



Iron solubility in crustal and anthropogenic aerosols: The Eastern Mediterranean as a case study

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ABSTRACT

We report seawater dissolution experiments for aerosol samples simultaneously collected (October 2007) across the Levantine Basin (LB, Eastern Mediterranean Sea), a marine system influenced by seasonal atmospheric inputs. Two distinct populations exhibited contrasting kinetic profiles; those representative of strong Saharan dust events which had variable iron release profiles with a maximum solubility of $0.94 \pm 1.48\%$ (1 s.d.) whereas those which had a relatively greater anthropogenic influence had consistent profiles (fast release, ≤ 2 h, of dissolved iron in seawater followed by removal) with a maximum solubility of $11.5 \pm 9.3\%$ (1 s.d.). First estimates of atmospheric fluxes of soluble iron are presented, ranging from $8.64 \pm 10.76 \text{ mg m}^{-2} \text{ y}^{-1}$ for the Northern LB to $6.48 \pm 7.78 \text{ mg m}^{-2} \text{ y}^{-1}$ for the Southern LB. Estimates of Fe fluxes to oceanic basins are important for constraining the global iron budget, and dust dissolution kinetic profiles provide information on the mechanisms involved during the release of aerosol Fe in seawater post atmospheric deposition.

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1. Introduction

Natural and anthropogenic dominated aerosol populations play an important role in many biogeochemical global processes and supply bioactive trace metals and nutrients to the ocean surface. In this context, iron (Fe) as an essential micronutrient for marine organisms has been the focus of many recent research studies. Iron has a significant impact on phytoplankton metabolism and hence on primary productivity (Falkowski et al., 1998), growth and species composition of marine phytoplankton communities (Boyd et al., 2000; Coale et al., 1996). The dominant external source of iron to the surface open ocean is from the atmosphere, by dry and wet deposition of Aeolian dust (Jickells and Spokes, 2001), originating mainly from the arid regions of the northern hemisphere, i.e. North Africa and Arabian Peninsula deserts (Jickells and Spokes, 2001; Pye, 1987).

The solubility of iron in seawater is poorly constrained and varies from $<1\%$ to $\sim 80\%$ (Aguilar-Islas et al., 2010 and references therein; Baker et al., 2006; Buck et al., 2006). Such variability is a result of environmental (i.e. aerosol composition, seawater dissolved organic material composition and biological activity) and experimental (i.e.

temperature, particle concentration, leach medium composition, Fe detection system, equilibration time) factors. Generally a single equilibration time is applied: e.g. instantaneous (e.g. Buck et al., 2010; Sedwick et al., 2007), 1 h (e.g. Chester et al., 1993; Guerzoni et al., 1999a) or one week (e.g. Bonnet and Guieu, 2004). In this study we investigate the kinetics of dissolution of aerosol iron in seawater over three time periods (2, 4 and 8 h). It is crucial when carrying out Fe solubility studies to apply a well defined (constant temperature, stirring rate, dark) and consistent experimental approach under realistic environmental conditions.

The Mediterranean Sea has one of the largest fluxes of mineral dust due to its close proximity to the Saharan desert (Guerzoni et al., 1999b) and is one of the most oligotrophic seas in the world (Krom et al., 1991), with the eastern basin being ultra-oligotrophic (Herut et al., 2005; Kress and Herut, 2001) owing to the lack of significant upwelling of the nutrient rich deep-water mass (Azov, 1991). The Mediterranean coastline has large population centers, with two contrasting regions: northern (NB) and southern (SB) boundaries (Chester et al., 1996; Kubilay and Saydam, 1995). The NB is surrounded by industrialized nations (Europe), which provide a background of relatively lower crustal/higher anthropic influenced aerosols to the Mediterranean marine aerosol, leading to the enrichment in some trace metals such as Pb, Cd and Cu (Chester et al., 1996; Erel et al., 2006; Teutsch et al., 2001). In contrast, the SB is

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characterized by arid and desert regions, including the Sahara, Saudi Arabian and Syrian deserts, and is therefore a source of crustal derived aerosols rich in Al, Fe and Mn minerals transported during seasonal episodic pulses (Chester et al., 1996). Intense dust events occur during the transitional period (March–May, October) over the Eastern Mediterranean (Koçak et al., 2005; Kubilay et al., 2000).

A large variation in solubility is expected as no one aerosol population is either completely “crustal” or “anthropogenic” in nature, but is in reality a mixture of varying proportions of these two “end-member” populations (e.g. Baker et al., 2006; Sedwick et al., 2007). The observed difference between the populations is supported by observations in the literature (Bonnet and Guieu, 2004; Baker et al., 2006; Sedwick et al., 2007; Mendez et al., 2010). The degree to which trace metals present in these populations are enriched or depleted, relative to a specific source, can be assessed by the enrichment factor (EF, Rahn et al., 1979). Iron solid state speciation (phases that iron is associated with) has been suggested as an important factor impacting on its solubility (Shi et al., 2009). Anthropogenically influenced aerosols tend to have a proportionally higher iron content in the “exchangeable” and “oxide/carbonate” phases compared with those aerosol populations having a relatively greater contribution of crustal material (Chester et al., 1989; Koçak et al., 2007) and exhibit a higher solubility of iron (Aguilar-Islas et al., 2010 and references therein; Baker et al., 2006; Mendez et al., 2010; Sedwick et al., 2005). Moreover, the impact of mineralogy on the solubility of iron from anthropogenically influenced and crustally derived aerosols has recently been highlighted. Schroth et al. (2009) demonstrated the importance of mineralogy on the release of iron from particulate materials with decreasing cumulative solubilities in iron from oil fly ash (~79%) to arid soil (~0.29%) while Journet et al. (2008) observed decreasing solubilities of iron (5.25% to 0.003%) from crustally dominated aerosols containing increasing iron content (0.13 to 77.4% w/w), present in iron (hydro-) oxide, clay and feldspar.

In terms of global marine systems, the Mediterranean Sea is an ideal natural laboratory to characterize the aeolian inputs of iron and their impacts on its water. Aeolian inputs of iron are amongst the highest in the world and are important for primary production (Bonnet et al., 2005; Herut et al., 2005). The Mediterranean Sea receives aeolian fluxes of iron along with other trace metals such as Al, Mn, Zn and Pb, and nutrients, N and P. The impact of these inputs is not negligible (e.g. Bonnet et al., 2005; Markaki et al., 2003). The eastern Mediterranean Sea is reported to be P limited (Krom et al., 1991) and some studies (Özsoy and Saydam, 2001; Statham and Hart, 2005) indicated that this region is unlikely to be Fe limited. However, iron biogeochemical cycling impacts on the P cycle in this part of the Mediterranean Sea (Krom et al., 1991). Eastern Mediterranean dust contains a high proportion of Fe oxides and poorly crystalline clay minerals; both having a high affinity for dissolved PO_4^{3-} . Krom et al. (1991) suggested that the deposition of dust may scavenge PO_4^{3-} . More recently, some workers, e.g. Bonnet and Guieu (2006), reported that the supply of soluble Fe is important to the Mediterranean as it has been shown that post spring blooms, dissolved Fe concentrations in the surface layers may become depleted. Atmospheric inputs are therefore an important supply of nutrients to the mixed layer and it has been suggested that these inputs have a fertilizing impact (Bonnet et al., 2005). Moreover, estimates of Fe fluxes/inputs to an oceanic basin are important numbers for constraining the global iron budget.

Owing to regular intense seasonal dust events, the Eastern Mediterranean Sea is an ideal region to investigate the Fe seawater dissolution process associated with aerosol populations being influenced to different degrees by contrasting sources (anthropic and crustal). Therefore, given the potential impact of atmospheric inputs in the marine environment, it is crucial to define the availability of nutrients, post deposition, to the sea surface. Hence the aim of this study was to determine the soluble fraction of Fe in seawater, over time, from contrasting Eastern Mediterranean aerosol

populations, naturally exposed to atmospheric processing, highlighting for the mixed aerosol populations (i) the relative potential changes in the solubility of Fe in seawater and (ii) the kinetics of the dissolution process under carefully controlled experimental conditions. Combined with literature data for spatial aerosol Fe concentrations across the Levantine Basin and aerosol Fe settling velocities (Koçak et al., 2005), a first estimate of the atmospheric fluxes of soluble Fe to the Levantine Basin is presented.

2. Methods

2.1. Aerosol collection

Daily high volume aerosol (flow rate around $1 \text{ m}^3 \text{ min}^{-1}$) samples at different sites were collected simultaneously over 24 h periods, during October 2007 until the 1st of November (October is one of the transition months when Saharan dust events are most likely to occur) (Koçak et al., 2004). Samples were collected from three rural coastal locations (i) Erdemli (Er), Turkey ($36^\circ 33' 54'' \text{ N}$ and $34^\circ 15' 18'' \text{ E}$), (ii) Heraklion (He), Crete, Greece ($35^\circ 18' 29'' \text{ N}$ and $25^\circ 04' 48'' \text{ E}$) and (iii) Tel-Shikmona (TS), Israel ($32^\circ 49' 34'' \text{ N}$ and $34^\circ 57' 24'' \text{ E}$), (Fig. 1). Aerosol filter samples were collected from (i) the top of a designed sampling tower in Erdemli (22 m high located, ~20 m from the shore) (ii) the roof of the University of Crete, Heraklion (Voutes campus; on the north coast of Crete, 20 m above ground and 96 m above sea level, 3.3 km from the shore) and (iii) the roof of the National Institute of Oceanography in Tel-Shikmona (located partly in the inter-tidal zone; 22 m above sea level). For more details of the sampling sites at Erdemli and Tel-Shikmona see Koçak et al. (2004) and Herut et al. (2001), for more details of the sampling site at Heraklion see Theodosi et al. (2010).

Aerosol samples were collected on acid washed Whatman 41 fibrous cellulose acetate filters, following a cleaning protocol modified from Baker et al. (2006). Specially designed holding trays were made “in house” from high density polyethylene onto which acid washed polypropylene meshes were glued with epoxy resin. Operational blanks were set aside for each batch of acid washed filters during the sampling campaign. These were achieved by placing the filter onto the anodized aluminum filter holder of the sampler using acid-washed tweezers, the secured frame was then put back and the sampler closed for about 1 min (high volume pump switched off). The filter was then removed, folded and placed in a re-sealable bag. A total of 73 aerosol samples were collected ($n = 24 \text{ Er}$; $n = 23 \text{ TS}$; $n = 26 \text{ He}$) along with 11 operational blanks. Once collected, samples were stored frozen to minimize any potential decrease in the solubility of Fe in seawater (Buck et al., 2006). All manipulations of filters were carried out in a class-100 laminar flow cabinet to minimize contamination.

2.2. Seawater matrix

A 20 L sample of open ocean seawater was collected from the Canary Basin in 2006 (20.58° N , 29.22° W , $S = 33.2$) from a towed fish and was filtered in-line using $0.2 \mu\text{m}$ pore size cartridge filters (Sartobran™, Sartorius Stedim, Biotech.) and stored unacidified in a 20 L acid washed carboy in the dark for 2 y before use. The dissolved iron (dFe) concentration was $2.38 \pm 0.23 \text{ nM}$ while the concentration of total Fe complexing ligands was $2.78 \pm 0.68 \text{ nM}$. The measurements of dissolved Fe and total Fe complexing ligands were made on aged seawater (18 months) prior to the dissolution experiments which were carried out over a short period of time (2–3 weeks) to ensure a constant complexing ligand capacity. The complexing capacity is in the reported range (0.8 to 4.8 nM) of the Western Mediterranean Sea (Wagener et al., 2008) while the concentration of dFe was in the same range (0.23 to >5 nM in the top 26 m) as the concentrations reported by Statham and Hart (2005) in the Cretan Sea.

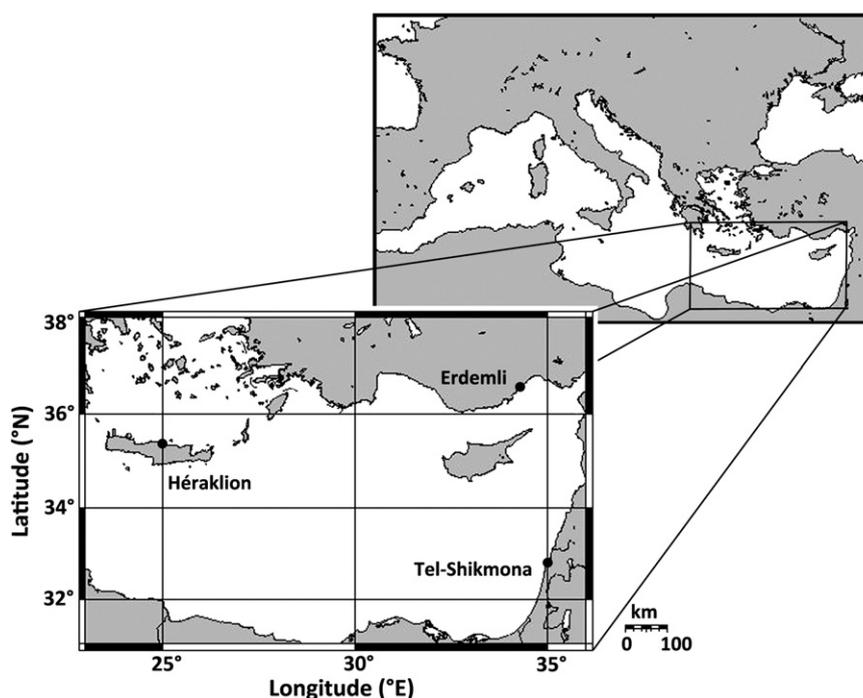


Fig. 1. Location of the three sampling sites across the Levantine Basin: Heraklion (35°18'29" N and 25°04'48" E), Erdemli (36°33'54" N and 34°15'18" E) and Tel-Shikmona (32°49'34" N and 34°57'24" E).

2.3. Sample processing and analysis

All samples and blanks (both procedural and operational) underwent total acid digestion in parallel with different reference materials (MESS-3, NIST 1648, Estuarine Sediment 1646a, Coal Fly Ash 1633a). A HF/aqua regia (1:1) mixture was applied on samples from Tel-Shikmona and Heraklion (Herut et al., 2001) while a HF/HNO₃ (18:5) mixture was used for samples from Erdemli (Biscombe, 2004), both digestion procedures being already established in the respective laboratories. Total digests of samples and blank filters along with reagent blanks, in 1% nitric acid, were analyzed for Fe and Al along with a range of minor and major elements, using a Varian 725 ES ICP-OES instrument and an X Series 2 Thermo Scientific ICP-MS instrument. The percentage recoveries for both elements, for the two techniques over the three sites, were >85% for the HF/HNO₃ and >95% for the HF/aqua regia digestion approaches, respectively. Operational blank contributions were calculated using the operational blanks and the mean digest concentrations. Operational blank contributions to the overall collection of samples from the three sites for both elements were always <10% and in some cases <1%. The dissolved iron concentration (dFe) was determined by flow injection with chemiluminescence detection (FI-CL) using an on-line 8-hydroxyquinoline preconcentration micro-column (Bowie et al., 1998). The limit of detection was 0.041 ± 0.034 nM and the precision of each measurement (n=4) was <10% *rsd*. The accuracy of the system was assessed with a standard reference seawater (NASS-4, National Research Council, $1.88 \text{ nM} \pm 0.28 \text{ nM}$) and an "in-house" reference material (0.85 ± 0.02 nM, collected from the Canary Basin in 2002 at 21.8° N, 25.4°) and good agreement (95% confidence) was found: 1.94 ± 0.16 nM (NASS-4) and 0.85 ± 0.07 nM ("in-house" reference material). Total Fe complexing ligand concentration in the seawater was measured using competitive ligand exchange-adsorptive cathodic stripping voltammetry (CLE-ACSV, Croot and Johansson, 2000) and the ligand 2-(2-thiazolylazo)-p-cresol (TAC, 10^{-5} M) by Dr M. Rijkenberg (NIOZ, Netherlands).

2.4. Aerosol back trajectories

Elemental concentrations and three-day mass back trajectory analyses were carried out in parallel for each sample to categorize aerosol source. Back trajectories arriving at Erdemli and Tel-Shikmona have historically been divided into up to six sectors (Koçak et al., 2004, 2005). However for the current study, a simpler categorization was adopted using only two sectors (i) northern air masses (relatively lower crustal to anthropogenic contributions) and (ii) southern air masses (crustal dust influence), due to the smaller number of samples (73) compared with Koçak et al. (2004, 2005) who used up to 621 samples. Three-day back trajectories arriving at 1000, 2000 and 4000 m levels were calculated for each sample commencing at 10.00 UTC using the HYSPLIT (HYBRID Single-Particle Lagrangian Integrated Trajectory) model from Air Resources Laboratory. Selected aerosol samples representative of the two contrasting air mass sectors were chosen to undergo dissolution experiments for the determination of Fe solubility from aerosol in seawater.

2.5. Procedure for dissolution experiments

The 2 L incubation vessel for the dissolution experiments was pre-cleaned daily in a 6 M hydrochloric acid bath while the magnetic stirrer was cleaned in a 2 M nitric acid bath; both were soaked for at least 24 h. Between each bath, labware was rinsed thoroughly with ultra high purity (UHP) de-ionized water ($\geq 18.2 \text{ M}\Omega \text{ cm}^{-1}$). The PTFE membranes (0.2 μm pore size, Pall Corporation) used to filter sub-samples were activated by soaking in high purity methanol (5 mL, Romil) for 5 min, followed by a rinse with 10 mL high purity HCl (1 M) and a 20 mL UHP de-ionized water rinse. Once activated, the filters were stored wet in re-sealable bags to avoid drying out. For each dissolution experiment, flow lines, fittings, activated PTFE filter and connectors of the autosampler were cleaned with 1 M HCl and 4 volumes of UHP de-ionized water prior to use.

A 4 cm² filter section was taken from each of the selected aerosol samples to ensure that the predicted release of Fe into the seawater would be in the low nM range, hence ensuring that the lowest practical particle “concentration” was used, while allowing reliable analytical detection. The calculated particle concentrations for both populations were based on the total concentration of iron from the digests, assuming 3.5% of iron by mass. The anthropogenic aerosol particle concentrations in seawater ranged between 0.1 and 0.38 mg L⁻¹ (mean 0.26 ± 0.13 mg L⁻¹) while crustal aerosol particle concentrations ranged between 1.1 and 3.7 mg L⁻¹ (mean 2.1 ± 1.2 mg L⁻¹) in the 2 L incubation vessel. These low aerosol concentrations were chosen to minimize the impact of the “particle concentration effect” on the observed iron solubility in seawater (e.g. Bonnet and Guieu, 2004; Spokes and Jickells, 1996). Aerosol filters were cut to size using an acid washed 2 cm² plastic template and ceramic scissors.

Each 4 cm² filter portion was then carefully placed in a 2 L FEP incubation vessel containing 0.5 L of seawater. During each dissolution study, seawater sub-samples (10 mL) were extracted from the incubation vessel at 2 h, 4 h and 8 h, the sampling strategy being adopted from knowledge derived from previous dissolution studies for both crustal and anthropogenic dominated end-member aerosol materials (Séguret, 2008). Sub-samples were filtered in-line (0.2 µm pore size) and collected using an automated sampler (Séguret et al., 2008), controlled by virtual instrument (VI) software (Ruthern Instruments) written in LabVIEW version 7.1 (National Instruments Corp. Ltd.), to minimize handling and the risk of contamination. Each dissolution study was conducted within strictly controlled experimental conditions, i.e. 25 ± 0.2 °C (typical seawater temperature in October in the first 10 m layer, Gertman and Hecht, 2002), in the dark (removing the impact of photochemical effects) at a low constant stirring rate in 0.5 L of seawater. Sub-samples were then acidified to pH 2 (0.012 M HCl, SpA, Romil) and stored for 2 weeks before analysis. All manipulations of filters, dissolution set up and sub-samples were carried out in a class-100 laminar flow cabinet to minimize contamination.

Initial dissolution experiments included triplicate leaches of the operational blank filters from each sampling site to define the blank contributions of the filters and sample handling. The filter blank concentrations were determined, using FI-CL, by subtraction of the mean seawater iron concentration from the concentration of iron following an 8 h incubation with the filter present. The means and standard deviations of blank filters after an 8 h equilibration time with seawater were 0.14 ± 0.10 nM for TS (n = 36), 0.11 ± 0.23 nM for He (n = 12) and <0.02 nM for Er (n = 32). The data clearly indicated minimal contamination from the added filter portions to the seawater, no adsorption of dissolved iron in seawater onto the filter and minimal adsorption of Fe to the incubator container walls.

The potential adsorption of dissolved Fe onto the walls of the incubation vessel (as well as contamination from the vessel) was investigated by rinsing the incubation vessel and stirrer with 30 mL of 0.012 M HCl (pH = 2; SpA, Romil) prepared in UHP de-ionized water after each dissolution study. The effective decrease in dFe concentrations as a result of adsorption was calculated as:

$$(dFe)_{\text{adsorption}} = (dFe)_{\text{acidic leach}} / (2,000 / 30) \quad (1)$$

where dFe_{acidic leach} is the concentration in the 30 mL rinse of the wall, 2000 (mL) corresponds to the 2 L incubation vessel and 30 is the 30 mL rinse of the incubation vessel wall. The calculated effective decrease in dFe concentrations as a result of adsorption was 0.061 ± 0.053 nM (n = 13). The FEP bottles were therefore a good choice due to negligible adsorption of dFe onto the walls.

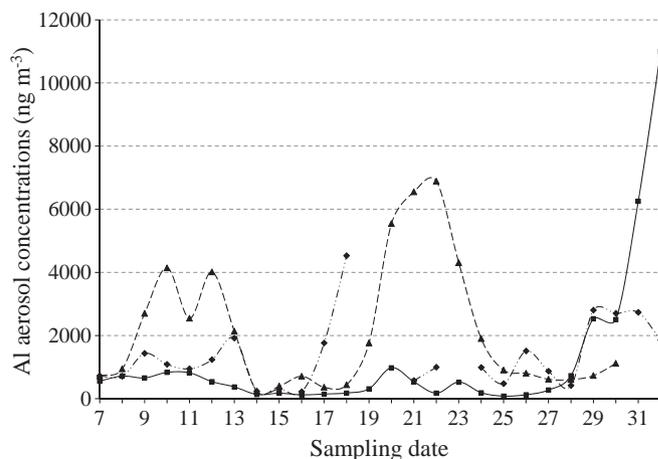


Fig. 2. Temporal variation of aluminum concentrations (ng m⁻³) for the three sites, Erdemli (triangle), Heraklion (square) and Tel-Shikmona (diamond).

The concentration of iron released, during dissolution studies, from the aerosols in seawater was converted to percent solubility using Eq. (2):

$$\% \text{Solubility} = (\text{amount of Fe released in seawater} \div \text{total Fe present in added aerosol}) \times 100. \quad (2)$$

3. Results and discussion

3.1. Selection of aerosol samples for dissolution studies

The temporal variation of total aerosol Al concentrations for the identification of Saharan dust events is presented in Fig. 2 and Table 1, while the temporal variation in the total aerosol Fe concentrations at each site is shown in Fig. 3.a–d as well as mass back trajectories of selected aerosol samples and their respective solubilities (see Section 3.2). For all sites the total aerosol iron had significant correlations with total aluminum (Rank–Spearman correlation coefficient $r > 0.96$). Similar significant correlations ($p < 0.05$) were observed with other elements having predominantly crustal sources

Table 1
Aluminum, iron, copper and lead concentrations (ng m⁻³), their respective enrichment factors and the crustal contributions from the crustally derived and anthropogenically influenced samples from the three sites. (–) non detectable.

| | Elemental concentration (ng m ⁻³) | | | | Enrichment factor | | | Crustal contribution (%) |
|---------------------|---|-------|------|------|-------------------|-------|-------|--------------------------|
| | Al | Fe | Cu | Pb | EF Fe | EF Cu | EF Pb | |
| Erdemli | | | | | | | | |
| 08-oct | 962 | 710 | 7.2 | 5.0 | 1.2 | 14 | 11.0 | 85.3 |
| 10-oct | 4,160 | 2,961 | 8.6 | 16.9 | 1.1 | 3.7 | 8.7 | 88.5 |
| 12-oct | 4,032 | 2,829 | 6.9 | 13.1 | 1.1 | 3.1 | 6.9 | 89.8 |
| 17-oct | 380 | 257 | 5.4 | 2.7 | 1.1 | 26 | 14.9 | 93.1 |
| 22-oct | 6,908 | 4,671 | 8.3 | 11.2 | 1.1 | 2.2 | 3.5 | 93.2 |
| 27-oct | 634 | 384 | 9.3 | 8.3 | 1.0 | 27 | 28.0 | 103.9 |
| Heraklion | | | | | | | | |
| 17-oct | 120 | 215 | 4.1 | 3.4 | 2.8 | 61.6 | 60.8 | 42.2 |
| 18-oct | 145 | 239 | 1.5 | 6.1 | 2.6 | 19.5 | 89.6 | 44.3 |
| 20-oct | 312 | 614 | 0.9 | 2.6 | 3.1 | 5.4 | 17.7 | 82.2 |
| 30-oct | 2505 | 1569 | 7.5 | 5.5 | 1.0 | 5.4 | 4.7 | 100.6 |
| 01-nov | 11,002 | 6170 | 9.4 | 2.8 | 0.9 | 1.6 | 0.5 | 112.3 |
| Tel-Shikmona | | | | | | | | |
| 18-oct | 4,441 | 3,262 | 13.1 | 5.5 | 1.1 | 5.4 | 2.6 | 85.8 |
| 28-oct | 331 | 332 | – | 2.1 | 1.6 | – | 13.3 | 62.8 |
| 29-oct | 2,717 | 1,674 | 1.3 | 1.4 | 1.0 | 0.9 | 1.1 | 102.3 |
| 01-nov | 1,817 | 1,074 | – | 1.6 | 0.9 | – | 1.9 | 106.6 |

such as Mn, Ti and Ca. High iron ($Fe > 700 \text{ ng m}^{-3}$) and aluminum ($Al > 1,000 \text{ ng m}^{-3}$) aerosol concentrations along with lower minor EF_{CRUST} calculated using element/Al ratios from Koçak (2006) revealed several dust events (in this case as defined by $Al > 1000 \text{ ng m}^{-3}$, Chester et al., 1990) over the three sites during October 2007 (Table 1). At Erdemli (Fig. 3.a), the initial dust event (9th–13th) was a result of higher altitude transport of dust from the North Eastern Saharan/middle east region while the second event (19th–24th) originated from the West, Central and Eastern Saharan desert. At Heraklion (Fig. 3.b), an intense event (29th–31st) developed as a

result of dust transport from the Eastern Saharan desert. At Tel Shikmona (Fig. 3.c), the first three dust events (9th–10th, 12th–13th, 17th–18th) were a result of dust transport from the Eastern Saharan desert (the initial two events coinciding with those observed at Erdemli). The last dust event (29th–31st) originated from the Central Saharan desert, similar to the large dust event that occurred at Heraklion during the same period. Low total iron concentrations for the three sites were observed as a result of their northern air mass origin (and hence a comparatively lower crustal dust contribution). Therefore, “crustal” derived (defined as high crustal Al, Fe and Mn

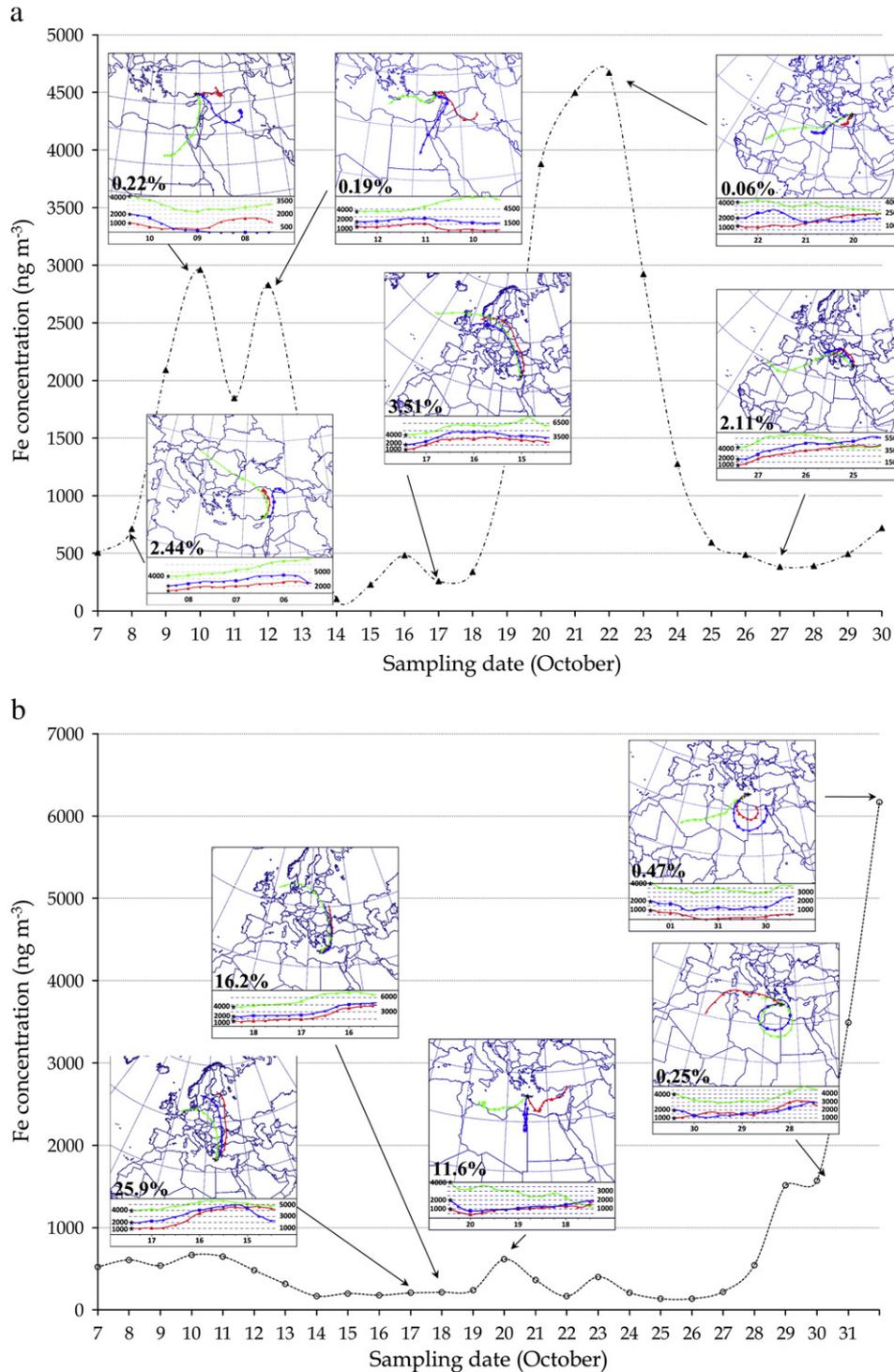


Fig. 3. Temporal variation of iron concentrations (ng m^{-3}) for the three sites along with maximum solubility (%), a) Erdemli, b) Heraklion, c) Tel-Shikmona, in October/November 2007.

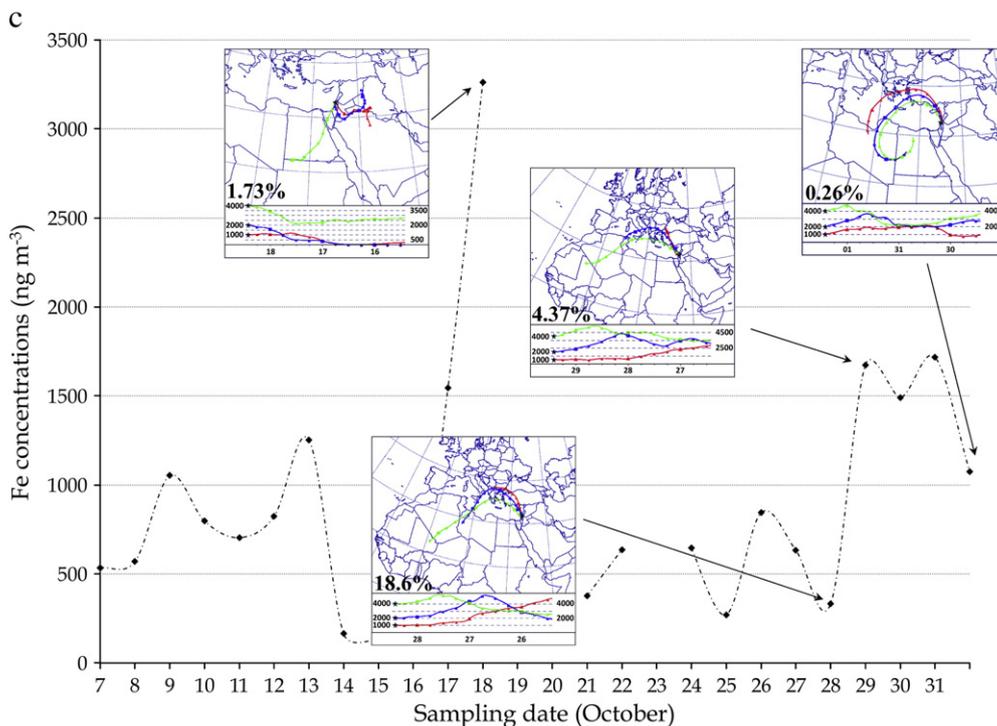


Fig. 3 (continued).

elemental concentrations and derived mainly from Saharan region) and “anthropogenically” influenced (defined as generally northerly derived aerosol populations characterized by an enrichment factor, $EF > 10$, such as for Pb and Cu) aerosol samples from the three sites were selected to undergo dissolution.

3.2. Kinetic dissolution profiles of the two aerosol populations

All anthropogenically influenced aerosols showed similar dissolution profiles (Fig. 4.a) with the maximum dFe concentration occurring after 2 h of contact with seawater, followed by a fast decrease. The absolute difference between the measured iron concentration released and the filter blank was significantly different (95% confidence level) for all aerosol samples according to the recommended method of the European Reference Material Commission (Linsinger, 2005). The data show that a short equilibration time (2 h) is most appropriate for determining the maximum solubility of anthropogenically influenced aerosols and agrees with the findings of other workers (Buck et al., 2006; Chen et al., 2006; Chester et al., 1993). The mean maximum solubility for these aerosols was $11.5 \pm 9.3\%$. The same type of profile has previously been reported for the urban end-member NIST 1648 (Séguret, 2008; Séguret et al., 2008). The decrease in solubility after 2 h may be a result of (i) re-adsorption onto the aerosol particles on the filter (not the filter itself as no adsorption was apparent while equilibrating the blank filter in seawater) and/or (ii) conversion of dissolved Fe to particulate species and/or organic complexes. A decrease in dFe concentrations in seawater over time has also been observed in batch experiments using aerosols from the Washington coast (Crecelius, 1980) and NIST 1648 (Bonnet and Guieu, 2004).

Depending upon the exposure time, dissolved seawater Fe concentrations may have become saturated for some of the anthropogenically influenced samples, leading to precipitation of oxy-hydroxides. This potential saturation for the anthropogenically influenced aerosols would result in an underestimation of the “total potential” soluble fraction of Fe associated with the aerosol material. The mean seawater concentrations of released dissolved Fe for each of

the equilibration periods (2, 4 and 8 h) were 11.5 ± 9.3 nM; 4.0 ± 3.5 nM; 2.9 ± 3.4 nM respectively (Table 2.a). After 8 h, four aerosol samples had dFe concentrations > 2.0 nM. This indicates either (i)

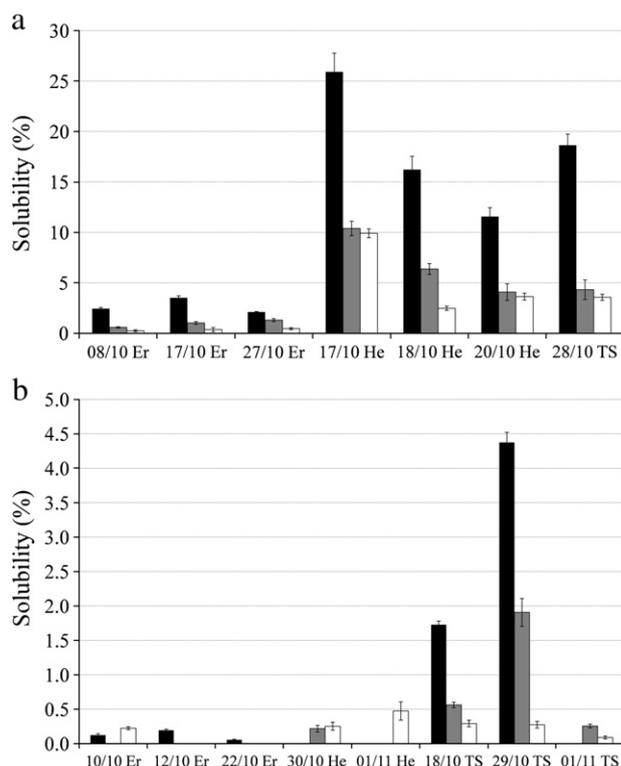


Fig. 4. Percent solubility of iron during dissolutions of a) anthropogenically influenced samples ($n = 8$) and b) crustally derived samples ($n = 7$) from the three sites over time (h). ER = Erdemli, HE = Heraklion, TS = Tel-Shikmona with the corresponding sampling dates (day/month) in 2007. Black bars = 2 h, gray bars = 4 h and white bars = 8 h. Error bars = ± 1 s.d.

Table 2.a

Solubility (%) and concentration (nM) of iron released from the anthropogenic influenced samples in seawater at the three sub-sample times, after subtraction of the filter blank. (–) non detectable released concentrations.

| Sub-samples | Solubility (%) | Concentration (nM) | Solubility (%) | Concentration (nM) | Solubility (%) | Concentration (nM) | |
|--------------|----------------|--------------------|----------------|--------------------|----------------|--------------------|--|
| Erdemli | | 08-oct | | 17-oct | | 27-oct | |
| 2 h | 2.44 ± 0.11 | 7.3 ± 0.32 | 3.51 ± 0.19 | 4.00 ± 0.22 | 2.11 ± 0.04 | 3.50 ± 0.07 | |
| 4 h | 0.57 ± 0.06 | 1.70 ± 0.19 | 1.02 ± 0.14 | 1.20 ± 0.16 | 1.30 ± 0.15 | 2.10 ± 0.24 | |
| 8 h | – | – | – | – | 0.45 ± 0.10 | 0.70 ± 0.16 | |
| Heraklion | | 17-oct | | 18-oct | | 20-oct | |
| 2 h | 25.9 ± 1.85 | 18.0 ± 1.28 | 16.2 ± 1.32 | 13.0 ± 1.05 | 11.6 ± 0.88 | 11.2 ± 0.85 | |
| 4 h | 10.4 ± 0.72 | 7.20 ± 0.50 | 6.37 ± 0.54 | 5.10 ± 0.43 | 4.08 ± 0.82 | 3.90 ± 0.79 | |
| 8 h | 9.90 ± 0.44 | 6.90 ± 0.30 | 2.47 ± 0.20 | 2.00 ± 0.16 | 3.63 ± 0.34 | 3.50 ± 0.33 | |
| Tel-Shikmona | | 28-oct | | | | | |
| 2 h | 18.6 ± 1.10 | 10.7 ± 0.63 | | | | | |
| 4 h | 4.31 ± 0.97 | 2.50 ± 0.56 | | | | | |
| 8 h | 3.56 ± 0.30 | 2.00 ± 0.17 | | | | | |

equilibrium between dissolved and particulate Fe was not reached after 8 h or (ii) equilibrium may have been reached but soluble organic material had also been released, stabilizing higher dFe concentrations. For three of these four aerosol samples, dFe concentrations were not significantly different after 4 and 8 h of dissolution, suggesting that equilibrium had been reached and hence the release of soluble organic matter played an important role. These dFe concentrations are higher than would be predicted based on the theoretical iron solubility. However, previous studies have indicated that both anthropogenic and crustal aerosol material contribute metal complexing organic ligands to seawater (Nimmo et al., 1996; Nimmo and Fones, 1996). Wagener et al. (2008) highlighted the impact of natural ligand concentrations on aerosol Fe seawater solubility and dust dissolution rates. Furthermore bacterial colonies, which have the potential to produce iron binding ligands, have been associated with aerosol material in the Eastern Mediterranean atmosphere (Griffin et al., 2007).

The changes in solubility of crustal aerosol samples with time of seawater equilibration are plotted in Fig. 4.b. The overall mean maximum solubility was $0.94 \pm 1.48\%$ for all the samples considered and the maximum was reached at different equilibration times. In contrast to the anthropogenic aerosols, different kinetic trends were observed; (i) a maximum solubility reached within 2–4 h followed by a decrease, (ii) an increase in solubility without the attainment of equilibrium during the 8 h study period, and (iii) no change in solubility with time. These differences illustrate the contrasting behavior of aerosols from different sources due to their chemical composition and

atmospheric aging processes. For comparative purposes the maximum solubility was used for each sub-sample. Evaluation of any statistical difference between the filter blanks and the measured iron concentration released from each crustally derived sample was carried out using the recommended method (Linsinger, 2005). When a sub-sample was not significantly different at the 95% confidence level, the calculated solubility was not reported in Fig. 4.b or Table 2.b. Therefore for future studies, a longer equilibration time and/or a larger filter portion (and hence a greater aerosol mass) is recommended.

The mean maximum solubilities of the crustally derived and anthropogenically influenced aerosol samples were $0.94 \pm 1.48\%$ and $11.5 \pm 9.3\%$ respectively, and were reached after different equilibration times. The overall solubility of iron from all of the aerosol samples was $5.9 \pm 8.2\%$ ($n = 15$). Bonnet and Guieu (2004) observed contrasting dissolution profiles for a Saharan soil and an urban particulate reference material equilibrated for 24 h and 7 days in Western Mediterranean seawater. The Saharan soil showed slow dFe release over 7 days whereas the urban sample reached equilibrium after 24 h. The variability in iron solubility between different aerosol source types found in this study agrees with previous Atlantic Ocean studies. Sedwick et al. (2007) used an instantaneous deionized water (pH 5.5) leach (Buck et al., 2006) and showed that the fractional iron solubility of aerosols collected in Bermuda increased from 0.5 to 14% as the dominant aerosol source shifted from crustal (Saharan) to anthropogenic (North American). Similarly, Baker et al. (2006) reported the contrasting solubility of Atlantic Ocean aerosols originating from Europe (15–54%) and the Sahara (1.4–4.1%) using an ammonium acetate leach at pH 4.7.

Table 2.b

Solubility (%) and concentration (nM) of iron released from the crustally derived samples in seawater at the three sub-sample times, after subtraction of the filter blank. (–) non detectable released concentrations.

| Sub-samples | Solubility (%) | Concentration (nM) | Solubility (%) | Concentration (nM) | Solubility (%) | Concentration (nM) | |
|--------------|----------------|--------------------|----------------|--------------------|----------------|--------------------|--|
| Erdemli | | 10-oct | | 12-oct | | 22-oct | |
| 2 h | 0.12 ± 0.02 | 1.6 ± 0.26 | 0.19 ± 0.02 | 2.3 ± 0.2 | 0.06 ± 0.01 | 1.00 ± 0.16 | |
| 4 h | – | – | – | – | – | – | |
| 8 h | 0.22 ± 0.02 | 2.90 ± 0.27 | – | – | – | – | |
| Heraklion | | 30-oct | | 01-nov | | | |
| 2 h | – | – | – | – | | | |
| 4 h | 0.22 ± 0.05 | 1.39 ± 0.30 | – | – | | | |
| 8 h | 0.25 ± 0.06 | 1.61 ± 0.37 | 0.47 ± 0.13 | 0.45 ± 0.13 | | | |
| Tel-Shikmona | | 18-oct | | 29-oct | | 01-nov | |
| 2 h | 1.73 ± 0.05 | 9.20 ± 0.29 | 4.37 ± 0.15 | 12.6 ± 0.43 | – | – | |
| 4 h | 0.56 ± 0.04 | 3.00 ± 0.22 | 1.91 ± 0.20 | 5.50 ± 0.59 | 0.26 ± 0.03 | 1.08 ± 0.12 | |
| 8 h | 0.29 ± 0.05 | 1.60 ± 0.26 | 0.28 ± 0.05 | 0.80 ± 0.14 | 0.09 ± 0.02 | 0.38 ± 0.09 | |

The solid state speciation of iron in aerosol particles will also impact on both the solubility and rate of Fe dissolution. [Schroth et al. \(2009\)](#) observed different release rates in ultra pure water for iron associated with contrasting mineral phases and suggested that iron (II) present in primary and secondary silicate minerals dissolved slowly whereas iron present as iron(III) sulfate salts, such as those present in oil fly ash, was released immediately. [Mendez et al. \(2010\)](#) showed both a fast initial release of iron and a second release after >14 days. Therefore the solid state speciation of iron in dust impacts on the operationally defined maximum solubility of iron released and on the dissolution rates. [Séguret \(2008\)](#) showed that the urban reference material NIST 1648 exhibited maximum solubility within 2 h (experiments carried out over 7 days) and that a Saharan derived sample collected from Tel-Shikmona exhibited a maximum solubility after 8 h (experiments carried out over 24 h). According to [Ridame and Guieu \(2002\)](#), this time-scale corresponds with the retention time of particles in the surface mixed layer which is likely to be highly variable depending upon a range of factors (such as particle size, mixing regime, mixed depth layer and biological processes). It is noted, however, that longer retention times of several months have been reported by [Statham and Hart \(2005\)](#) in the Cretan Sea.

3.3. Fe crustal contribution versus solubility

The highest Fe solubility values from the whole data set were detected at Heraklion on the 17th October, amounting to 25.9%, with corresponding 3-day air mass back trajectories all indicating central European sources (at all altitudes). The lowest solubility was detected in the sample collected at Erdemli on the 22nd of October, having a solubility of 0.06%. This sample was collected at the peak of a dust event lasting several days (19th–24th of October), with the iron aerosol concentration being in excess of 4500 ng m^{-3} and the 3-day air mass back trajectories toward the latter part of the event indicating sources from the Western Central to the Mid Northern Saharan desert. All of the other samples exhibited values between these two extremes and were generally consistent with the relative different contributions of contrasting sources and mixture of sources depicted by each of the accompanying 3-day air mass back trajectories. They showed generally low iron solubility for Saharan derived samples and higher solubility for low dust anthropogenically influenced samples.

Therefore in reality each collected samples represented a range of mixed aerosol populations, with different proportions of contrasting sources. Thus the iron solid state speciation characteristics of aerosol populations, and possibly the iron solubility in seawater, are influenced by the relative proportions of mixing of major sources or end-members. To further investigate the range of aerosol mixtures for samples that underwent dissolutions in seawater, the percent crustal contribution of iron for each aerosol sample was determined from the following equation:

$$\% \text{crustal contribution} = \left\{ \frac{(C_{\text{Al aero}} \times (C_{\text{Fe}}/C_{\text{Al}})_{\text{crust}})}{C_{\text{Fe aero}}} \right\} \times 100 \quad (3)$$

where $C_{\text{Fe aero}}$ and $C_{\text{Al aero}}$ are the particulate concentrations (ng m^{-3}) of iron and aluminum in the air, and $(C_{\text{Fe}}/C_{\text{Al}})_{\text{crust}}$ is the ratio (0.63 ± 0.02) of their concentrations in crustal material (coarse fraction), taken from [Andreae et al. \(2002\)](#) during a dust event occurring over 4 days. This ratio was calculated from a very intense dust event, even though a range of ratios was observed. The choice of this ratio is consistent with the aim of this study and previous studies ([Guieu et al., 2002](#); [Koçak et al., 2007](#)).

[Fig. 5.a–c](#) highlights the relationship at 2, 4 and 8 h between the crustal contribution ([Table 1](#)) to the iron aerosol concentration and the soluble fraction from the samples collected at the three sites. The majority of the samples had a high percentage crustal contribution to the total aerosol iron (>80%), while some samples were anthropo-

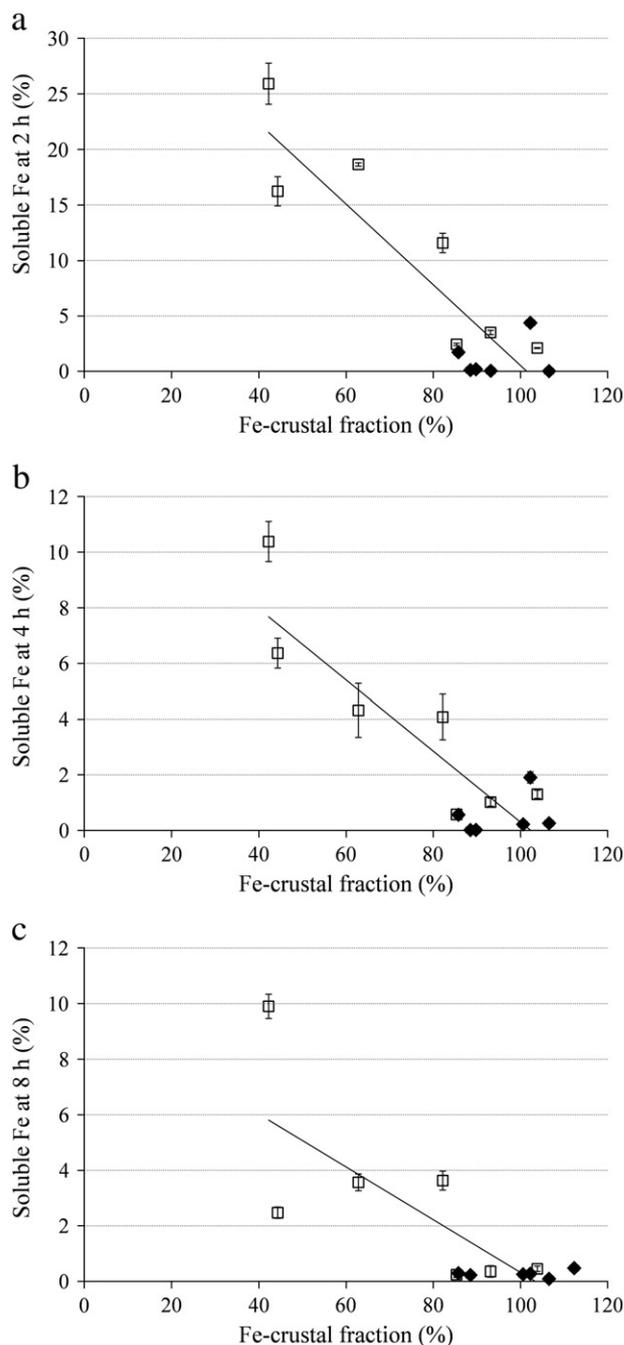


Fig. 5. Percentage of the soluble iron fraction against the crustal fraction contribution of iron in aerosols from the three sites. Soluble iron fraction versus the iron crustal contribution of the aerosol population, a) after a 2 h contact time, b) after a 4 h contact time, c) after a 8 h contact time. Solid diamonds=crustally derived aerosol and open squares=anthropogenically influenced aerosol. Error bars= ± 1 s.d.

genically influenced, exhibiting a comparatively lower crustal contribution (down to 40%). For five samples, a crustal contribution of >100% was calculated, indicating variability in the aerosol Fe/Al precursor crustal material or within the variability of the Fe/Al ratios used in Eq. (2). Despite the limited number of samples ($n=15$), and the assumption made in the percent crustal contribution calculation, a statistically significant linear (Pearson product-moment correlation coefficient, $p < 0.01$) response was found over the lifetime of the experiment: $r=0.882$ at 2 h ([Fig. 5.a](#)), $r=0.885$ at 4 h ([Fig. 5.b](#)) and $r=0.781$ at 8 h ([Fig. 5.c](#)) although the strength of the relationship decreased with longer equilibration times. This suggests that for the Eastern Mediterranean marine aerosol the short term solubility in

seawater (<8 h) of the aerosol population may be influenced by the relative contributions of the contrasting end-member aerosol populations. Moreover, extrapolating the linear regression (at 2 h) gives a maximum solubility of 38% for the anthropogenically influenced samples. This is similar to the findings of Baker et al. (2006) who observed up to 54% release of iron from aerosols originating from the North Atlantic/Europe region, using an ammonium acetate leach. Dissolution of a larger number of anthropogenically influenced samples from this region with a wide range of anthropogenic contribution (samples with <40% crustal contribution) should be carried out to improve this estimation.

3.4. Dry atmospheric fluxes of seawater soluble iron over the Levantine Basin

The atmospheric dry depositional flux of soluble iron in seawater for both sites was estimated (Eq. (4)), taking into account the solubility of crustally derived and anthropogenically influenced samples. It is assumed that the flux calculated for Tel-Shikmona represents the flux over the Southern Levantine Basin (SLB) and the flux calculated at Erdemli represents the flux over the Northern Levantine Basin (NLB). Generally the flux at each site is given by:

$$F = ((\text{Fe})_N \times V_d \times R_N \times S_{\text{anthrop}}) + ((\text{Fe})_S \times V_d \times R_S \times S_{\text{crust}}) \quad (4)$$

where $(\text{Fe})_N$ and $(\text{Fe})_S$ are the geometric means of Fe aerosol concentrations for the northern and southern air mass sectors at Tel Shikmona and Erdemli respectively, V_d is the mean of the elemental settling velocities (1.73 m s^{-1}). R_N and R_S are the anthropogenic and crustal dust event frequency (%) at each of the two sites (temporal influence) originating from the northern and southern airflow sectors and calculated from Koçak et al. (2004, 2005), based on daily back trajectories carried out over several years (1991–2002). S_{anthrop} and S_{crust} are the mean maximum solubilities of iron in seawater associated with Saharan dominated and anthropogenically influenced aerosol samples from Erdemli (NLB) and Tel Shikmona (SLB). The aerosol concentrations were taken from Koçak et al. (2005) and were geometric means based on three years of continuous sampling (between 1999 and 2002). The dry deposition settling velocity (V_d) corresponded to the mean values of V_d previously used by Koçak et al. (2005) that were calculated using the approach adopted by Spokes et al. (2001) using aerosol size fractional data.

Hence the calculated soluble iron fluxes for the two Levantine sub-basins were $8.79 \pm 10.23 \text{ mg m}^{-2} \text{ y}^{-1}$ for the NLB and $9.01 \pm 9.94 \text{ mg m}^{-2} \text{ y}^{-1}$ for the SLB. Having calculated the depositional fluxes it is then possible to calculate the atmospheric inputs across the Northern and Southern Basins, assuming the surface areas are 111,000 and 436,000 km^2 respectively (Ludwing and Maybeck, 2003). The soluble iron inputs for the two basins ranged from $960 \pm 1100 \text{ t y}^{-1}$ for NLB to $3900 \pm 4300 \text{ t y}^{-1}$ for SLB. The NLB had lower inputs of soluble iron compared with the SLB, mainly as a result of the larger defined surface area of the SLB. Such a difference between the two basins has also been observed by Koçak et al. (2005). In their study, the soluble Fe fluxes were calculated in a similar manner to that above, using data from sequential leach studies on Eastern Mediterranean aerosol samples of contrasting sources. Specifically the first stage “exchangeable” Fe (using an ammonium acetate leach solution) fraction was used in the flux calculations.

4. Conclusions

The utilization of elemental concentrations and back trajectories allowed two populations of aerosol samples to be categorized. The crustal derived samples exhibited a variable kinetic profile for the release of Fe into seawater from the particles with a mean maximum

solubility of $0.94 \pm 1.48\%$. In contrast, the anthropogenically influenced samples exhibited consistent kinetic profiles (fast release <2 h; followed by removal of dissolved iron from seawater) with a mean maximum solubility of $11.5 \pm 9.3\%$ (up to 25.9%). The maximum solubility was used to calculate the soluble iron fluxes for the Levantine Basin: $8.64 \pm 10.76 \text{ mg m}^{-2} \text{ y}^{-1}$ for the Northern Levantine Basin and $6.48 \pm 7.78 \text{ mg m}^{-2} \text{ y}^{-1}$ for the Southern Levantine Basin. The atmospheric dry inputs of soluble iron to both basins were then estimated: $960 \pm 1200 \text{ t y}^{-1}$ for NLB and $2820 \pm 3390 \text{ t y}^{-1}$ for SLB. The Northern Basin (higher solubility) had lower inputs of soluble Fe compared with the Southern Basin. Estimates of Fe fluxes/inputs to an oceanic basin like the Eastern Mediterranean Sea are essential for constraining a more appropriate representation of aerosol Fe deposition for coastal and more enclosed ocean basins. Moreover, we clearly highlighted the importance of the aerosol source and the equilibration time on the apparent Fe solubility determined, with no “ideal” or applicable universal equilibration time, as different aerosol populations exhibited contrasting kinetic profiles. For future studies, we recommend the simultaneous determination of the Fe colloidal fraction (<0.4 μm) to investigate the effect of Fe speciation on the dissolution process.

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