Iron speciation was studied in wet and dry deposition samples collected at two locations on the island of Crete (Greece), in the Levantine Basin, Eastern Mediterranean, from November 2004 to February 2007. Iron solubility ranged from 27.2% for pH between 4 and 5 (polluted rainwater) to 0.5% for pH close to 8 (Sahara dust episodes), indicating that Fe solubility, and therefore Fe bioavailability to ecosystems, is enhanced in the presence of acidic species.

During the studied period, Dissolved Reactive Iron (DSRFe) levels deposited in the Eastern Mediterranean Sea were sufficient to account for the dissolved iron levels in seawater reported by Statham and Hart [Statham, P.J., Hart, V., 2005. Dissolved iron in the Cretan Sea (Mediterranean), Limnology Oceanography, 118–124.]. Therefore dissolved iron in the Mediterranean Sea could be exclusively attributed to atmospheric deposition. The biogeochemical implications of atmospheric dissolved iron on phytoplankton growth and nitrogen fixation were also investigated. During summer and autumn less than 5% of the deposited dissolved Fe is required for phytoplankton growth (i.e., when water stratification is at its maximum). The calculated nitrogen fixation potential induced by the measured deposition dissolved iron, was found to be at least 1.5 to 3 times smaller than the atmospheric nitrogen deposition, indicating the significant role of atmospheric deposition in the biogeochemical N cycle in the Mediterranean.

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Despite its potential role, the majority of studies on the role of the atmosphere as a source of iron in the Mediterranean have been performed in the western basin (Bonnet and Guieu, 2004, 2006; Guieu et al., 2002a,b; 2005). For the eastern basin there is only one study (Özsoy and Saydam, 2001), examining the role of wet deposition on the iron cycle. Wet deposition is limited to the winter months and dry deposition is the main mechanism of atmospheric input during summer and autumn (Markaki et al., 2003; Kouvarakis et al., 2002a,b; 2005). For the eastern basin there is only one study (Özsoy and Saydam, 2001), examining the role of wet deposition on seawater productivity in the Mediterranean will be discussed.

2. Experimental

2.1. Sampling site

Rainwater and dry deposition samples were collected on the island of Crete (Greece), located at a central position in the Mediterranean Basin, relatively far from Saharan and anthropogenic emissions. Consequently, the data from this site could be considered representative of the open Eastern Mediterranean Sea.

Apart from the main sampling site, which was situated at Finokalia (35°20′N, 25°40′E), a coastal site in northern Crete, there was a secondary station at the University of Crete, 6 km south of Heraklion (35°20′N, 25°07′E) to examine the spatial variability in Fe concentration detected in wet deposition. Characterization of the sites and the prevailing meteorology can be found in Arsene et al. (2007) (Fig. 1).

2.2. Sampling and analytical techniques

Rainwater was collected at both locations, on an event basis, using wet-only collectors (Van Essen) with a lid activated by the rain sensor. Since iron is biologically labile and can be photo reduced, samples were immediately filtered and frozen at the cessation of the event (see below).

At Finokalia station, bulk deposition samples have been collected in parallel to the wet deposition samples. Bulk deposition was estimated based on the collection of particles on a flat surface covered by multiple layers of glass beads which can trap larger particles, thus avoiding resuspension. Dry deposition refers to bulk samples not affected by wet deposition. The glass beads were positioned on a funnel installed 3 m above the ground as described by Kouvarakis et al. (2001). The glass beads system was exposed to the atmosphere for 1 to 2 weeks at a time. After which the system was washed with ultrapure water (300 ml). More details on sample collection can be found in Kouvarakis et al. (2001).

Wet and bulk/dry deposition samples have been filtered immediately after collection, through a pre-weighed 0.45 μm cellulose filter and the pH of the rinse solution was determined. Then the samples were stored in the freezer until analysis, which was performed within a month. The crustal mass was estimated by weighing the cellulose filters before and after the filtration.

Dissolved Reactive Iron (DSRFe: Fe(II) and Fe(III)) was determined spectrometrically using the Ferrozine colometric method developed by Stookey (1970). Fe(II) was quantified using the same procedure without any addition of hydroxylamine hydrochloride (reducing reagent), while Fe(III) was calculated indirectly as the difference between DSRFe and Fe(II). The absorbance was measured at 562 nm using a 5 cm cell. The detection limit was 0.010 μM with a corresponding precision of 4% RSD at typical rainwater concentrations. It should be noted that the detection limit was estimated as the mean of the blank sample plus three times the standard deviation obtained on the blank value. To check for possible interferences from matrix, standard addition tests were performed. The recovery was about 98.3% for both DSRFe and Fe(II) (n = 6; both polluted and Sahara-influenced rainwater samples).

Particulate Iron (PFe) was also determined, after acid digestion with HNO3, using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Iron recovery obtained using three certified marine sediments reference materials (MESS-3, GBW 07313 and BCSS-1, about 20 mg of each reference material) were 91.2 ± 3.4%, 94.2 ± 2.3% and 91.5 ± 0.2% respectively. Finally Total Iron (TFe) was calculated by adding both dissolved and particulate iron.

3. Results

3.1. Iron speciation

Due to the oxidizing environment in rain water samples, Fe(III) has been assumed to be the dominant species present in atmospheric samples (Moore et al., 1984, Zhuang et al., 1990). However the present study reveals that a significant fraction of DSRFe was in the form of Fe(II). This trend has been observed also in other studies (Behra and Sigg, 1990, Pehkonen et al., 1992; Zhuang et al., 1995; Siefert et al., 1998; Willey et al., 2000; Özsoy and Saydam, 2001). More specifically Fe(II) accounts for on average 82 ± 49% (median value = 78%, slope = 0.74, R² = 0.91) and 74 ± 27% (median = 73%, slope = 0.80, R² = 0.97) of the dissolved reactive iron in rainwater samples (n = 125) collected at Heraklion and Finokalia respectively, while the
percentage in bulk deposition at Finokalia (n = 61) was 73 ± 23% (median = 71%, slope = 0.75, R² = 0.90) (Fig. 2).

Although Fe(II) undergoes rapid transformation when it enters the surface seawater, it is clear that atmospheric input by both wet and dry deposition is a very important direct source of soluble Fe(II) in the surface seawater.

3.2. Iron atmospheric fluxes

3.2.1. Wet deposition

During the sampling period (November 2004–February 2007), 76 and 49 rainwater samples were collected at the two sampling sites Heraklion and Finokalia, respectively. The monthly volume weighted mean (VWM) of various Fe species in wet deposition samples from both stations are presented in Fig. 3a,b. The levels of Fe(II), Fe(III) and Total Fe observed in this work (average of 0.09 μM, 0.27 μM and 15.87 μM, respectively) compare very well with those reported by Ozsoy and Saydam (2001) in their study conducted at Erdemli (Turkey) (average values of 0.03 μM, 0.11 μM and 24.31 μM, respectively).

To examine the factors controlling total and dissolved iron concentrations in wet deposition, back trajectories were calculated for each rainwater sample using the HYPLIT 4 model (Hybrid Single Particle Langrangian Integrated Trajectory) (http://www.arl.noaa.gov/ready/hyplit4.html). On the basis of air mass backtrajectory analysis, our data have been classified into 4 categories corresponding to the 4 main wind sectors in the Eastern Mediterranean (N/NW; E/NE; W; S/SW/SE). Table 1 reports the DSRFe/TFe ratio as a function of the air mass origin and the variation of rainwater pH. Iron concentrations associated with Southern derived air masses (i.e. Saharan) were higher (by up to 10 times) than those associated with air masses associated with dust events from the 14.1 mg for the Finokalia samples (see further discussion in Section 3.4).

Indeed our data set highlights the importance of one extreme Saharan dust event on 24 February 2006, which affected the annual Fe fluxes at both sampling sites for the year 2006. This event leads to higher mass input and consequently higher TFe. Such large dust amounts are associated with low DSRFe and thus reduce the dissolved iron annual fluxes. The specific event was more efficient at Finokalia adding 105.58 mg Fe m⁻² year⁻¹ to the TFe flux during Nov-Oct 06, in contrast to almost half this contribution (85.37 mg Fe m⁻²) measured at Heraklion station (55% and 62% of the total annual iron input, respectively). Soluble iron at Heraklion was found to be almost 2 times higher than observed at Finokalia during this specific period (Nov 05–Oct 06). The above observation can be explained, to some extent, by the 3 times lower dust content in Heraklion samples, mean value of 4.1 mg, compared to the 14.1 mg for the Finokalia samples (see further discussion in Section 3.4).

3.3. Origin of total and dissolved iron in precipitation

To understand the origin of iron in deposition samples, total iron mass has been compared with insoluble dust estimated by pre- and post-weighing of the filter. A significant correlation has been observed with a slope (TFe/insoluble dust mass) equal to 3.8 ± 0.6% (median = 4.0%, slope = 3.8, R² = 0.97) (n = 68, Fig. 5a). This value is in good agreement with the crustal iron content quoted in the literature (3.5%, Meschediz et al., 2005) and/or in western Mediterranean samples (4.3%, Guieu et al., 2002b).

In deposition samples dissolved iron was found to correlate significantly with dissolved aluminium with a (DSRFe/DSAl) ratio equal to 72 ± 50% (median = 81%, slope = 0.69, R² = 0.80) (n = 90, Fig. 5b). A similar ratio has been reported for earth’s crust, as well as for western Mediterranean dust samples (Guieu et al., 2002b) and demonstrates similar solubility for both elements in deposition samples in the Eastern Mediterranean.

3.4. Factors controlling the solubility of iron

The present section examines the behavior of the different forms of iron as a function of pH, as well as the solubility of Fe. Solubility is defined as the percentage of the dissolved iron concentration divided by the total (dissolved plus particulate) iron concentration (Baker et al., 2006).

Chemical, biotic and physical processes such as pH, presence of dissolved organic complexing ligands, particle size and concentration, bacteria, phytoplankton, and temperature, can influence the extent of metal dissolution (Chester et al., 1990, 1993; Lim et al., 1995; Bonnet and Guieu, 2004; Biscombe et al., 2004).

Fig. 6a,b reports on the variability of DSRFe as a function of pH, distinguishing between wet and dry deposition samples. DSRFe decreases with pH increase. A similar pattern is also valid for each of the soluble forms of Fe (Fe(II) and Fe(III) separately: not shown) for both wet and dry deposition samples, indicating a clear influence of pH on iron solubility. Indeed iron solubility (Fig. 6c,d) reaches a maximum value of 27.2% for pH between 4 and 5, characteristic of polluted rainfall (Lore-Pilot and Morelli, 1988) and a minimum value of 0.5% for pH close to 8, characteristic of Saharan-influenced rain (Mahowald et al., 2005). Iron solubility in wet and dry deposition samples was estimated to be 4% and 1.7%, respectively, similar to recent estimations of iron solubility in rain water and aerosol samples, respectively (Stevens and Spokes, 2001). Thus the presence of acidic species enhances iron solubility and therefore the capacity to induce soluble, bioavailable iron to the marine ecosystem.

On the other hand TFe shows an opposite trend compared to DSRFe, as it clearly increases as pH increases (Fig. 6e,f). The above observation can be attributed to the presence of high dust loads, particularly when pH ranges from 7 to 8, characteristic of Saharan-influenced rain. Saharan dust is considered to be a rich source of iron, especially iron oxides such as hematite. In addition the presence of the higher dust load will influence the iron solubility as progressively higher particle concentrations would be present in solution. Decreased Fe solubility with particle concentration in aqueous
solutions has been observed in our samples (Fig. 6g,h), but such behavior is not unexpected, given the opposite trend between total and dissolved iron and the increase of total iron with dust load (see Section 3.3).

4. Discussion—Biochemical implications for the Eastern Mediterranean

4.1. Role of atmospheric deposition in dissolved and total iron levels in the water column

Statham and Hart (2005) reported concentrations of dissolved iron in the water column of the Cretan sea in the Eastern Mediterranean during March and September.

The concentration of DSRFe in the water column \( C_x \) derived from atmospheric deposition of dissolved iron \( F_x \) can be estimated from the following equation:

\[ F_x = \frac{C_x \cdot H}{t_x}, \]

where \( H \): the water column depth and \( t_x \): the lifetime of dissolved Fe in the water.

Based on the dissolved atmospheric iron inputs in the Eastern Mediterranean of 5.94 to 12.25 mg Fe m\(^{-2}\) year\(^{-1}\) as deduced from this work, and taking into account an average mixed layer depth of 80 m and a lifetime of 1 year (Statham and Hart, 2005), the potential DSRFe concentration in surface seawater can be estimated from Eq. (1). The DSRFe thus calculated in seawater as a result of atmospheric input ranges from 1.33 to 2.74 nmol Fe L\(^{-1}\).

The above estimation is in good agreement with the values of 1.44 and 1.95 nmol L\(^{-1}\) in March and September respectively, reported for the Eastern Mediterranean, by Statham and Hart (2005). Even though the atmospheric dissolved iron is expected to be lower when it enters the sea, since a conversion to insoluble iron will occur, the estimation presented above indicates that the dissolved iron concentration in the water column of the Mediterranean could be exclusively attributed to atmospheric deposition. Note also that during the dry period the mean solubility of 1.5% estimated for this work during the dry period is in excellent agreement with the mean dissolution of 2% reported by Chen et al., 2007 to explain the dissolved iron levels in the Gulf of Aqaba, Red Sea.

The measured atmospheric deposition of total iron of 0.2 to 0.6 g Fe m\(^{-2}\) year\(^{-1}\) (average 0.4 g Fe m\(^{-2}\) year\(^{-1}\)) (Table 2) during 2005–2006 have been compared to sediment traps deployed in the Cretan Sea during a seven year survey (1999–2005; Markaki, 2007). The mean value of atmospheric iron deposition of 0.4 g Fe m\(^{-2}\) year\(^{-1}\) compares very well to the value of 0.5 g Fe m\(^{-2}\) year\(^{-1}\) derived from sediment trap deployment and confirms the significant role of atmospheric iron input.

### Table 1

Four main wind sectors responsible for air masses to Heraklion during the rainy period.

<table>
<thead>
<tr>
<th>Sector</th>
<th>Event %</th>
<th>Precipitation %</th>
<th>VWM DSRFe (μM)</th>
<th>VWM TFe (μM)</th>
<th>Average solubility</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-NW (n=33)</td>
<td>45.8</td>
<td>(39.6)</td>
<td>0.15</td>
<td>1.31</td>
<td>170 ± 8.7</td>
<td>5.2</td>
</tr>
<tr>
<td>E-NE (n=11)</td>
<td>15.3</td>
<td>(27.5)</td>
<td>0.23</td>
<td>1.25</td>
<td>242 ± 13.5</td>
<td>5.3</td>
</tr>
<tr>
<td>W (n=4)</td>
<td>5.6</td>
<td>(7.9)</td>
<td>0.27</td>
<td>0.84</td>
<td>29.8 ± 13.1</td>
<td>5.1</td>
</tr>
<tr>
<td>S-SW-SE (n=24)</td>
<td>33.3</td>
<td>(25.0)</td>
<td>0.17</td>
<td>9.61</td>
<td>4.7 ± 4.2</td>
<td>6.6</td>
</tr>
</tbody>
</table>

The numbers indicate for each wind sector (i) the percentage of air masses originating within each wind sector and associated with rain events, (ii) the percentage of precipitation within each sector, (iii) the per sector VWM (μM) of DSRFe and (iv) VWM (μM) of TFe, (v) the average solubility and (vi) the pH value.
4.2. Dissolved iron and phytoplankton growth

Atmospheric input of Fe can control phytoplankton growth in high nitrate low chlorophyll (HNLC) regions (Behrenfeld et al., 1996; Boyd et al., 2000). Fe can also be a rate-limiting nutrient to diazotrophic microorganisms and therefore may influence nitrogen fixation in oligotrophic areas, such as the Eastern Mediterranean (Falkowski, 1997; Gruber and Sarmiento, 1997). An estimation of the role of atmospheric input of dissolved Fe on marine phytoplankton (non-diazotrophic) development (FeR) can be obtained using the following equation:

$$\text{FeR} = \frac{N^{\text{atm}}}{(\text{Fe}/N)_{\text{phyto}}}$$  \hspace{1cm} (2)

where $N^{\text{atm}}$ is the atmospheric nitrogen deposition flux and $(\text{Fe}/N)_{\text{phyto}}$ is the cellular Fe:N ratio of non-diazotrophic phytoplankton, which equals to 86 μmol/mol (Baker et al., 2003).

During the dry period, summer and autumn, when the water column is stratified and the contribution of nutrients from deeper layers is reduced, the atmospheric influence on new production is maximized.

Table 2

<table>
<thead>
<tr>
<th></th>
<th>TFe (mg m$^{-2}$ year$^{-1}$)</th>
<th>DSRFe (mg m$^{-2}$ year$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rain Heraklion</td>
<td>Nov 04–Oct 05</td>
<td>111.06</td>
</tr>
<tr>
<td></td>
<td>Nov 05–Oct 06</td>
<td>138.17</td>
</tr>
<tr>
<td>Rain Finokalia</td>
<td>Nov 04–Oct 05</td>
<td>71.88</td>
</tr>
<tr>
<td></td>
<td>Nov 05–Oct 06</td>
<td>305.19</td>
</tr>
<tr>
<td>Dry Finokalia</td>
<td>May 05–Oct 05</td>
<td>131.50</td>
</tr>
<tr>
<td></td>
<td>May 06–Oct 06</td>
<td>256.05</td>
</tr>
</tbody>
</table>

Fig. 4. Temporal variability of monthly averaged Fe flux in wet (a) and dry deposition (b) samples collected at Finokalia during the sampling period November 2004–February 2007.

Fig. 5. Relation between (a) Total Fe and dust and (b) dissolved Fe and Al.
Considering the dissolved N and Fe aeolian deposition during the dry period of 30.0 mmol m$^{-2}$ (Markaki et al., 2003 and Markaki, 2007) and 58.2 μmol m$^{-2}$ (this work), respectively, our data indicate that the fraction of dissolved atmospheric Fe removed through N-stimulated growth ($\text{Fe}^{\text{R/Faero}}$) was less than 5%. This percentage confirms that dry atmospheric deposition, is a major source of Fe inputs to the Eastern Mediterranean, providing over 95% of iron in excess.
The dissolved Fe concentration was found to be sufficient for supporting phytoplankton growth in the Eastern Mediterranean Sea, thus it cannot be considered as a limiting factor for phytoplankton growth in the area.

4.3. Nitrogen fixation potential induced by dissolved iron

Fe can also be a rate-limiting nutrient to diazotrophic microorganisms as it controls the N2 fixation in the oligotrophic ocean and the growth of natural and cultured populations of *Trichodesmium* spp. (Paerl et al., 1994). Howard and Rees (1996) indicated that Fe is a critical nutrient co-factor for the nitrogenase enzyme. In general, there is indication that the aeolian deposition of Fe to the oceans may ultimately serve as a nutrient co-factor for the nitrogenase enzyme. In general, there is indication that the aeolian deposition of Fe to the oceans may ultimately control the rate of N2 fixation on regional and global scales (Michaels et al., 1996; Falkowski, 1997).

Diazotrophs and especially *Trichodesmium*, the most prominent planktonic marine nitrogen fixer, is present throughout the open waters of oligotrophic tropical and subtropical oceans (Capone et al., 1997). *Trichodesmium* spp. are capable of contemporaneously fixing N2 and CO2 at relatively high rates and are considered a major contributor to oceanic primary production of C and N cycling (Paerl et al., 1994). This cyanobacterium supplies up to half of new nitrogen in the Mediterranean (from 24 to 29%) to be calculated by the following equation:

\[
N_{\text{fix}} = (\text{Fe}^{\text{aero}} - \text{Fe}^{\text{R}}) \left( \frac{\text{Fe}}{\text{N}_{\text{fix}}} \right)_{\text{err}}^{-1}
\]

where Fe\text{\textsuperscript{aero}} is the iron atmospheric deposition flux, Fe\text{\textsuperscript{R}} is the quantity of Fe removed by non-diazotrophic production stimulated by N atmospheric input as discussed above and \( \left( \frac{\text{Fe}}{\text{N}_{\text{fix}}} \right)_{\text{err}} \) is the cellular Fe:N ratio of N fixing organisms, which varies between 2.8 and 4.9 mmol/mol (Baker et al., 2003; Berman-Frank et al., 2001).

Thus, for the dry period, the maximum potential for N2 fixation by *Trichodesmium* sp. ranges between 11.3 and 19.7 mmol N m\(^{-2}\) y\(^{-1}\), values significantly lower (by a factor of 1.5–3) to the observed atmospheric N deposition fluxes. These factors could be considered as lower limits as dissolution of iron could be decreased when it enters the sea.

Therefore N fixation induced by dissolved iron deposition is much lower compared to atmospheric deposition of reactive nitrogen. This result highlights the significant role of atmospheric deposition of nitrogen in the Eastern Mediterranean productivity.

5. Conclusion

This work reports the first complete data of atmospheric deposition of iron in the Eastern Mediterranean, covering a 2 year period. This data set confirms that atmospheric deposition provides a sufficient amount of iron, in both particulate and dissolved forms, to the seawater of the Eastern Mediterranean. Iron deposition is found to be of comparable importance in both wet and dry deposition modes.

The solubility of Fe and its dependence on pH will therefore potentially increase the bioavailable fraction of iron to an ecosystem, with the enhanced presence of acidic species. The observed iron solubility ranged from 27.2% for pH between 4 and 5 (polluted rainwater), to 0.5% for pH close to 8 (Sahara dust case). The crustal solubility ranged from 27.2% for pH between 4 and 5 (polluted rainwater), to 0.5% for pH close to 8 (Sahara dust case). The observed iron solubility ranges between 11.3 and 19.7 mmol N m\(^{-2}\) y\(^{-1}\), is 1.5 to 3 times smaller than the measured total atmospheric nitrogen deposition in the same area, indicating the significant role of atmospheric deposition in the biogeochemical N cycle in the Mediterranean.

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