to the high regional SO₂ concentrations which neutralize NH₃ preventing the

¹ It is important to note that the values reported from Freyer (1991) for HNO₃, were strongly depleted compared to the fine mode particulate NO₃⁻ that presented enriched isotopic values (see Chapter 3)

formation of NH_4NO_3 (Seinfeld and Pandis 1997; Bardouki et al., 2003). The absence of NH_4NO_3 from the atmosphere of the EMS is important since this is unusual compared to other European areas, where the presence of NH_4NO_3 is very common (Putaud et al., 2004). This observation can imply that in the atmospheric environment of the EMS the major source of nitrate input is the coarse mode ($>1\mu\text{m}$ diameter) of particulate nitrates, $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 respectively, that in general can represent 50% of the total particulate in the offshore-flowing air (Spokes et al., 2000; Yeatman et al. 2001). Furthermore it can suggest that the isotopic signature of particulate atmospheric NO_3^- established by Freyer (1991) for Northern and Western Europe is unlikely to be the same in the EMS, due to different dominance of the particulate nitrate species.

The presence of the coarse mode of particulate nitrate and the absence of NH_4NO_3 , which is the dominant representative of the fine mode particulate nitrate, make the atmospheric input characteristics differ between the two sub-basins of the Mediterranean Sea. For example, ammonium nitrate has been reported by several authors in the atmosphere of the Western Mediterranean (Sellegri et al., 2001; Querol et al., 2004), in contrast, as already mentioned, to the Eastern basin. Sellegri et al. (2001) showed that NH_4NO_3 can be present even at 100–200 km offshore, especially when the air masses originate from Western Europe. Because NH_4NO_3 has enriched $\delta^{15}\text{N}$ (Freyer, 1991) and because its deposition velocity is much lower compared to the other nitrate species, this difference in the dominant speciation of reactive nitrogen in the atmosphere is likely to cause the west-to-east gradient in $\delta^{15}\text{N}$ of atmospheric N inputs to the surface water masses of the Mediterranean Sea that was recorded in previous studies (Pantoja et al., 2002).

Chapter 2. Outline and experimental design of the thesis

2.1 Thesis outline

This thesis is based on a collection of samples, novel analyses, and multi-faceted datasets that make a start on the interpretation of the information recorded for the isotopic composition of nitrate both in the atmospheric and marine environments of the EMS. Nitrogen (N) isotopic data are the common theme in all Chapters. The obtained atmospheric data which are mentioned in this dissertation are used to establish the isotopic fingerprint of nitrate input from the atmosphere to the EMS. Concerning the assessment in the marine environment of EMS, the main objective was to document the stable isotope ratios in nitrate ($\delta^{15}\text{N-NO}_3$, $\delta^{18}\text{O-NO}_3$), in dissolved organic nitrogen ($\delta^{15}\text{DON+NH}_4^-$) and in particulate N of both suspended particles ($\delta^{15}\text{N}_{\text{susp}}$) and sinking particles ($\delta^{15}\text{N-SNP}$), that can be used to estimate the recycling portion of nitrate.

The focus on producing a more complete portrait of $\delta^{15}\text{N-NO}_3$ through the measurement of multiple parameters has enabled this study a) to establish the isotopic signature of nitrate in the atmosphere of EMS; b) to examine whether the depleted $\delta^{15}\text{N-NO}_3^-$ in deep waters of the EMS may be explained by atmospheric deposition alone without N_2 -fixation playing a significant role and c) to estimate the portion of nitrate in the surface layer of water column of EMS, that must have derived from regenerated N.

The following individual Chapters of this thesis constitute the basis of 2 articles that are submitted to peer-reviewed scientific journals:

Chapter 3

Mara, P., Mihalopoulos, N., Gogou, A., Dähnke, K., Schlarbaum, T., Emeis, K.-C., Krom, M., (2009), **Isotopic composition of nitrate in wet and dry atmospheric deposition on Crete/ Eastern Mediterranean Sea**, *Global Biogeochemical Cycles* 23, GB4002 11pp.doi:10.1029/2008GB003395.

Chapter 4

Emeis, K.-C., Mara, P., Schlarbaum, T., Möbius, J., Dähnke, K., Struck, U., Mihalopoulos, N., Krom, M., (2010), **Isotope ratios of nitrate, dissolved reduced**

and particulate nitrogen in the Eastern Mediterranean Sea trace external N-inputs and internal N-cycling, *Journal of Geophysical Research-Biogeoscience*, doi:10.1029/2009JG001214, in press.

My contribution to Chapter 4 (Emeis et al., 2010):

- analysis and determination of the stable isotope ratio of nitrogen ($^{15}\text{N}/^{14}\text{N}$) and oxygen ($^{18}\text{O}/^{16}\text{O}$) of nitrate (NO_3) in samples collected from the water column during the M71-3 cruise (part of the data set).
- recovery, analysis and determination of nitrogen stable isotope ratio ($^{15}\text{N}/^{14}\text{N}$) in samples of the sediment-water interface deriving from multicorer deployments, during the same cruise.
- recovery, analysis and determination of the oxygen stable isotope ratio ($^{18}\text{O}/^{16}\text{O}$) in atmospheric dry deposition samples, part of the data set presented for the Δ (15,18) calculation.
- co-work in the manuscript discussion and preparation.

2.2 Experimental design

The natural isotopic variations of nitrate (NO_3^-), provide an important integrative tool for studying the nitrogen cycle. As already discussed, depending on the environment the $\delta^{15}\text{N}$ can provide information for the major transformations of the internal cycling and transport of nitrates, as well as the nitrogen balance of inputs and losses that occur in the ocean. The $^{18}\text{O}/^{16}\text{O}$ ratio of nitrate ($\delta^{18}\text{O}\text{-NO}_3$) has been studied in freshwater and terrestrial systems and has been shown to provide additional and important constraints on natural processes (Kendall, 1998), since oxygen and nitrogen atoms in nitrate do not record identical aspects of the nitrogen cycle (Casciotti et al., 2002). Furthermore as will be extensively discussed below, the in parallel determination of $\delta^{18}\text{O}\text{-NO}_3$ and $\delta^{15}\text{N}\text{-NO}_3$, can assign a factor which is helpful in the discrimination of the isotopic signature of the regenerated nitrogen, a parameter that is important for the productivity in oligotrophic environments.

2.2.1 Studing Area

A) Atmospheric deposition

The collection of atmospheric deposition samples was carried out in two different places in the island of Crete. These two stations represent an urban and a relatively pristine setting respectively.

The main station that collected bulk, wet and aerosol deposition was located in Finokalia ($25^{\circ}40'E$, $35^{\circ}20'N$), with an elevation of 130 m where no significant human activities occur within a range of 20 km. Finokalia is located in the northern part of Crete, and faces the sea within the sector 270° - 90° . The second station which collected wet deposition events only, is located in the University of Crete ($25^{\circ}4'E$, $35^{\circ}18'N$) situated 6 km south of the city of Heraklion (Fig. 2.1).

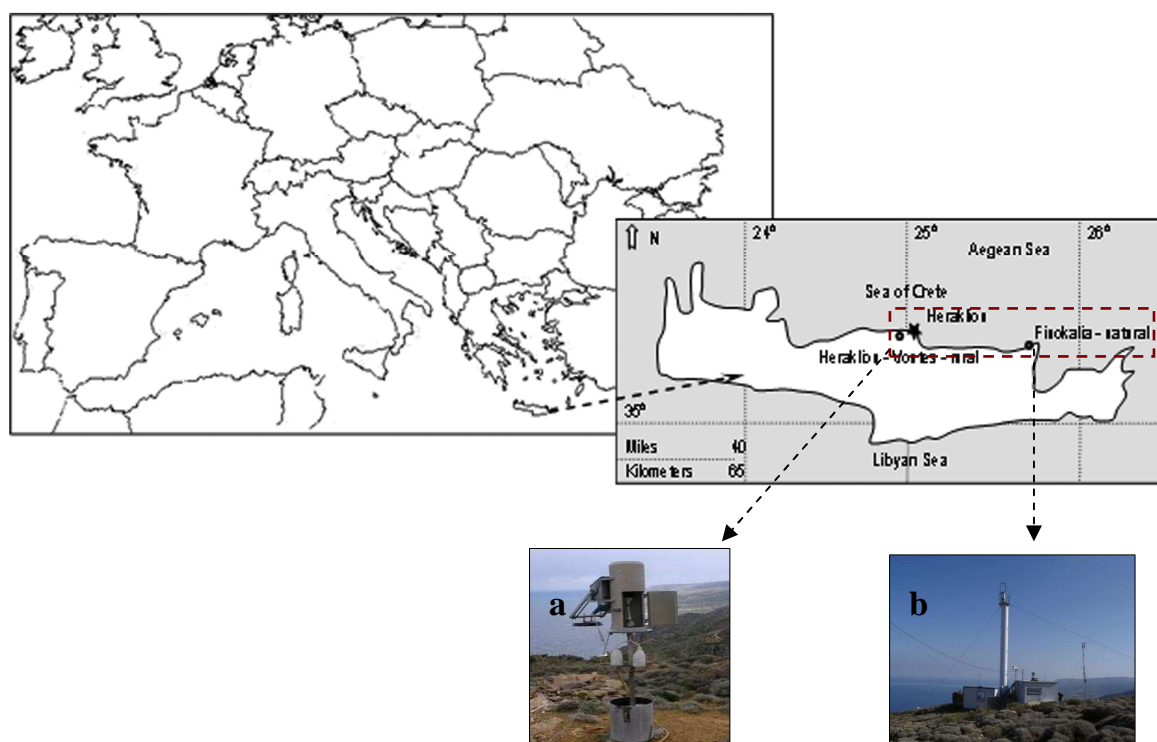


Fig. 2.1. Location of the sampling sites:a) Heraklion station b) Finokalia station

B) Marine samples

Samples were collected on board the R/V METEOR during a 17-day sampling campaign, undertaken in January/February 2007. All stations were aligned on E-W and N-S transects covering a wide grid of stations located mainly in the pelagic zone of the EMS (Fig.2.2). The arrangement of the stations attempted to cover all the major basins and water masses recorded in the region².

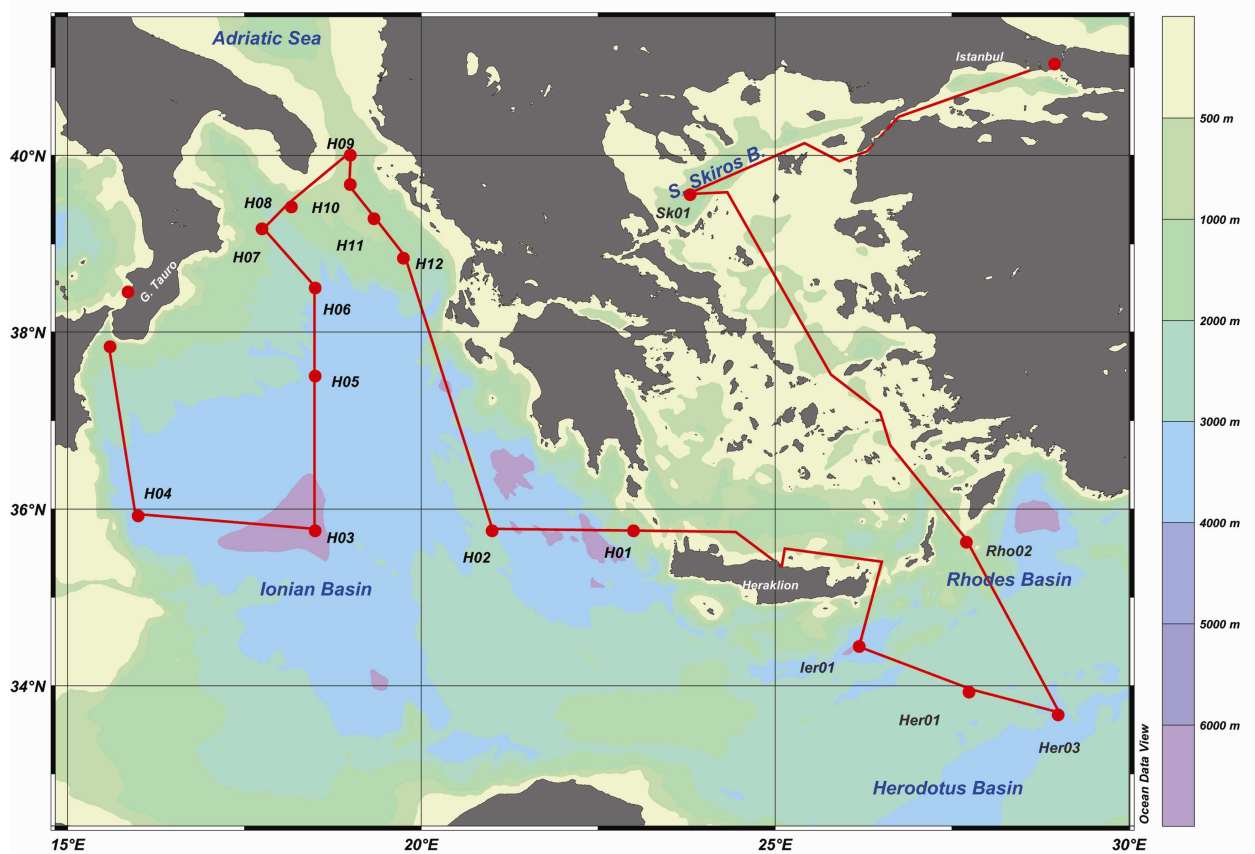


Fig. 2.2. Sampling stations as conducted during the R/V Meteor cruise 71-3 in the Eastern Mediterranean Sea (January-February/2007).

² The analytical details concerning the sampling campaigns that were performed for the needs of the thesis are fully presented in the following chapters

2.2.2 Applied Methods

Denitrifier method

For the needs of this thesis, a method using denitrifying bacteria for measuring nitrogen and oxygen isotopic composition of nitrate at the natural-abundance level was used, following the analytical protocols described by Sigman et al., (2001) and Casciotti et al., (2002). The denitrifier method takes advantage of naturally occurring denitrifying bacterial strains such as *P.chlororaphis* and *P.aureofaciens*, that lack an important gene (*nosZ*) (Christensen and Tiedje, 1988; Glockner et al., 1993) which encodes an enzyme responsible for the reduction of N₂O to N₂ (Zumft and Vega, 1979).

The classical bacterial denitrification pathway (Fig.2.3) consists of nitrate (NO₃) respiration that leads to nitrite (NO₂), nitrite respiration which is combined with nitric oxide (NO) reduction, and nitrous oxide (N₂O) respiration with final result dinitrogen (N₂).

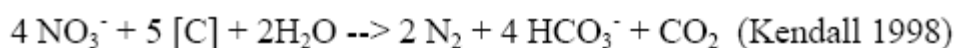
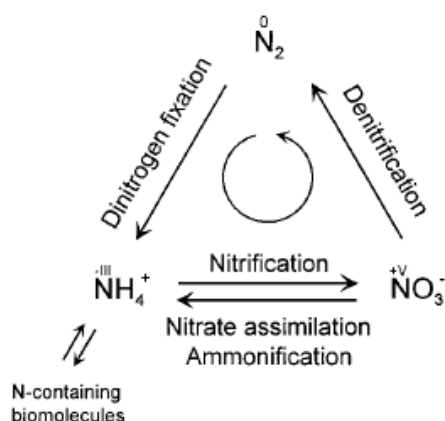


Fig. 2.3. Biogeochemical nitrogen cycle sustained by prokaryotes. The Roman numerals give the formal oxidation state of the principal nitrogen species of the cycle. The equation beneath the scheme presents the denitrification pathway that is mediated by the *Pseudomonas* denitrificans.

For nitrogen isotopes, if the conversion is complete and there are no additional nitrogen pools being converted to N₂O, mass balance requires that the δ¹⁵N of the product N₂O be identical to that of the initial nitrate. In the case of oxygen, the calculation of isotopic composition cannot be considered as a mass balance equation. Casciotti et al., (2002) established approaches for quantifying and correcting both

fractionation and oxygen exchange that are inherent in the denitrifier method for $\delta^{18}\text{O}$ analysis of nitrate.

The denitrifier method compared to other isotopic methods has the advantage of achieving much higher sensitivity levels (Sigman et al., 2001; Casciotti et al., 2002). The main advantage lies in the fact that it can be characterized as a nanomole level method which realizes the critical needs of the isotopic analysis (e.g low sample size) providing reproducible isotopic analysis of samples in low nitrate concentrations that can go down to 1 μM (Sigman et al., 2001). Furthermore, it has the capacity to analyze the oxygen isotope composition of seawater nitrate, in parallel with the nitrogen isotopic ratio.

Chapter 3. Establishing the nitrate isotopic signature in the atmosphere of Crete (eastern Mediterranean Sea)

3.1 Brief Introduction

The Eastern Mediterranean Sea (EMS) is an ultra-oligotrophic environment characterised by extremely low annual primary productivity, dissolved nutrient concentrations in the surface and deep waters, chlorophyll-*a* concentrations, and phytoplankton biomass (Krom et al., 2003). The annual phytoplankton bloom occurs in winter, when all the wet atmospheric deposition takes place (Psarra et al., 2000, Kouvarakis et al., 2001). At that time, the typical mixing depth is around 200 m; during the summer, when much of the dry deposition occurs, the water column is well stratified. An N- budget calculation for the EMS (Krom et al., 2004) that used wet and dry atmospheric fluxes determined on the island of Crete and in Israel (Kouvarakis et al., 2001, Herut et al., 1999) suggested that 60% of the total reactive N and 30% of the total P is supplied by atmospheric input. This represents a more significant fraction of total supply than in many other ocean areas (Duce et al., 2008).

Interestingly, the $\delta^{15}\text{N}$ of NO_3^- in deep water of the EMS ($\sim 2.5\text{‰}$; Pantoja et al., 2002) is substantially lower in the deep waters of other oceans ($5\pm 0.5\text{‰}$; Liu and Kaplan, 1989; Sigman et al., 2000) and is in the same range as that found in thermocline nitrate of other oligotrophic ocean regions (Knapp et al., 2005; Casciotti et al., 2008). The EMS differs from these regions not only in the thermocline nitrate pool, but also in the deep-water pool and in all particulate N-compartments such as phytoplankton (Sachs and Repeta, 1999), suspended matter (Struck et al., 2001; Pantoja et al., 2002; Çoban-Yildiz et al., 2006), and surface sediments (Struck et al., 2001) have $\delta^{15}\text{N} < 5\text{‰}$.

Up to now, the excess of reactive nitrogen concentrations and the depleted N-isotope ratios in NO_3^- of EMS intermediate and deep waters, was explained mainly by the N_2 -fixation hypothesis (Béthoux and Copin-Montegut, 1986; Pantoja et al., 2002). According to the nitrogen fixation explanation, the excess N dominates the EMS system, because there are no significant areas of anaerobic sediments where denitrification could occur. This is due to the ultra-oligotrophic nature of the basin

caused by the anti-estuarine circulation in the EMS, and to low organic carbon concentrations in the sediments. The only requirement of the procedure is that the diazotrophic organisms, especially in the EMS, continue to fix atmospheric nitrogen while P starved. This is contrary to the results obtained for such organisms in other regions such as the Atlantic ocean (Mills et al., 2004).

The presence of low $\delta^{15}\text{N-NO}_3$ values in the intermediate and deep water has been used to support the high N_2 -fixation explanation (Pantoja et al., 2002, Koppelman et al., 2003) without however considering the isotopic signature of the nitrogen input through atmospheric deposition. The fact that the atmospheric input plays such a prominent role is due to the specific setting of the EMS and has been highlighted in recent literature which has revealed the importance of the atmospheric flux in the oceans. Specifically, Baker et al., (2007) have shown that ignorance of the $\delta^{15}\text{N-N}$ of the atmospheric flux in the tropical Atlantic resulted in an over-estimate of the N_2 -fixation rate by a factor of 2. Similarly, Knapp et al., (2008b) suggested that atmospheric deposition of nitrogen may account for a substantial portion of low- $\delta^{15}\text{N}$ in the nitrate pool of subtropical thermoclines.

In this Chapter are presented the first data on the isotopic composition of nitrogen in both wet and dry deposition of NO_3^- in the EMS on samples from the island of Crete over a period of more than a year. The data establish the isotopic fingerprint of nitrate input from the atmosphere to this important area of the ocean, which represents a boundary region between the anthropogenically affected air masses from Europe and the relatively unpolluted air masses from N. Africa. The main scope of the Chapter is to examine whether the depleted $\delta^{15}\text{N-NO}_3^-$ in the deep waters of the EMS may be explained by atmospheric deposition alone without N_2 -fixation playing a significant role.

3.2. Materials and Methods

3.2.1. Sampling

The sampling period started in April 2006 and ended in September 2007. During this period, wet and bulk deposition as well as aerosol samples were collected for the analysis of NO_3^- and its nitrogen isotopic composition (Table 3).

Stations	Samples	Sequence	Period	# samples
Finokalia	Bulk Deposition	1 sample/ 10-15 days	April 2006- September 2007	35
	Wet Deposition	Single events	April 2006- September 2007	14
	Aerosols	1 sample/ 3 days	June-July 2007	6
Heraklion	Wet Deposition	Single events	April 2006- September 2007	24

Table 3. Sampling protocol for the wet and dry deposition during the period 2006-2007

A) Wet deposition

Rainwater was collected on an event basis using wet-only collectors installed at two localities on the island of Crete, that were frequently referred to in the previous Chapter. The collection of the rain samples was done in PolyTetraFluoroEthylene (PTFE) vials, which were thoroughly washed in deionized water before exposure, and stored at -20 °C until further analysis.

B) Bulk deposition

Bulk deposition of dissolved inorganic nitrogen (DIN) was carried out by collecting particles on a flat surface covered by glass beads, positioned on a funnel, and situated at Finokalia at 3 m above the ground. The deposition measured using this technique corresponds to the total deposition (i.e., wet + dry). Because no rain events occurred from May to September 2006, the measured total deposition during that period corresponds to the dry deposition. The glass bead system was exposed to the atmosphere for 10-15 days and washed with nanopure water. The eluant was processed as the rainwater samples. It should be noted that there is no well-established and accepted technique for the direct determination of dry deposition. The advantage of the technique employed here compared to other techniques using funnels or flat

surfaces, is that the multiple layers of glass beads can trap larger particles and thus avoid resuspension.

The bulk collector was previously validated by comparing the nitrogen deposition measured with the glass beds with the sum of the deposition of gaseous and particulate nitrogen species measured *in parallel* (Kouvarakis et al., 2001). Both deposition techniques expressed the same seasonal variability in terms of nitrogen deposition, but the glass-bead technique was found to collect about 60% more. Given that there are large uncertainties encountered with the estimation of deposition velocities (V_d) of the various gaseous and particulate nitrogen species (Kouvarakis et al., 2001), the agreement is quite good.

C) Aerosol samples

In order to make the link between bulk and aerosol deposition in terms of their isotopic composition, aerosol samples were also collected at Finokalia during June and July 2007 using a virtual impactor (VI; Loo and Cork, 1988). The impactor was modified to divide particles into two size fractions: fine (aerodynamic particle diameter $D_a < 1.3 \mu\text{m}$) and coarse particles ($D_a > 1.3 \mu\text{m}$). The VI was run in parallel with the bulk deposition collector, and the average sampling time for the aerosols was 24 h. After collection, each filter was extracted with 20 mL Milli-Q water for 45 min in an ultrasonic bath. The extraction efficiency of this method is higher than 98% for all compounds of interest (Kouvarakis et al., 2001). After extraction, samples were stored at $-20 \text{ }^\circ\text{C}$ for further analysis.

3.2.2 Analytical methods

A) Nitrogen isotopic composition in NO_3^-

The $\delta^{15}\text{N}$ in NO_3^- were determined with the denitrifier method (Sigman et al., 2001; Casciotti et al., 2002) which is based on the isotopic analysis of nitrous oxide (N_2O) produced by denitrifying *Pseudomonas* strains. The details and the advantages of the method have already been discussed in Chapter 2. The N_2O that was the final product of the denitrification procedure was concentrated and purified on a Gas Bench (Thermo Finnigan Gas Bench II) and the isotopic composition was determined using

an isotope ratio mass spectrometer (Delta Plus XP) calibrated with ultra high purity N_2 gas against $\delta^{15}N$ in air as standard (Mariotti, 1984).

To avoid concentration-dependent fractionation effects, sample size was adjusted to achieve a final amount of 20 nmol N_2O . For each sample, duplicate measurements were performed, and an international KNO_3 -standard (IAEA-N3; $\delta^{15}N$ of 4.7‰ versus air N_2) was analysed with each batch of samples. The standard deviation on the IAEA- NO_3 was below 0.2 ‰ ($n = 5$) for $\delta^{15}N$.

B) Atmospheric nutrients

The analysis of the main atmospheric anions, including NO_3^- , was carried out by Ion Chromatography using a Dionex AS4A-SC column with ASRS-I suppressor in autosuppression mode of operation. The reproducibility of the measurements was better than 2 % and the detection limit was 0.08 μM of NO_3^- .

3. 3. Results

The EMS is characterized by the existence of two well-distinguished meteorological seasons equally distributed within the year: the dry season (from May to September) and the wet season (from October to April). Each season has typical circulation patterns: the dry season is mainly characterized by winds of North/North-East direction (Central and Eastern Europe and Balkans), which from July to September correspond to 90 % of the wind occurrences. During the wet season (October to April) the prevalence of N/NW sector is less pronounced and especially during March/April and October/November, winds from the North/North-West South/South-West (North Africa) and West sectors (marine influence) are roughly equally distributed. The seasonality is reflected in the amount, the mode of deposition and the isotopic composition of NO_3^- deposited on Crete.

3.3.1. NO_3^- concentrations and isotopic composition in rain water

The concentrations and deposition of NO_3^- on Crete (Finokalia and Heraklion) from April 2006 up to September 2007 ranged from 5.6 to 157 μM of NO_3^- (Fig. 3.1a) and from 0.02 to 2.45 $\text{mmol/m}^2/\text{rain event}$ (median value: 0.41 $\text{mmol/m}^2/\text{rain event}$), respectively. Very few single rain events were recorded during spring and summer which means that the available data are mainly for the autumn and winter periods. Per event NO_3^- fluxes in the rain water samples are in good agreement with those reported by Kouvarakis et al. (2001) which ranged from 0.01 to 1.16 $\text{mmol/m}^2/\text{rain event}$ (median 0.18 $\text{mmol/m}^2/\text{rain event}$).

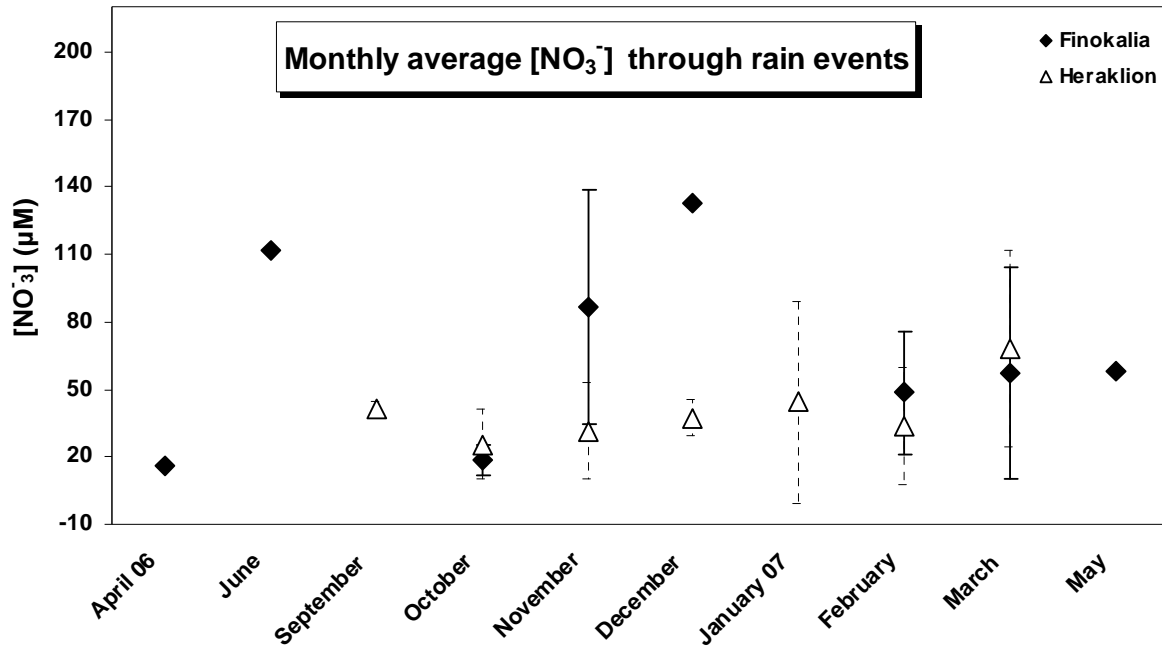


Fig.3.1.a. Monthly average nitrate levels in μM collected at two locations on the island of Crete (Heraklion and Finokalia).

The mean $\delta^{15}\text{N}$ of NO_3^- in rainwater ranged from -5.7‰ (April 06) to -3.4‰ (November 06) (Fig. 3.1b).

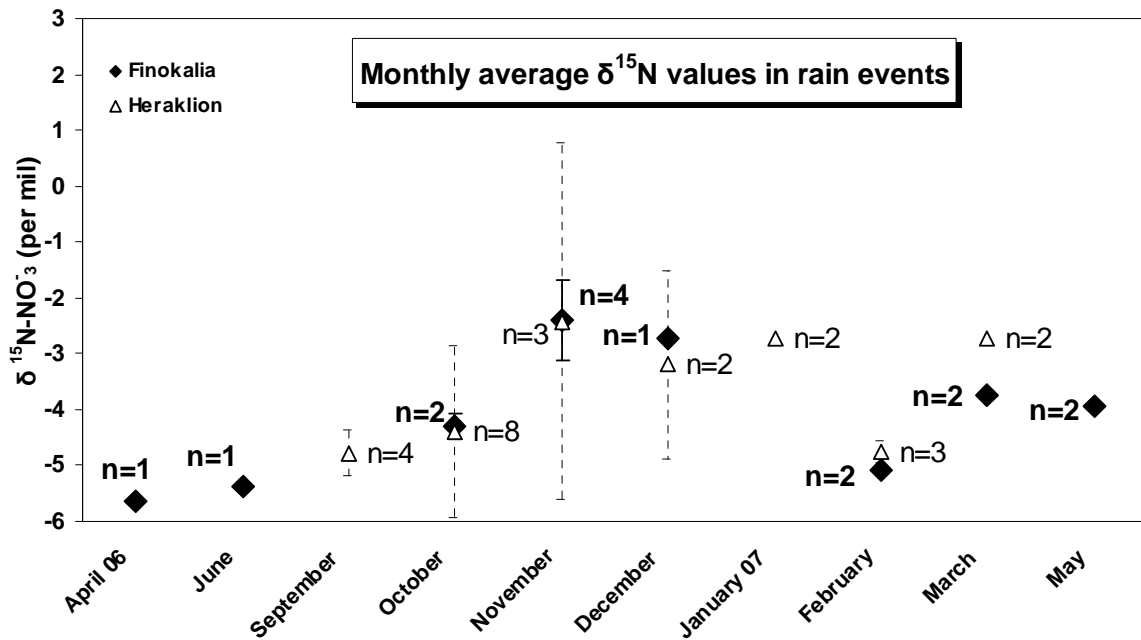


Fig.3.1.b. The $\delta^{15}\text{N}$ in wet deposition samples collected at two locations on the island of Crete (Heraklion and Finokalia).

Interestingly, the $\delta^{15}\text{N}$ values between Heraklion ($n=24$) and Finokalia ($n=15$) were not statistically different, despite the difference in anthropogenic influence

between these two locations (*t-test*, $\alpha = 0.05$). This suggests that the isotopic composition of NO_3^- in rain on Crete is mainly influenced by long-range transport phenomena rather than by local sources. Although local influence is of minor importance, it may explain the slightly enriched values observed at Heraklion during March 2007. More specifically, the rain events that occurred on different days at the two sampling locations during this month (March 2007) reflect the local rather than regional precipitation forcing.

Table 4 compares the $\delta^{15}\text{N}-\text{NO}_3^-$ in rain from Crete with those reported from other locations (Freyer, 1991; Hastings et al., 2003). In general, the data from Crete agree with the range of $\delta^{15}\text{N}$ values of atmospheric NO_3^- reported in the literature.

Season	Region						
	Jülich/ Germany (moderately polluted)	Ahrensburg/ Germany (moderately polluted)	Deuselbach/ Germany (rural)	Le Conquet/ France (coastal)	Pretoria/ South Africa (polluted)	Bermuda/ UK (mixed influence)	Crete/ Greece
Spring	-3.8± 1.7	-2.7± 3.0	-2.2± 2.7	-5.4± 2.3	-5± 5.2	Warm season -2.1± 1.5	-4.4±1.0
Summer	-5.5± 0.8	-4.3± 2.5	-4.5± 2.5	-6.5± 3.7	-4.9± 3.0		-5.4
Autumn	-0.5± 0.6	-3.1± 3.9	-3.1± 3.2	-3.6± 2.2	-3.3± 5.1	Cold season -5.9± 3.3	-3.7±1.2
Winter	0.3± 0.4	-0.1± 1.4	-0.1± 1.4	-1.7± 1.0	0.3± 3.6		-3.7±1.1

Table 4. Comparison of average $\delta^{15}\text{N}-\text{NO}_3^-$ values (*per mil*) in rain on Crete with those reported in the literature for Europe and South Africa (Freyer,1991) and Bermuda (Hastings et al., 2003).

3.3.2. Isotopic composition in bulk deposition

Bulk deposition of $\delta^{15}\text{N}-\text{NO}_3^-$ is displayed in Fig. 3.2. The horizontal error bars indicate the duration of the collection period in Julian dates. Figure 3.2 also shows the rainfall (h) in millimeters and the existence of the two seasons: the dry season (from May to September) and the wet season (from October to April). The majority of rainfall occurs during the wet season, whereas during the dry season the rain events are scarce. All samples had negative $\delta^{15}\text{N}-\text{NO}_3^-$ that ranged from -5.0 ‰

to -1.3 ‰, with a clear minimum during the spring and summer seasons that contrasts with enriched $\delta^{15}\text{N-NO}_3^-$ in autumn and winter (Fig. 3.2). Up to now, no data on $\delta^{15}\text{N}$ in bulk deposition samples exist in the literature so it is not possible to compare the obtained data with data from other regions of the world.

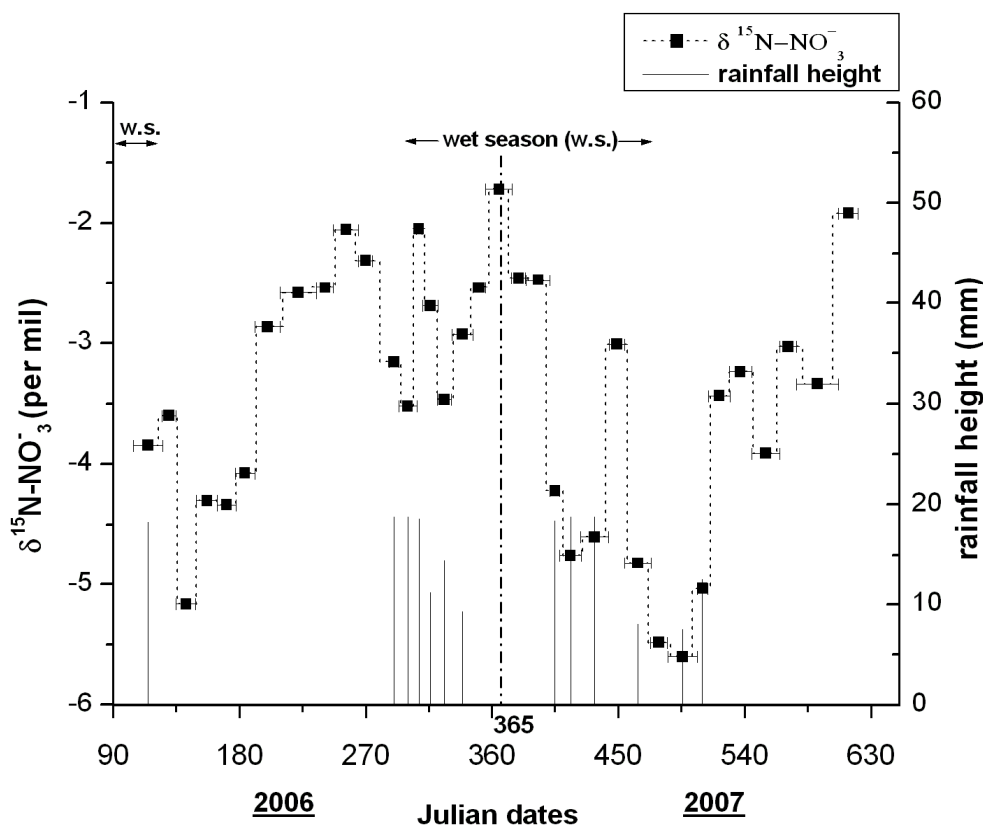


Fig. 3.2. Temporal variation (in Julian date) of nitrate $\delta^{15}\text{N}$ values and rainfall height (h) during the period April 2006-September 2007, at Finokalia.

3.4. Discussion

3.4.1. Factors controlling isotopic composition in wet and dry deposition

The $\delta^{15}\text{N-NO}_3^-$ in wet and bulk deposition on Crete was always < 0 ‰ over the sampling period from January to December 2006, but the isotopic composition of the two modes of deposition differed during the wet and dry seasons (Fig. 3.3).

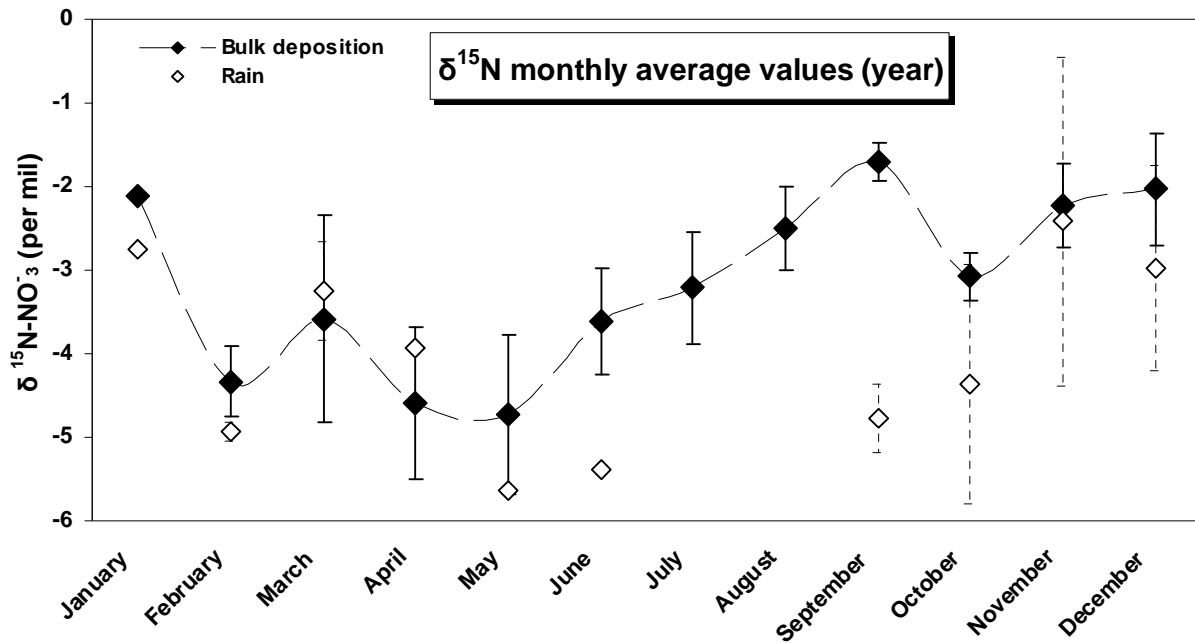


Fig.3.3. Monthly nitrate $\delta^{15}\text{N}$ values in both bulk and wet deposition samples on Crete. The data from the two sampling locations (Heraklion and Finokalia) have been combined.

During the rainy season (October to April), there is no statistically significant difference in $\delta^{15}\text{N}$ between rain and bulk samples (*t-test*, $\alpha = 0.05$). This is in agreement with the dominant role of rain as the main parameter controlling the fate of NO_3^- in the atmosphere.

The similarity of $\delta^{15}\text{N}$ in rain and bulk deposition disappears during the dry period (from May to September). At that time, bulk deposition continues to be depleted ($\delta^{15}\text{N}$: -2.2 to -5.0 ‰) and the few rain events (1 in June and May and 2 in September) that occurred during the dry period were more ^{15}N -depleted than dry deposition ($\delta^{15}\text{N}$: -5.4 to -5.6 ‰).

In the following sections, the $\delta^{15}\text{N}$ measured in the bulk deposition during the dry period (after removing the cases with the rain events) will be referred to as dry deposition and its sources will be examined below.

3.4.2. Isotope fingerprints and sources of dry deposited material

Dry deposition of NO_3^- is mediated by two compounds: aerosol (i.e. particulate) and gaseous NO_3^- , the latter mainly in the form of nitric acid (HNO_3 ; e.g. Kouvarakis et al., 2001).

Table 5 reports $\delta^{15}\text{N}$ for both gaseous and particulate NO_3^- reported by Freyer (1991) and compares these values with the obtained dry deposition data of this thesis.

Season	Region			
	Julich/ Germany $\delta^{15}\text{N}(\text{NO}_3^-)$ (‰)	Julich/ Germany $\delta^{15}\text{N}$ (HNO_3) (‰)	Crete $\delta^{15}\text{N}(\text{NO}_3^-)$ (‰) in coarse-mode aerosols	Crete $\delta^{15}\text{N}(\text{NO}_3^-)$ (‰) in dry deposition
Spring	5.5± 2.7	-2.2± 0.5		-4.2± 1.3 (n= 4)
Summer	3.7± 0.9	-3.0± 1.5	-3.4± 1.9 (n= 6)	-3.2± 0.6 (n= 11)
Autumn	6.8± 2.9	-2.6± 1.1		-1.7± 0.7 (n= 3)
Winter	9.2± 2.0	-2.7± 1.0		-2.0± 0.2 (n= 3)

Table 5. Nitrate $\delta^{15}\text{N}$ mean values (including standard deviation) in dry deposition and aerosol samples collected in Crete and comparison with the results reported in the literature (Germany; Freyer, 1991).

In Freyer's data concerning Germany (Freyer, 1991), HNO_3 had negative $\delta^{15}\text{N}$ throughout the year without any significant seasonal variation, whereas $\delta^{15}\text{N}-\text{NO}_3^-$ was always positive. In contrast the dry deposition data from Crete in 2006 had consistently negative $\delta^{15}\text{N}$, something very important since the collected samples are combined by aerosol NO_3^- and gaseous HNO_3 (Table 5). Kouvarakis et al. (2001) reported equal levels of gaseous HNO_3 and aerosol NO_3^- on Crete over the course of a year. It is difficult to reconcile the consistently negative $\delta^{15}\text{N}$ of dry deposition on Crete with the isotopic composition of NO_3^- and nitric acid obtained in Germany. The solution may lie in the different speciation of atmospheric reactive nitrogen compounds in the two areas.

The formation of HNO_3 involves anthropogenic sources because it is formed from the reaction of NO_2 with OH-radicals (Seinfeld and Pandis, 1997). Freyer (1991)

reported that the negative $\delta^{15}\text{N}$ values measured for HNO_3 (see Table 5) can indeed be reasonably estimated assuming a simple kinetic isotope fractionation that may occur during the reaction of NO_2 with OH-radicals. Kouvarakis et al. (2001) observed a clear seasonality in the concentrations of HNO_3 in the atmosphere over Crete, with the highest concentrations during the dry period. These authors attributed the HNO_3 behaviour to the seasonality in OH-radicals associated with an HNO_3 accumulation in the atmosphere due to the absence of rain. Because the mechanism of HNO_3 formation is common, the $\delta^{15}\text{N}$ values of HNO_3 obtained in Germany may be applied to the data from Crete.

This is not the case for particulate NO_3^- that exists, as already mentioned, in three forms. Specifically, when NH_4NO_3 is formed, it is present as fine mode particles and has low deposition velocities. Measurements performed in several locations in the EMS (Kouvarakis et al., 2001; Danalatos et al., 1995; Koçak et al., 2004) found no NH_4NO_3 during the dry period (May to September). The reasons for the absence were, as already mentioned, the high temperatures and the high concentrations of SO_2 as well as the decreased supply of ammonia from regional sources or from Eastern Europe compared to the more intensive agriculture practices in Western Europe. As a result, the isotopic signature of particulate atmospheric NO_3^- established by Freyer (1991) is unlikely to be characteristic for the EMS due to the difference in the particulate nitrate species.

Analysis of particulate NO_3^- collected during this work, as well as in several locations in the EMS (Koçak et al., 2004, 2007; Koulouri et al., 2008), indicate that the main types of particulate NO_3^- formed in the atmosphere over the EMS are NaNO_3 , and $\text{Ca}(\text{NO}_3)_2$ formed under the reactions that were described in Chapter 1. The prevalence of these species is the reason why the majority of particulate NO_3^- (more than 90 % of NO_3^-) is associated with coarse-mode particles which have much higher deposition velocities (up to a factor of 10) compared to fine-mode particles (Koulouri et al., 2008).

This is illustrated by the $\delta^{15}\text{N}$ of nitrate extracted from the six samples of coarse-mode aerosol deposition taken in the summer of 2006 using the VI collector (Table 5) which have an isotopic signature not significantly different (*t-test*, $\alpha = 0.05$) from that of NO_3^- in dry deposition collected at the same time. In addition, the isotopic signature of coarse-mode NO_3^- is very similar to that of HNO_3 in Germany (Freyer,

1991; Table 5). The depleted values of $\delta^{15}\text{N-NO}_3^-$ on Crete during the dry period are a strong indication for the formation of NaNO_3 and $\text{Ca(NO}_3)_2$ from the ^{15}N depleted precursor HNO_3 .

As already discussed, the Eastern compared to the Western basin of the EMS presents different atmospheric patterns in terms of NH_4NO_3 (Sellegri et al., 2001; Querol et al., 2004). As a result of the positive $\delta^{15}\text{N}$ values of NH_4NO_3 ($\delta^{15}\text{N} > 0\text{‰}$) (Freyer, 1991) and because of the lower deposition velocity compared to the other nitrate species, there is a difference in the dominant speciation of reactive nitrogen in the atmosphere of the two basins, something that can cause the west-to-east gradient in $\delta^{15}\text{N}$ of atmospheric N inputs to surface water masses of the Mediterranean Sea.

3.5. Implications for the N-cycle in the Eastern Mediterranean Sea

NO_3^- in both wet and dry deposition samples obtained from Crete has a $\delta^{15}\text{N}$ of -3.1‰ on flux-weighted annual average. In addition N: P ratio in deposition samples was of the order of 160 (Mihalopoulos, unpublished data), significantly higher than the seawater ratio. Because atmospheric deposition contributes $> 50\%$ of biologically available reactive N to the EMS (Krom et al., 2004), the depleted isotope signature of atmospheric input must be taken into account in explaining the depleted N-isotopic composition of the nitrate pool in this ocean basin and in other oligotrophic regions (Baker et al., 2007; Knapp et al., 2008a).

As already discussed the most widespread explanation for the unusually high N: P ratio in the deep water of the EMS, is the high rates of nitrogen fixation (Béthoux and Copin-Montegut, 1986; Gruber and Sarmiento, 1997; Pantoja et al., 2002; Ribera d'Alcala et al., 2003). One of the principal arguments in support of the postulated high contribution by diazotrophic N_2 fixation in the EMS (e.g., Mahaffey et al., 2005) is the depleted $\delta^{15}\text{N}$ of dissolved nitrate in the deep water masses ($2.5 \pm 0.1\text{‰}$ in the EMS, Pantoja et al., (2002)) compared to 4-6 ‰ in the Atlantic Ocean; (Brandes and Devol, 2002).

Based on recent literature, there are only three measurement-based estimates of N_2 -fixation rates in the EMS, and the results of the measurements are contradictory. Rees et al., (2006) determined very high rates of nitrogen fixation ($129 \text{ nmoles N L}^{-1} \text{ d}^{-1}$) during a single set of measurements carried out in the centre of the Cyprus Eddy.

These rates were 128-240 % of the maximum rates determined in the NE Atlantic Ocean (Voss et al., 2004). If this were to be the case over the entire EMS, the amount of N₂ fixed would be 1420 * 10⁹ moles N/y for the entire EMS, or 780 % of the total reactive N exported to the Western Mediterranean Sea through the Straits of Sicily (Krom et al., 2004). In contrast, a series of N₂ fixation measurements carried out by Berman-Franck et al., (2007) on the coast of Israel found rates ~ 1 nmole N L⁻¹ d⁻¹ in winter and 0 nmole N L⁻¹ d⁻¹ in summer. Ibello et al. (2010) have found similarly low values on a transect carried out across the EMS. Again if this were to be the case over the entire area of the EMS, these low rates would result in a calculated fixed N production of < 10 * 10⁹ moles N/y, or around 5 % of the total N exported through the Straits of Sicily (Krom et al., 2004). Clearly, the direct evidence for significant diazotrophic N₂ fixation in the EMS is at present ambiguous.

An indirect approach to assessing the contribution of newly fixed N₂ is based on the nitrogen isotopic composition of particulate nitrogen and nitrate and has been used in support of and to quantify N₂ fixation in the EMS (Pantoja et al., 2002; Sachs and Repeta, 1999). Based on data available at that time, Pantoja et al., (2002) estimated relative contributions of N from N₂ fixation (assumed as having a δ¹⁵N of -2.6 ‰) and deep-water nitrate (assumed as having a δ¹⁵N-NO₃⁻ of 2.4 ‰) needed to explain an observed δ¹⁵N of -2 ‰ of algal biomass found in their samples from the EMS. These authors concluded that up to 90 % of assimilated N in the EMS derives from N₂-fixation. Using this simple approach, but using the present measured values for atmospheric input, it is calculated that an algal biomass in the EMS with a δ¹⁵N of -2 ‰ may equally well derive from 80 % atmospheric input (at the -3.1 ‰ found in the results of this thesis) and 20 % thermocline nitrate (at the 2.5 ‰ given by Pantoja et al., 2002) without the need for a contribution from N₂-fixation.

In a second study, Sachs and Repeta (1999) also used information on the δ¹⁵N of particles and on δ¹⁵N-NO₃⁻ (which they had determined to be 0.7 ‰ in two samples from the EMS deep water mass), as well as assumptions on the isotope signature of external N inputs to the EMS to calculate that 46-70 % of the nitrate pool in the EMS originates from N₂ fixation. Their isotope balance equation of the form:

$$\delta_{\text{fix}} * x + \delta_{\text{other}} * (1-x) = \delta_{\text{nitrate}}$$

included the $\delta^{15}\text{N}$ of fixed nitrogen (δ_{fix} , assumed as -2.6‰), δ_{nitrate} (at 0.7‰), and the weighted $\delta^{15}\text{N}$ of all external nitrogen sources (δ_{other}), which Sachs and Repeta (1999) varied between 1‰ and 4‰ .

The δ_{other} parameter can be constrained with the present data on the $\delta^{15}\text{N}$ of atmospheric deposition (Table 6), and using the more realistic value of 2.5‰ for the δ_{nitrate} of Pantoja et al., (2002), the required contribution of N_2 fixation in the estimate of Sachs and Repeta (1999) vanishes.

	Mass-N	$\delta^{15}\text{N}$ (‰) (a)	weighted $\delta^{15}\text{N}$ (‰)	$\delta^{15}\text{N}$ (‰) (b)	weighted $\delta^{15}\text{N}$ (‰)
Sources (10^9 Mole/a)	198		0.46		1.53
Inflow Sicily	16	5	0.40	5	0.40
Inflow Adriatic/Po River	20	5	0.51	8	0.81
Inflow Black Sea	8	5	0.20	8	0.32
Inflow Nile River	15	5	0.38	8	0.61
Inflow other rivers	28	5	0.71	8	1.13
Atmospheric deposition	111	-3.1	-1.74	-3.1	-1.74

Table 6. $\delta^{15}\text{N}$ of external inputs to the EMS based on the budget of Krom et al., (2004) and the $\delta^{15}\text{N}$ of the atmospheric input (thesis results) and surface water in the Western Mediterranean Sea (Pantoja et al., 2002). For lack of data, the $\delta^{15}\text{N}$ of nitrate from rivers and inflow from the Black Sea vary from 5‰ (case a) to 8‰ (case b). In either case, the $\delta^{15}\text{N}$ of external nitrate sources is more depleted than nitrate in the deep-water nitrate pool ($2.5 \pm 0.1\text{‰}$; Pantoja et al., 2002).

Table 6 shows the Krom et al., (2004) estimates of present-day nitrogen inputs into the EMS, and estimations of their $\delta^{15}\text{N}$ signatures. The resulting $\delta^{15}\text{N}$ of all external inputs is calculated by summing the relative weight (contribution to total inputs; in 10^9 Moles/y) of each individual source N_i with its specific isotope composition $\delta^{15}\text{N}_i$:

$$\delta^{15}\text{NO}_3 \text{ inputs} = \frac{\sum_i \delta^{15}\text{N}_i * \text{input}N_i}{\sum \text{input}N}$$

Well constrained in the calculation of annual steady-state $\delta^{15}\text{NO}_3 \text{ inputs}$ is the $\delta^{15}\text{N}$ of atmospheric deposition (-3.1‰ obtained values), less well constrained (but corroborated by data from surface waters of the western Mediterranean Sea; Pantoja et al., 2002) is the $\delta^{15}\text{NO}_3$ of inflow to the EMS at Sicily at 5‰ . Due to the lack of data, there is an assumption that $\delta^{15}\text{NO}_3$ of nitrate inputs by rivers (Po, Nile and other rivers) is either 5‰ (case a) or 8‰ (case b). This range of $\delta^{15}\text{NO}_3$ is typical for rivers

draining industrialised catchments in North America and Europe, and for groundwater in Egypt (Aly et al., 1982; Mayer et al., 2002; Johannsen et al., 2008); $\delta^{15}\text{NO}_3$ of nitrate from the Black Sea inflow also varies between 5 ‰ and 8 ‰. With these assumptions, calculated $\delta^{15}\text{NO}_{3\text{inputs}}$ ($=\delta_{\text{others}}$) is between 0.5 ‰ (case a) and 1.5‰ (case b) and in both cases, the combined inputs are more depleted than the EMS deep-water nitrate pool, requiring no input from N_2 fixation in the Sachs and Repeta (1999) isotope balance mentioned above. This calculation shows that the presence of isotopically light particles and nitrate in the deep waters of the EMS cannot be used as definitive evidence for extensive nitrogen fixation in the basin, but may reflect the dominance of atmospheric deposition in external nitrogen inputs. However, the similarity between the measured $\delta^{15}\text{N}$ estimate for atmospheric deposition of NO_3^- (-3.1 ‰) and the inferred isotope value of nitrate originating from N_2 -fixation (-2.6‰) will always result in ambiguous conclusions in isotope mixing calculations.

Assuming that N_2 -fixation is not a relevant contributor to the isotope mixture in nitrate in the EMS, can the low $\delta^{15}\text{N-NO}_3$ of the deep-water nitrate pool be explained by atmospheric inputs alone? This requires that atmospheric input (or rather that part transferred into the deep water of the EMS over the last decades) was and is large enough to impact the deep nitrate pool. In the present evaluation, there is a benefit from the relatively simple water mass circulation pattern of the EMS. As described in Chapter 1, the Modified Atlantic Water (MAW) flows in through the Strait of Sicily at the surface, sinks in the Eastern part of the EMS and feeds the Levantine Intermediate Water (LIW). This is a high temperature, high salinity water mass at depths between 200 and 500 m that constitutes the return flow of the general circulation when leaving the EMS as a westward current at depth in the Sicily Strait. Below this surface circulation cell (>500 m) is the Eastern Mediterranean Deep Water (EMDW; Wüst, 1961; Malanotte-Rizzolli and Bergamasco, 1989) of interest here. The volume of EMDW below 500 m (not including Adriatic and Aegean sub-basins) is of the order of $1.7 \cdot 10^{15} \text{ m}^3$ and the average NO_3 -concentration is 4.6 mmol m^{-3} (MEDAR, 2002; Schlitzer, 2008). The nitrate inventory of deep water is thus of the order of $7600 \cdot 10^9$ Moles, today having an average $\delta^{15}\text{NO}_3$ of 2.5 ± 0.1 ‰ (Pantoja et al., 2002).

The process that would transfer external N-inputs ($=\delta^{15}\text{NO}_{3\text{inputs}}$ or δ_{others}) to EMDW is remineralisation of particles produced by assimilation of nitrate in surface

water. For reasons of simplicity, there is an assumption that nitrate in the surface layer is quantitatively assimilated over the course of a year, so that the particles produced from nitrate in the surface have the same isotopic composition as $\delta^{15}\text{NO}_{3\text{inputs}}$.

The mass flux of N to EMDW from mineralisation of particles can be roughly calculated from published estimates of export production. Using oxygen data at the Straits of Sicily, Béthoux (1989) estimated the export production in the EMS as approximately 1.6×10^{12} mol C/a, which translates to an N-export flux of 240×10^9 Mole/a at a C: N molar ratio of 106: 16 of sinking material. Most of that export flux is mineralised in the LIW interval and is exported to Sicily: Krom et al., (2004) quantified the loss at Sicily at a minimum of 142×10^9 Mole/a (range $153\text{-}227 \times 10^9$ Mole/a; Ribera d'Alcala et al., 2003), and loss to sediment deposition and sediment denitrification of N to 37×10^9 Mole/a. From the difference between export flux and sinks, the amount of N-export production that is mineralised in EMDW should be approximately 61×10^9 mol/a, or roughly 25% of export flux. The residence time ($\tau = 7600/61$) of the deep-water nitrate of the EMDW in the present estimation is thus 125 years, which agrees with the 100-130 years residence time estimated from oxygen and tritium contents of EMDW (Roether et al., 1996; Roether and Schlitzer, 1991).

To gauge the leverage that $\delta^{15}\text{NO}_3$ from remineralized particles has on $\delta^{15}\text{NO}_3$ of EMDW, there is an assumption that the deep nitrate pool had a $\delta^{15}\text{NO}_3$ of 5 ‰ before significant atmospheric inputs, and that the mass of nitrate remained stable at 7600×10^9 Moles. Although the assumed $\delta^{15}\text{NO}_3$ conforms to the global average of oceanic waters > 2000 m (Sigman et al., 2000), it should be pointed out that this choice is somewhat arbitrary, because EMDW is not connected to global ocean deep water, and in consequence its pre-industrial $\delta^{15}\text{NO}_3$ may have been different (Brandes and Devol, 2002).

Under these assumptions, it has been calculated that approximately 40-60 % of EMS deepwater nitrate must have been replaced by external nitrate having $\delta^{15}\text{NO}_{3\text{inputs}}$ of between 0.5‰ and 1.5‰ (Table 6) over the course of the last decades, to arrive at the 2.5 ‰ observed today. At fluxes comparable to those of today, the time required to depress the deep $\delta^{15}\text{NO}_3$ to the observed 2.5‰ from an initial 5 ‰ would be in the order of 60-70 years, but would be shorter, if the original $\delta^{15}\text{NO}_3$ of the deep nitrate pool was initially lower.

With little variation, the average mass of atmospheric NO_x deposition over the EMS area since 1980 is estimated to be around 110*10⁹ Mole/a (EMEP; <http://www.emep.int/index.html>). Considering that emissions in Europe quadrupled from 1950 to 1980 (van Aardenne et al., 2001; Preunkert et al., 2003) and have remained high since then, and that river nitrate loads increased in step (Vollenweider et al., 1996), it can be said that a significant portion of the extant EMDW nitrate pool derives from ¹⁵N-depleted external N-inputs instead of N₂-fixation. If external inputs continue at current rates and N-isotope composition, EMDW δ¹⁵NO₃ should converge with δ¹⁵NO_{3inputs} and thus should become progressively depleted.

Chapter 4. The isotopic ratios of nitrate, dissolved and particulate nitrogen in the Eastern Mediterranean Sea (EMS): *An attempt to provide a comprehensive data set of $\delta^{15}N$ in N-pools of the water column and to explain the processes causing the unusual isotopic ratios in the deep water of EMS*

4.1 Overview

As already mentioned, the currently Eastern Mediterranean Sea (EMS) is a highly oligotrophic oceanic environment (Antoine et al., 1995; Béthoux, 1989). The primary production presents, approximately, half of the values observed in the mid-ocean gyres such as the Sargasso Sea or the Northeast Pacific (Krom et al., 2003). This low productivity is caused by the anti-estuarine circulation in the EMS which was extensively described in Chapter 1. The Levantine Intermediate Water (LIW) which is fed by the flows of sinking water masses that originate from the Atlantic Ocean, is characterized by a high temperature and salinity pattern at depths from 200-500 m. Below the surface circulation, at a depth of > 500m, the Eastern Mediterranean Deep Water (EMDW)³ (Malanotte-Rizzoli and Bergamasco, 1989; Wüst, 1961) gains sufficient density after winter cooling (Lascaratos et al, 1999).

The loss of nutrients while the LIW is exported through the Sicily Straits, causes the deep waters of the EMS to be nutrient-depleted relative to the deep water in other parts of the global ocean: nitrate concentrations in EMDW are 4-6 μM compared to 8 μM in deep water of the adjacent Western Mediterranean Sea, and 20 μM at similar depths in the Atlantic Ocean. The EMS also presents unusually high nitrate: phosphate ratio (28: 1) in the deep water (Krom et al., 1991) and it is described as a phosphate-starved system (Krom et al., 2005). As a result, the primary production during the winter phytoplankton bloom is limited by phosphate rather than by nitrate (Krom et al., 1991). In winter, the phosphates in the surface water is highly depleted while an excess of nitrates remains (Kress and Herut, 2001). However, soon after the seasonal thermocline develops in spring, both nitrate and phosphate become depleted in the photic zone (Kress and Herut, 2001; Krom et al., 2005) and phytoplankton productivity becomes N- and P- co-limited (Thingstad et al., 2005; Zohary, 2005).

³ EMDW is formed when LIW entrains into surface waters of the two northern sub-basins of the EMS (Aegean or Adriatic Sea)

As already discussed, the main theme of the present dissertation is the isotopic signature of nitrogen in the region of EMS. Besides the description about the depleted isotopic atmospheric input given in Chapter 3, depleted isotopic values have been also recorded in deep-water nitrate, suspended matter, and surface sediments in the EMS (Struck et al., 2001; Pantoja et al., 2002; Çoban-Yildiz et al., 2006). The levels of $\delta^{15}\text{N}$ are unusually low compared to the relative values observed in other open-ocean environments.

Some possible explanations have been suggested for these low levels of $\delta^{15}\text{N}$. The incomplete uptake of nitrates by phytoplankton would result in products (such as particulate nitrogen or dissolved organic nitrogen) depleted in ^{15}N , while unprocessed residual nitrate would be enriched in ^{15}N . Together, residue and products have the original nitrate signature, and establishing the isotope fingerprints of all compartments is a tool to quantify individual processes in the N-cycle (Altabet, 1988).

The second possible reason, extensively discussed in Chapters 1 and 3, concerns the biological nitrogen fixation. Nitrogen fixation can reasonably explain the low $\delta^{15}\text{N}$ levels and the high N: P ratios in the EMS (Sachs and Repeta, 1999; Pantoja et al., 2002), because the newly fixed nitrogen is isotopically depleted. According to Minagawa and Wada (1986) and Montoya et al., (2002), the isotopic nitrogen values for the newly fixed nitrogen may range from -2 to 0 ‰ and can explain the observed values reported in previous studies (Pantoja et al., 2002). However, observational evidence for N_2 -fixation in the EMS is ambiguous (Rees et al., 2006; Berman-Frank et al., 2007; Ibello et al., 2010). So far the annual input of the diazotrophic nitrogen fixation process estimates ranges from 0 (Berman-Frank et al., 2007; Krom et al., 2004) to $120 \cdot 10^9$ mol/a (Béthoux and Copin-Montegut, 1986). The estimation made by Béthoux and Copin-Montegut (1986), corresponds to two thirds (2/3) of the total nitrate exported through the Straits of Sicily.

The third possible reason for the low $\delta^{15}\text{N}$ levels in the EMS is the atmospheric NO_x input. A detailed measurement of the levels of $\delta^{15}\text{N}$ of nitrates in the region of EMS, was presented in Chapter 3. As pointed out the atmospheric deposition of NO_x at present dominates the external nitrogen inputs. Furthermore, the regional atmospheric loads have noticeably increased over the last decades (Kouvarakis et al., 2001; Fagerli et al., 2007) and the input of new nitrate from the atmosphere to the surface water mass of the EMS presently can account for almost

60% of reactive N inputs. The atmospheric NO_3^- source is strongly depleted in dry and wet deposition and, as pointed out in Chapter 3, has an annual average of $\delta^{15}\text{N-NO}_3$ around -3.1 ‰. Still, what is interesting is that the $\delta^{15}\text{N}$ signature of N_2 fixation and of atmospheric inputs presents similarly low values. But while the fixed N has to be oxidised to nitrate in the mixed layer, atmospheric NO_x is a direct input of nitrate that is known also to have a high $\delta^{18}\text{O-NO}_3$ (Kendall, 1998; Sigman et al., 2009; Wankel et al., 2009).

In oligotrophic environments nitrate can be regenerated from particulate nitrogen and possibly from dissolved organic nitrogen via ammonia and nitrite oxidation (Bronk, 2002; Knapp et al., 2008), instead of being available as a large source (thermocline nitrate) that can be provided by the mixed layer in the oceans. Thus, the regenerated nutrients from particulate or dissolved organic nitrogen can be particularly important in the oligotrophic region of the Eastern Mediterranean Sea (Diaz and Raimbault, 2000), since the contribution to the primary production can be significant (Yool et al., 2007).

The applied method used for the needs of the thesis concerning the analysis of $\delta^{15}\text{N}$ in the atmospheric as well as the marine samples obtained from the EMS, was discussed in Chapter 2. The denitrifier method reported by Sigman et al., (2001) and Casciotti et al., (2002) can simultaneously determine the $\delta^{15}\text{N}$ as well as the $\delta^{18}\text{O}_3$ of NO_3 . The ability to measure $\delta^{18}\text{O}$ is essential especially in nitrogen cycles that involve internal oceanic sources and sinks (Casciotti et al., 2008). The determination of $\delta^{18}\text{O-NO}_3$ in parallel with $\delta^{15}\text{N-NO}_3$ in the mixed layer can provide answers concerning the nitrates in the mixed layer. With the in parallel analysis of $\delta^{18}\text{O-NO}_3$ and $\delta^{15}\text{N-NO}_3$ it can be seen whether the deep winter mixing or if other sources besides thermocline nitrate, contribute to the nitrates of the mixed layer.

Nitrification as a process can provide a characteristic isotopic signature on the $\delta^{18}\text{O-NO}_3$ and $\delta^{15}\text{N-NO}_3$ of the regenerated nitrate (Casciotti et al., 2003; Wankel et al., 2006) and can be used to quantify the contribution of regenerated nitrate (Sigman et al., 2009). The dissolved total reduced nitrogen which is composed of $\text{DON}+\text{NH}_4^+$ can be a key component in the recycling of reactive N in the EMS (Thingstad et al., 2005), and its isotopic composition must reflect active participation in the N-cycle (Knapp et al., 2005).

The present Chapter shows the nitrogen and oxygen isotope ratios of nitrate ($\delta^{15}\text{N-NO}_3$, $\delta^{18}\text{O-NO}_3$), dissolved total reduced nitrogen and of particulate N in suspended particles ($\delta^{15}\text{N}_{\text{susp}}$) obtained from filtration from the mixed-layer and deep-water pools in the region of EMS. Furthermore an approach has been made to present the mass fluxes and the $\delta^{15}\text{N}$ data of sinking particles intercepted by sediment traps. The results obtained from the marine environment of the EMS will be able to provide a comprehensive data set of $\delta^{15}\text{N}$ in several N-pools of the water column, and possibly help explain the processes which cause the unusual isotopic ratios in the deep water. Furthermore, together with the atmospheric results that were reported and discussed in Chapter 3, there will be an attempt to test if the unusually low levels of $\delta^{15}\text{N}$ are a consequence of incomplete nitrate utilisation in the euphotic zone due to the P-limited phytoplankton blooms, or if internal N-recycling or external inputs (N_2 fixation or NO_x inputs respectively) are a significant source of mixed-layer nitrate.

4.2 Materials and Methods

The marine samples were obtained during an expedition of the R/V METEOR in the EMS. The cruise was conducted in January/February 2007 and as shown in Fig. 2.2 (Chapter 2), it consisted of 17 stations (see Table C.1. data appendix). Water samples were taken with a rosette sampler equipped with a Seabird 911 CTD; an aliquot of the bottom water at the sediment-water interface was also taken from multicorer deployments. Water samples were immediately filtered through pre-combusted, rinsed GF/C filters and transferred into PE bottles for shore-based analyses of nutrient concentrations, total dissolved nitrogen (TDN) content and N-isotopic signature ($\delta^{15}\text{TDN}$), and $\delta^{15}\text{N}/\delta^{18}\text{O}$ of nitrate ($\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$). Samples for nitrate isotope analysis were frozen on board ship for further analysis onshore, samples for TDN analysis were oxidised immediately after filtration on the ship with persulfate and then stored frozen in brown glass bottles until further analysis in the shore-based laboratory (Schlarbaum et al., 2010). Samples for nutrient analyses were poisoned with 3.5 % mercury chloride solution and stored at room temperature. Nutrient and TDN concentrations were analysed immediately after the expedition using a Bran+Luebbe Autoanalyzer 2 with standard colorimetric techniques (Grasshoff et al., 1999).

Large water samples (10-50 L) were filtered through pre-combusted GF/F filters for analyses of total nitrogen concentrations in suspended solids (particulate nitrogen PN_{susp}), as well as for $\delta^{15}\text{N}$ of PN_{susp} ($\delta^{15}\text{N}_{\text{susp}}$). Filters were frozen on board but were lyophilised and weighed before any further analysis in the laboratory.

During the cruise, a mooring system MID-03 (Mediterranean Ierapetra Deep) was deployed in the Ierapetra Deep off Crete (34°26.63' N, 026°11.58' E, bottom depth 3620 m) (Fig. 2.2; Chapter 2), with the sampling covering the period 30.01.07 – 03.09.07. The system consisted of one sediment trap McLane PARFLUX MARK 7G-21 at 1508 m water depth (MID-03 Shallow) and one Kiel Sediment Trap K/MT 234 at 2689 m water depth (MID-03 Deep). The cups were filled with filtered (GF/F, combusted) sea water from the respective depths. In addition, 35 g L⁻¹ NaCl and 3.3 g L⁻¹ HgCl₂ were added in order to avoid diffusion and bacterial decomposition during the deployment. The particle flux was sampled at intervals of 12 days. Subsequent to trap recovery, trapped materials were sieved into > 1 and < 1 mm fractions, the wet sample material was filtered onto pre-weighed nucleopore filters and dried at 40°C. The dry weights of the < 1 mm fraction are used for calculating the total fluxes, and the filter cake was homogenised with an agate mortar prior to analysis. The same site has seen intermittent sediment trap deployments at 2700 m water depth in 1999 (30 January to 13 April, 1999) and in 2001/2002 (5 November 2001 to 1 April, 2002) (Warnken, 2003), and the data from these earlier deployments are used to complement data obtained from the latest trapping period.

4.2.1. Analytical methods

A) Nitrogen ($\delta^{15}\text{N}$) and oxygen ($\delta^{18}\text{O}$) analysis in nitrate (NO_3^-) and total reduced dissolved nitrogen ($\delta^{15}\text{N}$ -TDN)

The samples for determinations of $\delta^{15}\text{N}$ - NO_3^- and $\delta^{18}\text{O}$ - NO_3^- and $\delta^{15}\text{N}$ -TDN were thawed in the shore-based laboratory, and nitrate isotopic composition was determined with the denitrifier method (Sigman et al., 2001; Casciotti et al., 2002). The untreated filtered water samples or persulfate-digested TDN samples, were injected into a suspension of *Pseudomonas aureofaciens* for combined analysis of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, or *P. chlororaphis* for $\delta^{15}\text{N}$ analysis of TDN only. The resulting N_2O gas was flushed by purging the sample vials with helium, concentrated and purified on a GasBench II

(ThermoFinnigan), and analyzed on a Delta Plus XP mass spectrometer (ThermoFinnigan), as described in the analysis of the atmospheric samples.

For each sample, replicate measurements were performed, and an international standard (IAEA-N3) was measured with each batch of samples. The standard values were 4.7 ‰ for $\delta^{15}\text{N}$ and 25.6 ‰ for IAEA-N3 referenced to Standard Mean Ocean Water, ^{18}O (Böhlke et al., 2003; Lehmann et al., 2003; Sigman et al., 2005). The contribution of nitrite (NO^-) was below $< 1\text{‰}$ and thus the effect on $\delta^{18}\text{O}$ values is negligible (Casciotti and Mcilvin, 2007). Therefore NO^- was not considered in the calculations. The standard deviation for IAEA-N3 was better than 0.2 ‰ ($n = 5$) for $\delta^{15}\text{NO}_3$ and better than 0.4 ‰ for $\delta^{18}\text{O-NO}_3$. As in the case of the atmospheric samples, potassium nitrate (KNO_3) was used as an alternative internal standard, besides the IAEA-N3. The standard deviation for the internal standard was within the same specification for both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ as IAEA-N3. The duplicate analyses suggest an overall average standard deviation for $\delta^{15}\text{N-NO}_3$ of 0.2‰ and for $\delta^{18}\text{O-NO}_3$ of 0.3‰. The standard deviations of duplicate analyses of $\delta^{18}\text{O-NO}_3$ increased to 0.5 ‰ in samples with low nitrate concentrations in the mixed layer and upper thermocline.

For calculations of the $\delta^{15}\text{N}$ of total reduced nitrogen mass balance calculations were made using the measured concentrations of nitrate and TRN, and $\delta^{15}\text{N-TDN}$ values of the oxidised sample, the reagent blank and the $\delta^{15}\text{N-NO}_3$ of the original (not oxidised) sample (Knapp et al, 2005):

$$\delta^{15}\text{TRN} = \delta^{15}\text{N-TDN} * \frac{c(\text{TDN})}{c(\text{TRN})} - [\delta^{15}\text{N-NO}_3^- * \frac{c(\text{NO}_3^-)}{c(\text{Blank})}] / c(\text{TRN})$$

The pH of the digested samples of TRN analysis was ~ 6.0 so no pH adjustment was necessary (Schlarbaum et al., 2010). Yield of the persulfate digestion procedure has been tested with different standards and the oxidation efficiency was between 98-105 % (Schlarbaum et al., 2010). A urea standard (in solid form analysed by combustion in an elemental analyser) was used for quality control in $\delta^{15}\text{N-TRN}$ measurements ($\delta^{15}\text{N}$ of solid was $0.5 \pm 0.2\text{‰}$; $\delta^{15}\text{N}$ after persulfate digestion and conversion to N_2O by the denitrifier method was $0.4 \pm 0.2\text{‰}$). Because of low concentrations and error propagation, the calculated standard deviation of $\delta^{15}\text{TRN}$ analyses ranged from 0.2 to 2.0‰ with a mean value of 0.9 ‰, and the calculated

mean standard deviation for TRN concentration was 1.7 μM . The mean standard deviation for $\delta^{15}\text{N}$ -TRN (0.9 ‰) was calculated with standard deviations of actual measurements of $\delta^{15}\text{N}$ - NO_3 and $\delta^{15}\text{N}$ -TDN (after digestion), which were in part better than the 0.2 ‰ estimated as the overall standard deviation for the $\delta^{15}\text{N}$ - NO_3 measurements. It must be noted that $\delta^{15}\text{N}$ -TRN was not corrected for any contribution from ammonium. The only published data on ammonium from the EMS found values in the range of 40-80 nM with no major trend with depth (Krom et al., 2005). In the same profiles the DON concentration was \sim 2-4 μM in deeper water, similar to the values measured in this study. It is thus likely that most of the isotopic signal is due to DON.

B) $\delta^{15}\text{N}$ analysis of particulate nitrogen in suspended solids (PN_{susp})

Total particulate nitrogen concentrations in suspended solids (PN_{susp}) and in sinking material captured by the sediment trap (SPN) were analysed after high-temperature flash combustion in a Carlo Erba NA-2500 elemental analyzer at 1100°C (Rixen et al., 2000). $\delta^{15}\text{N}$ values were determined using a Finnigan MAT 252 gas isotope mass spectrometer coupled to an elemental analyzer. Pure tank N_2 calibrated against the reference standards International Atomic Energy Agency (IAEA)-N-1 and IAEA-N-2 was used as a working standard. The within-lab standard-deviation was found to be $<$ 0.2 ‰ based on a set of replicate measurements of six sediment samples.

4.3 Results

4.3.1 Concentrations of nitrogen compounds

The sampling campaign in the EMS took place in winter when the water column at most stations was well mixed with a thermocline situated at depths of around 100 m⁴ to 250 m⁵ water depth (see Table C.1. data appendix). Fluorescence profiles (Fig. 4.1) showed elevated fluorescence (uncalibrated chlorophyll

⁴ Refers to Stations H07 to H12 in the northern Ionian Basin, in the following abbreviated as NIS, maximum water depth 1688 m, and station Sk01 in the northern Aegean Sea; see Fig. 2.2 in Chapter 2).

⁵ Refers to Stations in the deep Ionian Basin, Ierapetra and Herodotus Basin, termed as pelagic stations.

concentrations) in the surface mixed layer typical of the winter phytoplankton bloom observed in the EMS (Krom et al., 2003). Concentration versus depth plots of nitrate, phosphate, TRN and PN_{susp} for all stations showed that the thermocline in all cases coincided with the nitracline. Based on the criterion of nitrate concentrations, samples were grouped as: above the nitracline, in the nitracline, and below the nitracline (deep-water samples) for each station set (Table 7; Table C.2. data appendix).

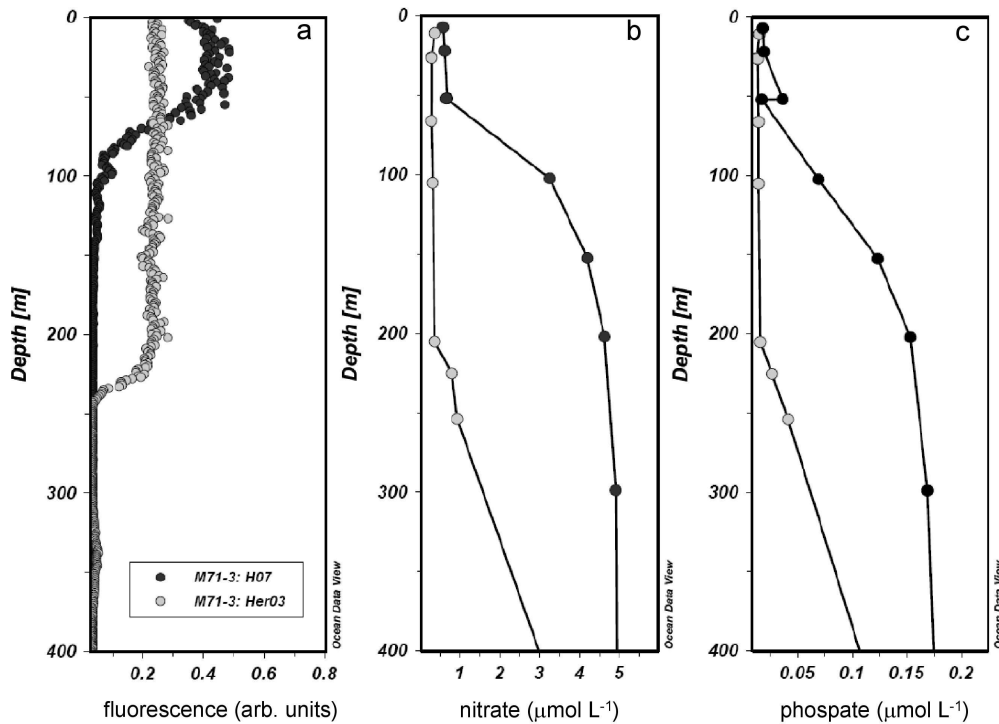


Fig.4.1. Profiles of fluorescence (a), nitrate (b) and phosphate (c) concentrations in the upper 400 m at 2 stations representative of NIS (H07) and pelagic stations (Her03) show stratification between the 80 and 230 m water depth and indicate the biologically active mixed layer. An ongoing phytoplankton bloom in the northern Ionian Sea (at station H07) is sustained by nitrate and phosphate provided from ongoing regional thermocline deepening, whereas station Her03 illustrates the mature and thick mixed layer with very low nutrient concentrations at pelagic sites.

Nitrate concentrations were low but measurable in the mixed layers of both the NIS and the pelagic stations, (Fig. 4.2a; Table 7; Table C.2. data appendix) while phosphate concentrations were below the effective detection limit of the nutrient procedures being used (estimated to $0.05 \mu\text{M}$) (Li et al., 2008). TRN concentrations varied around averages of $1.6 \mu\text{M}$ in the mixed layer of NIS and pelagic stations, and $3.3 \mu\text{M}$ in the northern Aegean station (Fig. 4.2b; Table 7; Table C.2. data appendix). Suspended PN concentrations in the mixed layer of the NIS were on average $0.5 \mu\text{mol N L}^{-1}$ ($0.4 \mu\text{mol N L}^{-1}$ in the mixed layer of the pelagic stations, and $0.5 \mu\text{mol N L}^{-1}$ in the northern Aegean) (Fig. 4.2c; Table 7; Table C.2. data appendix).

Table 7.1. Average concentrations and isotopic composition/northern Ionian Sea stations

Nitrate	Phosphate	TRN	PN	$\delta^{15}\text{N-NO}_3$	$\delta^{18}\text{O-NO}_3$	$\delta^{15}\text{TRN}$	$\delta^{15}\text{PN}$
($\mu\text{mol L}^{-1}$)	($\mu\text{mol L}^{-1}$)	($\mu\text{mol L}^{-1}$)	($\mu\text{mol L}^{-1}$)	(‰)	(‰)	(‰)	(‰)

mixed layer above nitracline

Average	0.48	0.02	1.6	0.5	5.6	10.7	-0.2	2.2
Sd	0.32	0.01	0.8	0.1	2.7	7.1	1.8	1.1
N	24	24	24	3	11	7	2	3
Range	0.06-0.97	0.01-0.04	0.6-3.5	0.4-0.6	1.0-9.9	3.1-21.5	-1.1-1.5	1.0-3.1

in nitracline

Average	3.55	0.1	1.5	no data	2.1	5.1	2.9	no data
Sd	0.95	0.04	0.7		0.8	2.5	3.3	
N	14	14	14		13	10	7	
Range	1.75-4.45	0.03-0.14	0.6-3.2		1.3-3.8	2.8-9.5	-2.4-6.6	

below nitracline to total depth

Average	4.49	0.16	1.4	0.2	2	3.2	2.4	7.9
sd	0.47	0.02	0.7	0.0	0.3	0.7	3.5	0.6
n	25	25	25	3	24	11	8	3
Range	3.53-5.09	0.11-0.19	0.6-3.2	0.1-0.2	1.1-2.5	2.3-4.4	-1.4-7.7	7.3-8.4

Table 7.2. Average concentrations and isotopic composition/pelagic stations*Mixed layer above nitracline*

Average	0.24	0.02	1.6	0.40	2.3	5.2	1.1	1.1
sd	0.26	0.01	1.1	0.10	3.4	0.0	1.1	0.5
n	57	57	56	24	3	2	2	23
Range	0.03-0.93	0.01-0.04	0.8-5.4	0.2-0.5	0.1-6.3	5.2	5.2	0.1-2.4

in nitracline

Average	3.45	0.12	1.6	0.2	1.6	5.0	3.4	7
sd	1.44	0.06	1.6	0.1	0.5	1.4	3.5	0.7
n	21	20	20	10	20	13	9	10
Range	0.93-5.53	0.02-0.21	0.6-7.0	0.1-0.3	0.6-3.3	2.8-7.2	0.6-12.2	6.0-8.1

Below nitracline to total depth

Average	4.77	0.18	1.3	0.1	2.2	3.8	6.7	7.2
sd	0.45	0.02	0.7	0.1	0.3	0.8	3.5	0.8
n	52	52	52	21	47	14	33	20
Range	3.76-5.98	0.13-0.22	0.5-3.6	0.0-0.4	1.3-2.9	2.4-5.5	1.1-14.4	5.2-8.5

Table 7.3. Average concentrations and isotopic composition/North Aegean station*mixed layer above nitracline*

Average	0.33	0.02	3.3	0.5	4.1	no data	-0.6	1.9
sd	0.31	0.01	0.3	0.0	2.6		n/a	0.3
n	4	4	4	2	2		1	2
range	0.07-0.67	0.02-0.03	3.1-3.6	0.5-0.6	2.2-5.9		n/a	1.7-2.1

in nitracline

average	2.27	0.1	3.6	0.2	2.0	4.4	2.8	7.7
sd	0.9	0.05	1.8	n/a	0.4	2.3	0.8	n/a
n	5	5	5	1	5.0	4.0	5.0	1
range	1.28-3.53	0.05-0.17	2.2-6.6	n/a	1.6-2.5	2.7-7.7	2.2-4.0	n/a

below nitracline to total depth

average	4.7	0.23	3.6	0.1	2.3	no data	3.6	8.1
sd	0.11	0.01	0.8	0.0	0.1		1.3	0.3
n	3	3	3	2	3		3	2
range	4.61-4.82	0.22-0.24	2.7-4.2	0.1	2.2-2.4		2.1-4.5	7.8-8.3

Table 7. Average concentrations and isotopic composition in water samples from above, in and below the nitracline during the Meteor expedition 71-3 in the EMS: Northern Ionian Sea (NIS; 6 stations, Table 7.1.), pelagic stations (10 stations, Table 7.2.) and northern Aegean Sea (1 station Table 7.3.) Tables C.1., C.2., and C.3. in the data appendix provide analytically all the data used in this Chapter.

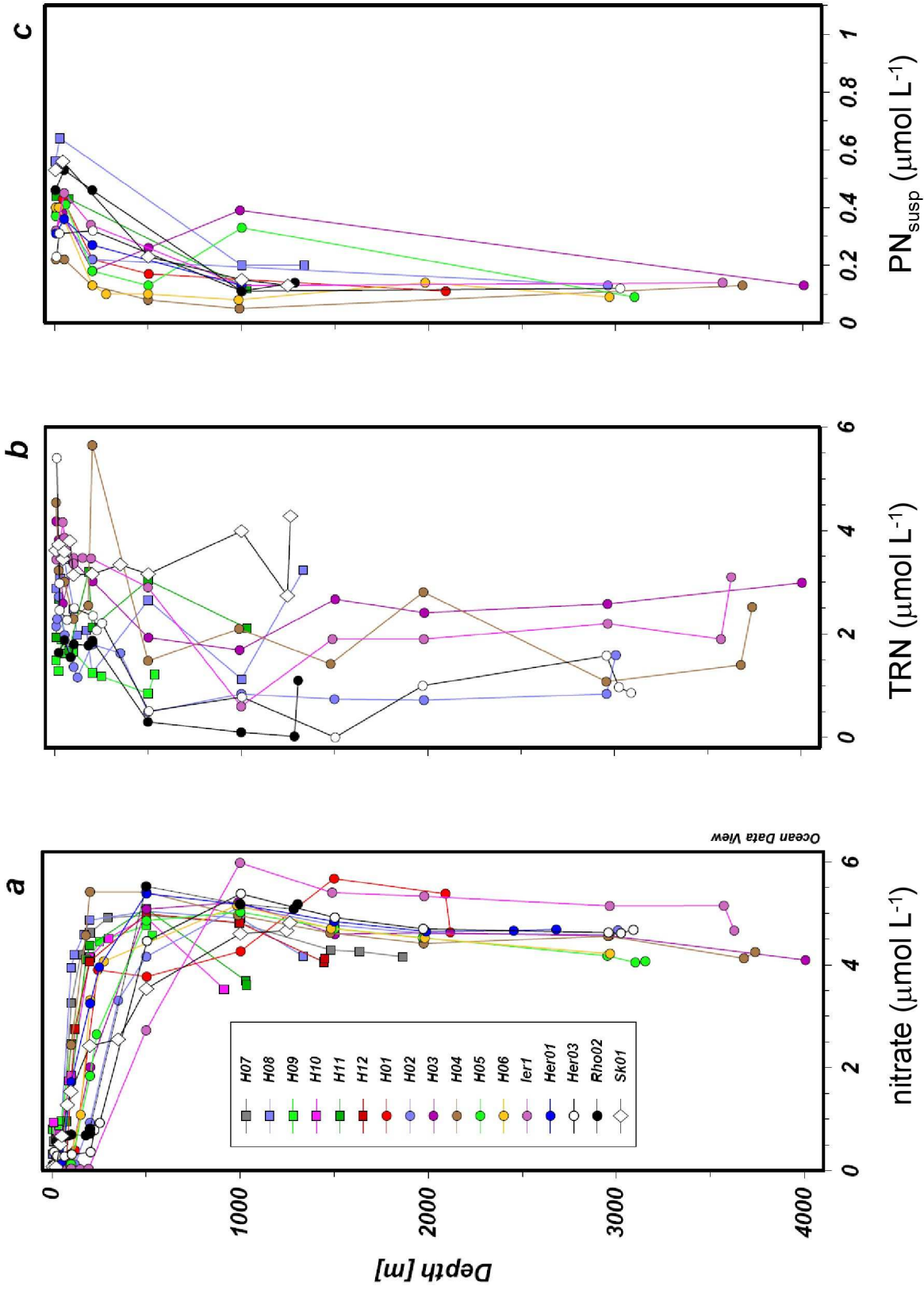


Fig. 4.2. Concentrations of nitrate (a), TRN (b) and particulate N in total suspended solids (c) plotted against water depth for all stations.

The intermediate water mass had average nitrate concentrations around $3.5 \mu\text{mol L}^{-1}$ and average phosphate concentrations between 0.10 and $0.12 \mu\text{mol L}^{-1}$. The mean N: P ratio in the intermediate water was around 30. TRN concentrations were around $1.5 \mu\text{mol N L}^{-1}$ in intermediate waters at NIS and pelagic stations, and $3.6 \mu\text{mol N L}^{-1}$ in the Aegean station (see Table C.3. data appendix). The TRN concentrations in the intermediate waters in the stations, showed a large scattering due to measurement uncertainties at the low concentration levels measured. Suspended PN (not determined in the intermediate waters of NIS stations) averaged $0.2 \mu\text{mol N L}^{-1}$ at both pelagic stations and the single northern Aegean station (see Table C.3. data appendix).

Concentrations of most dissolved and particulate constituents in samples below the nitracline to total depth were more uniform than in the biologically active surface (Fig. 4.2): Average nitrate (4.5 to $4.8 \mu\text{mol L}^{-1}$) and phosphate (0.16 to $0.23 \mu\text{mol L}^{-1}$) concentrations over all stations resulted in an average N: P ratio of > 27 , similar to previous measurements across the EMS (Kress and Herut, 2001). Average TRN concentrations varied around $1.3 \mu\text{mol N L}^{-1}$ in the deep water of the NIS and the pelagic stations, but were elevated (average $3.6 \mu\text{mol N L}^{-1}$) in the northern Aegean. Average suspended PN concentration was below $0.2 \mu\text{mol N L}^{-1}$ in all the water samples below the nitracline to total depth.

The two sediment traps deployed over 216 days from February to September 2007 at station Ierapetra (SE of Crete, see Fig. 2.2; Chapter 2) monitored a total sinking particulate N (SPN) flux in the shallow trap (at 1500 m) of $5.7 \text{ mmol N m}^{-2}$ (or $26.3 \mu\text{mol N m}^{-2} \text{ d}^{-1}$) over that period, while the deep trap (at 2700 m) collected $1.4 \text{ mmol N m}^{-2}$ ($6.5 \mu\text{mol N m}^{-2} \text{ d}^{-1}$) of SPN over the same period. Earlier sediment trap deployments at the MID location (Warken, 2003), reported similar N fluxes in the deep traps (MID-01, February to April 1999, $4.5 \mu\text{mol N m}^{-2} \text{ d}^{-1}$; and MID-02, November 2001 to March 2002, $6.0 \mu\text{mol N m}^{-2} \text{ d}^{-1}$); unfortunately, sampling in the shallower trap failed during those deployments.

4.3.2 Isotopic composition of nitrogen compounds

At all stations, the isotopic composition of nitrogen-bearing species differed not only between the mixed layer and the intermediate and deep water masses (Fig. 4.3; Table C.3. data appendix), but also among station sets.

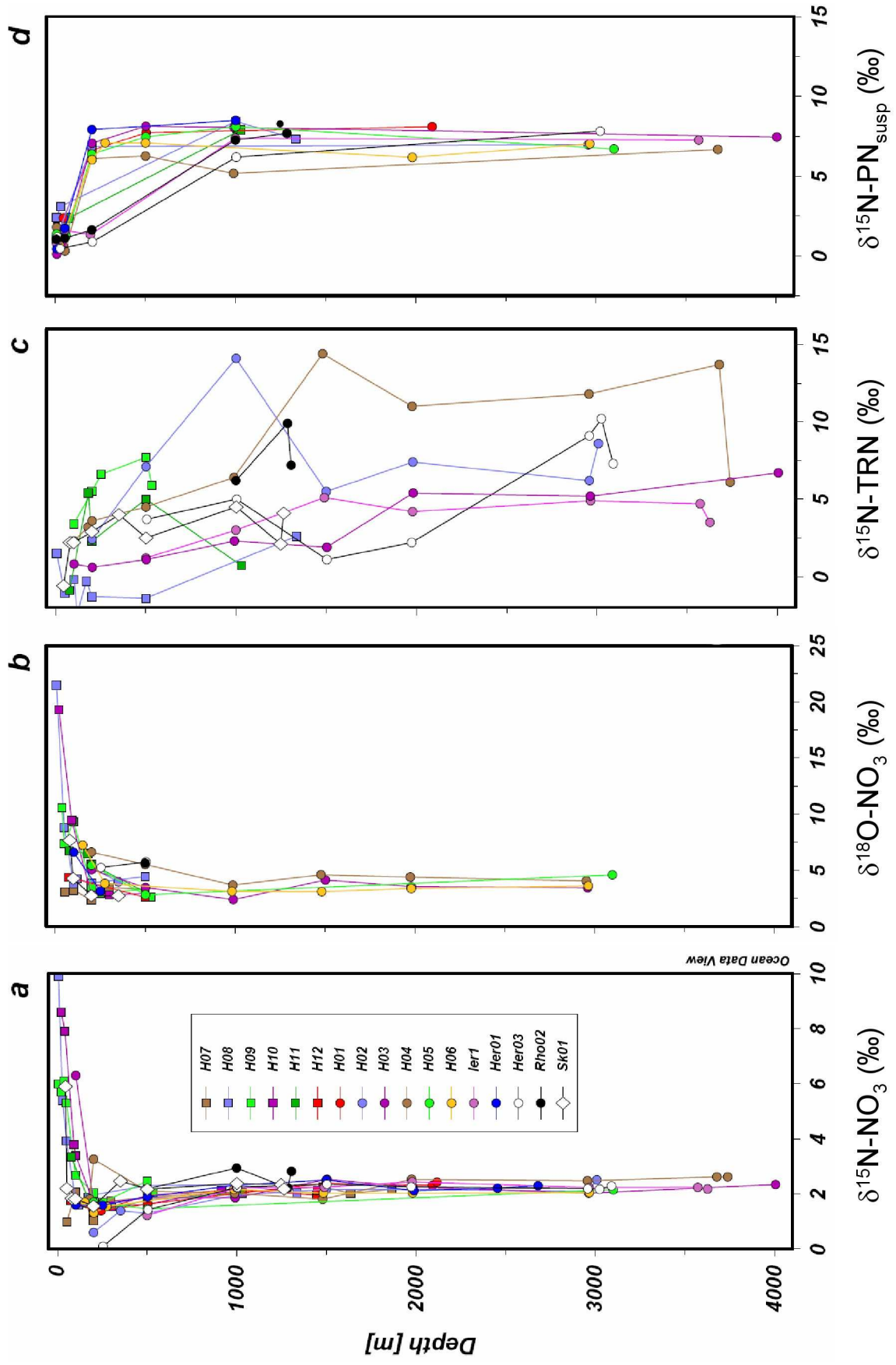


Fig. 4.3. Isotopic composition of $\delta^{15}\text{N-NO}_3$ (a) $\delta^{18}\text{O-NO}_3$ (b) $\delta^{15}\text{N-TRN}$ (c) and $\delta^{15}\text{N}$ of suspended PN (d) plotted against water depth for all stations.

Mixed-layer nitrate had average $\delta^{15}\text{N-NO}_3$ of 5.6‰, 2.3‰, and 4.1‰ at NIS, pelagic, and northern Aegean stations, respectively. The $\delta^{18}\text{O-NO}_3$ was 10.7‰ at NIS stations, and 5.2‰ at pelagic stations; no sample yielded a reliable value in the northern Aegean. $\delta^{15}\text{N}$ of suspended PN in the mixed layer was low ($\delta^{15}\text{N}_{\text{susp}}$ average of all stations = 1.3 ± 0.7 ‰), and TRN in the surface layer (average $\delta^{15}\text{TRN}$ of all stations = 0.0 ± 1.1 ‰) was roughly similar to the $\delta^{15}\text{N}_{\text{susp}}$.

The average isotopic composition of nitrate in samples from the nitracline was similar in all stations: $\delta^{15}\text{NO}_3$ averaged 1.6 and 2.1 ‰ in samples below the mixed layers of the pelagic and NIS stations, respectively, and 2.0 ‰ in the thick nitracline in the northern Aegean. $\delta^{18}\text{O-NO}_3$ of samples from the nitracline had averages of 5.1‰ (NIS stations), 5.0 ‰ (pelagic stations), and 4.4‰ in the northern Aegean nitracline. Values of $\delta^{15}\text{N-TRN}$ and $\delta^{15}\text{N}_{\text{susp}}$ were higher in the thermocline samples than in the mixed layer (Table 7; Table C.3. data appendix).

In deep waters, $\delta^{15}\text{N-NO}_3$ averaged between 2.0 ‰ and 2.3 ‰ in the three stations sets, and $\delta^{18}\text{O-NO}_3$ had an average between 3.2 ‰ (NIS stations) and 3.8 ‰ for pelagic sites, respectively. These deep water values were not statistically different. Suspended matter in deep waters at all stations had high $\delta^{15}\text{N}_{\text{susp}}$ averages of 7.2 ‰ to 8.1 ‰, while $\delta^{15}\text{N-TRN}$ measurements averaged between 2.4 ‰ and 6.7 ‰ over all sites. Part of the high variability is attributed to the measurement artefacts at the low concentrations that were encountered. Samples of deep water below the nitracline at pelagic sites, where a relatively large sample pool was measured, had an average $\delta^{15}\text{N-TRN}$ of 6.7 ± 3.5 ‰ (Table 7; Table C.3. data appendix).

The $\delta^{15}\text{N}$ of sinking material ($\delta^{15}\text{N-SPN}$) collected by the two sediment traps during the deployment in 2007 (MID-03) differed significantly from the $\delta^{15}\text{N}$ of suspended matter collected by filtration in deep water, and was essentially the same as $\delta^{15}\text{N}_{\text{susp}}$ found in the mixed layer during the expedition. The upper trap had an average $\delta^{15}\text{N-SPN}$ of 0.9 ± 0.8 ‰ within the 216-day sampling period (1.0 ‰ flux weighted), whereas the lower trap average $\delta^{15}\text{N-SPN}$ was 0.8 ± 1.0 ‰. This is lower compared to the $\delta^{15}\text{N-SPN}$ of the 1999 deployment (MID-01; $\delta^{15}\text{N-SPN} = 2.2 \pm 0.4$ ‰), but is in agreement with data from trap MID-02 (deployment 2001/2002) that collected sinking particles with a mean $\delta^{15}\text{N-SPN}$ of 1.2 ± 0.6 ‰ (Warnken, 2003). Together the three deployments cover a period from November to October, and thus the biologically

active season for which the bulk of particle transport of the mixed layer is expected to occur. In a composite annual cycle constructed from all three deployments at 2700 m water depth (Figure 4.4), SPN- flux peaks in March, whereas the highest values of the $\delta^{15}\text{N}$ -SPN (1.8 ‰) were obtained in November and December. In general, seasonality in $\delta^{15}\text{N}$ -SPN is limited and varies around an annual average of 1.1 ‰ with low values from April to May (0.3-0.5 ‰) and higher values (1.2–1.8 ‰) later in the year from June to December.

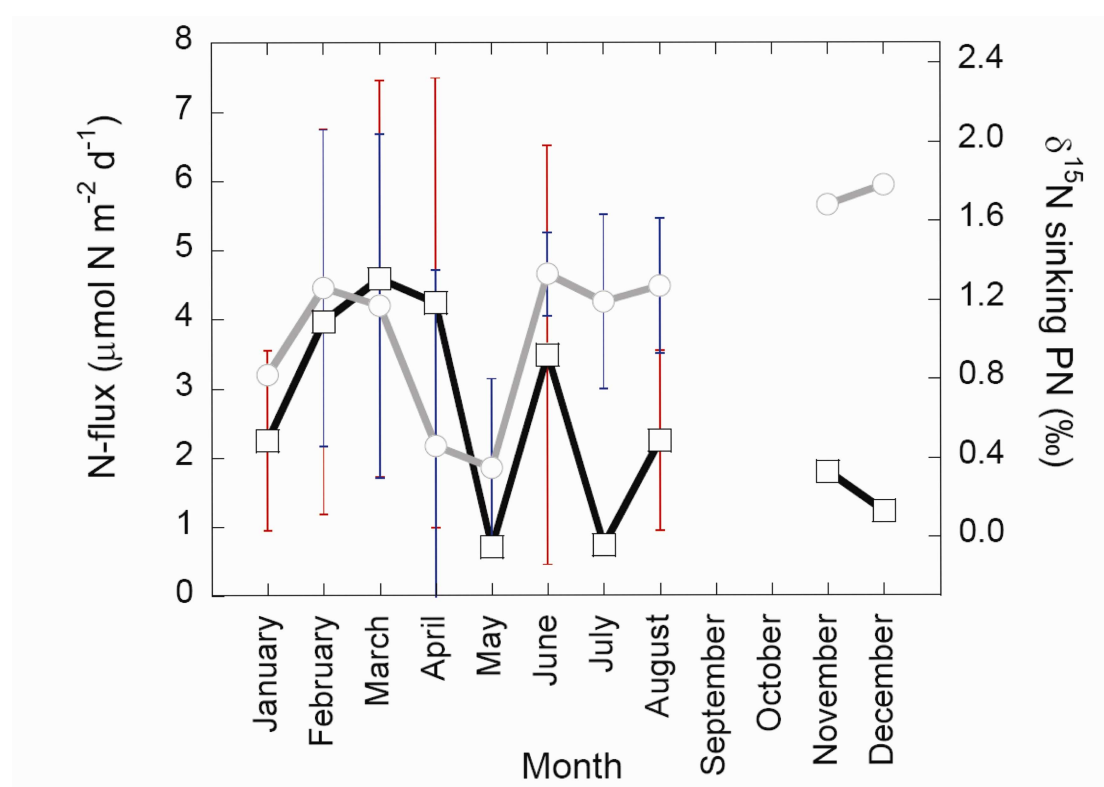


Fig.4.4. Composite seasonal diagram of sinking PN fluxes (squares) and $\delta^{15}\text{N}$ of sinking PN (circles) and their standard deviations at 2600 m water depth at Ierapetra station. Fluxes (squares, black line and s.d. in red) and $\delta^{15}\text{N}$ -SPN (circle, grey line, s.d. in blue) for three deployment periods (MID-1: 01/30/1999 to 04/13/1999), MID-2: 11/05/2001 to 04/01/2002 and MID-3: 01/30/2007 to 09/05/2007) at 2700 m water depth have been assembled in a surrogate annual cycle.

4.4 Discussion

Table 8 is a compilation of inventories and $\delta^{15}\text{N}$ of different water masses in the EMS and in different compartments of reactive N based on the present data, according to which the mass-weighted and depth-integrated $\delta^{15}\text{N}$ of the EMS is 2.8‰. The calculation of the inventories (given in gigamol N) are based on water volumes

for the EMS without Adriatic and Aegean sub-basins and weight $\delta^{15}\text{N}$ values by average concentrations found during the 2007 METEOR cruise (M71-3). Judging from that value, the inventory of reactive N in the EMS is fundamentally different from the inventories of other oceans or regional marine systems studied so far, because the overall level of $\delta^{15}\text{N}$ is clearly lower than elsewhere.

In this section measurements reported in this thesis on the individual compartments of N in the EMS will be compared with previous data, as well as with from data other areas. Furthermore the possible reasons for the unusual ^{15}N depletion will be discussed and tested against the isotopic evidence.

Interval (m)	Interval volume (km ³)	Mass nitrate (Gmol)	Interval weighted $\delta^{15}\text{N}$ -NO ₃ (‰)	Mass suspended PN (Gmol)	Interval weighted $\delta^{15}\text{N}$ -PN _{SUSP} (‰)	Mass TRN (Gmol)	Interval weighted $\delta^{15}\text{N}$ -TNR(‰)	Sum reactive N (Gmol)	weighted $\delta^{15}\text{N}$ reactive N(‰)
0-200	306200	357	2.4	112	1.6	876	1.1	1345	1.5
200-500	365300	1411	1.8	59	6.4	700	6.2	2171	3.3
> 500	1719000	7949	2.2	249	7.2	3510	5.2	11709	3.2
all	2390500	9717	2.1	421	5.6	5086	4.6	15224	3.0

Table 8. Estimation of reactive N-inventories of the EMS in different depth intervals and mass-weighted $\delta^{15}\text{N}$ of different components (nitrate, particulate nitrogen PN and total reduced nitrogen, TRN; data in Tables C.1.-C.3. in the data appendix). The last column gives the integrated and mass-weighted $\delta^{15}\text{N}$ values over all components of reactive N for each interval. The last line shows the integrated inventories and the $\delta^{15}\text{N}$ values of the entire water column.

4.4.1 Isotopic composition of reactive nitrogen in sub-nitracline and deep water masses

The starting point of this discussion is the isotopic composition of the large reactive nitrogen in the deep-water pool and the depth interval below the nitracline and in the deep-water pool, which integrates the isotopic signal over all internal and external nitrate sources over the deep-water residence time of 50-80 years (Roether et al., 1996). Differing from the pool in surface waters, this deep nitrate pool is isotopically homogeneous in the EMS and the discussion does not differentiate between different station settings. There are three previous data sets of widely differing $\delta^{15}\text{N}$ -NO₃ in deep and intermediate water masses. Initially, Sachs and Repeta (1999) determined the $\delta^{15}\text{N}$ -NO₃ to -0.7 ± 0.1 ‰ in two samples of deep water (depths not given) from the EMS, analysed by the ammonia diffusion method (Sigman et al.,

1997). Some years later Struck et al. (2001), also using the ammonia diffusion method, gave a mean of 7.3 ± 2.8 ‰ in six samples of waters from between 200 and 400 m water depth. Finally Pantoja et al., (2002), using the denitrifier method, presented six data points below 500 m in the EMS, but the authors gave the $\delta^{15}\text{NO}_3$ value (2.5 ± 0.1 ‰) for only four samples.

The data presented in this Chapter confirm that $\delta^{15}\text{N-NO}_3$ of nitrate in the deep water of the EMS (below 500 m) is indeed lower (2.2 ± 0.3 ‰; $n = 68$) compared to the narrow range of 4.7 to 5.4 ‰ for global ocean deep-water nitrate (Sigman et al., 2009). Furthermore, this dataset shows that nitrate in the LIW water mass from the base of nitracline to 500 m is even more ^{15}N -depleted (1.8 ± 0.4 ‰; $n = 29$). The deep water nitrate in the Western Mediterranean Sea has a $\delta^{15}\text{N-NO}_3$ of 3.0 ± 0.1 ‰ below 1500 m water depth (Pantoja et al., 2002), while in the adjacent NE subtropical Atlantic Ocean, the $\delta^{15}\text{N-NO}_3$ is around 5 ‰ in waters > 800 m depth (Bourbonnais et al., 2009). In Chapter 3, the residence time of deep-water nitrate in the EMS has been estimated to be 125 years. The pool is not directly linked to deep waters outside the EMS which is fed mainly by mineralisation/nitrification of particles sinking from the mixed layer and by preformed nitrate downwelled during deep-water formation without subsequent modification by denitrification. The main nitrate sink is the LIW water mass that exports nitrate to the Western Mediterranean Sea at depths between 150 and 500 m. As already described in Chapter 1, the external sources are N_2 -fixation and atmospheric NO_x since, as pointed out in Chapter 3, the runoff of rivers is considered to be an important source in the EMS.

The comparatively small size of the deep-water nitrate pool in the EMS, its relatively short residence time compared to that of other oceans, the low $\delta^{15}\text{N}$ of external nitrate sources and the lack of mid-water denitrification, are the principal parameters, which, in conjunction, decrease the overall level of $\delta^{15}\text{N}$. As mentioned in Chapter 3, depleted inputs imply that over a residence time (~ 125 years) the deep water $\delta^{15}\text{N-NO}_3$ should decrease to approach the $\delta^{15}\text{N}$ of inputs. The only data of $\delta^{15}\text{NO}_3$ available (also determined by the denitrifier method and with the same internal standard deviation of the method) to gauge possible systematic time-dependent changes are those four samples taken in 1999 in the EMS by Pantoja et al., (2002). These data had an average of 2.5 ± 0.1 ‰ below 500 m depth. Average $\delta^{15}\text{N-NO}_3$ in the present samples taken from below 500 m water depth eight years later is

$2.2 \pm 0.3 \text{ ‰}$ ($n = 68$). While the difference in isotopic ratio between the two datasets is in good accord with a gradual decrease of $\delta^{15}\text{N-NO}_3$ over time, the amount of the change is not large enough to confirm the hypothesis. However, it must be noted that the interval-integrated and mass-weighted $\delta^{15}\text{N}$ of reactive N in the EMS (Table 7) has a gradient from lighter to heavier values with depth, and that the surface layer, which has a much lower residence time than deep water (on the order of years), is within the $\delta^{15}\text{N}$ range of estimated external N inputs.

The EMS deep-water ($> 500 \text{ m}$) nitrate pool is even more unusual in that it has higher $\delta^{18}\text{O}$ ($3.7 \pm 0.9 \text{ ‰}$, $n=25$) than other deep-water pools in the world ocean (Sigman et al., 2009). Available data for the $\delta^{18}\text{O}$ of deep nitrate from a variety of other deep oceanic environments are reported, and all are lower (1.8 to 2.8 ‰, except in the water depth interval from 300 to 1500 m in the Eastern tropical Pacific with a $\delta^{18}\text{O}$ of 7.0 ‰) than the EMS deep nitrate pool. One previous reported value for the $\delta^{18}\text{O-NO}_3$ of deep water in the Western Mediterranean Sea (Sigman et al., 2009) was 2.6 ‰ for the depth range of 1500 m to the seafloor, and $3.1 \pm 0.1 \text{ ‰}$ for a composite value of in parallel measurements of four samples in deep water.

A probable reason for higher $\delta^{18}\text{O-NO}_3$ in EMS deep water than in other deep ocean pools may be that the EMS is a concentration basin where evaporation exceeds precipitation and river runoff (E/P+R ratio of 1.2 in winter and 1.83 in summer) (Gat et al., 1996). The average $\delta^{18}\text{O}$ in water samples deeper than 500 m is $1.43 \pm 0.18 \text{ ‰}$ and $1.44 \pm 0.16 \text{ ‰}$ in the 0-500 m depth range (Pierre, 1999), and thus is around 1.4‰ heavier than in other ocean basins (LeGrande and Schmidt, 2006). Based on experiments, Granger et al., (2004) suggested that nitrification does not involve dissolved O_2 for the required electron transfer to oxidise NH_4^+ to NO_2^- and subsequently to NO_3^- (Sigman et al., 2009). The authors argue that it is very likely that the $\delta^{18}\text{O-NO}_3$ is inherited from the $\delta^{18}\text{O}$ of ambient water with a positive offset of approximately 2 ‰. This offset observed in deep waters of the global ocean is thought to result in part from nitrification (in low latitudes with essentially complete nitrate assimilation in surface waters) while a small positive shift in $\delta^{18}\text{O}$, and added positive shift from admixture of preformed nitrate with elevated $\delta^{18}\text{O-NO}_3$ due to partial assimilation in high latitudes (Sigman et al., 2009). An analogous situation may be in play in the Eastern Mediterranean: deep water formation in the northern basins (Aegean and Adriatic Seas), where surface water cools and sinks during winter

months, exports performed and ^{18}O enriched nitrate (from partial assimilation) from the sea surface to the deep eastern Mediterranean Sea, where it mixes with nitrate from nitrification.

The concentrations of TRN (predominantly DON) in EMS deep and sub-nitracline intermediate waters are also very low compared with other environments (Berman and Bronk, 2003) and match the low PN concentrations (Table 7; Table C.3. data appendix). So far, no data exist on $\delta^{15}\text{N}$ -TRN from deep waters of the global ocean, but $\delta^{15}\text{N}$ -TRN in the deep (> 500 m) EMS is clearly higher (6.0 ± 3.7 ‰, $n=39$) than in EMS surface waters. It is also higher than in the subtropical (3.9 ± 0.4 ‰) and equatorial NW Atlantic (4.1 ± 0.6 ‰), and the subtropical NE Atlantic (2.6 ± 0.4 ‰). They are however in the range of values reported from shallower depths of the subtropical North Pacific (5.4 ± 0.8 ‰) (Knapp et al., 2005; Meador et al., 2007; Bourbonnais et al., 2009).

This ^{15}N -enriched TRN in EMS deep water coexists with low concentrations of even more ^{15}N enriched suspended PN, whereas the data from the sediment trap suggest that the $\delta^{15}\text{N}$ of sinking material from the mixed layer is low over the entire year, differing from other observations (Altabet, 1988; Gaye-Haake et al., 2005) and apparently not enriched in ^{15}N , during its passage through the water column. But there was a significant decrease in the flux measured at different water depths, with the flux of particulate sinking N in the upper sediment trap being $5.7 \text{ mmol N m}^{-2}$ over the period of 216 days, decreasing to $1.4 \text{ mmol N m}^{-2}$ at 2700 m water depth (second trap). This implies a loss of 75% of particulate N flux to disintegration and remineralisation over an 1100 m water column. Because both the concentrations of suspended PN and TRN in ambient water are low, and also decrease with depth, most of the loss can be attributed to ammonification and to the rapid nitrification to nitrate. In consequence, both TRN and suspended PN in deep water are very likely enriched residues of mineralisation, from which some lighter product originated. Because at the same time all meso-zooplankton size classes in EMS deep waters (Koppelman et al., 2009) and surface sediments (Struck et al., 2001) of the EMS are also enriched over the sinking PN flux, the product with low $\delta^{15}\text{N}$ is likely to be nitrate.

4.4.2. Nitrate in the surface layer: Testing the model of incomplete nitrate utilisation

The intermediate water nitrate pool provides the bulk of nitrate available for assimilation in the euphotic zone of the EMS. The phytoplankton bloom takes place over the winter period (October-March), and nutrients are mixed into the surface layer. Nutrients are removed from the mixed layer until all of the phosphate has been taken up and excess nitrate remains together with biomass and TRN produced; sinking particles leave the mixed layer across the pycnocline.

At all stations sampled during the M71-3 cruise there was excess nitrate remaining in the surface mixed layer. The average nitrate remaining in the euphotic zone was between 0.24 and 0.48 μM , and the actual amount of residual nitrate varied accordingly to location and stage of thermocline evolution. These concentrations are similar to those found previously for the average winter residual nitrate across the Southern Levantine basin ($0.6 \pm 0.5 \mu\text{M}$) (Kress and Herut, 2001). In contrast, phosphate was entirely depleted in most surface water samples, with all values being below the detection limit for dissolved phosphate in samples from the EMS that have been preserved by freezing prior to analysis ($< 20 \text{ nM}$) (Krom et al., 2005).

If the concept of the incomplete nitrate utilisation is correct, and no other sources are involved, then the residual nitrate evolves isotopically from the nitrate provided by mixing (Mariotti et al., 1981). The initial mixed-layer nitrate pool in a closed system is progressively assimilated and it will become enriched in ^{15}N (and ^{18}O) in the course of assimilation in analogy to the Rayleigh distillation process (Mariotti et al., 1981):

$$\delta^{15}\text{NO}_3\text{residual} = \delta^{15}\text{NO}_3\text{initial} + {}^{15}\epsilon \times f \times \ln(f)$$

where $f = [\text{NO}_3]_{\text{residual}}/[\text{NO}_3]_{\text{initial}}$, and ${}^{15}\epsilon$ expresses the fractionation factor (in *per mil*) between product and substrate. The range of ${}^{15}\epsilon$ reported in the literature is large and though it differs for different primary producers from -16 to 6 ‰ (York et al., 2007), it is commonly assumed to be -5 ‰. Available field and experimental data suggest equal separation factors ${}^{15}\epsilon$ and ${}^{18}\epsilon$ for nitrate assimilation (Casciotti et al., 2002; Granger et al., 2004; Lehmann et al., 2005).

Simplifying the mixed layer to closed systems and using the Rayleigh closed-system approach as described above, it is assumed an initial nitrate concentration in

the mixed layer of approximately half the concentration below the thermocline and at the nitrate isotope signature of water below the thermocline before the onset of phytoplankton assimilation. The initial nitrate concentration would be $1.8 \mu\text{mol L}^{-1}$ and is similar in value to previous estimates for the amount of nitrate mixed into surface waters in the EMS (Krom et al., 2003). The Rayleigh model predicts that by the time that 73 % of the initial nitrate in the NIS mixed layer is assimilated into PN, SPN and TRN (such as is the case in the average profile over all stations there), the residual nitrate would have a $\delta^{15}\text{N-NO}_3$ of 8.6 ‰, which is significantly higher than the 5.6 ‰ found in the samples. Surface layer nitrate concentrations at the pelagic stations were only 15 % of the assumed initial nitrate and should have a $\delta^{15}\text{N-NO}_3$ of 11.5 ‰, whereas in this study it is found to be 2.3 ‰. The low $\delta^{15}\text{N-NO}_3$ of nitrate remaining in the mixed layers in both cases suggests an additional source of nitrate with a low $\delta^{15}\text{N-NO}_3$.

4.4.3 Constraints from differences in $\delta^{15}\text{NO}_3$ and $\delta^{18}\text{NO}_3$

At all stations (NIS and pelagic), a second and related indicator for a deviation from simple enrichment due to assimilation of thermocline nitrate is the differential behaviour of $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ of residual nitrate in the mixed layer. This is illustrated in Figs. 4.3a and b, where the $\delta^{18}\text{O-NO}_3$ in surface samples is significantly higher than the corresponding $\delta^{15}\text{N-NO}_3$. Although this could be an effect of unequal separation factors for $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ it nevertheless runs counter to available evidence from culture studies and field observations (Casciotti et al., 2002; Granger et al., 2004; Lehmann et al., 2005). If this is accepted, the two isotopes of nitrate should evolve in parallel, if only one nitrate source were assimilated. In the present case, $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ in mixed layer samples should plot a 1:1 enrichment line originating from the composition of nitrate at the base of the thermocline. Any deviation from 1:1 line originating from the nitrate source may be expressed as a nitrate isotope anomaly $\Delta(15,18)$ (Sigman et al., 2005):

$$\Delta(15,18) = (\delta^{15}\text{N}_{\text{measured}} - \delta^{15}\text{N}_{\text{source}}) - \varepsilon^{15}/\varepsilon^{18} \times (\delta^{18}\text{O}_{\text{measured}} - \delta^{18}\text{O}_{\text{source}})$$

Figure 4.5 presents a depth plot of $\Delta(15,18)$ for different station sets over the top 500 m and is calculated by using the average $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ of EMS deep water as $\delta^{15}\text{N}_{\text{source}}$ and $\delta^{18}\text{O}_{\text{source}}$, respectively.

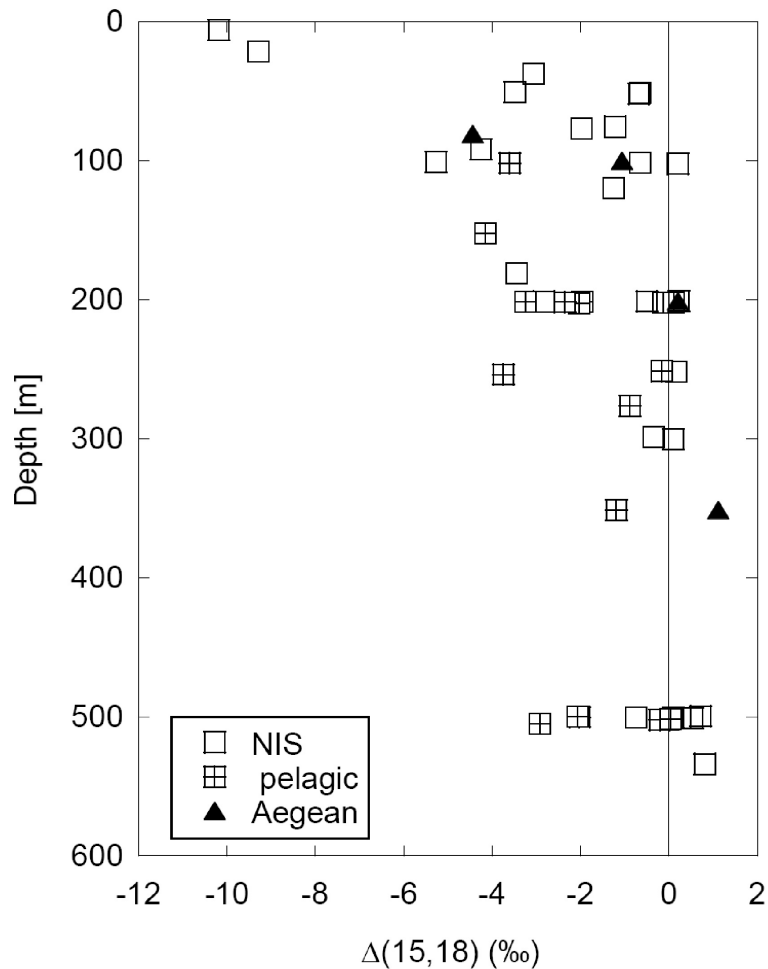


Fig.4.5. Depth plot of $\Delta(15,18)$ of nitrate for different station sets in the upper 500 m of the water column.

The data points presented are scarce in the nitrate-depleted mixed layers, but suggest an average $\Delta(15,18)$ of EMS mixed layer nitrate of around -3 ‰, and both station sets suggest a decrease towards the sea surface. The negative values imply that nitrate in the surface layer is not solely a residue of an initial pool or nitrate provided by cross-thermocline transport; in this case $\Delta(15,18)$ should be 0‰ because $\delta^{15}\text{N}_{\text{source}}$ and $\delta^{18}\text{O}_{\text{source}}$ would evolve in parallel.

This deviation indicates an additional source with lower $\delta^{15}\text{N-NO}_3$ (or higher $\delta^{18}\text{O-NO}_3$) than the residual thermocline nitrate, and suggests either nitrate generation

via nitrification while nitrate in the mixed layer is being assimilated, or external input of nitrate with a different isotopic makeup than the thermocline nitrate (Sigman et al., 2005). These alternatives are discussed below.

5. Nitrification of fixed N or recycled N

Nitrification in the presence of nitrate assimilation, via ammonification of particulate N and/or DON, is the standard mechanism causing a negative $\Delta(15,18)$ in euphotic zones. In the few oligotrophic environments studied so far, observed negative $\Delta(15,18)$ values have been attributed to nitrification of comparatively light PN produced from fixation and possibly DON (Bourbonnais et al., 2009; Casciotti et al., 2008; Knapp et al., 2008a). In these cases, the isotopic composition of (in this case “new”) nitrate is set by the $\delta^{15}\text{N}$ of fixed N ($\sim -1\text{‰}$) on the one hand, and by the $\delta^{18}\text{O}$ of ambient seawater with a positive offset of 2 ‰, so that nitrate deriving from N_2 fixation is added to the mixed-layer nitrate pool with a $\delta^{15}\text{N-NO}_3$ of $\sim -1\text{‰}$ and $\delta^{18}\text{O-NO}_3$ of $\sim 2\text{‰}$ (Bourbonnais et al., 2009). In the EMS with its higher $\delta^{18}\text{O}$ of seawater, it is expected that the recycled nitrate has a $\delta^{15}\text{N-NO}_3$ equivalent to $\delta^{15}\text{SPN}$ and a $\delta^{18}\text{O-NO}_3$ of $\sim 3.4\text{‰}$.

Partitioning of ammonium released from PN to either nitrification or ammonium uptake has also been shown to cause a range of $\Delta(15,18)$ values, because both processes have different $^{15}\epsilon$ (Sigman et al., 2005; Wankel et al., 2006). Negative $\Delta(15,18)$ values in residual nitrate may ensue, because nitrate returned from PN mineralisation via ammonium oxidation is relatively more depleted in ^{15}N than the residual nitrate pool, whereas its $\delta^{18}\text{O}$ is pegged to ambient water. Because on the other hand ammonium uptake has a lower preference for ^{15}N than nitrification (Cifuentes et al., 1989; Casciotti et al., 2003), significant ratios of ammonium assimilation versus nitrification will cause biomass, and thus PN, to be relatively enriched over the recycled nitrate. Since no indication was found for enriched SPN or PN in the mixed layers, and the sediment trap data suggest that SPN is on annual average even more depleted in ^{15}N than thermocline nitrate in the EMS, it is believed that assimilation of mineralised ammonium is unlikely to play a major role as a substrate for phytoplankton growth in the EMS mixed layer, and as a cause for negative $\Delta(15,18)$. But the isotopic data do not completely rule out assimilation of remineralized ammonium: if relatively little nitrification takes place, particulate N may be remineralized and ammonium completely reassimilated without involving isotope fractionation.

6. Input of atmospheric NO_x

Besides the internal source of nitrate, a second source that potentially causes negative $\Delta(15,18)$ values in the mixed layer of the EMS, namely atmospheric inputs of NO_x, must exist. Two previous studies (Knapp et al., 2008a; Bourbonnais et al., 2009) acknowledge (though they dismiss) the possibility that the negative $\Delta(15,18)$ observed in mixed layer nitrate of the oligotrophic Sargasso Sea and subtropical NE Atlantic Ocean indicates atmospheric NO_x inputs, which have very high $\delta^{18}\text{O-NO}_3$ at low $\delta^{15}\text{N-NO}_3$ (Kendall, 1998). Such an input, if it is not immediately assimilated due to phosphate limitation, would introduce nitrate with low $\delta^{15}\text{N-NO}_3$ and high $\delta^{18}\text{O-NO}_3$ into the surface mixed layer of the EMS. There is evidence suggesting that NO_x inputs play a relatively larger role in the EMS than elsewhere: modelled average annual total NO_x inputs in wet and dry deposition to the EMS surface range between 200 and 400 mg N m⁻² a⁻¹. Reduced N deposition is lower (200 - 20 mg N m⁻² a⁻¹), and both inputs have a pronounced N-S gradient, with reduced N having a steeper land-sea gradient. An estimated 14-29 mmol NO_x m⁻² a⁻¹ of industrial origin is thus supplied annually to the basin, along with a smaller contribution of reduced N.

In Chapter 3 it was shown that the atmospheric deposition on the island of Crete in the winter months of 2006/2007 had a mean $\delta^{15}\text{N-NO}_3$ of -2.0 ‰. Further analysis of the samples revealed a high $\delta^{18}\text{O-NO}_3$: thirteen samples of dry atmospheric deposition (no rain events recorded) collected on the island of Crete during June-September 2007 had an average $\delta^{18}\text{O-NO}_3$ of 67.5 ± 4.2 ‰. Although these data do not cover the time of predominantly wet deposition in winter, the values are within the range reported from other environments (Kendall, 1998) and from the nearby northern Red Sea (Wankel et al., 2009). There, $\delta^{15}\text{N}$ values of water-soluble nitrate in aerosol samples ranged from -6.9 to +1.9 ‰ and $\delta^{18}\text{O}$ was found to range from 65.1 to 84.9 ‰ with the highest $\delta^{18}\text{O}$ values occurring in the winter. That nitrate was deposited from air masses deriving from the Mediterranean Sea and western Europe (Wankel et al., 2009). Thus, although only < 10 % of nitrate remaining in the mixed layer of the EMS might have originated from the atmospheric source over a period of four months, the effects on average $\delta^{18}\text{O-NO}_3$ and $\Delta(15,18)$ values are quite important due to the small amount of nitrate in the mixed layer of the EMS and the high $\delta^{18}\text{O-NO}_3$ of atmospheric inputs. Other authors (Knapp et al., 2008a;

Bourbonnais et al., 2009) have speculated that the nitrate isotope anomaly observed in other oligotrophic ocean mixed layers may be caused by the input of NO_x . Of all of these, the Eastern Mediterranean surface mixed layer is arguably the most sensitive place in the world ocean to register that input. The nitrate pool in the Eastern Mediterranean is very small and the system is phosphate-limited. Most other upper ocean waters receiving a sizeable NO_x input (Duce et al., 2008) are N-limited, so that any nitrate entering the surface ocean there should be immediately assimilated. This assimilation (and subsequent recycling to nitrate) would eradicate the $\delta^{18}\text{O}$ signal diagnostic of atmospheric NO_x and would make it impossible to trace.

The isotopic signatures of internal (recycling) and external (N_2 fixation and NO_x) inputs together with an estimate of N export flux can be used in a conceptual steady-state mass and isotope balance model to explore the effects of externally and internally supplied N on $\Delta(15,18)$. The model is the same as that used in the subtropical SE Atlantic (Bourbonnais et al., 2009).

Figure 4.6 is a conceptual diagram of sources, sinks and transformations in the N-cycle of the eastern Mediterranean Sea to illustrate the rationale and the modelling approach: the nitrate pool in surface water is fed by external (NO_x , N_2 fixed, and nitrate from cross-thermocline mixing, ku) and internal (mineralisation and nitrification of PN in the surface mixed layer) sources. The nitrate sink for the surface layer is assimilation into particulate N produced (with TRN/DON as a by-product) and export of sinking particulate nitrogen across the thermocline.

The nitrate below the thermocline is a mixture of a standing stock of nitrate in deep/intermediate water and an addition from the mineralisation of sinking particulate nitrogen. In the present interpretation, the difference between deep-water suspended matter and TRN on the one hand and sinking PN and nitrate on the other hand may arise, when small particles shed from the sinking PN are a substrate for ammonification, and partition into ^{15}N -depleted ammonia that is completely oxidised to nitrate and small residual small particles (suspended PN) enriched in ^{15}N . A by-product of this suspended particulate nitrate may be TRN/DON that is also enriched in ^{15}N as compared to the sinking material. Nitrification of ammonia liberated from sinking PN or from fixed N_2 water adds nitrate with a $\delta^{18}\text{O}$ (marked in blue in Fig. 4.6) approximately 2 ‰ higher than ambient seawater – in the case of the EMS, this nitrate is expected to have a $\delta^{18}\text{O}\text{-NO}_3$ of 3.4 ‰.

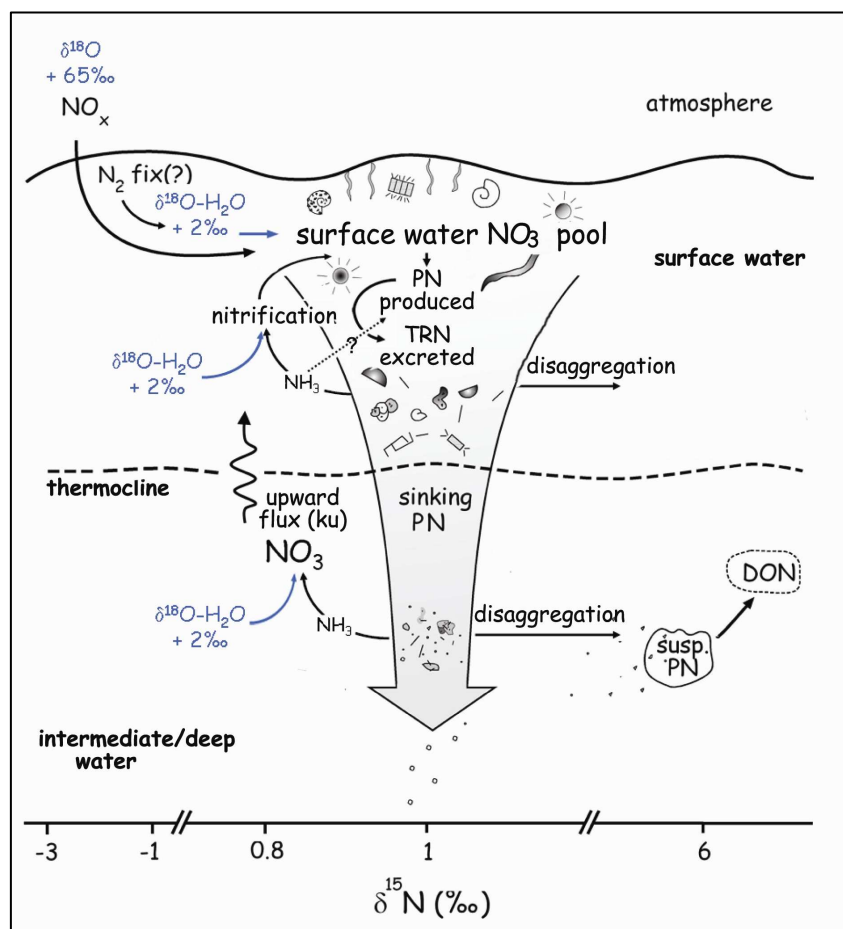


Fig.4.6. Conceptual diagram of the processes that determine the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate in the surface and intermediate water masses of the eastern Mediterranean Sea; this diagram is also a schematic illustration of the model used to calculate $\Delta(15,18)$ of nitrate under assumptions of different sources as explained in the text.

It is pointed out that nitrate added from the mineralisation of fixed N_2 or from sinking PN produced from assimilation of thermocline nitrate both acquire the same $\delta^{18}\text{O}$ after nitrification (through exchange with ambient water), but the two N-sources have different $\delta^{15}\text{N}$, and both these additions cause negative excursions in $\Delta(15,18)$: Because this term expresses the deviation in the dual isotopes of nitrate from the isotopic composition of nitrate provided by the thermocline flux ku and enriched in parallel during assimilation with a 1:1 slope, $\Delta(15,18)$ would remain 0‰, regardless of the extent of nitrate assimilated, if ku only were the source of nitrate in the surface. The other possible source of nitrate (NO_x from the atmosphere) has a high $\delta^{18}\text{O}$ of 65‰ at a low $\delta^{15}\text{N}$ of -2 ‰. If not assimilated immediately, this atmospheric input lowers the $\delta^{15}\text{N}$ - NO_3 while raising the $\delta^{18}\text{O}$ - NO_3 of the surface nitrate pool, and would also cause a negative $\Delta(15,18)$ though for a different reason.

The model for the calculation of $\Delta(15,18)$ (Bourbonnais et al., 2009), was adapted to conditions in the Eastern Mediterranean Sea. The appropriate boundary conditions were chosen for the thermocline nitrate isotopic composition (Table 7; Table C.3. data appendix), the $\delta^{18}\text{O}$ of seawater, and the observed N-export production of 56 mmol per year. This production is fixed; added inputs from N_2 fixation or NO_x reduce ku by the equivalent amount. If nitrification of particulate N occurs in the surface layer, this requires that the amount of nitrate assimilated in the surface layer is higher by the amount nitrified to maintain the export flux, but it does not affect ku . All N sources have a specific $\delta^{15}\text{N}$ signature, and the nitrate mixture in the surface layer integrates these isotopic contributions. That pool of nitrate is assimilated into the biomass, and the residual nitrate pool in the surface layer is isotopically enriched during phytoplankton assimilation with equal fractionation factors $^{15}\epsilon = ^{18}\epsilon = -5\text{‰}$: at any stage of assimilation, the $\delta^{15}\text{N}$ of sinking PN is 5 ‰ more depleted than the residual nitrate pool, while the $\delta^{18}\text{O}$ signal of the assimilated nitrate is lost. In the model, recycled nitrate (nitrification) inherits the $\delta^{15}\text{N}$ of sinking PN (that has or does not have a contribution from N_2 fixation) and the $\delta^{18}\text{O}$ of seawater (with an offset of +2 ‰).

An hypothetical calculation of $\Delta(15,18)$ was conducted for a range of input conditions from 0-40 mmol N from N_2 fixation and 0-40 mmol N of recycled nitrate, both of which acquire a $\delta^{18}\text{O}\text{-NO}_3$ of 3.4 ‰. Nitrate input from N_2 -fixation needs to be 40 mmol $\text{m}^{-2} \text{a}^{-1}$ (> 70% of the 56 mmol $\text{m}^{-2} \text{a}^{-1}$ PN export flux) to create a $\Delta(15,18)$ of around -2‰ ; input of 40 mmol $\text{m}^{-2} \text{a}^{-1}$ of recycled nitrate yielded a $\Delta(15,18)$ of -3.6‰ , which is close to the roughly -3‰ observed. For an assumed unassimilated NO_x input of only 5 mmol m^{-2} , which is well within the known atmospheric NO_x flux to the Eastern Mediterranean, the model calculates a $\Delta(15,18)$ of -5.8‰ . This is due to the somewhat lower $\delta^{15}\text{N}$ and grossly higher $\delta^{18}\text{O}$ as compared to thermocline nitrate.

These calculations suggest a number of possible combinations of external and internal sources that can theoretically result in the nitrate isotope anomaly observed in the mixed layer. They are inconclusive because the $\Delta(15,18)$, which is well suited to diagnose nitrate sources in other areas of the oligotrophic surface ocean, is somewhat blunt in the EMS due to the similarities in isotopic composition of all external and internal sources. However, the preferred interpretation of the data is that they

represent a mixture of regenerated nitrate and NO_x input, because both are known to be inputs to the mixed layer in the necessary magnitudes and isotopic ranges to fully describe the changes observed.

The input from N_2 fixation is considered to be unlikely for the time of the M71-3 cruise, because a) the cruise was conducted over the winter period and b) N_2 fixation measurements were very low even when performed in the summer of 2007 (June) across the region of EMS (Ibello et al., 2010). There is ample evidence that primary production in the EMS is supported by regenerated nutrients that are entrained into a microbial loop operating in surface waters (Zohary and Robarts, 1998; Thingstad et al., 2005). Nutrient budgets (Ribera d' Alcala et al., 2003) and experimental work (Thingstad and Rassoulzadegan 1989; Thingstad et al., 2005) both imply that surface productivity is to a significant extent supported by regenerated nitrate. In addition, recent genetic investigations suggest that ammonia-oxidizing *Archaea* in mesopelagic waters of the Eastern basin may have a central role in the nitrification of ammonium liberated from particulate N (De Corte et al., 2009). The data presented in the Chapter 4 underline the importance of recycled nitrate, but also stress that atmospheric NO_x inputs to the basin must be taken into account in mass-based and isotope-based budgets of the N-cycle in the eastern Mediterranean Sea.

Chapter 5. Conclusions and outlook

5.1 Conclusions

In this thesis different perspectives of the nitrogen cycle in the atmospheric and marine environment of the Eastern Mediterranean Sea (EMS) were examined, using stable isotopes as an additional tool to assess sources, sinks and processing of reactive nitrogen or nitrate. It has been shown that nitrogen isotope ratios, and, possibly even more so, oxygen isotopes of nitrate, could shed light on nutrient processing in this oligotrophic environment.

To quantify the role of atmospheric NO_3^- deposition in the N-cycle in the eastern Mediterranean, NO_3^- and its $^{15}\text{N}/^{14}\text{N}$ ratio, ($\delta^{15}\text{N}\text{-NO}_3$), samples of dry and wet deposition from April 2006 to September 2007 were analysed, in the island of Crete. Both dry and wet deposition samples showed consistently negative values ($< 0 \text{ ‰}$) of $\delta^{15}\text{N}\text{-NO}_3$, implying a ^{15}N -depleted atmospheric source. The $\delta^{15}\text{N}\text{-NO}_3$ values in wet deposition were in agreement with data reported in other regions (Freyer, 1991; Hastings et al., 2003). Interestingly the low $\delta^{15}\text{N}\text{-NO}_3$ values in both dry and wet deposition can be attributed to the formation of ^{15}N - depleted NaNO_3 and $\text{Ca}(\text{NO}_3)_2$, as well as in the presence of HNO_3 that was reported in this study to have depleted $\delta^{15}\text{N}$ values in dry deposition samples. The difference in the dominant aerosol NO_3^- speciation in the Mediterranean atmosphere should result in the west-to-east gradient in $\delta^{15}\text{N}$ values of atmospheric NO_3^- inputs presented in the Mediterranean Sea. Indeed, in addition to NaNO_3 and $\text{Ca}(\text{NO}_3)_2$ that show depleted $\delta^{15}\text{N}$ values, NH_4NO_3 formation which has relatively enriched $\delta^{15}\text{N}$ values, has been reported only for the Western Mediterranean atmosphere, while no formation of the compound has been, so far, reported to occur in the Eastern basin.

The presence of isotopically depleted NO_3^- (as compared to deep ocean nitrate) in the intermediate and deep waters of the EMS cannot alone be used to prove the importance of N_2 -fixed nitrogen in creating the unusually low $\delta^{15}\text{N}\text{-NO}_3$ in EMS deep water. Based on the data shown in Chapter 3, the atmospheric input dominates the $\delta^{15}\text{NO}_3$ of N-inputs to surface waters in the EMS. This surface water signal is communicated to the deep water mass in the EMS via particle flux, and the impact

over the last decades is likely to have been large enough to depress $\delta^{15}\text{N}$ of the EMS deep nitrate pool.

In order to explain the processes causing the unusual isotopic ratios in the deep water of EMS and to reveal the importance of providing a comprehensive data set of $\delta^{15}\text{N}$ in N-pools of the water column, a research cruise using the R/V METEOR was conducted during January/February 2007. The analysis of the samples collected from 17 stations during the cruise, showed that the total pool of reactive nitrogen (nitrate, dissolved total reduced nitrogen, particulate nitrogen) in the EMS has depleted values of ^{15}N compared to the global ocean. In particular, the low $\delta^{15}\text{N}$ of nitrate, which represents the largest N-pool, must be to a large extent due to the isolation and the anti-estuarine circulation of the EMS (extensively described in Chapter 1). The anti-estuarine circulation prevents the communication of the EMS with the global deep-water nitrate pool that is very homogeneous and presents $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ values around 5 ‰ and 2 ‰, respectively (Sigman et al., 2009).

As discussed in Chapter 4, the low level of $\delta^{15}\text{N}$ in the EMS reflects the dominance of an isotopically depleted N-source, since processes that enrich ^{15}N (e.g. denitrification) are lacking in action in the EMS. The data presented in this study were collected over the winter period, which coincided with a typical winter bloom at one set of stations in the northern Ionian basin and with an (unusually early) mature thermocline at maximum depth in the remaining pelagic set of stations. Although they provide only a snapshot of a seasonal cycle in the mixed layer, the data from the two situations (depending thermocline and mature thermocline) in that cycle permit an initial assessment of different nitrate sources to the mixed layer.

The low levels of $\delta^{15}\text{N}$ in NO_3 , TRN and PN cannot result only from the partial N uptake caused by the extant P-limited phytoplankton bloom. A source of isotopically distinct nitrate, which may be internal (recycled nitrates) or external (N_2 fixation or NO_x input) is also required. Possible ranges for the nitrate isotope anomaly $\Delta(15,18)$ in the mixed layer calculated in Chapter 4 by a simple model, pointed towards nitrification and/or a realistic contribution of atmospheric nitrate with characteristically low $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ as an important source of additional nitrate.

Clearly, as already suggested by Hastings et al., (2003) and Knapp et al. (2005) for the Sargasso Sea, the input of atmospheric NO_3^- cannot be neglected when

investigating the present-day N-cycle in the oligotrophic EMS. It is known that EMS receives a significant supply of anthropogenic NO_x , that together with known recycling processes can adequately describe the isotope distribution. These patterns could also be caused by extensive N_2 fixation, but that would require very high rates of diazotrophy in winter when, even in summer, very low levels of fixation are measured in the region. Furthermore this would be in conflict with the knowledge provided in Chapter 3 on the amount and isotopic composition of anthropogenic NO_x input in the EMS.

5.2 Outlook

While it was possible to answer many of the questions related to the nitrogen cycling in the EMS, the conclusions outlined above have posed a number of new questions.

One important sub-basin of the EMS is the Aegean Sea which lies to the northeast of the Eastern Mediterranean and is landlocked on its north and west coasts by the Greek mainland, to the east by the coast of Turkey and to the south by the island of Crete (Velaoras and Lascaratos, 2005). It is separated by the Cyclades plateau into two sub-cells, the North Aegean (N.Aegean) and the South Aegean (S.Aegean), each with significantly different hydrographic characteristics. Specifically, the water-column structure of the N. Aegean is influenced by the input of less saline waters from the Black Sea (BSW) through the Dardanelles Straits and from fresh water discharges from rivers which are located in mainland Greece. These features create an interesting structure which seems to have a significant role in the productivity status of the area (Ignatiades et al., 2002).

An important aspect concerning the Aegean Sea is the contribution of the area to the total deep water circulation of EMS. As has been shown, bottom-arrested currents represent a significant mechanism for the export of dense water masses produced by oceanic convection, the process which sets and maintains the abyssal circulation of the world ocean (Rubino et al., 2003). Until the eighties, the Adriatic Sea was historically considered to be the source of the Eastern Mediterranean Deep and Bottom Waters (EMDW). Data obtained from the 1987 (Schlitzer et al., 1991) and 1995 (Roether et al., 1996) METEOR cruises revealed that the thermohaline circulation in the Eastern Mediterranean had been abruptly changed. This change is

referred to as the Eastern Mediterranean Transient (EMT) and was attributed to the dramatic climatic change that took place in the Eastern Mediterranean Sea in the nineties. During the EMT the cold and relatively fresh Adriatic Deep Water was replaced substantially by waters of high density (warmer and saltier) formed in the Aegean, outflowing from the straits of the Cretan Arc and replacing mainly bottom layers of the Ionian Sea (Klein et al., 1999). Distinct lenses from the Aegean Sea were identified at depths between 700 and 1100 m resulting from changes in either the circulation or the large-scale water budget (Roether et al., 1996). Zervakis et al. (2000) suggested that the reduced Black Sea outflow into the North Aegean could facilitate dense water formation during the influence of cold atmospheric fronts in the winter.

The change in the deep water had extensive consequences for the entire circulation of the eastern Mediterranean Sea. One result was the uplifting of the residing water column by as much as about 500 m, which appeared to be strongest in the Ionian Basin (Lascaratos et al., 1999). With the uplifting a rise of the nutricline over large parts of the Eastern Mediterranean to depths as shallow as 150 m has been observed (Klein et al., 1999).

The disruption observed in the circulation of the EMS due to the EMT brings to the surface two important issues that can be considered as future aspects for debate. The first deals with the nutrient cycling in the EMS and has to be more comprehensively discussed and presented as a future outlook. This may be particularly relevant to the biogeochemical cycling of $\delta^{15}\text{N}$ when considering the nutrient data obtained from the METEOR 71-3 cruise conducted in the EMS in 2007, in comparison with the nutrient data from METEOR 1 cruise that took place in 1987. The samples in both cruises were also analysed and measured by applying the same methods as described in this thesis. In this case, it would be interesting to see if there has been a change in nutrient ratios since then, building on the idea that N presents a trend to increase in the EMS. The idea of providing an overview concerning nutrient ratios also arose from the hypothesis that these ought to have changed if the atmosphere delivered more N than P over the last decades. Furthermore the nutrient data from the two METEOR campaigns can also present other important variables for the region of EMS.

The second important issue deals with the deep water formation procedure and more specifically the contribution of the deep water mass to the $\delta^{15}\text{N}$ of the region. The Eastern Mediterranean Transient caused important changes in the structure of the water column; the data obtained from the region concerning the $\delta^{15}\text{N}$ - NO_3 in deep water have to be enhanced with new information that will come from future cruises in order to reveal the magnitude of the contribution to the isotopic ratio of nitrogen in the basin. With this in mind, the idea of having an extensive mass-isotope budget for the entire Mediterranean may be feasible. This budget can be conducted taking into account the contribution of the data that were collected and presented in this thesis together with other studies that have been conducted and/or will be conducted in the region. A full mass-isotope budget will be also an important step for a modelling approach of N-cycling in the EMS.

Acknowledgments

I am deeply indebted to my advisors, Prof. Dr. Kay-Christian Emeis, and Prof. Dr. Nikos Mihalopoulos for their support, their invaluable advice and critical comments. Without their help, this Ph.D. dissertation would not have been possible.

I am very grateful to Prof. Dr. Emeis, because he gave the opportunity to be part of his research group in Germany and offered me the opportunity to participate in a very important sampling cruise in the Eastern Mediterranean Basin during January 2007.

I would like to thank Prof. Dr. Tasso Eleftheriou for taking the time to evaluate this thesis as a co-referee, and for the useful remarks that he made during the writing of this thesis.

I would also like to thank Dr. Aleka Gogou from the Hellenic Centre for Marine Research (HCMR), for her advice and patience which was very much appreciated.

My Ph.D. studies were accomplished mostly thanks to the support from my colleagues in GKSS where I spent most time when analysing samples in Germany. I was fortunate to be part of a group of scientifically ambitious researchers at the Institute of Coastal Research in GKSS, such as Dr. Kirsten Daehnke, Dr. Tim Schlarbaum, Dr. Enno Bahlmann, as well as Dr. Juergen Moebius who is a member of the Institut für Biogeochemie und Meereschemie in Hamburg University and many other people such as Dr. Birgit Gaye. Their help certainly motivated me to continue.

At this point, I would like to express my everlasting gratitude to my friends in Greece for their patience and support, providing the main energy supply for me to finish this thesis. I wish to extend my heartfelt thanks to my parents who are no longer

with us, whose continuous encouragement used to lighten my path into higher education.

This work was funded by **EUROCEANS** network of excellence under the contract number **WP5 SYSMS-1054**.

References

- Altabet, M. A. (1988), Variations in nitrogen isotopic composition between sinking and suspended particles: implications for nitrogen cycling and particle transformation in the open ocean, *Deep-Sea Research*, **35**: 535-554.
- Altabet, M. A., and R. Francois (1994), The use of nitrogen isotopic ratio for reconstruction of past changes in surface ocean nutrient utilization, *In: Carbon Cycling in the Glacial Ocean: Constraints on the Ocean's Role in Global Change*, (Zahn, R., Pedersen, T. F., Kaminski, M. A., Labeyrie, L. D., eds) Springer-Verlag, Heidelberg.
- Aly, A. I. M., Mohamed, M. A., Hallaba, E., (1982), Natural variations of ^{15}N -content of nitrate in ground and surface waters and total nitrogen of soil in the Wadi El-Natron area in Egypt, *In: Stable Isotopes*, (Schmidt, H.-L., Förstel, H., Heinzinger, K., eds) pp. 475–481, Elsevier, Amsterdam.
- Amman, M., Siegwolf, R.T.W., Pichelmayer, F., Suter, M., Saurer, M., Brunold, C., (1999), Estimating the uptake of traffic derived NO_2 from ^{15}N abundance in needles of Norway spruce, *Oecologia*, **118**: 124-131.
- Antoine, D., Morel, A. André, J.M., (1995), Algal pigment distribution and primary production in the eastern Mediterranean as derived from coastal zone color scanner observations, *Journal of Geophysical Research*, **100**(C8): 16193-16209.
- Arimoto, R., Duce, R. A., Ray, B. J., Ellis Jr, W. G., Cullen, J. D., Merrill J.T, (1995), Trace elements in the atmosphere over the North Atlantic, *Journal of Geophysical Research*, **100**: 1199–1213.
- Azov, Y., (1991), Eastern Mediterranean—a marine desert?, *Marine Pollution Bulletin*, **23**: 225-232.
- Baker, A., Kelly, S., Biswas, K., Witt, M., Jickells, T., (2003), Atmospheric deposition of nutrients to the Atlantic Ocean, *Geophysical Research Letters* **30** (24), doi:10.1029/2003GL018518.
- Baker, A. R., K. Weston, S. D. Kelly, M. Voss, P. Streu, J. N. Cape (2007), Dry and wet deposition of nutrients from the tropical Atlantic atmosphere: Links to primary productivity and nitrogen fixation, *Deep Sea Research, Part I*, **54**, 1704–1720.

- Bardouki, H., Liakakou, H., Economou, C., Sciare, J., Smolik, J., Zdimal, V., Eleftheriadis, K., Lazaridis, M., Dye, C., Mihalopoulos N., (2003), Chemical composition of size-resolved atmospheric aerosols in the eastern Mediterranean during summer and winter, *Atmospheric Environment*, **37**: 195–208.
- Berg B. and H. Staaf (1981), Leaching, accumulation and release of nitrogen in decomposing forest litter, *In: Terrestrial Nitrogen Cycles*, (F.E. Clark and T. Rosswall, eds) Swedish Natural Science Research Council, Stockholm :163–178.
- Berland, B.R., Bonin, D.J., Maestrini, S.Y., (1980), Nitrogen or phosphorous? Considerations on the “nutritional paradox” of the Mediterranean Sea, *Oceanologica Acta*, **3**: 135–141.
- Berman-Franck, I., Yogev, T., Aharonovich, D., Beja O., (2007), Nitrogen fixation in the Eastern Mediterranean Sea, *in IUGG XXIV General Assembly, 2-13 July 2007*, Perugia, Italy PS001 5773.
- Berman, T., and D. A. Bronk (2003), Dissolved organic nitrogen: a dynamic participant in aquatic ecosystems, *Aquat. Microb. Ecol.*, **31**: 279-305.
- Béthoux, J.P. and G., Copin-Montegut, (1986), Biological fixation of atmospheric nitrogen in the Mediterranean Sea, *Limnology & Oceanography*, **31**(6): 1353-1358.
- Béthoux, J.P.(1989), Oxygen consumption, new production, vertical advection and environmental evolution of the Mediterranean Sea., *Deep Sea Research*, **36**(5): 769-781.
- Béthoux, J. P., Morin, P., Chaumery, C., Connan, O., Gentili, B., Ruiz-Pino, D., (1998), Nutrients in the Mediterranean Sea, mass balance and statistical analysis of concentrations with respect to environmental change, *Marine Chemistry*, **63**: 155–169.
- Bolin, B., and Cook, R. B. (1983), *The Major Biogeochemical Cycles and their Interactions*, John Wiley and Sons, Chichester.
- Böhlke, J. K., Mroczkowski, S.J., Coplen, T.B., (2003), Oxygen isotopes in nitrate: new reference materials for ^{18}O : ^{17}O : ^{16}O measurements and observations on nitrate-water equilibration, *Rapid Communications in Mass Spectrometry*, **17**(16): 1835-1846.
- Bonnet, S., and C. Guieu, (2006), Atmospheric forcing on the annual iron cycle in the western Mediterranean Sea: a 1 year survey, *Journal of Geophysical Research*, **111** (C09010) doi:10.1029/2005JC003213.

- Bourbonnais, A., Lehmann, M. F., Waniek, J. J., Schulz-Bull, D. E., (2009), Nitrate isotope anomalies reflect N₂ fixation in the Azores Front region (subtropical NE Atlantic), *Journal of Geophysical Research*, **114** (C03003): 1-16.
- Brandes, J. A., and A. H. Devol (2002), A global marine-fixed nitrogen isotopic budget: Implications for Holocene nitrogen cycling, *Global Biogeochemical Cycles*, **16**(4): 1120, doi:10.1029/2001GB001856.
- Bronk, D. A. (2002), Dynamics of DON, in *Biogeochemistry of Marine Dissolved Organic Matter*, (Hansell, D.A. and C. A. Carlson, eds), Academic Press, New York, pp. 153-247.
- Burt, T.P., Heathwaite, A. L., Trudgill, S.T., (1993), Nitrate: Processes, Patterns and Management, John Wiley & Sons, Inc., New York, Chapters 5 & 10.
- Casciotti, K. L., Sigman, D., Galanter M., Hastings, M., Böhlke, J. K., Hilkert, A.,(2002), Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method, *Analytical Chemistry*, **74**: 4905-4912.
- Casciotti, K. L., Sigman D. M., Ward, B. B., (2003), Linking diversity and stable isotope fractionation in ammonia-oxidizing bacteria, *Geomicrobiology Journal*, **20**(4), 335-353.
- Casciotti K. L. and M. R., Mcilvin (2007), Isotopic analyses of nitrate and nitrite from reference mixtures and application to eastern tropical North Pacific waters, *Marine Chemistry*, **107**: 184–201.
- Casciotti, K.L., Trull, T.W., Glover, D.M., Davies D., (2008), Constraints on nitrogen cycling at the subtropical North Pacific Station ALOHA from isotopic measurements of nitrate and particulate nitrogen, *Deep Sea Research Part II*, **55**(14-15): 1661-1672.
- Chen, Y., and R. Siefert, (2004), Seasonal and spatial distributions and dry deposition fluxes of atmospheric total and labile iron over the tropical and sub-tropical North Atlantic Ocean, *Journal of Geophysical Research*, **109** (D09305), doi:10.1029/2003JD003958.
- Christaki U., Giannakourou, A., van Wambeke F., Grégori G., (2001), Nanoflagellate predation on auto- and heterotrophic picoplankton in the oligotrophic Mediterranean Sea, *Journal of Plankton Research*, **23** (11): 1297-1310.
- Christensen, S. and J. M., Tiedje, (1988), Sub-parts-per-billion nitrate method: Use of an N₂O producing denitrifier to convert NO₃⁻ or ¹⁵NO₃⁻ to N₂O, *Applied & Environmental Microbiology*, **54**: 1409-1413.

- Cifuentes, L. A., Fogel, M. L., Pennock, J. R., Sharp, J. H., (1989), Biogeochemical factors that influence the stable nitrogen isotope ratio of dissolved ammonium in the Delaware Estuary., *Geochim Cosmochim Acta* **53**: 2713–2721.
- Çoban-Yildiz, Y., Altabet, M.A., Yilmaz, A. Tugrul, S., (2006), Carbon and nitrogen isotopic ratios of suspended particulate organic matter (SPOM) in the Black Sea water column, *Deep Sea Research II*, **53**: 1875-1892.
- Cornell, S., Rendell, A., Jickells, T., (1995), Atmospheric inputs of dissolved organic nitrogen to the oceans *Nature*, **376**: 243-246.
- Danalatos, D., Glavas, S., Kambezidis, H., (1995), Atmospheric nitric acid concentrations in a Mediterranean site, Patras, Greece, *Atmospheric Environment*, **29**: 1849-1852.
- Delwiche, C.C., (1970), The nitrogen-cycle, *Scientific American*, **223**(3):136-147.
- Deutsch, C., Sarmiento, J. L., Sigman, D. M., Gruber, N., Dunne J. P., (2007), Spatial coupling of nitrogen inputs and losses in the ocean, *Nature*, **445**: 163-167.
- De Corte, D., Yokokawa, T., Varela, M. M., Agogué, H., Herndl, G. J. (2009), Spatial distribution of Bacteria and Archaea and amoA gene copy numbers throughout the water column of the Eastern Mediterranean Sea, *The ISME Journal*, **3** (2): 147-158.
- Diaz, F., and P. Raimbault (2000), Nitrogen regeneration and dissolved organic nitrogen release during spring in a NW Mediterranean coastal zone (Gulf of Lions): implications for the estimation of new production, *Marine Ecology Progress Series*, **197**: 51-65.
- Dingman, S. L., (1994), Physical Hydrology, Prentice-Hall, Inc., Englewood Cliffs, NJ.
- Dolan, J. R., (2000), Tintinnid ciliate diversity in the Mediterranean Sea: longitudinal patterns related to water column structure in late spring-early summer, *Aquatic Microbial Ecology*, **22**: 69–78.
- Duce, R.A., LaRoche, J., Altieri, K., Arrigo, K.R., Baker, A.R., Capone, D. G., Cornell, S., Dentener, F., Galloway, J., Ganeshram, R. S., Geider, R. J., Jickells, T., Kuypers, M. M., Langlois, R., Liss, P. S., Liu, S. M., Middelburg, J. J., Moore, C. M., Nickovic, S., Oschlies, A., Pedersen, T., Prospero, J., Schlitzer, R., Seitzinger, S., Sorensen, L. L., Uematsu, M., Ulloa, O., Voss, M., Ward, B., Zamora L., (2008), Impacts of atmospheric anthropogenic nitrogen on the open ocean, *Science*, **320** (5878): 893-897.

- Elliott, E.M., Kendall, C., Wankel, S.D., Burns, D.A., Boyler, E. W., Harlin, K., Bain, D.J., Butler, T.J., (2007), Nitrogen isotopes as indicators of NO_x source contributions to atmospheric nitrate deposition across the Midwestern and Northeastern United States, *Environmental Science & Technology*, **41** (22): 7661–7667.
- Fagerli, H., Legrand, M., Preunkert, S., Vestreng, V., Simpson, D., Cerqueiraet, M., (2007), Modeling historical long-term trends of sulfate, ammonium, and elemental carbon over Europe: A comparison with ice core records in the Alps, *Journal of Geophysical Research*, **112**: D23S13.
- Fairchild, R.G., (1983), *In: Synthesis and applications of isotopically labeled compounds*, (Duncan W.P., Susan A.B., eds), Elsevier, Amsterdam, pp. 155-165.
- Fanning, K.A., (1989), Influence of atmospheric pollution on nutrient limitation, *Nature*, **339**: 460–463.
- Ferm, M., (1998), Atmospheric ammonia and ammonium transport in Europe and critical loads—a review, *Nutrient Cycling in Agroecosystems*, **51**: 5–17.
- Fogel, M. L., and H. W., Paerl, (1993), Isotopic tracers of nitrogen from atmospheric deposition to coastal waters, *Chemical Geology*, **107**: 233-236.
- Freyer, H. D., (1991), Seasonal variation of ¹⁵N/¹⁴N ratios in atmospheric nitrate species, *Tellus*, **43B**: 30-44.
- Gat, J. R., Shemesh, A., Tziperman, E., Hecht, A., Georgopoulos, D., Basturk, O., (1996), The stable isotope composition of waters of the Eastern Mediterranean Sea, *Journal of Geophysical Research* **101**(C3): 6441-6451.
- Gaye-Haake, B., Lahajnar, N., Emeis, K.-C., Unger, D., Rixen, T., Suthhof, A., Ramaswamy, V., Schult H., Paropkari, A. L., Guptha, M. V. S., Ittekkot, V., (2005), Stable nitrogen isotopic ratios of sinking particles and sediments from the northern Indian Ocean, *Marine Chemistry*, **96**: 243-255.
- Glockner, A.B., Jüngst A., Zumft, W.G., (1993), Copper-containing nitrite reductase from *Pseudomonas aureofaciens* is functional in a mutationally cytochrome cd1-free background (NirS-) of *Pseudomonas stutzeri*, *Archives of Microbiology*, **160**(1):18–26.
- Graedel, T. E. and P. J. Crutzen, (1993), *Atmospheric Change: An Earth System Perspective*, W.H. Freeman and Company, New York.

- Granger, J., Sigman, D. M., Needoba, J. A., Harrison, P. J., (2004), Coupled nitrogen and oxygen isotope fractionation of nitrate during assimilation by cultures of marine phytoplankton, *Limnology & Oceanography*, **49**(5): 1763-1773.
- Grasshoff, K., Ehrhardt, M., Kremling, K., (1999), *Methods of Seawater Analysis*, Verlag Chemie, Weinheim 632 pp.
- Gruber, N. and J. Sarmiento (1997), Global patterns of nitrogen fixation and denitrification, *Global Biogeochemical Cycles*, **11**: 235-266.
- Guerzoni S., Chester, R., Dulac, F., Herut, B., Loÿe-Pilot, M.D., Measures, C., Migon, C., Molinaroli, E., Moulin, C., Rossini, P., Saydam, C., Soudine, A., P., Ziveri, (1999), The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea, *Progress in Oceanography*, **44**(1-3): 147-190.
- Guieu, C., Chester, R., Nimmo, M., Martin, J. M., Guerzoni, S., Nicolas, E., Mateu, J., Keyse S., (1997), Atmospheric input of dissolved and particulate metals to the north western Mediterranean, *Deep Sea Research II*, **44**: 665–674.
- Hastings, M. G., Sigman, D. M., Lipschultz F., (2003), Isotopic evidence for source changes of nitrate in rain at Bermuda, *Journal of Geophysical Research*, **108** (D24): 4790, doi:10.1029/2003JD003789.
- Hastings, M.G., Steig, E.J., Sigman, D.M., (2004), Seasonal variations in N and O isotopes of nitrate in snow at Summit, Greenland: implications for the study of nitrate in snow and ice cores, *Journal of Geophysical Research*, **109**: D20306.
- Heaton, T.H.E., (1986), Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review, *Chemical Geology (Isotope Geoscience Section)*, **59**: 87-102.
- Heaton, T.H.E., (1987), $^{15}\text{N}/^{14}\text{N}$ ratios of nitrate and ammonium in rain at Pretoria, South Africa, *Atmospheric Environment*, **21**: 843- 852.
- Heaton, T.H.E., Spiro, B., Robertson S. M. C., (1997), Potential canopy influences on the isotopic composition of nitrogen and sulphur in atmospheric deposition, *Oecologia*, **109**: 600-607.
- Heaton, T.H.E., Wynn, P., Tye, A.M., (2004), Low $^{15}\text{N}/^{14}\text{N}$ ratios for nitrate in snow in the high Arctic (79 N), *Atmospheric Environment*, **38**: 5611–5621.
- Herut, B., Krom, M. D., Pan, G., Mortimer, R., (1999), Atmospheric input of nitrogen and phosphorus to the Southeast Mediterranean: Sources, fluxes, and possible impact, *Limnology & Oceanography*, **44**: 1683– 1692.

- Herut, B., Nimmo, M., Medway, A., Chester, R., Krom, M., (2001), Dry atmospheric inputs of trace metals at the Mediterranean coast of Israel (SE Mediterranean): sources and fluxes, *Atmospheric Environment*, **35**: 803–813.
- Herut, B., Collier, B., Krom, M.D., (2002), The role of dust in supplying nitrogen and phosphorus to the South East Mediterranean, *Limnology & Oceanography*, **47**: 870–878.
- Hicks, B.B., and P.S. Liss, (1976) Transfer of SO₂ and other reactive gases across the air-sea interface, *Tellus*, **28**: 348-354.
- Hoering, T.C., (1957), The isotopic composition of the ammonia and nitrate in rain, *Geochimica et Cosmochimica Acta*, **12**: 97–102.
- Hubner H., (1986), Isotope effects of nitrogen in the soil and biosphere, *In: Handbook of Environmental Isotope Geochemistry 2* (P. Fritz and J. Ch. Fontes eds), Terrestrial Environment, Elsevier, Amsterdam pp. 361-425.
- Ibello, V., Cantoni, C., Cozzi, S., Civitarese, G., (2010), First basin-wide experimental results on N₂ fixation in the open Mediterranean Sea, *Geophysical Research Letters*, **37**(3): 1-5.
- Ignatiades, L., Psarra, S., Zervakis, V., Pagou, K., Souvermezoglou, E., Assimakopoulou G., Gotsis-Skretas, O., (2002), Phytoplankton size-based dynamics in the Aegean Sea (Eastern Mediterranean), *Journal of Marine Systems*, **36**: 11–28.
- Ignatiades L., (2005), Scaling the trophic status of the Aegean Sea, eastern Mediterranean, *Journal of Sea Research*, **54**: 51– 57.
- IPCC (1995), IPCC Second Assessment in Climate Change 1995 (<http://www.ipcc.ch/pdf/climate-changes-1995/ipcc-2nd-assessment/2nd-assessment-en.pdf>).
- Johannsen, A., Dähnke K., Emeis K.-C., (2008), N-isotope composition of riverine nitrogen loads of four German rivers discharging into the North Sea, *Organic Geochemistry*, **39**: 1678-1689.
- Junk G. and H.J. Svec (1958), The absolute abundance of the nitrogen isotopes in the atmosphere and compressed gases from various sources, *Geochimica et Cosmochimica Acta*, 234–243.
- Kelly, S.D., C. Stein, T.D. Jickells (2005), Carbon and nitrogen isotopic analysis of atmospheric organic matter, *Atmospheric Environment*, **39**: 6007–6011.

- Kendall, C., (1998), Tracing nitrogen sources and cycling in catchments, *In: Isotope Tracers in Catchment Hydrology*, Kendall, C., McDonnell, J.J. (Eds.), Elsevier, Amsterdam, pp. 519–576.
- Klein, B., Roether, W., Manca, B., Bregant, D., Beitzel, V., Kovacevic, V., Luchetta, A., (1999), The large deep water transient in the Eastern Mediterranean, *Deep-Sea Research I*, **46**: 371–414.
- Knapp A. N., Sigman, D. M., Lipschultz, F., (2005), N isotopic composition of dissolved organic nitrogen and nitrate at the Bermuda Atlantic Time-series Study site, *Global Biogeochem. Cycles*, **19** (GB1018): doi:10.1029/2004GB002320.
- Knapp, A., DiFiore, P. J., Deutsch, C., Sigman, D. M., Lipschultz, F., (2008a), Nitrate isotopic composition between Bermuda and Puerto Rico: Implications for N₂ fixation in the Atlantic Ocean, *Global Biogeochemical Cycles*, **22**: (GB3014), 1-14.
- Knapp, A.N., Hastings, M.G., Sigman, D.M., Lipschultz, F., Galloway, J.M., (2008b), The flux and isotopic composition of reduced and total nitrogen in Bermuda rain, *Marine Chemistry, In Press, Corrected Proof* doi: 10.1016/j.marchem.2008.08.007.
- Koçak, M., Kubilay N., Mihalopoulos N., (2004), Ionic composition of the lower tropospheric aerosols in a NE Mediterranean site: Implication regarding sources and long-range transport, *Atmospheric Environment*, **38**: 2067-2077.
- Koçak, M., Kubilay, N., Herut, B., Nimmo, M., (2005), Dry atmospheric fluxes of trace metals (Al, Fe, Mn, Pb, Cd, Zn, Cu) over the Levantine Basin: a refined assessment, *Atmospheric Environment*, **29**: 2289–2300.
- Koçak, M., Mihalopoulos, N., Kubilay, N., (2007), Chemical composition of the fine and coarse fraction of aerosols in the northeastern Mediterranean, *Atmospheric Environment*, **41**(34): 7351-7368.
- Koppelman, R., Fabian, H., Weikert, H., (2003), Temporal variability of deep-sea zooplankton in the Arabian Sea, *Marine Biology*, **142**:959–970.
- Koppelman, R., Böttger-Schnack, R., Möbius, J., Weikert, H., (2009), Trophic relationships of zooplankton in the eastern Mediterranean Sea based on stable isotope measurements, *Journ. of Plankton Research*, **31**(6): 669-686.
- Koulouri E., Saarikoski, S., Theodosi, C., Markaki, Z., Gerasopoulos, E., Kouvarakis, G., Mäkelä, T., Hillamo, R., Mihalopoulos, N., (2008), Chemical composition and sources of fine and coarse aerosol particles in the Eastern Mediterranean, *Atmospheric Environment*, **42**: 6542–6550.

Kouvarakis, G., Mihalopoulos, N., A. Tselepidis, A., Stavrakakis, S., (2001), On the importance of atmospheric inputs of inorganic nitrogen species on the productivity of the eastern Mediterranean Sea, *Global Biogeochemical Cycles*, **15**(4): 805–817.

Kreitler, C.W., (1975), Determining the source of nitrate in ground water by nitrogen isotope studies, *Report of Investigations* (83), Bureau of Economic Geology, Univ. Texas, Austin, Texas.

Kress, N., and B. Herut (2001), Spatial and seasonal evolution of dissolved oxygen and nutrients in the Southern Levantine Basin (Eastern Mediterranean Sea): Chemical characterisation of the water masses and inferences on the N: P ratios, *Deep-Sea Research Part I*, **48**: 2347-2372.

Kress, N., Manca, B.B., Klein, B., Deponte, D., (2003), Continuing influence of the changed thermohaline circulation in the eastern Mediterranean on the distribution of dissolved oxygen and nutrients: physical and chemical characterization of the water masses, *Journal of Geophysical Research*, **108** (C9): 1–20.

Krom, M. D., Brenner, S., Kress, N., Gordon, L. I., (1991), Phosphorus limitation of Primary Productivity in the E.Mediterranean sea, *Limnology & Oceanography*, **36**: 424-432.

Krom, M. D., Groom, S., Zohary, T., (2003), The Eastern Mediterranean, *In: The Biogeochemistry of Marine Systems* (Black, K.D. and G.B., Shimmield, eds), Blackwell Publishing, Oxford, pp. 91-122.

Krom, M.D., Herut, B., Mantoura, R.F.C., (2004), Nutrient budget for the Eastern Mediterranean: Implications for P limitation, *Limnology & Oceanography*, **49**: 1582-1592.

Krom, M. D., Woodward, E. M. S., Herut, B., Kress, N., Carbo, P., Mantoura, R. F. C., Spyres, G., Thingstad, T. F., Wassmann, P., Wexels Riser, C., Kitidis, V., Law, C. S., Zodiatis, G., (2005), Nutrient cycling in the south east Levantine basin of the Eastern Mediterranean: results from a phosphorus starved system, *Deep Sea Research Part II*, **52**(22-23): 2879-2896.

Lascazatos, A., Roether, W., Nittis, K. Klein, B., (1999), Recent changes in deep water formation and spreading in the eastern Mediterranean Sea: a review, *Progress in Oceanography*, **44**: 5–36.

LeGrande, N. A., and G.A. Schmidt (2006), Global gridded data set of the oxygen isotopic composition in seawater, *Geophysical. Research Letters*, **33** (L12604).

- Lehmann, M. F., Reichert, P., Bernasconi, S. M., Barbieri, A., McKenzie, J. A., (2003), Modelling nitrogen and oxygen isotope fractionation during denitrification in a lacustrine redox-transition zone, *Geochimica et Cosmochimica Acta*, **67** (14): 2529-2542.
- Lehmann, M. F., Sigman, D. M., McCorkle, D. C., Brunelle, B. G., Hoffmann, S., Kienast, M., Cane, G., Clement, J., (2005), The origin of the deep Bering Sea nitrate deficit - Constraints from the nitrogen and oxygen isotopic composition of water-column nitrate and benthic nitrate fluxes, *Global Biogeochemical Cycles*, **19**: (GB4005), doi:10.1029/2005GB002508.
- Letolle R., (1980), Nitrogen-15 in the natural environment, *In Handbook of Environmental Isotope Geochemistry 1* (P. Fritz and J. Ch. Fontes eds), The Terrestrial Environment, Elsevier, Oxford, pp. 407-433.
- Li, Q. P., Hansell, D. A., Zhang, J.- Z., (2008), Underway monitoring of nanomolar nitrate plus nitrite and phosphate in oligotrophic seawater, *Limnology & Oceanography: Methods*, **6**: 319-326.
- Liu, K.-K. and I. R., Kaplan, (1989), The eastern tropical Pacific as a source of ¹⁵N-enriched nitrate in seawater off southern California, *Limnology Oceanography*, **34**: 820–830.
- Loo, B.W. and C. P., Cork, (1988), Development of high efficiency virtual impactor, *Aerosol Science & Technology*, **9**: 167-170.
- Lohrenz, S.E., Wiesenburg, D.A., DePalma, I.P., Johnson, K.S., Gustafson Jr., D.E., (1988), Interrelationships among primary production, chlorophyll, and environmental conditions in frontal regions of the western Mediterranean Sea, *Deep-Sea Research*, **35**: 793–810.
- Mahaffey, C., Michaels, A., Capone, D.G., (2005), The conundrum of marine nitrogen fixation, *American Journal of Science*, **305**: 546–595.
- Malanotte-Rizzoli, P., and A., Bergamasco, (1989), The circulation of the eastern Meditterean, Part 1, *Oceanologica Acta*, **12**: 335-351.
- Mariotti, A., Germon, C. Hubert, P. Kaiser, P. Letolle, R., Tardieux, A., P. Tardieux, P., (1981), Experimental determination of nitrogen kinetic isotope fractionation: some principles; illustration for the denitrification and nitrification processes, *Plant Soil*, **62**: 413-430.

- Mariotti, A., (1983), Atmospheric nitrogen as a reliable standard for natural ^{15}N abundance measurements, *Nature*, **303**: 685–687.
- Mariotti, A., (1984), Natural ^{15}N abundance measurements and atmospheric nitrogen standard calibration, *Nature*, **311**: 251-252.
- Markaki, Z., Oikonomou, K., Koçak, M., Kouvarakis, G., Chaniotaki, A., Kubilay, N., Mihalopoulos, N., (2003), Atmospheric deposition of inorganic phosphorus in the Levantine basin, eastern Mediterranean: Spatial and temporal variability and its role in seawater productivity, *Limnology & Oceanography*, **48**: 557–1568.
- Martin, J. H., Elbaz-Poulichet, F., Guieu, C., Loye-Pilot, M.D., Han, G., (1989), River versus atmospheric input of material to the Mediterranean: An overview, *Marine Chemistry*, **28**: 159–182.
- Mayer, B., Boyer, E. W., Goodale, C., Jaworski, C., van Breemen, N. A., Howarth, N., Seitzinger, R. W., Billen, S., Lajtha, G., Nosal, L. J., Paustian, K., (2002), Sources of nitrate in rivers draining sixteen watersheds in the northeastern US: Isotopic constraints, *Biogeochemistry*, **57**(1): 171-197.
- Meador, T. B., Aluwihare, L. I. Mahaffey, C., (2007), Isotopic heterogeneity and cycling of organic nitrogen in the oligotrophic ocean, *Limnology & Oceanography*, **52**(3): 934-947.
- Medar Group, (2002), MEDATLAS/2002 database. Mediterranean and Black Sea database of temperature salinity and bio-chemical parameters, IFREMER Edition (CD version).
- Metzger, S., Mihalopoulos, N., Lelieveld J., (2006), Importance of mineral cations and organics in gas- aerosol partitioning of reactive nitrogen compounds: case study based on MINOS results, *Atmospheric Chemistry & Physics*, **6**: 2549–2567.
- Migon, C., Journal, B., Nicolas, E., (1997), Measurement of trace metal wet, dry and total atmospheric fluxes over the Ligurian Sea, *Atmospheric Environment*, **40**: 889–896.
- Mihalopoulos N., Stephanou, E., Pilitsidis, S., Kanakidou, M., Bousquet P., (1997), Atmospheric aerosol composition above the Eastern Mediterranean region, *Tellus*, **49B**: 314-326.
- Miller, A.R., (1983), The Mediterranean Sea, A. Physical aspects, *In: Ecosystems of the World*, 26: Estuaries and Enclosed Seas, (Ketchum, B.H., ed.), Elsevier, Amsterdam, pp. 219–238.

- Mills, M. M., Ridame, C., Davey, M., La Roche, J., Geider, R. J., (2004), Iron and phosphorus co-limit nitrogen fixation in the eastern tropical North Atlantic, *Nature*, **429**: 292-294.
- Minagawa, M., and E. Wada (1986), Nitrogen isotope ratios of red tide organisms in the East China Sea: A characterization of biological nitrogen fixation, *Marine Chemistry*, **19**: 245-249.
- Montoya, J. P., Carpenter, E. J., Capone, D.G., (2002), Nitrogen fixation and nitrogen isotope abundance in zooplankton of the oligotrophic North Atlantic, *Limnology & Oceanography*, **47**: 1617– 1628.
- Moore, H., (1977), The isotopic composition of ammonia, nitrogen dioxide and nitrate in the atmosphere, *Atmospheric Environment*, **11**: 1239–1243.
- Moretti, M., Sansone, E., Spezie, G., De Maio, A., (1993), Results of investigation in the Sicily Channel (1986-1990), *Deep-Sea Research*, **40**: 1181-1192.
- Mulvaney, R. L., Ashraf, M., Azam, F., Brooks, P. D., Herman, D. J., (1994), Evaluation of methods for nitrogen-15 analysis of inorganic nitrogen in soil extracts: I. Steam distillation methods *Communications in Soil Science & Plant Analysis*, **25**: 2187-2200.
- Owens, N. J. P., Galloway, J. N., Duce, R. A., (1992), Episodic atmospheric nitrogen deposition to oligotrophic oceans, *Nature*, **357**: 397–399.
- Pan, G., Krom, M. D., Herut, B., (2002), Adsorption-desorption of phosphate on airborne dust and river borne particulates in East Mediterranean seawater, *Environmental Science & Technology*, **36**: 3519– 3524.
- Pantoja, S., Repeta, D.J., Sachs, J. Sigman, D., (2002), Stable isotope constraints on the nitrogen cycle of the Mediterranean Sea water column, *Deep-Sea Research Part I*, **49**: 1609-1621.
- Peterson B.J. and B. Fry, (1987), Stable isotopes in ecosystem studies, *Annual Review of Ecology & Systematics*, **18**: 293-320.
- Pierre, C. (1999), The oxygen and carbon isotope distribution in the Mediterranean water masses, *Marine Geology*, **153**: 41-55.
- Pitta, P., Giannakourou, A., Christaki, U., (2001), Planktonic ciliates in the oligotrophic Mediterranean Sea: longitudinal trends of standing stocks, distributions and analysis of food vacuole contents, *Aquatic Microbial Ecology*, **24**: 297–311.

- Psarra, S., Tselepidis, A., Ignatiades, L., (2000), Primary productivity in the oligotrophic Cretan Sea (NE Mediterranean): Seasonal and interannual variability, *Progress in Oceanography*, **46**: 187–204.
- Prieur, L., and A., Sournia, (1994), ‘‘Almofront-1’’ (April–May 1991): an interdisciplinary study of the Almeria-Oran geostrophic front, SW Mediterranean Sea, *Journal of Marine Systems*, **5**: 187–203.
- Preunkert, S., Wagenbach, D., Legrand, M., (2003), A seasonally resolved alpine ice core record of nitrate: Comparison with anthropogenic inventories and estimation of preindustrial emissions of NO in Europe, *Journal of Geophysical Research*, **108**(D21): 4681, doi:10.1029/2003JD003475.
- Putaud P., Baltensperger, U., Facchini, M.-C., Fuzzi, S., Gehrig, R., Hansson, H.-C., Harrison, R. M., Jones, A. M., Laj, P., Maenhaut, W., Mihalopoulos, N., Palmgren, F., Querol, X., Raes, F., Rodriguez, S., Brink, H. T., Tunved, P., van Dingenen, R., Wehner, B., Weingartner, E., Wiedensohler A., W ahlin, P. (2004), A European aerosol phenomenology—2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe, *Atmospheric Environment*, **38**: 2579–2595.
- Querol, X., Alastuey, A., Rodriguez, S., Viana, M. M., Artinano, B., Salvador, P., Mantilla, E., Garcia do Santos, S., Patier, R. F., de La Rosa, J., Sanchez de la Campa, A., Menendez, M., Gill, J. J., (2004), Levels of particulate matter in rural, urban and industrial sites in Spain, *Science of the Total Environment*, **334–335**: 359–376.
- Redfield, A.C., (1958), The biological control of chemical factors in the environment, *American Scientist*, **46**: 205–221.
- Rees A. P., Law, C. S., Woodward E. M. S., (2006), High rates of nitrogen fixation during an in-situ phosphate release experiment in the Eastern Mediterranean Sea, *Geophysical Research Letters*, **33**(10607): 1–4.
- Ribera d’Alcala, M. R., Civitarese, G., Conversano, F., Lavezza, R., (2003), Nutrient ratios and fluxes hint at overlooked processes in the Mediterranean Sea, *Journal of Geophysical Research*, **108**: doi:10.1029/2002JC001650.
- Ridame, C., Guieu, C., Loye-Pilot, M., (1999), Trend in total atmospheric fluxes of aluminum, iron and trace metals in the northwestern Mediterranean over the past decade (1985–1997), *Journal of Geophysical Research*, **104**: 30127–30138.

- Ridame, C., Moutin, T., Guieu, C., (2003), Does the adsorption process of phosphate onto Saharan dust explain the unusual N/P ratio in the Mediterranean sea ? *Oceanologica Acta* **26**: 629-634.
- Rixen, T., Ittekkot, V., Haake-Gaye, B., Schäfer, P., (2000), The influence of the SW monsoon on the deep-sea organic carbon cycle in the Holocene, *Deep Sea Research Part II*, **47** (14): 2629-2651.
- Roether, W., and R., Schlitzer, (1991), Eastern Mediterranean deep water renewal on the basis of chlorofluoromethanes and tritium, *Dynamics of Atmospheres and Oceans*, **15**: 333–354.
- Roether, W., Manca, B. B., Klein, B., Bregant, D., Georgopoulos, D., Beitzel, V., Kovacevic, V., Luchetta, A., (1996), Recent changes in Eastern Mediterranean deep waters, *Science*, **271**: 333-335.
- Rubino, A., Budillon, G., Pierini, S., Spezie, G., (2003), A model for the spreading and sinking of the Deep Ice Shelf Water in the Ross Sea, *Antarctic Science*, **15**: 25–30.
- Russell, K. M., Galloway, J. N., Macko, S. A., Moody, J. L., Scudlar, J. R., (1998), Sources of nitrogen in wet deposition to the Chesapeake Bay region, *Atmospheric Environment*, **32**: 2453-2465.
- Sachs, J.P., and D.J., Repeta, (1999), Oligotrophy and nitrogen fixation during Eastern Mediterranean sapropel events, *Science*, **286**: 2485–2488.
- Sarmiento, J., Herbert, L. T., Toggweiler, R., (1988), Mediterranean nutrient balance and episodes of anoxia, *Global Biogeochemical Cycles*, **2**: 427–444.
- Schlarbaum, T., Daehnke, K., Emeis, K.-C., (2010), Dissolved organic nitrogen in the Elbe River and estuary: Results of nitrogen isotope investigations, *Marine Chemistry*.
- Schlitzer, R., Roether, W., Oster, H., Junghans, H.-G., Johnnsen, H., Michelato, A., (1991), Chlorofluoromethane and oxygen in the eastern Mediterranean, *Deep-Sea Research*, **38**: 1531–1551
- Schlitzer, R., (2004), Ocean Data View. AWI-Bremerhaven, Bremerhaven. <http://awi-bremerhaven.de/GEO/ODV>
- Schlitzer, R., (2008), Ocean Data View, <http://odv.awi.de>.

Seinfeld, J., and S. Pandis (1997), *Atmospheric Chemistry and Physics: From Air Pollution to Climate Changes*, John Wiley, Hoboken, N. J., p. 1326.

Sellegrì, K., Gourdeau, J., Putaud, J. P., Despiiau, S., (2001), Chemical composition of marine aerosol in a Mediterranean coastal zone during the FETCH experiment, *Journal of Geophysical Research*, **106**: 12023–12037.

Sigman, D. M., Altabet, M. A., Michener, R., McCorkle, D.C., Fry, B., Holmes, R. M., (1997), Natural abundance-level measurement of the nitrogen isotopic composition of oceanic nitrate: an adaptation of the ammonia diffusion method, *Marine Chemistry*, **57**(3-4): 227-242.

Sigman, D.M., Altabet, M. A., McCorkle, D. C., Francois, R., Fischer, G., (2000), The $\delta^{15}\text{N}$ of nitrate in the Southern Ocean: nitrogen cycling and circulation in the ocean interior, *Journal of Geophysical Research*, **105**: 19599–19614.

Sigman, D. M., Casciotti, K. L., Andreani, M., Barford, C., Galanter, M., Böhlke, J. K., (2001), A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater, *Analytical Chemistry*, **73** (17): 4145-4153.

Sigman, D. M., Granger, G., DiFiore, P. J., Lehmann, M. M., Ho, R., Cane, J., van Geen, A., (2005), Coupled nitrogen and oxygen isotope measurements of nitrate along the eastern North Pacific margin, *Global Biogeochemical Cycles*, **19**(GB4022): 14, doi:10.1029/2005GB002458.

Sigman, D. M., DiFiore P. J., Hain, M.P., Deutsch C., Wank, Y., Karl, D.M., Knapp, A.N., Lehmann, N.F., Pantoja, S., (2009), The dual isotopes of deep nitrate as a constraint on the cycle and budget of oceanic fixed nitrogen, *Deep-Sea Research Part I*, **56** (9): 1419-1439.

Slawk, G., and P. Raimbault (1995), Simple procedure for simultaneous recovery of dissolved inorganic and organic nitrogen in ^{15}N -tracer experiments and improving the isotopic mass balance, *Marine Ecology Progress Series*, **124**: 289-299.

Spokes, L.J., Yeatman, S.G., Cornell, S.E., Jickells, T.D., (2000), Nitrogen deposition to the eastern Atlantic Ocean. The importance of south-easterly flow, *Tellus*, **52B**: 37-49.

Sprent, J.I. ,(1987), *The Ecology of the Nitrogen Cycle*, Cambridge University Press, New York.

Stevenson, F.J. (1972), *In: The encyclopedia of geochemistry and environmental sciences*, (Fairbridge, R.W., ed), Van Nostrand, New York.

Struck, U., Emeis, K.-C., Rau, G.H., Voss, M., Krom, M., (2001), Biological productivity during sapropel S5 formation in the eastern Mediterranean Sea - Evidence from stable isotopes of nitrogen and carbon, *Geochimica et Cosmochimica Acta*, **65**(19): 3241-3258.

Stumm W. and J.J., Morgan, (1981), *Aquatic Chemistry: An introduction emphasizing chemical equilibria in natural waters*, Wiley-Interscience, N.Y.

Thingstad, T. F., and F. Rassoulzadegan (1999), Conceptual models for the biogeochemical role of the photic zone microbial food web, with particular reference to the Mediterranean Sea, *Progress in Oceanography*, **44**: 271–286.

Thingstad, T.F., Krom, M.D., Mantoura, R.F.C., Flaten, G.A.F., Groom, S., Herut, B., Kress, N., Law, C.S., Pasternak, A., Pitta, P., Psarra, S., Rassoulzadegan, F., Tanaka, T., Tselepidis, A., Wassmann, P., Woodward, E.M.S., Wexels Riser, C., Zodiatis, G., Zohary, T., (2005), Nature of Phosphorus limitation in the ultraoligotrophic Eastern Mediterranean, *Science*, **309**: 1068-1071.

van Wambeke F., Christaki U., Giannakourou A., Moutin T., Souvemerzoglou K., (2002), Longitudinal and Vertical Trends of Bacterial Limitation by Phosphorus and Carbon in the Mediterranean Sea, *Microbial Ecology*, **43**:119-133.

Velaoras, D. and A. Lascaratos, (2005), Deep water mass characteristics and interannual variability in the North and Central Aegean Sea, *Journal of Marine Systems*, **53**: 59-85.

Vitousek, P.M., Aber, J., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., Tilman. G.D. (1997), Human Alteration of the Global Nitrogen Cycle: Causes and Consequences, *Issues in Ecology*, **1**: 1-15.

Vollenweider, R. A., Rinaldi, A., Viviani, R., Todini, E., (1996), Assessment of the state of eutrophication in the Mediterranean Sea, *In: Mediterranean Action Plan Technical Report*, Mediterranean Action Plan, Athens, pp.1-449.

Voss, M., Croot, P., Lochte, K., Mills, M. L., Peeken I., (2004), Patterns of nitrogen fixation along 10°N in the tropical Atlantic, *Geophysical Research Letters*, **31**(L23S09): doi:10.1029/2004GL020127.

Wankel, S. D., Kendall C., Francis C. A., Paytan A., (2006), Nitrogen sources and cycling in the San Francisco Bay Estuary: A nitrate dual isotopic composition approach, *Limnology & Oceanography*, **51** (4): 1654-1664

Wankel S.D., Chen Y., Kendall C., Post A.F., Paytan A., (2009), Sources of aerosol nitrate to the Gulf of Aqaba: Evidence from $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate and trace metal chemistry, *Marine Chemistry*, *In press*, *Corrected Prof*, doi:10.1016/j.marchem.2009.01.013

Warnken, C. (2003), Biogeochemie von Schwebstoffen, Sinkstoffen und Sedimenten im Ierapetra-Tief (östliches Mittelmeer), M.Sc. Thesis, University of Hamburg, Hamburg, pp 80.

Wüst, G., (1961), On the vertical circulation of the Mediterranean Sea, *Jouranl of Geophysical Research*, **66**: 3261-3271.

Yeatman, S.G., Spokes L. J., Jickells T. D., (2001), Comparisons of coarse-mode aerosol nitrate and ammonium at two polluted coastal sites, *Atmospheric Environment*, **35**, 1321-1335.

Yool, A., Martin, A. P., Fernandez, C., Clark, D. R., (2007), The significance of nitrification for oceanic new production, *Nature*, **447**: 999-1002.

York, J. K., Tamasky, J., Valiela, I., Repeta, D. J., (2007), Stable isotopic detection of ammonium and nitrate assimilation by phytoplankton in the Waquoit Bay estuarine system, *Limnology & Oceanography*, **52**: 144–155.

Zervakis, V., Georgopoulos, D., Drakopoulos, P.G., (2000), The role of the North Aegean in triggering the recent Eastern Mediterranean climatic changes, *Journal of Geophysical Research*, **105**: 26103-26116.

Zohary, T. and R. D., Robarts, (1998), Experimental study of microbial P limitation in the eastern Mediterranean, *Limnology & Oceanography*, **43**(3): 387-395.

Zohary, T., (2005), Nature of Phosphorus limitation in the ultraoligotrophic Eastern Mediterranean, *Science*, **309**: 1068-1071.

Zumft, W.G. and J. M., Vega, (1979), Reduction of nitrate to nitrous oxide by a cytoplasmic membrane fraction from the marine denitrifier *Pseudomonas perfectomarinus*, *Biochimica et Biophysica Acta*, **548**: 484-499.

Internet Sources

EMEP; <http://www.emep.int/index.html>

Figure Captions

Fig. 1.1. Generalized diagram of a biogeochemical cycle within ecosystems

Fig. 1.2. Biochemical cycle of nitrogen

Fig. 1.3. Depiction of NO_x cycling pathways leading to the formation of aerosol HNO_3 (or NO_3^-). Solid lines, represent reactions that occur during day time, while dashed lines correspond to the reactions performed at night (after Wankel et al., 2009).

Fig. 2.1. Location of the sampling sites:a) Heraklion station b) Finokalia station

Fig. 2.2. Sampling stations as conducted during the R/V Meteor cruise 71-3 in the EMS (January-February/2007)

Fig. 2.3. Biogeochemical nitrogen cycle sustained by prokaryotes. The Roman numerals give the formal oxidation state of the principal nitrogen species of the cycle. The equation beneath the scheme presents the denitrification pathway that is mediated.

Fig. 3.1.a. Monthly average nitrate levels in μM collected at two locations on Crete Island (Heraklion and Finokalia)

Fig. 3.1.b. The $\delta^{15}\text{N}$ in wet deposition samples collected at two locations on Crete Island (Heraklion and Finokalia)

Fig. 3.2. Temporal variation (in Julian date) of nitrate $\delta^{15}\text{N}$ values and rainfall height (h) during the period April 2006-September 2007, at Finokalia.

Fig. 3.3. Monthly nitrate $\delta^{15}\text{N}$ values in both bulk and wet deposition samples on Crete. The data from the two sampling locations (Heraklion and Finokalia) have been combined.

Fig. 4.1. Profiles of fluorescence (a), nitrate (b) and phosphate (c) concentrations in the upper 400 m at 2 stations representative of NIS (H07) and pelagic stations (Her03) show stratification between the 80 and 230 m water depth and indicate the biologically active mixed layer. An ongoing phytoplankton bloom in the northern Ionian Sea (at station H07) is sustained by nitrate and phosphate provided from

ongoing regional thermocline deepening, whereas station Her03 illustrates the mature and thick mixed layer with very low nutrient concentrations at pelagic sites.

Fig. 4.2. Concentrations of nitrate (a), TRN (b) and particulate N in total suspended solids (c) plotted against water depth for all stations.

Fig. 4.3. Isotopic composition $\delta^{15}\text{N-NO}_3$ (a), $\delta^{18}\text{O-NO}_3$ (b), $\delta^{15}\text{N-TRN}$ (c), and δ^{15} of suspended PN (d) plotted against water depth for all stations.

Fig. 4.4. Composite seasonal diagram of sinking PN fluxes (squares) and δ^{15} of sinking PN (circles) and their standard deviations at 2600 m water depth at Ierapetra station. Fluxes (squares, black line and s.d. in red) and $\delta^{15}\text{SPN}$ (circle, grey line, s.d. in blue) for three deployment periods (MID-1: 01/30/1999 to 04/13/1999), MID-2: 11/05/2001 to 04/01/2002 and MID-3: 01/30/2007 to 09/05/2007) at 2700 m water depth have been assembled in a surrogate annual cycle.

Fig. 4.5. Depth plot of $\Delta(15,18)$ of nitrate for different station sets in the upper 500 m of the water column.

Fig. 4.6. Conceptual diagram of the processes that determine the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate in the surface and intermediate water masses of the eastern Mediterranean Sea; this diagram also is a schematic illustration of the model used to calculate $\Delta(15,18)$ of nitrate under assumptions of different sources as explained in the text.

Table Captions

Table 1. α_i values for different compounds

Table 2. Median concentrations of nitrate and phosphate in water masses below 300m depth (Schlitzer, 2004).

Table 3. Sampling protocol for the wet and dry deposition during the period 2006-2007.

Table 4. Comparison of average $\delta^{15}\text{N-NO}_3^-$ values in rain on Crete with those reported in the literature for Europe and South Africa (Freyer,1991) and Bermuda (Hastings et al., 2003).

Table 5. Nitrate $\delta^{15}\text{N}$ mean values (including standard deviation) in dry deposition and aerosol samples collected in Crete and comparison with the results reported in the literature (Germany; Freyer 1991).

Table 6. $\delta^{15}\text{N}$ of external inputs to the EMS based on the budget of Krom et al. (2004) and the $\delta^{15}\text{N}$ of the atmospheric input (thesis results) and surface water in the Western Mediterranean Sea (Pantoja et al., 2002). For lack of data, the $\delta^{15}\text{N}$ of nitrate from rivers and inflow from the Black Sea vary from 5‰ (case a) to 8‰ (case b). In either case, the $\delta^{15}\text{N}$ of external nitrate sources is more depleted than nitrate in the deep-water nitrate pool ($2.5\pm 0.1\%$; Pantoja et al., 2002).

Table 7. Average concentrations and isotopic composition in water samples from above, in and below the nitracline during the Meteor expedition 71-3 in the EMS: Northern Ionian Sea (NIS; 6 stations, Table 7.1.), pelagic stations (10 stations, Table 7.2.) and northern Aegean Sea (1 station Table 7.3.). Tables C.1., C.2., and C.3. in the data appendix provide analytically all the data used in Chapter 4.

Table 8. Estimation of reactive N-inventories of the EMS in different depth intervals and mass-weighted $\delta^{15}\text{N}$ of different components (nitrate, particulate nitrogen PN and total reduced nitrogen, TRN; Table C.1. data appendix). The last column is the integrated and mass-weighted $\delta^{15}\text{N}$ over all components of reactive N for each interval, the last line are the integrated inventories and $\delta^{15}\text{N}$ of the entire water column.

List of abbreviations

ASW = Atlantic Surface Water

DIN = Dissolved Inorganic Nitrogen

DON = Dissolved Organic Nitrogen

δ = isotope ratio

ϵ = isotope fractionation factor

EMDW = Eastern Mediterranean Deep Water

EMS = Eastern Mediterranean Sea

LDW = Levantine Deep Water

LIW = Levantine Intermediate Water

MAW = Modified Atlantic Water

MID = Mediterranean Ierapetra Deep

MUC = MultiCore

NIS = Northern Ionian Sea

PN = Particulate Nitrogen

SPN = Sinking Particulate Nitrogen

TDN = Total Dissolved Nitrogen

TRN = Total dissolved Reduced Nitrogen

TOC = Total Organic Carbon

Data Appendix

The basic data used in the Chapters of this thesis, are listed in the following appendix.

A. Data from the Finokalia atmospheric station (25°40'E, 35°20'N)

Table A.1. Sampling dates, nitrate concentrations, fluxes, and nitrogen isotope values from dry deposition samples collected in the atmospheric station of Finokalia (Crete). The duration of sampling lasted over than a year (April 2006- September 2007). The collection of the samples performed on a flat surface covered by glass beads, situated 3 m above the ground.

Months	Sampling period		Code	Nitrate ($\mu\text{mol L}^{-1}$)	Nitrate fluxes ($\text{mgr m}^{-2} \text{day}^{-1}$)	$\delta^{15}\text{N}$ - nitrate (‰)
April 2006	14.04.2006	05.05.2006	D-46	104.02	11.20	-3.63
May	05.05.2006	15.05.2006	D-47	225.35	20.97	-3.36
May	15.05.2006	29.05.2006	D-48	233.98	16.66	-5.08
June	29.05.2006	13.06.2006	D-49	211.59	14.38	-4.13
June	16.06.2006	26.06.2006	D-51	350.86	23.32	-4.17
July	26.06.2006	10.07.2006	D-52	268.69	19.14	-3.88
July	10.07.2006	28.07.2006	D-53	343.31	19.44	-2.55
August	28.07.2006	23.08.2006	D-54	472.38	18.12	-2.24
August	23.08.2006	04.09.2006	D-55	215.79	18.53	-2.19
September	04.09.2006	22.09.2006	D-56	572.77	31.38	-1.66
September	22.09.2006	02.10.2006	D-57	400.00	41.21	-1.94
October	13.10.2006	20.10.2006	D-59	20.66	6.87	-2.87
October	20.10.2006	02.11.2006	D-60	10.50	1.88	-3.27
November	02.11.2006	06.11.2006	D-61	44.05	25.38	-1.65
November	06.11.2006	17.11.2006	D-62	84.94	10.69	-2.36
November	17.11.2006	27.11.2006	D-63	79.98	14.36	-3.21
December	27.11.2006	12.12.2006	D-64	240.06	18.44	-2.62
December	12.12.2006	21.12.2006	D-65	88.52	8.72	-2.19
December	21.12.2006	09.01.2007	D-66	230.92	12.12	-1.29
January 2007	09.01.2007	19.01.2007	D-67	N.A	N.A	-2.10
January	19.01.2007	05.02.2007	D-68	147.89	18.51	-2.12
February	05.02.2007	12.02.2007	D-69	39.47	12.87	-4.04
February	12.02.2007	27.02.2007	D-70	91.44	14.18	-4.63
March	27.02.2007	19.03.2007	D-72	242.19	28.17	-4.46
March	19.03.2007	30.03.2007	D-73	269.18	44.46	-2.71
April	30.03.2007	18.04.2007	D-74	138.51	7.27	-4.70
April	18.04.2007	30.04.2007	D-75	422.85	67.15	-5.43
May	30.04.2007	21.05.2007	D-76	78.44	3.48	-5.56
May	21.05.2007	29.05.2007	D-77	135.80	26.33	-4.94
June	29.05.2007	13.06.2007	D-78	261.67	40.97	-3.18
June	13.06.2007	29.06.2007	D-79	384.74	25.31	-2.96
July	29.06.2007	19.07.2007	D-80	300.77	15.00	-3.70
July	19.07.2007	31.07.2007	D-81	886.79	74.50	-2.73
August	31.07.2007	30.08.2007	D-82	765.97	26.87	-3.07
September	30.08.2007	13.09.2007	D-83	300.18	18.29	-1.51

Table A.2. Sampling dates, nitrate concentrations, fluxes, and oxygen isotope values from dry deposition samples collected in the atmospheric station of Finokalia.

Months	Sampling period		Code	Nitrate ($\mu\text{mol L}^{-1}$)	Nitrate fluxes ($\text{mgr m}^{-2} \text{day}^{-1}$)	$\delta^{18}\text{O}$ - nitrate (‰)
April 2006	14.04.2006	05.05.2006	D-46	104.02	11.20	69.92
May	05.05.2006	15.05.2006	D-47	225.35	20.97	66.06
May	15.05.2006	29.05.2006	D-48	233.98	16.66	68.31
June	29.05.2006	13.06.2006	D-49	211.59	14.38	68.77
June	16.06.2006	26.06.2006	D-51	350.86	23.32	66.96
July	26.06.2006	10.07.2006	D-52	268.69	19.14	64.82
July	10.07.2006	28.07.2006	D-53	343.31	19.44	64.84
August	28.07.2006	23.08.2006	D-54	472.38	18.12	67.64
August	23.08.2006	04.09.2006	D-55	215.79	18.53	67.05
September	04.09.2006	22.09.2006	D-56	572.77	31.38	57.02
September	22.09.2006	02.10.2006	D-57	400.00	41.21	
October	13.10.2006	20.10.2006	D-59	20.66	6.87	
October	20.10.2006	02.11.2006	D-60	10.50	1.88	
November	02.11.2006	06.11.2006	D-61	44.05	25.38	
November	06.11.2006	17.11.2006	D-62	84.94	10.69	
November	17.11.2006	27.11.2006	D-63	79.98	14.36	
December	27.11.2006	12.12.2006	D-64	240.06	18.44	
December	12.12.2006	21.12.2006	D-65	88.52	8.72	
December	21.12.2006	09.01.2007	D-66	230.92	12.12	
January 2007	09.01.2007	19.01.2007	D-67	n.a	n.a	
January	19.01.2007	05.02.2007	D-68	147.89	18.51	
February	05.02.2007	12.02.2007	D-69	39.47	12.87	
February	12.02.2007	27.02.2007	D-70	91.44	14.18	
March	27.02.2007	19.03.2007	D-72	242.19	28.17	
March	19.03.2007	30.03.2007	D-73	269.18	44.46	73.98
April	30.03.2007	18.04.2007	D-74	138.51	7.27	73.21
April	18.04.2007	30.04.2007	D-75	422.85	67.15	
May	30.04.2007	21.05.2007	D-76	78.44	3.48	
May	21.05.2007	29.05.2007	D-77	135.80	26.33	69.19
June	29.05.2007	13.06.2007	D-78	261.67	40.97	
June	13.06.2007	29.06.2007	D-79	384.74	25.31	70.47
July	29.06.2007	19.07.2007	D-80	300.77	15.00	
July	19.07.2007	31.07.2007	D-81	886.79	74.50	
August	31.07.2007	30.08.2007	D-82	765.97	26.87	
September	30.08.2007	13.09.2007	D-83	300.18	18.29	

Table A.3. Sampling dates, nitrate concentrations, fluxes, and nitrogen isotope values from aerosols collected from June 2007 to July 2007, in the atmospheric station of Finokalia. The samples were collected in Teflon filters (Millipore, Fluoropore membrane filters) using a virtual impactor, modified to collect particles with diameter less than 1.3 μm (PM1.3) and particles with diameters between 1.3 and 10 μm (PM1.3–10).

Months	Sampling Dates		Code	Nitrate ($\mu\text{mol L}^{-1}$)	Nitrate fluxes ($\text{mgr cm}^{-3} \text{ day}^{-1}$)	$\delta^{15}\text{N}$ -nitrate (‰)
June 2007	22.06.2007	23.06.2007	C-03	6.03	11.76	-2.68
June	23.06.2007	24.06.2007	C-04	12.60	25.10	-2.36
June	29.06.2007	30.06.2007	C-10	30.81	23.06	-2.03
July	02.07.2007	03.07.2007	C-13	32.65	22.77	-5.89
July	10.07.2007	11.07.2007	C-21	12.84	13.15	-1.63
July	14.07.2007	15.07.2007	C-25	36.23	25.9	-5.84

Table A.4. Sampling dates, nitrate concentrations, fluxes, precipitation height (H) and nitrogen isotope values from rainwater single events collected in the atmospheric station of Finokalia, from April 2006 to September 2007. The collection of the rain samples was done in PolyTetraFluoroEthylene (PTFE) vials.

Months	Sampling period		Code	Height (mm)	Nitrate ($\mu\text{mol L}^{-1}$)	Nitrate fluxes ($\text{mgr m}^{-2} \text{ event}^{-1}$)	$\delta^{15}\text{N}$ -nitrate (‰)
April 2006	14.04.2006	05.05.2006	D-45	24.66	16.21	24.79	-5.63
June	10.06.2006	16.06.2006	D-50	1.25	112.09	8.69	-5.38
October	13.10.2006	20.10.2006	R-35-36	41.01	14.11	35.88	-4.56
October	20.10.2006	02.11.2006	R-037	37.88	23.32	54.78	-4.15
November	02.11.2006	06.11.2006	R-038	5.63	51.00	17.80	-2.44
November	06.11.2006	13.11.2006	R-039	1.43	156.73	13.89	-1.49
November	13.11.2006	17.11.2006	R-040	3.84	43.26	10.31	-3.26
November	17.11.2006	27.11.2006	R-041	1.79	94.75	10.50	-2.44
December	28.11.2006	08.12.2006	R-042	1.25	132.78	10.30	-2.74
February 2007	05.02.2007	12.02.2007	R-043	12.69	28.83	62.60	-5.12
February	12.02.2007	27.02.2007	R-044	23.05	67.86	154.12	-5.07
March	27.02.2007	07.03.2007	R-045+ R-046	35.02	24.08	6.67	-3.70
March	07.03.2007	17.04.2007	R-047+ R-048	36.63	90.62	65.26	-3.80
May	21.05.2007	29.05.2007	R-049	4.47	57.97	37.25	-3.93

**B. Data from Heraklion station situated in the University Campus in Crete
(25°4'E, 35°18'N)**

Table B.1. Sampling dates, nitrate concentration and fluxes, precipitation height (H) and nitrogen isotope values from rainwater single events collected in the atmospheric station of Heraklion (University Campus), from April 2006 to September 2007.

Months	Sampling period		Code	H (mm)	Nitrate ($\mu\text{mol L}^{-1}$)	Nitrate fluxes (mgr m^{-2} event ⁻¹)	$\delta^{15}\text{N}$ - nitrate (‰)
September 2006	21.09.2006	25.09.2006	RH 55	5.05	39.72	12.45	-5.07
September	25.09.2006	29.09.2006	RH 56	0.57	43.46	1.52	-4.49
October	06.10.2006	09.10.2006	RH 57	2.05	49.15	6.23	-2.90
October	09.10.2006	11.10.2006	RH 58	18.53	18.67	21.45	1.86
October	11.10.2006	13.10.2006	RH 59	17.57	30.76	33.51	-2.98
October	13.10.2006	16.10.2006	RH 60	10.23	42.99	27.26	-5.73
October	16.10.2006	17.10.2006	RH 61	14.44	22.43	20.09	-4.44
October	17.10.2006	18.10.2006	RH 62	46.09	7.92	22.63	-2.77
October	18.10.2006	20.10.2006	RH 63	12.03	26.58	19.83	-5.61
October	31.10.2006	01.11.2006	RH 64	31.29	5.64	10.95	-6.42
November	02.11.2006	06.11.2006	RH 65	19.98	56.19	69.60	0.97
November	07.11.2006	13.11.2006	RH 66	54.88	19.15	65.14	-2.82
November	24.11.2006	28.11.2006	RH 68	8.42	18.74	9.79	-5.41
December	04.12.2006	06.12.2006	RH 69	3.37	31.89	6.66	-4.40
December	22.12.2006	08.01.2007	RH 70	22.38	42.93	59.58	-2.00
January 2007	16.01.2007	05.02.2007	RH 73	27.44	22.02	37.47	-2.74
February	06.02.2007	12.02.2007	RH 74	10.35	26.32	16.89	-4.63
February	15.02.2007	20.02.2007	RH 75	26.96	12.34	20.63	-2.58
February	21.02.2007	26.02.2007	RH 76	44.05	62.40	170.41	-4.91
March	27.02.2007	15.03.2007	RH 77	21.18	63.58	83.49	-5.14
March	21.03.2007	23.03.2007	RH 79	12.03	26.67	19.90	-2.74

C. Data from the METEOR Cruise (M71-3) conducted in the Eastern Mediterranean Sea

Table C.1. Sampling locations, physicochemical parameters and oxygen concentrations from the METEOR cruise (M71-3) conducted in the Eastern Mediterranean Sea during January-February/2007. Samples were taken in several depths of the water column and from the sediment-water interface deriving from multicorer deployments (MUC).

Stations	Lon (°E)	Lat (°N)	Bot. Depth (m)	Depth (m)	Temperature (°C)	Salinity (psu)	Oxygen ($\mu\text{mol L}^{-1}$)
H07	17.75	39.17	1866	7.22	14.51	38.48	5.43
H07	17.75	39.17	1866	22.09	14.52	38.48	5.47
H07	17.75	39.17	1866	51.97	14.51	38.49	5.44
H07	17.75	39.17	1866	52.07	14.51	38.49	5.17
H07	17.75	39.17	1866	102.47	14.43	38.75	5.44
H07	17.75	39.17	1866	152.58	14.45	38.84	4.59
H07	17.75	39.17	1866	202.07	14.37	38.87	4.46
H07	17.75	39.17	1866	298.80	14.10	38.82	4.46
H07	17.75	39.17	1866	502.03	13.89	38.79	4.47
H07	17.75	39.17	1866	992.57	13.74	38.75	4.40
H07	17.75	39.17	1866	1482.03	13.75	38.76	4.61
H07	17.75	39.17	1866	1634.50	13.76	38.76	4.64
H07_MUC	17.75	39.17	1866	1866			
H12	19.75	38.83	1450	5.70	16.00	38.22	5.31
H12	19.75	38.83	1450	21.28	16.01	38.23	5.28
H12	19.75	38.83	1450	50.85	15.72	38.39	4.81
H12	19.75	38.83	1450	75.64	15.57	38.43	5.30
H12	19.75	38.83	1450	75.66	15.56	38.44	5.29
H12	19.75	38.83	1450	121.25	14.69	38.76	4.66
H12	19.75	38.83	1450	201.17	14.48	38.86	4.47
H12	19.75	38.83	1450	201.29	14.48	38.86	4.49
H12	19.75	38.83	1450	499.68	13.94	38.80	4.38
H12	19.75	38.83	1450	998.13	13.74	38.75	4.24
H12	19.75	38.83	1450	1443.76	13.71	38.76	4.59
H12_MUC	19.75	38.83	1450	1450			
H10	19.00	39.92	1008	6.98	15.11	38.40	5.35
H10	19.00	39.92	1008	21.67	14.83	38.38	5.38
H10	19.00	39.92	1008	41.56	14.34	38.32	5.47
H10	19.00	39.92	1008	41.68	14.34	38.32	
H10	19.00	39.92	1008	91.91	14.23	38.63	5.03
H10	19.00	39.92	1008	101.53	14.23	38.66	4.97
H10	19.00	39.92	1008	201.23	14.23	38.80	4.48
H10	19.00	39.92	1008	300.51	14.14	38.81	4.47
H10	19.00	39.92	1008	500.53	13.95	38.80	4.41
H10	19.00	39.92	1008	914.47	13.46	38.76	4.91
H08	18.17	39.42	1360	6.29	14.95	38.45	5.45
H08	18.17	39.42	1360	21.37	14.95	38.45	5.47
H08	18.17	39.42	1360	28.93	14.82	38.48	5.34
H08	18.17	39.42	1360	50.64	14.50	38.53	5.24

Table C.1. continued

Stations	Lon (°E)	Lat (°N)	Bot. Depth (m)	Depth (m)	Temperature (°C)	Salinity (psu)	Oxygen ($\mu\text{mol L}^{-1}$)
H08	18.17	39.42	1360	101.57	14.52	38.83	
H08	18.17	39.42	1360	119.99	14.47	38.84	4.50
H08	18.17	39.42	1360	170.16	14.36	38.86	4.46
H08	18.17	39.42	1360	201.32	14.27	38.85	4.42
H08	18.17	39.42	1360	500.54	13.88	38.79	4.42
H08	18.17	39.42	1360	1000.87	13.74	38.75	4.34
H08	18.17	39.42	1360	1333.56	13.73	38.76	4.72
H04	16.00	35.92	3750	7.09	16.49	37.98	5.37
H04	16.00	35.92	3750	21.95	16.48	37.98	5.43
H04	16.00	35.92	3750	52.34	16.00	38.05	5.28
H04	16.00	35.92	3750	101.26	15.01	38.61	4.71
H04	16.00	35.92	3750	179.58	14.52	38.86	
H04	16.00	35.92	3750	201.56	14.40	38.86	4.32
H04	16.00	35.92	3750	500.26	13.84	38.78	4.31
H04	16.00	35.92	3750	988.35	13.74	38.75	
H04	16.00	35.92	3750	1478.85	13.78	38.75	4.50
H04	16.00	35.92	3750	1975.66	13.82	38.75	4.55
H04	16.00	35.92	3750	2955.99	13.92	38.74	4.54
H04	16.00	35.92	3750	3677.42	14.03	38.74	4.68
H04_MUC	16.00	35.92	3750	3738			
H03	18.50	35.75	4087	7.97	16.64	38.24	5.31
H03	18.50	35.75	4087	23.10	16.61	38.28	5.33
H03	18.50	35.75	4087	43.94	16.54	38.36	5.32
H03	18.50	35.75	4087	102.12	16.18	38.46	5.23
H03	18.50	35.75	4087	202.83	15.04	38.83	4.91
H03	18.50	35.75	4087	502.34	14.16	38.84	4.25
H03	18.50	35.75	4087	990.97	13.75	38.75	4.22
H03	18.50	35.75	4087	1503.23	13.77	38.74	
H03	18.50	35.75	4087	1981.42	13.81	38.74	4.41
H03	18.50	35.75	4087	2963.19	13.90	38.73	4.44
H03	18.50	35.75	4087	4005.52	14.10	38.74	4.64
H05	18.50	37.50	3154	7.04	16.46	38.21	5.28
H05	18.50	37.50	3154	22.17	16.46	38.21	5.34
H05	18.50	37.50	3154	59.25	16.33	38.21	5.32
H05	18.50	37.50	3154	101.65	16.22	38.22	5.28
H05	18.50	37.50	3154	201.91	14.85	38.74	4.86
H05	18.50	37.50	3154	237.17	14.80	38.83	4.73
H05	18.50	37.50	3154	501.57	14.23	38.86	4.35
H05	18.50	37.50	3154	1001.12	13.78	38.76	4.30
H05	18.50	37.50	3154	1501.63	13.79	38.75	4.36
H05	18.50	37.50	3154	1970.42	13.82	38.75	4.44
H05	18.50	37.50	3154	2952.44	13.91	38.74	4.59
H05	18.50	37.50	3154	3100.41	13.92	38.75	4.66
H05_MUC	18.50	37.50	3154	3154			
H06	18.50	38.50	3040	7.31	16.23	38.21	5.35
H06	18.50	38.50	3040	12.91	16.22	38.20	5.36
H06	18.50	38.50	3040	22.92	16.22	38.20	5.34
H06	18.50	38.50	3040	52.94	16.23	38.20	5.38
H06	18.50	38.50	3040	102.27	16.03	38.21	5.22
H06	18.50	38.50	3040	152.57	15.16	38.66	5.00

Table C.1. continued

Stations	Lon (°E)	Lat (°N)	Bot. Depth (m)	Depth (m)	Temperature (°C)	Salinity (psu)	Oxygen ($\mu\text{mol L}^{-1}$)
H06	18.50	38.50	3040	202.97	14.81	38.82	4.54
H06	18.50	38.50	3040	276.29	14.54	38.88	4.51
H06	18.50	38.50	3040	500			
H06	18.50	38.50	3040	983.89	13.77	38.75	4.46
H06	18.50	38.50	3040	1483.27	13.79	38.75	4.38
H06	18.50	38.50	3040	1981.05	13.83	38.75	4.26
H06	18.50	38.50	3040	2966.31	13.92	38.75	4.58
H09	18.53	39.67	543	6.06	14.17	38.35	5.44
H09	18.53	39.67	543	21.10	14.17	38.35	5.46
H09	18.53	39.67	543	37.78	14.18	38.36	5.48
H09	18.53	39.67	543	51.18	14.20	38.37	5.48
H09	18.53	39.67	543	100.81	14.23	38.66	4.86
H09	18.53	39.67	543	202.03	14.23	38.81	4.49
H09	18.53	39.67	543	251.89	14.17	38.82	4.48
H09	18.53	39.67	543	501.10	13.67	38.76	4.37
H09	18.53	39.67	543	534.03	13.67	38.76	4.53
H11	19.33	39.28	1035	7.02	16.19	38.22	5.33
H11	19.33	39.28	1035	21.97	16.19	38.22	5.49
H11	19.33	39.28	1035	52.09	16.20	38.22	5.36
H11	19.33	39.28	1035	77.29	15.53	38.39	5.04
H11	19.33	39.28	1035	181.01	14.58	38.86	4.48
H11	19.33	39.28	1035	201.43	14.45	38.85	4.52
H11	19.33	39.28	1035	500.32	13.95	38.80	4.34
H11	19.33	39.28	1035	1030.59	13.54	38.76	4.92
H11_MUC	19.33	39.28	1035	1035			
H02	21.00	35.75	3008	7.23	17.00	38.70	5.18
H02	21.00	35.75	3008	12.77	17.01	38.70	5.24
H02	21.00	35.75	3008	22.60	17.00	38.70	5.20
H02	21.00	35.75	3008	53.01	17.01	38.70	5.25
H02	21.00	35.75	3008	102.15	17.11	38.73	
H02	21.00	35.75	3008	121.77	16.91	38.70	5.19
H02	21.00	35.75	3008	201.68	15.23	38.80	5.10
H02	21.00	35.75	3008	351.38	14.80	38.94	4.62
H02	21.00	35.75	3008	500.54	14.41	38.90	4.48
H02	21.00	35.75	3008	1000.26	13.76	38.75	4.15
H02	21.00	35.75	3008	1499.45	13.79	38.75	4.26
H02	21.00	35.75	3008	1979.26	13.83	38.75	4.26
H02	21.00	35.75	3008	2957.72	13.91	38.73	4.39
H02_MUC	21.00	35.75	3008	3008			
H01	23.00	35.75	2117	8.89	16.05	38.57	5.32
H01	23.00	35.75	2117	23.80	16.05	38.57	5.32
H01	23.00	35.75	2117	44.56	15.50	38.50	5.40
H01	23.00	35.75	2117	52.99	15.48	38.50	5.40
H01	23.00	35.75	2117	103.81	15.70	38.60	
H01	23.00	35.75	2117	122.42	15.02	38.48	
H01	23.00	35.75	2117	204	14.81	38.88	
H01	23.00	35.75	2117	243.27	14.72	38.93	4.61
H01	23.00	35.75	2117	503.59	14.33	38.91	4.71
H01	23.00	35.75	2117	1002.07	13.74	38.75	5.33
H01	23.00	35.75	2117	1499.26	13.81	38.76	

Table C.1. continued

Stations	Lon (°E)	Lat (°N)	Bot. Depth (m)	Depth (m)	Temperature (°C)	Salinity (psu)	Oxygen ($\mu\text{mol L}^{-1}$)
H01	23.00	35.75	2117	2091.36	13.86	38.76	4.35
H01_MUC	23.00	35.75	2117	2117			
ler01	26.19	34.44	3626	8.32	19.16	39.19	4.98
ler01	26.19	34.44	3626	23.35	19.18	39.19	
ler01	26.19	34.44	3626	43.05	19.18	39.19	4.98
ler01	26.19	34.44	3626	52.04	19.18	39.19	4.99
ler01	26.19	34.44	3626	101.70	19.18	39.19	5.02
ler01	26.19	34.44	3626	101.94	19.18	39.18	5.01
ler01	26.19	34.44	3626	149.33	19.17	39.18	5.03
ler01	26.19	34.44	3626	194.87	19.13	39.18	5.05
ler01	26.19	34.44	3626	500.09	15.15	39.01	4.69
ler01	26.19	34.44	3626	999.34	13.81	38.76	
ler01	26.19	34.44	3626	1488.97	13.79	38.75	4.18
ler01	26.19	34.44	3626	1978.32	13.93	38.78	4.26
ler01	26.19	34.44	3626	2964.50	14.04	38.77	4.28
ler01	26.19	34.44	3626	3571.22	14.11	38.76	4.25
ler01_MUC	26.19	34.44	3626	3626			
Her01	27.74	33.92	2680	7.58	16.75	39.10	5.19
Her01	27.74	33.92	2680	12.11	16.75	39.10	
Her01	27.74	33.92	2680	22.40	16.75	39.10	5.16
Her01	27.74	33.92	2680	37.07	16.74	39.10	5.21
Her01	27.74	33.92	2680	52.17	16.61	39.10	5.26
Her01	27.74	33.92	2680	101.94	15.69	39.05	4.75
Her01	27.74	33.92	2680	202.26	15.00	39.00	4.57
Her01	27.74	33.92	2680	251.50	14.66	38.95	4.47
Her01	27.74	33.92	2680	501.93	13.93	38.81	4.07
Her01	27.74	33.92	2680	1000.94	13.69	38.74	4.10
Her01	27.74	33.92	2680	1499.90	13.83	38.76	4.23
Her01	27.74	33.92	2680	1988.78	13.97	38.79	4.26
Her01	27.74	33.92	2680	2453.97	14.04	38.79	4.32
Her01_MUC	27.74	33.92	2680	2680			
Her03	29.00	33.67	3090	10.91	17.13	39.11	5.07
Her03	29.00	33.67	3090	26.03	17.15	39.11	
Her03	29.00	33.67	3090	26.47	17.15	39.11	5.08
Her03	29.00	33.67	3090	66.20	17.16	39.11	5.12
Her03	29.00	33.67	3090	105.21	17.16	39.11	5.09
Her03	29.00	33.67	3090	205.17	17.13	39.10	5.05
Her03	29.00	33.67	3090	225.15	16.86	39.04	4.92
Her03	29.00	33.67	3090	253.95	16.58	39.03	4.89
Her03	29.00	33.67	3090	504.86	14.49	38.92	4.33
Her03	29.00	33.67	3090	1003.40	13.74	38.75	4.04
Her03	29.00	33.67	3090	1503.02	13.79	38.75	4.16
Her03	29.00	33.67	3090	1972.83	13.93	38.78	4.27
Her03	29.00	33.67	3090	2958.08	14.12	38.79	4.23
Her03	29.00	33.67	3090	3024.26	14.13	38.79	4.18
Her03_MUC	29.00	33.67	3090	3090			
Rho02	27.70	35.62	1305	5.00			
Rho02	27.70	35.62	1305	22.81	16.15	39.24	5.08
Rho02	27.70	35.62	1305	52.10	16.10	39.23	5.15
Rho02	27.70	35.62	1305	85.44	16.07	39.22	5.06

Table C.1. continued

Stations	Lon (°E)	Lat (°N)	Bot. Depth (m)	Depth (m)	Temperature (°C)	Salinity (psu)	Oxygen ($\mu\text{mol L}^{-1}$)
Rho02	27.70	35.62	1305	102.23	16.07	39.22	5.01
Rho02	27.70	35.62	1305	180.54	16.08	39.22	5.15
Rho02	27.70	35.62	1305	201.58	16.07	39.22	5.10
Rho02	27.70	35.62	1305	201.59	16.07	39.22	5.09
Rho02	27.70	35.62	1305	499.92	13.97	38.82	4.10
Rho02	27.70	35.62	1305	999.08	13.76	38.76	4.06
Rho02	27.70	35.62	1305	1284.98	13.80	38.76	4.06
Rho02_MUC	27.70	35.62	1305	1305			
Sk01	23.80	39.56	1264	1.00			
Sk01	23.80	39.56	1264	6.63	13.68	38.14	5.59
Sk01	23.80	39.56	1264	21.63	13.70	38.15	5.61
Sk01	23.80	39.56	1264	44.75	14.99	38.70	5.24
Sk01	23.80	39.56	1264	52.54	14.80	38.72	5.23
Sk01	23.80	39.56	1264	81.12	14.91	38.90	5.08
Sk01	23.80	39.56	1264	100.45	14.70	38.90	5.00
Sk01	23.80	39.56	1264	201.24	14.09	38.89	4.95
Sk01	23.80	39.56	1264	351.65	13.80	38.94	5.06
Sk01	23.80	39.56	1264	501.70	13.68	38.98	
Sk01	23.80	39.56	1264	1001.34	13.35	39.04	4.38
Sk01	23.80	39.56	1264	1247.40	13.38	39.04	4.39
Sk01_MUC	23.80	39.56	1264	1264			

Table C.2. Sampling locations and nutrient concentrations in several depths and in the sediment-water interface (MUC) from the METEOR cruise M71-3.

Stations	Lon (°E)	Lat (°N)	Depth (m)	Nitrate ($\mu\text{mol L}^{-1}$)	Nitrite ($\mu\text{mol L}^{-1}$)	Ammonia ($\mu\text{mol L}^{-1}$)	Phosphate ($\mu\text{mol L}^{-1}$)	Silicate ($\mu\text{mol L}^{-1}$)
H07	17.75	39.17	22.09	0.61	0.16	1.17	0.02	1.51
H07	17.75	39.17	51.97	0.68	0.16	1.20	0.04	1.56
H07	17.75	39.17	52.07	0.65	0.16	1.22	0.02	1.56
H07	17.75	39.17	102.47	3.25	0.02	1.18	0.07	2.72
H07	17.75	39.17	152.58	4.20	0.02	1.31	0.12	3.29
H07	17.75	39.17	202.07	4.62	0.01	1.25	0.15	3.99
H07	17.75	39.17	298.80	4.91	0.01	1.20	0.17	4.52
H07	17.75	39.17	502.03	4.96	0.01	1.15	0.18	5.55
H07	17.75	39.17	992.57	4.81	0.00	1.20	0.18	7.43
H07	17.75	39.17	1482.03	4.29	0.01	1.18	0.15	6.17
H07	17.75	39.17	1634.50	4.26	0.01	1.17	0.15	6.26
H07_MUC	17.75	39.17	1866.00	4.15	0.00	1.31	0.15	5.82
H12	19.75	38.83	5.70	0.09	0.00	0.61	0.02	0.98
H12	19.75	38.83	21.28	0.06	0.00	0.63	0.02	1.03
H12	19.75	38.83	50.85	0.06	0.00	0.61	0.01	1.11
H12	19.75	38.83	75.64	0.17	0.01	0.60	0.01	1.12
H12	19.75	38.83	75.66	0.18	0.01	0.70	0.01	1.14
H12	19.75	38.83	121.25	2.75	0.01	0.76	0.04	2.14
H12	19.75	38.83	201.17	4.07	0.00	0.63	0.10	3.29
H12	19.75	38.83	201.29	4.07	0.00	0.61	0.12	3.25
H12	19.75	38.83	499.68	4.99	0.00	0.75	0.19	5.49
H12	19.75	38.83	998.13	4.82	0.00	0.63	0.18	7.75
H12	19.75	38.83	1443.76	4.06	0.00	0.62	0.13	5.85
H12_MUC	19.75	38.83	1450.00	4.12	0.01	1.61	0.17	6.45
H10	19.00	39.92	6.98	0.93	0.13	1.10	0.02	1.71
H10	19.00	39.92	21.67	0.35	0.01	1.13	0.01	1.18

Table C.2. continued

Stations	Lon (°E)	Lat (°N)	Depth (m)	Nitrate ($\mu\text{mol L}^{-1}$)	Nitrite ($\mu\text{mol L}^{-1}$)	Ammonia ($\mu\text{mol L}^{-1}$)	Phosphate ($\mu\text{mol L}^{-1}$)	Silicate ($\mu\text{mol L}^{-1}$)
H10	19.00	39.92	41.56	0.71	0.15	1.08	0.01	1.81
H10	19.00	39.92	41.68	0.50	0.07	1.14	0.02	1.45
H10	19.00	39.92	91.91	1.75	0.16	1.17	0.06	2.19
H10	19.00	39.92	101.53	1.85	0.10	1.14	0.03	2.20
H10	19.00	39.92	201.23	4.15	0.01	1.13	0.11	3.52
H10	19.00	39.92	300.51	4.52	0.01	1.12	0.15	4.10
H10	19.00	39.92	500.53	4.92	0.01	1.16	0.18	5.21
H10	19.00	39.92	914.47	3.53	0.01	1.16	0.12	4.14
H08	18.17	39.42	6.29	0.32	0.04	1.22	0.03	1.34
H08	18.17	39.42	21.37	0.31	0.04	1.17	0.03	1.32
H08	18.17	39.42	28.93	0.60	0.09	1.17	0.03	1.42
H08	18.17	39.42	50.64	0.94	0.18	1.15	0.02	1.62
H08	18.17	39.42	101.57	3.94	0.02	1.18	0.12	3.09
H08	18.17	39.42	119.99	4.20	0.01	1.18	0.13	3.36
H08	18.17	39.42	170.16	4.58	0.01	1.18	0.16	3.87
H08	18.17	39.42	201.32	4.87	0.01	1.15	0.17	4.41
H08	18.17	39.42	500.54	5.04	0.01	1.15	0.18	5.80
H08	18.17	39.42	1000.87	4.91	0.01	1.13	0.19	7.18
H08	18.17	39.42	1333.56	4.17	0.01	1.14	0.15	5.30
H04	16.00	35.92	7.09	0.10	0.01	1.09	0.02	0.82
H04	16.00	35.92	21.95	0.15	0.00	1.12	0.02	0.76
H04	16.00	35.92	52.34	0.17	0.01	1.11	0.02	0.98
H04	16.00	35.92	101.26	2.44	0.02	1.12	0.08	2.00
H04	16.00	35.92	179.58	4.57	0.01	1.13	0.15	3.84
H04	16.00	35.92	201.56	5.42	0.01	1.16	0.17	4.55
H04	16.00	35.92	500.26	5.41	0.00	1.14	0.21	6.65
H04	16.00	35.92	988.35	4.96	0.00	1.13	0.19	7.74
H04	16.00	35.92	1478.85	4.62	0.01	1.15	0.17	7.31
H04	16.00	35.92	1975.66	4.41	0.00	1.09	0.16	7.00

Table C.2. continued

Stations	Lon (°E)	Lat (°N)	Depth (m)	Nitrate ($\mu\text{mol L}^{-1}$)	Nitrite ($\mu\text{mol L}^{-1}$)	Ammonia ($\mu\text{mol L}^{-1}$)	Phosphate ($\mu\text{mol L}^{-1}$)	Silicate ($\mu\text{mol L}^{-1}$)
H04	16.00	35.92	2955.99	4.56	0.00	1.16	0.16	6.97
H04	16.00	35.92	3677.42	4.13	0.00	1.13	0.14	6.64
H04_MUC	16.00	35.92	3738.00	4.25	0.03	1.43	0.18	6.36
H03	18.50	35.75	7.97	0.10	0.00	1.21	0.02	0.81
H03	18.50	35.75	23.10	0.08	0.00	1.27	0.02	0.86
H03	18.50	35.75	43.94	0.11	0.00	1.21	0.02	0.87
H03	18.50	35.75	102.12	0.33	0.03	1.21	0.03	0.92
H03	18.50	35.75	202.83	2.01	0.01	1.31	0.05	1.55
H03	18.50	35.75	502.34	5.08	0.00	1.15	0.19	5.59
H03	18.50	35.75	990.97	5.22	0.01	1.11	0.21	8.11
H03	18.50	35.75	1503.23	4.60	0.00	1.13	0.18	7.51
H03	18.50	35.75	1981.42	4.62	0.00	1.12	0.18	7.65
H03	18.50	35.75	2963.19	4.57	0.00	1.13	0.17	7.56
H03	18.50	35.75	4005.52	4.09	0.00	1.11	0.14	6.45
H05	18.50	37.50	7.04	0.06	0.00	1.16	0.01	0.89
H05	18.50	37.50	22.17	0.06	0.01	1.17	0.01	0.91
H05	18.50	37.50	59.25	0.06	0.01	1.24	0.01	0.84
H05	18.50	37.50	101.65	0.13	0.03	1.22	0.01	0.92
H05	18.50	37.50	201.91	1.84	0.01	1.29		1.57
H05	18.50	37.50	237.17	2.65	0.01	1.16	0.07	1.99
H05	18.50	37.50	501.57	4.86	0.01	1.19	0.17	5.17
H05	18.50	37.50	1001.12	5.02	0.00	1.15	0.19	7.42
H05	18.50	37.50	1501.63	4.70	0.00	1.11	0.18	7.57
H05	18.50	37.50	1970.42	4.52	0.00	1.15	0.16	7.33
H05	18.50	37.50	2952.44	4.17	0.00	1.11	0.14	6.74
H05	18.50	37.50	3100.41	4.05	0.01	1.13	0.14	6.25
H05_MUC	18.50	37.50	3154.00	4.07	0.01	1.43	0.13	6.24
H06	18.50	38.50	7.31	0.07	0.00	1.20	0.03	0.87
H06	18.50	38.50	12.91	0.08	0.00	1.26	0.02	0.93

Table C.2. continued

Stations	Lon (°E)	Lat (°N)	Depth (m)	Nitrate ($\mu\text{mol L}^{-1}$)	Nitrite ($\mu\text{mol L}^{-1}$)	Ammonia ($\mu\text{mol L}^{-1}$)	Phosphate ($\mu\text{mol L}^{-1}$)	Silicate ($\mu\text{mol L}^{-1}$)
H06	18.50	38.50	22.92	0.05	0.00	1.22	0.02	0.94
H06	18.50	38.50	52.94	0.06	0.01	1.25	0.02	0.90
H06	18.50	38.50	102.27	0.32	0.05	1.34	0.02	0.97
H06	18.50	38.50	152.57	1.08	0.02	1.34	0.04	1.32
H06	18.50	38.50	202.97	3.32	0.02	1.41	0.10	2.50
H06	18.50	38.50	276.29	4.07	0.02	1.36	0.13	3.35
H06	18.50	38.50	500.00					
H06	18.50	38.50	983.89	5.16	0.03	1.42	0.19	7.85
H06	18.50	38.50	1483.27	4.70	0.02	1.30	0.17	7.78
H06	18.50	38.50	1981.05	4.52	0.02	1.36	0.16	7.46
H06	18.50	38.50	2966.31	4.22	0.02	1.37	0.15	6.58
H09	18.53	39.67	6.06	0.80	0.24	1.07	0.01	1.86
H09	18.53	39.67	21.10	0.79	0.24	1.08	0.01	1.87
H09	18.53	39.67	37.78	0.88	0.24	1.12	0.02	1.91
H09	18.53	39.67	51.18	0.97	0.24	1.25	0.02	1.93
H09	18.53	39.67	100.81	2.46	0.08	1.08	0.05	2.80
H09	18.53	39.67	202.03	4.15	0.01	1.09	0.11	3.53
H09	18.53	39.67	251.89	4.45	0.00	1.09	0.13	3.89
H09	18.53	39.67	501.10	4.77	0.00	1.11	0.17	7.14
H09	18.53	39.67	534.03	4.57	0.01	1.14	0.16	6.47
H11	19.33	39.28	7.02	0.11	0.00	1.22	0.03	0.90
H11	19.33	39.28	21.97	0.09	0.00	1.12	0.01	0.91
H11	19.33	39.28	52.09	0.10	0.10	1.16	0.02	0.95
H11	19.33	39.28	77.29	0.96	0.05	1.09	0.02	1.38
H11	19.33	39.28	181.01	4.11	0.01	1.16	0.14	3.20
H11	19.33	39.28	201.43	4.38	0.00	1.09	0.13	3.41
H11	19.33	39.28	500.32	5.10	0.00	1.15	0.17	5.56
H11	19.33	39.28	1030.59	3.69	0.01	1.18	0.14	3.89
H11_MUC	19.33	39.28	1035.00	3.61	0.01	1.43	0.12	3.75

Table C.2. continued

Stations	Lon (°E)	Lat (°N)	Depth (m)	Nitrate ($\mu\text{mol L}^{-1}$)	Nitrite ($\mu\text{mol L}^{-1}$)	Ammonia ($\mu\text{mol L}^{-1}$)	Phosphate ($\mu\text{mol L}^{-1}$)	Silicate ($\mu\text{mol L}^{-1}$)
H02	21.00	35.75	7.23	0.07	0.00	0.81	0.02	0.90
H02	21.00	35.75	12.77	0.05	0.00	0.83	0.02	0.89
H02	21.00	35.75	22.60	0.06	0.01	0.84	0.02	0.91
H02	21.00	35.75	53.01	0.06	0.00	0.77	0.02	0.88
H02	21.00	35.75	102.15	0.07	0.00	0.85	0.02	1.08
H02	21.00	35.75	121.77	0.12	0.03	0.78	0.01	0.91
H02	21.00	35.75	201.68	0.93	0.01	0.80	0.02	1.04
H02	21.00	35.75	351.38	3.31	0.00	0.74	0.10	2.95
H02	21.00	35.75	500.54	4.16	0.00	0.72	0.15	4.75
H02	21.00	35.75	1000.26	5.13	0.00	0.84	0.20	8.48
H02	21.00	35.75	1499.45	4.77	0.00	0.75	0.18	8.48
H02	21.00	35.75	1979.26	4.61	0.00	0.74	0.17	7.90
H02	21.00	35.75	2957.72	4.59	0.00	0.69	0.17	7.95
H02_MUC	21.00	35.75	3008.00	4.67	0.01	1.40	0.16	7.83
H01	23.00	35.75	8.89	0.07	0.00	0.53	0.03	0.90
H01	23.00	35.75	23.80	0.22	0.02	0.77	0.03	0.93
H01	23.00	35.75	44.56	0.09	0.02	0.61	0.02	0.92
H01	23.00	35.75	52.99	0.15	0.01	0.63	0.02	0.91
H01	23.00	35.75	103.81	0.06	0.01	0.62	0.02	1.04
H01	23.00	35.75	122.42	0.39		0.62	0.02	1.01
H01	23.00	35.75	204.00					
H01	23.00	35.75	243.27	3.90	0.00	0.61	0.11	3.02
H01	23.00	35.75	503.59	3.77	0.00	0.68	0.13	4.19
H01	23.00	35.75	1002.07	4.26	0.00	0.68	0.03	1.10
H01	23.00	35.75	1499.26	5.67	0.00	0.65	0.18	8.61
H01	23.00	35.75	2091.36	5.38	0.00	0.62	0.17	7.90
H01_MUC	23.00	35.75	2117.00	4.63	0.01	1.41	0.16	7.81
ler01	26.19	34.44	8.32	0.06	0.02	0.67	0.02	0.84
ler01	26.19	34.44	23.35	0.06	0.02	0.68	0.02	0.89

Table C.2. continued

Stations	Lon (°E)	Lat (°N)	Depth (m)	Nitrate ($\mu\text{mol L}^{-1}$)	Nitrite ($\mu\text{mol L}^{-1}$)	Ammonia ($\mu\text{mol L}^{-1}$)	Phosphate ($\mu\text{mol L}^{-1}$)	Silicate ($\mu\text{mol L}^{-1}$)
Ier01	26.19	34.44	43.05	0.04	0.02	0.69	0.02	0.92
Ier01	26.19	34.44	52.04	0.04	0.02	0.67	0.02	0.79
Ier01	26.19	34.44	101.70	0.03	0.02	0.59	0.03	0.91
Ier01	26.19	34.44	101.94	0.04	0.02	0.65	0.02	0.78
Ier01	26.19	34.44	149.33	0.03	0.02	0.64	0.02	0.81
Ier01	26.19	34.44	194.87	0.04	0.02	0.64	0.02	0.79
Ier01	26.19	34.44	500.09	2.73	0.01	0.65	0.08	2.88
Ier01	26.19	34.44	999.34	5.98	0.00	0.54	0.22	8.85
Ier01	26.19	34.44	1488.97	5.40	0.00	0.60	0.20	8.96
Ier01	26.19	34.44	1978.32	5.33	0.00	0.62	0.20	8.86
Ier01	26.19	34.44	2964.50	5.15	0.00	0.78	0.18	8.12
Ier01	26.19	34.44	3571.22	5.15	0.00	0.61	0.17	8.06
Ier01_MUC	26.19	34.44	3626.00	4.67	0.00	1.38	0.17	8.25
Her01	27.74	33.92	7.58	0.11	0.02	0.90	0.02	0.94
Her01	27.74	33.92	12.11	0.11	0.01	0.75	0.01	0.93
Her01	27.74	33.92	22.40	0.10	0.02	0.76	0.02	0.93
Her01	27.74	33.92	37.07	0.32	0.02	1.06	0.01	0.96
Her01	27.74	33.92	52.17	0.18	0.03	1.00	0.03	0.99
Her01	27.74	33.92	101.94	1.72	0.01	0.78	0.04	1.90
Her01	27.74	33.92	202.26	3.25	0.01	0.80	0.10	3.42
Her01	27.74	33.92	251.50	3.96	0.00	0.71	0.13	4.57
Her01	27.74	33.92	501.93	5.38	0.01	0.70	0.21	7.91
Her01	27.74	33.92	1000.94	5.17	0.00	0.71	0.20	9.47
Her01	27.74	33.92	1499.90	4.84	0.00	0.71	0.19	8.89
Her01	27.74	33.92	1988.78	4.65	0.00	0.69	0.17	8.47
Her01	27.74	33.92	2453.97	4.66	0.00	0.66	0.17	8.50
Her01_MUC	27.74	33.92	2680.00	4.69	0.02	1.29	0.19	8.49
Her03	29.00	33.67	10.91	0.36	0.02	0.69	0.02	0.87
Her03	29.00	33.67	26.03	0.28	0.01	0.63	0.01	0.84

Table C.2. continued

Stations	Lon (°E)	Lat (°N)	Depth (m)	Nitrate ($\mu\text{mol L}^{-1}$)	Nitrite ($\mu\text{mol L}^{-1}$)	Ammonia ($\mu\text{mol L}^{-1}$)	Phosphate ($\mu\text{mol L}^{-1}$)	Silicate ($\mu\text{mol L}^{-1}$)
Her03	29.00	33.67	105.21	0.31	0.01	0.65	0.01	0.85
Her03	29.00	33.67	205.17	0.36	0.01	0.58	0.02	0.84
Her03	29.00	33.67	225.15	0.79	0.01	0.89	0.03	0.95
Her03	29.00	33.67	253.95	0.93	0.01	0.68	0.04	1.05
Her03	29.00	33.67	504.86	4.46	0.00	0.65	0.15	5.33
Her03	29.00	33.67	1003.40	5.38	0.00	0.67	0.22	9.23
Her03	29.00	33.67	1503.02	4.92	0.00	0.65	0.19	9.23
Her03	29.00	33.67	1972.83	4.70	0.00	0.67	0.18	8.66
Her03	29.00	33.67	2958.08	4.63	0.00	0.65	0.17	8.48
Her03	29.00	33.67	3024.26	4.62	0.00	0.66	0.17	8.48
Her03_MUC	29.00	33.67	3090.00	4.68	0.00	1.27	0.18	8.52
Rho02	27.70	35.62	5.00					
Rho02	27.70	35.62	22.81	0.57	0.05	0.83	0.02	1.49
Rho02	27.70	35.62	52.10	0.64	0.05	0.78	0.02	1.58
Rho02	27.70	35.62	85.44	0.68	0.05	0.83	0.02	1.63
Rho02	27.70	35.62	102.23	0.70	0.05	0.82	0.02	1.61
Rho02	27.70	35.62	180.54	0.69	0.05	0.78	0.03	1.70
Rho02	27.70	35.62	201.58	0.72	0.05	0.78	0.02	1.65
Rho02	27.70	35.62	201.59	0.82	0.05	0.92	0.03	1.71
Rho02	27.70	35.62	499.92	5.52	0.00	0.74	0.21	8.17
Rho02	27.70	35.62	999.08	5.18	0.00	0.74	0.20	9.62
Rho02	27.70	35.62	1284.98	5.08	0.00	0.77	0.20	9.73
Rho02_MUC	27.70	35.62	1305.00	5.18	0.00	1.26	0.21	10.20
Sk01	23.80	39.56	1.00					
Sk01	23.80	39.56	6.63	0.08	0.00	0.63	0.02	1.39
Sk01	23.80	39.56	21.63	0.07	0.00	0.65	0.02	1.40
Sk01	23.80	39.56	44.75	0.51	0.04	0.72	0.02	1.61
Sk01	23.80	39.56	52.54	0.67	0.04	0.76	0.03	1.68
Sk01	23.80	39.56	81.12	1.28	0.02	0.70	0.05	1.92

Table C.2. continued

Stations	Lon (°E)	Lat (°N)	Depth (m)	Nitrate ($\mu\text{mol L}^{-1}$)	Nitrite ($\mu\text{mol L}^{-1}$)	Ammonia ($\mu\text{mol L}^{-1}$)	Phosphate ($\mu\text{mol L}^{-1}$)	Silicate ($\mu\text{mol L}^{-1}$)
Sk01	23.80	39.56	100.45	1.54	0.02	0.65	0.06	2.01
Sk01	23.80	39.56	201.24	2.43	0.01	0.77	0.09	2.67
Sk01	23.80	39.56	351.65	2.55	0.01	0.69	0.12	3.38
Sk01	23.80	39.56	501.70	3.54	0.00	0.64	0.17	5.19
Sk01	23.80	39.56	1001.34	4.61	0.00	0.72	0.22	9.15
Sk01	23.80	39.56	1247.40	4.66	0.00	0.72	0.23	9.94
Sk01_MUC	23.80	39.56	1264.00	4.82	0.00	1.32	0.24	10.25

Table C.3. Sampling locations and concentrations of the total nitrogen in suspended particles (PN_{susp}), total reduced nitrogen (TRN) and total carbon (TC), expressed in $\mu\text{mol L}^{-1}$ and $\mu\text{gr L}^{-1}$ respectively. Table C.3. contains also the isotopic values of nitrogen ($\delta^{15}\text{N}$) and oxygen ($\delta^{18}\text{O}$) in nitrate, as well as the isotopic values of $\delta^{15}\text{N}$ in suspended particles ($\delta^{15}\text{N-PN}_{\text{susp}}$) and in the total reduced nitrogen ($\delta^{15}\text{N-TRN}$), from several depths of the column and from the MUC. In the last column, the isotopic values of ^{13}C of the total organic carbon ($^{13}\text{C-TOC}$) in several depths of the water column are presented.

Station	Lon (°E)	Lat (°N)	Depth (m)	$\delta^{15}\text{N-NO}_3$ (‰)	$\delta^{18}\text{O-NO}_3$ (‰)	PN suspended ($\mu\text{mol L}^{-1}$)	$\delta^{15}\text{N-PN}_{\text{susp}}$ (‰)	TRN ($\mu\text{mol L}^{-1}$)	$\delta^{15}\text{N-TRN}$ (‰)	TC ($\mu\text{gr L}^{-1}$)	$\delta^{13}\text{C-TOC}$
H07	17.75	39.17	7.22								
H07	17.75	39.17	22.09								
H07	17.75	39.17	51.97								
H07	17.75	39.17	52.07	0.99	3.06						
H07	17.75	39.17	102.47	2.06	3.24						
H07	17.75	39.17	152.58	1.67							
H07	17.75	39.17	202.07	1.05	2.33						
H07	17.75	39.17	298.80	1.74	3.47						
H07	17.75	39.17	502.03	1.88	3.29						
H07	17.75	39.17	992.57	2.07							
H07	17.75	39.17	1482.03	2.26							
H07	17.75	39.17	1634.50	2.02							
H07_MUC	17.75	39.17	1866	2.17							
H12	19.75	38.83	5.70								
H12	19.75	38.83	21.28								
H12	19.75	38.83	50.85								
H12	19.75	38.83	75.64	1.75	4.36						
H12	19.75	38.83	75.66								
H12	19.75	38.83	121.25	1.71							
H12	19.75	38.83	201.17								
H12	19.75	38.83	201.29	1.34							
H12	19.75	38.83	499.68	1.94	2.61						
H12	19.75	38.83	998.13	2.15							
H12	19.75	38.83	1443.76	1.96							
H12_MUC	19.75	38.83	1450	2.13							
H10	19.00	39.92	6.98								

Table C.3. continued

Station	Lon (°E)	Lat (°N)	Depth (m)	$\delta^{15}\text{N-NO}_3$ (‰)	$\delta^{18}\text{O-NO}_3$ (‰)	PN suspended ($\mu\text{mol L}^{-1}$)	$\delta^{15}\text{N-PN}_{\text{susp}}$ (‰)	TRN ($\mu\text{mol L}^{-1}$)	$\delta^{15}\text{N-TRN}$ (‰)	TC ($\mu\text{gr L}^{-1}$)	$\delta^{13}\text{C-TOC}$
H10	19.00	39.92	21.67	8.6	19.28						
H10	19.00	39.92	41.56	7.9							
H10	19.00	39.92	41.68								
H10	19.00	39.92	91.91	3.8	9.45						
H10	19.00	39.92	101.53	3.4							
H10	19.00	39.92	201.23	1.66	2.82						
H10	19.00	39.92	300.51	1.54	2.83						
H10	19.00	39.92	500.53	1.63	2.93						
H10	19.00	39.92	914.47	2.12							
H08	18.17	39.42	6.29	9.9	21.48	0.56	2.39	2.88	1.50		
H08	18.17	39.42	21.37					3.47			
H08	18.17	39.42	28.93	5.4		0.64	3.09	3.07			
H08	18.17	39.42	50.64	3.93	8.81			3.45	-1.10		
H08	18.17	39.42	101.57	1.75	3.79			2.48	-0.20		
H08	18.17	39.42	119.99	1.6	4.24			1.98	-2.40		
H08	18.17	39.42	170.16	1.87				2.07	-0.30		
H08	18.17	39.42	201.32	1.97	3.86			1.25	-1.30		
H08	18.17	39.42	500.54	2.3	4.44			2.65	-1.40		
H08	18.17	39.42	1000.87	2.33		0.20	8.44	1.13			
H08	18.17	39.42	1333.56	2.03		0.20	7.32	3.24	2.60		
H04	16.00	35.92	7.09			0.22	1.79	4.54		0.94	-24.39
H04	16.00	35.92	21.95					3.23			
H04	16.00	35.92	52.34			0.22	0.31	3.01		0.84	-23.00
H04	16.00	35.92	101.26	1.78				2.29	2.30		
H04	16.00	35.92	179.58	1.82				2.55	3.20		
H04	16.00	35.92	201.56	3.26	6.61	0.13	6.10	5.65	3.60	0.47	-24.88
H04	16.00	35.92	500.26	2.1	5.51	0.08	6.26	1.48	4.50	0.40	-24.52
H04	16.00	35.92	988.35	2.02	3.68	0.05	5.17	2.10	6.40		
H04	16.00	35.92	1478.85	1.81	4.60			1.42	14.40		

Table C.3. continued

Station	Lon (°E)	Lat (°N)	Depth (m)	$\delta^{15}\text{N-NO}_3$ (‰)	$\delta^{18}\text{O-NO}_3$ (‰)	PN suspended ($\mu\text{mol L}^{-1}$)	$\delta^{15}\text{N-PN}_{\text{susp}}$ (‰)	TRN ($\mu\text{mol L}^{-1}$)	$\delta^{15}\text{N-TRN}$ (‰)	TC ($\mu\text{gr L}^{-1}$)	$\delta^{13}\text{C-TOC}$
H04	16.00	35.92	1975.66	2.53	4.39			2.81	11.00		
H04	16.00	35.92	2955.99	2.48	4.05			1.08	11.80		
H04	16.00	35.92	3677.42	2.62		0.13	6.67	1.40	13.70	0.91	-24.78
H04_MUC	16.00	35.92	3738	2.62				2.52	6.10		
H03	18.50	35.75	7.97			0.32	0.10	4.18			
H03	18.50	35.75	23.10					3.82			
H03	18.50	35.75	43.94			0.38	0.60	2.59			
H03	18.50	35.75	102.12	6.3				3.40	0.81		
H03	18.50	35.75	202.83	1.64	5.06	0.18	7.06	3.02	0.60		
H03	18.50	35.75	502.34	1.86	3.46	0.26	8.13	1.93	1.10		
H03	18.50	35.75	990.97	1.86	2.39	0.39	8.06	1.69	2.30		
H03	18.50	35.75	1503.23	2.53	4.13			2.67	1.90		
H03	18.50	35.75	1981.42	2.26	3.54			2.41	5.40		
H03	18.50	35.75	2963.19	2.03	3.44			2.58	5.20		
H03	18.50	35.75	4005.52	2.34		0.13	7.45	2.99	6.70		
H05	18.50	37.50	7.04			0.37	1.37			1.16	-22.89
H05	18.50	37.50	22.17								
H05	18.50	37.50	59.25			0.41	1.25			1.10	-24.67
H05	18.50	37.50	101.65								
H05	18.50	37.50	201.91	1.7	5.44	0.18	6.38			0.58	-24.95
H05	18.50	37.50	237.17								
H05	18.50	37.50	501.57	1.46	2.82	0.13	7.46			0.62	-24.27
H05	18.50	37.50	1001.12			0.33	8.10			0.66	-24.33
H05	18.50	37.50	1501.63								
H05	18.50	37.50	1970.42								
H05	18.50	37.50	2952.44								
H05	18.50	37.50	3100.41	2.15	4.59	0.09	6.70			0.48	-25.34
H05_MUC	18.50	37.50	3154								
H06	18.50	38.50	7.31			0.40	0.99			0.77	-21.90

Table C.3. continued

Station	Lon (°E)	Lat (°N)	Depth (m)	$\delta^{15}\text{N-NO}_3$ (‰)	$\delta^{18}\text{O-NO}_3$ (‰)	PN suspended ($\mu\text{mol L}^{-1}$)	$\delta^{15}\text{N-PN}_{\text{susp}}$ (‰)	TRN ($\mu\text{mol L}^{-1}$)	$\delta^{15}\text{N-TRN}$ (‰)	TC ($\mu\text{gr L}^{-1}$)	$\delta^{13}\text{C-TOC}$
H06	18.50	38.50	12.91								
H06	18.50	38.50	22.92			0.40	0.66			1.19	-23.68
H06	18.50	38.50	52.94								
H06	18.50	38.50	102.27								
H06	18.50	38.50	152.57	1.7	7.24						
H06	18.50	38.50	202.97	1.31		0.13	6.03			0.50	-24.42
H06	18.50	38.50	276.29	1.55	3.82	0.10	7.08				
H06	18.50	38.50	500			0.10	7.08			7.34	-24.98
H06	18.50	38.50	983.89	2.17	3.12	0.08					
H06	18.50	38.50	1483.27	2.03	3.10						
H06	18.50	38.50	1981.05	2.03	3.37	0.14	6.18			0.27	-24.54
H06	18.50	38.50	2966.31	2.05	3.61	0.09	7.02			0.45	-25.96
H09	18.53	39.67	6.06	6				1.49			
H09	18.53	39.67	21.10	5.7				1.29			
H09	18.53	39.67	37.78	6.1	10.55			1.90			
H09	18.53	39.67	51.18	5.3	7.34			1.63			
H09	18.53	39.67	100.81	2.67	9.33			1.66	3.40		
H09	18.53	39.67	202.03	2.03	3.55			1.25	5.50		
H09	18.53	39.67	251.89	1.69	2.92			1.18	6.60		
H09	18.53	39.67	501.10	2.47	3.33			0.85	7.70		
H09	18.53	39.67	534.03	2.05	2.63			1.22	5.90		
H11	19.33	39.28	7.02			0.44	1.02	1.93			
H11	19.33	39.28	21.97					2.68			
H11	19.33	39.28	52.09					1.94			
H11	19.33	39.28	77.29	3.34	6.71	0.43	2.38	1.68	-0.90		
H11	19.33	39.28	181.01	1.65	6.49			3.20	5.40		
H11	19.33	39.28	201.43	1.32	5.54			2.13	2.30		
H11	19.33	39.28	500.32	1.78	3.07			3.04	5.00		
H11	19.33	39.28	1030.59	2.03		0.12	7.90	2.11	0.70		

Table C.3. continued

Station	Lon (°E)	Lat (°N)	Depth (m)	$\delta^{15}\text{N-NO}_3$ (‰)	$\delta^{18}\text{O-NO}_3$ (‰)	PN suspended ($\mu\text{mol L}^{-1}$)	$\delta^{15}\text{N-PN}_{\text{susp}}$ (‰)	TRN ($\mu\text{mol L}^{-1}$)	$\delta^{15}\text{N-TRN}$ (‰)	TC ($\mu\text{gr L}^{-1}$)	$\delta^{13}\text{C-TOC}$
H11_MUC	19.33	39.28	1035								
H02	21.00	35.75	7.23			0.40	1.20	2.15		1.17	-21.68
H02	21.00	35.75	12.77			0.39	1.33	2.29		1.19	-22.59
H02	21.00	35.75	22.60					2.72			
H02	21.00	35.75	53.01					1.98			
H02	21.00	35.75	102.15					1.36			
H02	21.00	35.75	121.77					1.16			
H02	21.00	35.75	201.68	0.6	5.24	0.22	6.85	1.80	2.40	0.90	-24.58
H02	21.00	35.75	351.38	1.39	3.97			1.63			
H02	21.00	35.75	500.54	1.3				0.49	7.10		
H02	21.00	35.75	1000.26	1.96				0.84	14.10		
H02	21.00	35.75	1499.45	2.16				0.74	5.50		
H02	21.00	35.75	1979.26	2.17				0.72	7.40		
H02	21.00	35.75	2957.72	2.09		0.13	6.97	0.84	6.20	0.61	-25.51
H02_MUC	21.00	35.75	3008	2.51				1.59	8.60		
H01	23.00	35.75	8.89			0.38	0.70			0.60	-22.24
H01	23.00	35.75	23.80								
H01	23.00	35.75	44.56			0.43	2.36			0.75	-22.79
H01	23.00	35.75	52.99								
H01	23.00	35.75	103.81								
H01	23.00	35.75	122.42								
H01	23.00	35.75	204			0.22	6.63			1.11	-24.05
H01	23.00	35.75	243.27	1.39							
H01	23.00	35.75	503.59	1.64		0.17	7.72			0.97	-24.51
H01	23.00	35.75	1002.07								
H01	23.00	35.75	1499.26	2.39							
H01	23.00	35.75	2091.36	2.31		0.11	8.10			0.76	-24.96
H01_MUC	23.00	35.75	2117	2.43							
ler01	26.19	34.44	8.32			0.32	0.76	3.44			

Table C.3. continued

Station	Lon (°E)	Lat (°N)	Depth (m)	$\delta^{15}\text{N-NO}_3$ (‰)	$\delta^{18}\text{O-NO}_3$ (‰)	PN suspended ($\mu\text{mol L}^{-1}$)	$\delta^{15}\text{N-PN}_{\text{susp}}$ (‰)	TRN ($\mu\text{mol L}^{-1}$)	$\delta^{15}\text{N-TRN}$ (‰)	TC ($\mu\text{gr L}^{-1}$)	$\delta^{13}\text{C-TOC}$
ler01	26.19	34.44	23.35					3.56			
ler01	26.19	34.44	43.05					4.16			
ler01	26.19	34.44	52.04			0.45	1.60	3.86			
ler01	26.19	34.44	101.70					3.47			
ler01	26.19	34.44	101.94					3.36			
ler01	26.19	34.44	149.33					3.47			
ler01	26.19	34.44	194.87			0.34	1.33	3.46			
ler01	26.19	34.44	500.09	1.22				2.90	1.20		
ler01	26.19	34.44	999.34	2.23		0.13	7.37	0.60	3.00		
ler01	26.19	34.44	1488.97	2.24				1.90	5.10		
ler01	26.19	34.44	1978.32	2.44				1.90	4.20		
ler01	26.19	34.44	2964.50	2.23				2.20	4.90		
ler01	26.19	34.44	3571.22	2.24		0.14	7.26	1.90	4.70		
ler01_MUC	26.19	34.44	3626	2.18				3.10	3.50		
Her01	27.74	33.92	7.58			0.31	0.43			0.68	-22.03
Her01	27.74	33.92	12.11								
Her01	27.74	33.92	22.40								
Her01	27.74	33.92	37.07								
Her01	27.74	33.92	52.17			0.36	1.74			0.73	-22.93
Her01	27.74	33.92	101.94	1.6	6.59						
Her01	27.74	33.92	202.26	1.58		0.27	7.92			0.73	-24.40
Her01	27.74	33.92	251.50	1.59	3.14						
Her01	27.74	33.92	501.93	1.9							
Her01	27.74	33.92	1000.94	2.32		0.13	8.49			0.78	-24.47
Her01	27.74	33.92	1499.90	2.51							
Her01	27.74	33.92	1988.78	2.12							
Her01	27.74	33.92	2453.97	2.21							
Her01_MUC	27.74	33.92	2680	2.3							
Her03	29.00	33.67	10.91			0.23	1.19	5.40		1.22	-24.33

Table C.3. continued

Station	Lon (°E)	Lat (°N)	Depth (m)	$\delta^{15}\text{N-NO}_3$ (‰)	$\delta^{18}\text{O-NO}_3$ (‰)	PN suspended ($\mu\text{mol L}^{-1}$)	$\delta^{15}\text{N-PN}_{\text{susp}}$ (‰)	TRN ($\mu\text{mol L}^{-1}$)	$\delta^{15}\text{N-TRN}$ (‰)	TC ($\mu\text{gr L}^{-1}$)	$\delta^{13}\text{C-TOC}$
Her03	29.00	33.67	26.03					2.98			
Her03	29.00	33.67	26.47			0.31	0.45	2.46			
Her03	29.00	33.67	66.20					2.27			
Her03	29.00	33.67	105.21					2.50			
Her03	29.00	33.67	205.17			0.32	0.87	2.35			
Her03	29.00	33.67	225.15					2.07			
Her03	29.00	33.67	253.95	0.1	5.24			2.21			
Her03	29.00	33.67	504.86	1.43	5.74			0.51	3.70		
Her03	29.00	33.67	1003.40	2.24		0.11	6.19	0.78	5.00	0.78	-23.84
Her03	29.00	33.67	1503.02	2.35				0.00	1.10		
Her03	29.00	33.67	1972.83	2.26				1.00	2.20		
Her03	29.00	33.67	2958.08	2.19				1.58	9.10		
Her03	29.00	33.67	3024.26	2.17		0.12	7.82	0.97	10.20	0.71	-25.66
Her03_MUC	29.00	33.67	3090	2.29				0.86	7.30		
Rho02	27.70	35.62	5.00			0.46	1.04			1.29	-21.19
Rho02	27.70	35.62	22.81					1.64			
Rho02	27.70	35.62	52.10			0.53	1.11	1.88		1.70	-23.55
Rho02	27.70	35.62	85.44					1.55			
Rho02	27.70	35.62	102.23					1.80			
Rho02	27.70	35.62	180.54					1.78			
Rho02	27.70	35.62	201.58			0.46	1.62	1.84			
Rho02	27.70	35.62	201.59					1.87			
Rho02	27.70	35.62	499.92	2.18	5.64			0.30		1.24	-23.79
Rho02	27.70	35.62	999.08	2.94		0.11	7.26	0.10	6.20	0.71	-24.04
Rho02	27.70	35.62	1284.98	2.22		0.14	7.68	0.02	9.90	1.00	-24.81
Rho02_MUC	27.70	35.62	1305	2.82				1.10	7.20		
Sk01	23.80	39.56	1.00								
Sk01	23.80	39.56	6.63			0.53	2.13	3.62			
Sk01	23.80	39.56	21.63					3.73			

Table C.3. continued

Station	Lon (°E)	Lat (°N)	Depth (m)	$\delta^{15}\text{N-NO}_3$ (‰)	$\delta^{18}\text{O-NO}_3$ (‰)	PN suspended ($\mu\text{mol L}^{-1}$)	$\delta^{15}\text{N-PN}_{\text{susp}}$ (‰)	TRN ($\mu\text{mol L}^{-1}$)	$\delta^{15}\text{N-TRN}$ (‰)	TC ($\mu\text{gr L}^{-1}$)	$\delta^{13}\text{C-TOC}$
Sk01	23.80	39.56	44.75	5.9		0.56	1.72	3.45	-0.60		
Sk01	23.80	39.56	52.54	2.2				3.59			
Sk01	23.80	39.56	81.12	1.84	7.67			3.80	2.20		
Sk01	23.80	39.56	100.45	1.82	4.27			3.14	2.20		
Sk01	23.80	39.56	201.24	1.56	2.74			3.16	2.90		
Sk01	23.80	39.56	351.65	2.47	2.74			3.34	4.00		
Sk01	23.80	39.56	501.70	2.17		0.23	7.71	3.16	2.50		
Sk01	23.80	39.56	1001.34	2.38		0.15	7.83	3.99	4.50		
Sk01	23.80	39.56	1247.40	2.34		0.13	8.28	2.74	2.10		
Sk01_MUC	23.80	39.56	1264	2.18				4.28	4.10		

Curriculum Vitae

Paraskevi Mara

Diploma in Biology, Biology Dept. University of Crete, Greece

Born: 20.10. 1976 in Athens, Greece
Nationality: Greek
Home address: Geronymaki 33, 71306 Heraklion Crete, Greece

Education

Since

January 2006 Ph.D. student, Institut für Biogeochemie und Meereschemie, Universität Hamburg.
Thesis subject: “*The Nitrogen Cycle of the Eastern Mediterranean Sea from a Stable Isotope Perspective*”.

October 2002-July 2005 M.Sc in Natural Environmental Sciences, Chemistry Dept. University of Crete, Greece.
M.Sc.-Thesis: “*Influence of phytoplankton taxonomic profile in the distribution of total and dissolved DMSx compounds in the North Aegean Sea (Eastern Mediterranean)*”.

2001 Socrates Erasmus Student (spring semester) in *Environmental Engineering* at “Aalborg Universitet”, Aalborg, Denmark,

List of Publications:

Isari, S., Psarra, S., Pitta, P., Mara, P., Tomprou, O.M., et al., (2006), Differential patterns of mesozooplankters' distribution in relation to physical and biological variables of the northeastern Aegean Sea (Eastern Mediterranean), *Marine Biology*, **151**: 1559-1569, DOI 10.1007/s00227-006-0542-7.

Mara, P., Mihalopoulos, N., Gogou, A., Daehnke, K., Schlarbaum, T., Emeis, K-C., Krom, M., (2009), Isotopic composition of nitrate in wet and dry atmospheric deposition on Crete in the eastern Mediterranean Sea, *Global Biogeochemical Cycles* **23**: GB4002 11pp.doi:10.1029/2008GB003395.

Fragoulis, C., Psarra, S., Zervakis, S., Meador, T., Mara, P., et al., (2010), Connecting export fluxes to plankton food-web efficiency in the Black Sea waters inflowing into the Mediterranean Sea, *Journal of Plankton Research*, **32**(8): 1203-1216, doi: 10.1093/plankt/fbq010.

Emeis, K-C., Mara, P., Schlarbaum, T., Moebius, J., Daehnke, K., Struck, U., Mihalopoulos, N., Krom, M. (2010), Isotope ratios of nitrate, dissolved reduced and particulate nitrogen in the Eastern Mediterranean Sea trace external N-inputs and internal N-cycling, *Journal of Geophysical Research*, **115**: GB04041, doi:10.1029/2009JG001214.

Gogou A., Mara, P., Stavrakakis S., Krassakopoulou E., Lykousis V., Seasonal variations of $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}$ in settling particles from the open Eastern Mediterranean Sea (NESTOR site): a 4 year experiment (*in preparation*).

....μή πάντες απόστολοι; μή πάντες προφήται; μή πάντες διδάσκαλοι; μή πάντες δυνάμεις; μή πάντες χαρίσματα ἔχουσιν ἰαμάτων; μή πάντες γλώσσαις λαλοῦσι; μή πάντες διερμηνεύουσι; Ἐὰν ταῖς γλώσσαις τῶν ἀνθρώπων λαλῶ καὶ τῶν ἀγγέλων, ἀγάπην δὲ μὴ ἔχω, γέγονα χαλκὸς ἤχῳ ἢ κύμβαλον ἀλαλάζον...

Ἡ ἀγάπη μακροθυμεῖ, χρηστεύεται, ἡ ἀγάπη οὐ ζηλοῖ, ἡ ἀγάπη οὐ περπερεύεται, οὐ φυσιοῦται, οὐκ ἀσχημονεῖ, οὐ ζητεῖ τὰ ἑαυτῆς, οὐ παροξύνεται, οὐ λογίζεται τὸ κακόν, οὐ χαίρει τῇ ἀδικίᾳ, συγχαίρει δὲ τῇ ἀληθείᾳ· πάντα στέγει, πάντα ἐλπίζει, πάντα ὑπομένει.

-πρὸς Κορινθίους (ιβ´ 27 - ιγ´ 13)-

To my parents

&

*To Professor Tasso Eleftheriou and
his wife Margaret, for being always there for me*