

## RESEARCH ARTICLE

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## Key Points:

- This study compares the concentration of soluble ferrous iron in dust at source and deposition sites
- Dust from North Africa arriving in Sierra Nevada is greatly enriched in soluble ferrous iron
- The average enrichment ratio of iron is 15

## Supporting Information:

- Supporting Information S1

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## Soluble ferrous iron (Fe (II)) enrichment in airborne dust

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**Abstract** The input of soluble iron in dust delivered to the ocean and lakes is critical to their biogeochemistry and phytoplankton productivity. Most iron in soils and sediment deposits is insoluble, while only a tiny fraction is soluble and therefore suitable to meet the phytoplankton's requirements for photosynthesis and nitrogen assimilation. Aerosol deposition constitutes a major source of soluble iron to oceans and lakes, and in some regions the low phytoplankton productivity has been related to limitations in the supply of soluble iron from terrestrial sources. It is suggested that during atmospheric transport part of the insoluble iron is converted into soluble form. While the understanding of increased bioavailability of iron during atmospheric transport is improving, there are only a limited number of studies that actually quantify the increase in iron bioavailability in dust. In this study we compare the soluble ferrous iron, Fe (II) content in dust collected at deposition sites in the high-altitude mountains of the Sierra Nevada, Spain, to the source of dust in North Africa. We found that the dust is greatly enriched (on average 15 times) in Fe (II) relative to the fine fraction (<45  $\mu\text{m}$ ) of the parent soil collected from North African dust sources.

### 1. Introduction

North Africa is one of the largest and persistent sources of dust accounting for more than 50% of global dust emissions [Goudie and Middleton, 2006] and the primary source of dust across the Mediterranean to Europe [De Angelis and Gaudichet, 1991; Prospero et al., 2002]. Atmospheric dust has important implications to Earth's climate, hydrological, and biogeochemical cycles and human health [e.g., Ravi et al., 2011, and references therein]. The connectivity between the dust source and the far removed ecosystems dependent on dust inputs is maintained by atmospheric transport [Duce et al., 1991; Swap et al., 1992; Okin et al., 2004; Mahowald et al., 2005]. For example, the dependence of Saharan dust to the downwind ecosystems of the Caribbean [e.g., Shinn et al., 2000] and the Amazon basin [e.g., Swap et al., 1992] is well recognized in the literature.

Indeed, the biogeochemical impacts of dust are of premium interest, in particular, the concentration of soluble iron in dust because of its role in supplying this micronutrient that may be critical to ocean productivity [e.g., Martin and Fitzwater, 1988; Duce and Tindale, 1991]. The impact of dust on lake biogeochemistry, however, is seldom studied [Psenner, 1999; Morales-Baquero et al., 2006; Pulido-Villena et al., 2006], and it has been also suggested that iron, too, could be limiting the productivity of oligotrophic clearwater lakes [Vrede and Tranvik, 2006].

Although the percentage of iron depends on the mineralogy of source soil [e.g., Claquin et al., 1999], atmospheric processing plays a crucial role in increasing the bioavailability of iron in dust emitted from those sources [e.g., Zhuang et al., 1992; Spokes et al., 1994]. The average iron content in Earth's crust is 3.5% [Duce and Tindale, 1991]; the soluble or bioavailable portion of iron in soils and sediments is usually considered to be in the form of Fe (II) but only a tiny fraction of the total iron [Zhu et al., 1997]. Atmospheric processes favored by acidic environment and photochemical processes convert the iron from its insoluble form (i.e., Fe (III)) to soluble Fe (II) [Duce and Tindale, 1991; Zhuang et al., 1992; Mahowald et al., 2005]. While a number of studies have documented the large variability existing in iron solubility (soluble iron relative to total iron) in dust collected in source regions [e.g., Mahowald et al., 2005, Table S3], only a handful of authors have quantified soluble iron enrichment in dust during atmospheric transport [e.g., Zhuang et al., 1992; Zhu et al., 1997; Hand et al., 2004; Baker et al., 2006]. It is also important to note that enrichment of soluble iron is likely associated with combustion aerosols as they have higher iron solubility than mineral

aerosols [e.g., Luo *et al.*, 2008]. Of those studies, only one [e.g., Zhuang *et al.*, 1992] compares the Fe (II) concentrations at the source to the concentration in aerosols. Overall, because of the ease of dust sampling in source areas, dust geochemistry is better understood in source regions than in deposition areas, while we are not aware of any study comparing the concentration of soluble iron in dust at source and deposition sites. Thus, the process of iron enrichment in dust remains for most part poorly documented. To this end, the main goal of this study is to quantify the enrichment in the Fe (II) content of dust during atmospheric transport and elucidate the role of atmospheric processing in the increase in iron bioavailability in dust from major dust sources in North Africa. The close proximity of these sources to oligotrophic lakes in the Sierra Nevada makes it an ideal location to investigate this enrichment process, as the increase in Fe (II) during atmospheric transport may have an important impact on phytoplankton productivity in these lakes.

A few studies have demonstrated the influence of Saharan dust inputs to lake biogeochemistry [e.g., Morales-Baquero *et al.*, 2006; Mladenov *et al.*, 2008; Reche *et al.*, 2009]; however, the contribution to lake biogeochemistry of iron from dust deposition is yet to be examined. Crucial to the assessment of iron-in-dust impacts on lake geochemistry is the quantitative understanding of Fe (II) enrichment during atmospheric transport. To that end, here we assess the enrichment of Fe (II) by comparing the Fe (II) concentration in the dust collected at a site on the Sierra Nevada Mountains in Spain to the Fe (II) concentrations in fine and coarse fractions of sediments from North Africa, the primary source of atmospheric dust in Europe.

## 2. Methods

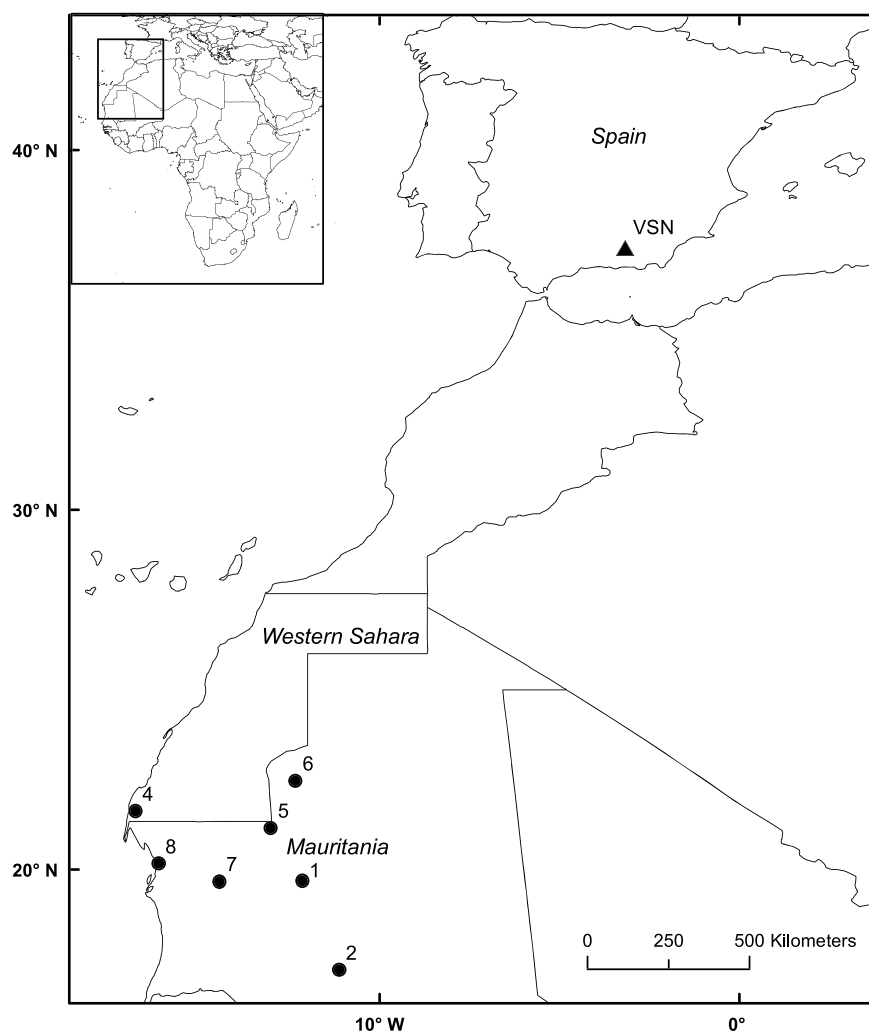
### 2.1. Soil Sampling and Dust Collection

Soil samples ( $n=7$ ) were collected from dust source regions in Western Sahara and Mauritania in North Africa in 2007 (samples 1, 2, and 4) and 2008 (samples 5–8) (Figure 1). A subsample of the soil from North Africa was analyzed using a particle size analyzer (LS 13-320, Beckman Coulter) for grain size analysis (Table 1). Soil samples from North Africa were sieved in the laboratory using a 45  $\mu\text{m}$  brass sieve placed on a Ro-tap sieve shaker and shaken for an hour. The fine fraction collected in a brass sieve pan was weighed and the percent yield ( $<45 \mu\text{m}$  fraction/parent soil) is reported in Table 1. The sieve was cleaned with distilled water and dried between each run to avoid sample contamination. The bulk parent soil was ground in a Picamill soil grinder, which had vials, spheres, and end buttons made of tungsten carbide, whereas the end caps were aluminum (Cianflone Scientific, Pittsburgh, PA, USA), and the ground bulk parent soil was used for iron analysis.

Samples of aerosol  $\text{PM}_{10}$  (total seven samples) were collected in 2008 at a remote location in the Sierra Nevada Mountains (Spain) at the Veleta Peak (VSN, 37°17'N, 3°11'W) at approximately 3000 m above sea level (asl) (Figure 1). Samples were collected on precombusted quartz and glass fiber filters by means of a high volume  $\text{PM}_{10}$  sampler MCV PM1025 (model CAV-A/MS) operated at an average flow rate of  $30 \text{ m}^{-3} \text{ h}^{-1}$  continuously for 60 h. Filters were wrapped in aluminum foil and stored in dry conditions in a cupboard until they were analyzed in the laboratory.

### 2.2. Iron Analysis

A piece of the filter was cut and weighed, and the dust collected in the filter was analyzed for soluble ferrous iron. Along with the filters, 0.25 g of the fine fraction and parent soil were soaked in 25 mL of 1 M NaCl acidified to a pH 2 for 5 min. Filter blanks and blanks (reagents only) were included as control for contamination during the analysis. A dissolution time of 5 min was used to extract the most mobile form of iron [Zhu *et al.*, 1997; Trapp *et al.*, 2010]. The aliquot was passed through a 0.45  $\mu\text{m}$  diameter Millipore filter to eliminate particulate matter. The pH was increased to 5.5 by adding an acetate buffer and Fe (II) concentration was measured in a spectrophotometer (Shimadzu 4100, detection limit:  $-4.000$  to  $+4.000$  Abs) at 562 nm by adding ferrozine (0.1 M). Linear calibrations was achieved using solutions between 0.05 mg/L and 10 mg/L concentrations of iron diluted from a stock solution of ammonium iron sulfate prepared in 1 M NaCl (acidified to a pH 2). For comparison between methods to analyze for Fe (II), the parent soil samples were analyzed following the method used in Bhattachan *et al.*'s [2015] study. The samples were run on the same day with the same set of reagents, while the only difference between the two methods is the duration that the sample was soaked in the aliquot (5 min versus shaken for an hour).



**Figure 1.** Map of the sampling sites in Western Sahara and Mauritania, Africa, and the sampling station at Veleta Peak (VSN) in the Sierra Nevada, Spain.

### 2.3. Trajectory Analysis

The origin of the aerosol samples was traced by using 5 day backward trajectories. These trajectories were obtained using the Hybrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT) [Draxler and Rolph, 2003] with archived data from the Global Data Assimilation System with 120 h run time. Two heights, 3000 m and 4000 m asl. were used, which represent the predominant altitude of Saharan dust intrusions arriving to the Sierra Nevada mountains [Mladenov et al., 2010]. The back trajectories were run for those days that

the dust was sampled at VSN. In addition, vertical profiles of atmospheric boundary layer in Granada, Spain, from Light Detection and Ranging (Lidar) data are obtained to detect the altitude at which Saharan dust is likely to be transported to the Sierra Nevada Mountains.

**Table 1.** The Grain Size Distribution of Soil Samples Collected From Dust Sources in North Africa (Figure 1)<sup>a</sup>

Sample ID	Clay (%)	Silt (%)	Sand (%)	Yield (%)
1	0.60	0.44	98.96	0.28
2	0.71	1.22	98.07	5.23
4	0	0.36	99.64	0.76
5	0.51	0.83	98.66	0.60
6	0.78	2.81	96.41	2.76
7	1.21	5.33	93.46	3.03
8	0.5	1.3	98.20	1.61

<sup>a</sup>The percent yield is calculated for the fine fraction (<45 μm).

### 3. Results

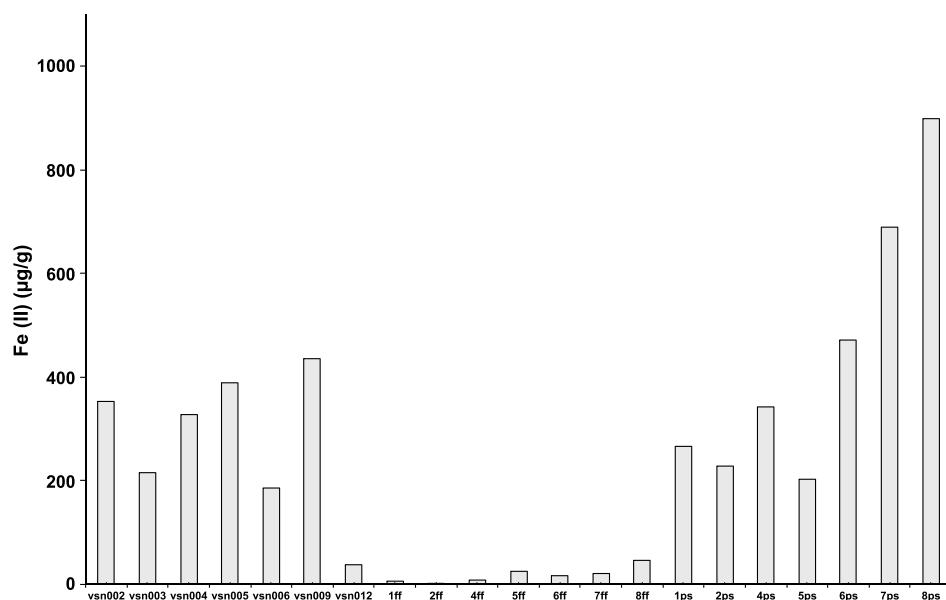
The grain size analysis shows that all samples are sandy in texture (greater

**Table 2.** The Soluble Ferrous Iron Content (Fe (II)) in Soil Samples (Parent Soil) From Mauritania and West Africa (See Figure 1)<sup>a</sup>

Sample ID	Parent Soil Fe (II) (μg/g)	Fine Fraction (<45 μm) Fe (II) (μg/g)
1	265.49	7.30
2	227.89	2.85
4	343.40	8.59
5	201.99	26.21
6	471.22	17.10
7	688.85	21.12
8	898.44	47.49
Average ± 1 standard deviation	442.47 ± 262.82	18.67 ± 15.15

<sup>a</sup>The samples are sieved through a 45 μm sieve, i.e., the fine fraction and analyzed for Fe (II) with samples soaked in the aliquot for 5 min. The average parent soil and fine fraction Fe (II) contents with ± 1 standard deviation are presented.

than 93% sand, Table 1) with less than 1% clay in almost all samples. The percent yield (calculated from sieving soil with a 45 μm sieve) ranges from as little as 0.3 (sample #1) to approximately 5 (sample #2). The soluble ferrous iron (Fe (II)) content for fine (<45 μm) and coarse (parent) fractions shows that Fe (II) is bounded to bulk parent soil (Table 2 and Figure 2). In the fine fraction, the smallest concentration of Fe (II) is 2.85 μg/g, whereas the largest concentration is 47.49 μg/g (sample #8ff). With regard to bulk parent soil, the smallest concentration is found in sample #5 ps (~202 μg/g), and the largest concentration is also in sample #8 ps (~900 μg/g). The average concentrations of Fe (II) in fine fraction and parent soil are 19 and 443 μg/g, respectively (Table 2). The reagent blanks and filter blanks had average absorbance values of 0.0208 and 0.0210, respectively. These relatively low values of absorbance resulted in extremely small measurement uncertainties as 0.05 mg/L and 1 mg/L of stock standard solution had absorbance value of 0.0260 and 0.0326, respectively. To estimate the Fe (II) solubility in dust arriving in the Sierra Nevada, we use the relationship between total Fe and PM<sub>10</sub> reported in *Mladenov et al.* [2010]. We find that the average Fe (II) solubility is approximately 0.9% (Table 3). Using HYSPLIT, the back trajectory analysis confirms that at least in two occasions (24 July and 30 August), the origin of dust emissions is clearly from the region in North Africa where soils were sampled (Figure 3). The back trajectory for other remaining days shows that air mass arrivals were generally from Europe or Africa, with few instances of air masses that had minimal contact with land (Figure S1 in the supporting information). The average concentration Fe (II) of these two sampling events (VSN004 and



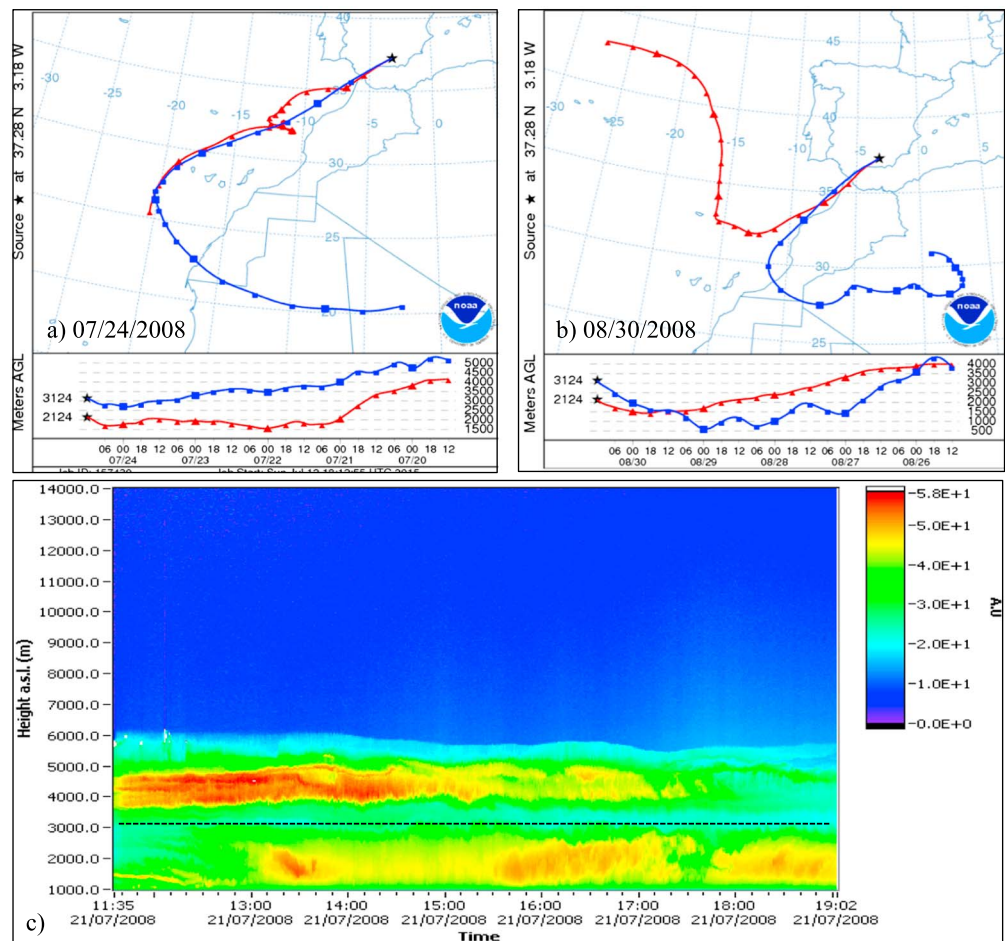
**Figure 2.** The concentration of Fe (II) (μg/g) in the PM<sub>10</sub> collected in filters at Veleta Peak (VSN), the fine fraction (<45 μm) denoted by notation “ff” and the parent soil denoted by notation “ps.”

**Table 3.** The Soluble Ferrous Iron Content (Fe (II)) in Dust Scavenged in Sierra Nevada Mountains in Spain at Veleta Peak Observatory (VSN)<sup>a</sup>

Sample ID	Date Retrieved	PM <sub>10</sub> (g)	Air Volume Filtered (m <sup>3</sup> )	PM10 (μg/m <sup>3</sup> )	Soluble Fe (II) (μg/g)	Total Fe/PM <sub>10</sub> (mg/g) <sup>b</sup>	Fe (II) Solubility (%) <sup>a</sup>
Dust in Filters							
VSN002	07/17/2008	0.055	1679	32.94	352.44	31.66	1.11
VSN003	07/21/2008	0.094	1678.7	55.88	214.63	33.44	0.64
VSN004	07/24/2008	0.067	1678.6	39.62	327.91	32.39	1.01
VSN005	07/31/2008	0.034	1679.3	20.31	388.17	28.96	1.34
VSN006	08/07/2008	0.038	1028.2	36.76	185.68	29.65	0.63
VSN009	08/30/2008	0.036	1679.6	21.31	435.90	29.30	1.49
VSN012	10/17/2008	0.059	1679	34.96	38.87	31.91	0.12
Average ± 1 standard deviation					227.66 ± 138.34		

<sup>a</sup>The mean and ± 1 standard deviation of Fe (II) is reported for the dust collected at VSN. The Fe (II) solubility (%) is the ratio of Fe (II) to Total Fe/PM<sub>10</sub>.  
<sup>b</sup>The relationship between Total Fe and PM<sub>10</sub> is from Mladenov *et al.* [2010] study.

VSN009) is 382 μg/g. Likewise, the average concentration of Fe (II) in dust captured in the filters is 228 μg/g. The comparison between the two methods for Fe (II) analysis shows that the concentrations of Fe (II) when the parent soil was shaken for an hour is on average 4 times higher than when it was soaked in the reagent for 5 min (Table S1).



**Figure 3.** The HYSPLIT-generated 5 day back trajectories for (a) 24 July and (b) 30 August 2008 were run at two heights, 3000 m and 4000 m above sea level. (c) A time series of LIDAR signal corresponding to a Saharan-dominated 21 July 2008 period. Absorbance units refers to absorbance from high (red) to low (violet) and the dashed line represents the 3000 m asl altitude.

#### 4. Discussion

From our results, the role of atmospheric processing during transport of dust is confirmed, as Fe (II) concentrations are relatively higher in the dust collected in the Sierra Nevada than in the fine fraction of the North African soils (Tables 2 and 3 and Figure 2). These results suggest that the insoluble form of iron (i.e., Fe (III)) in dust is converted to soluble form because of atmospheric processing. The role of combustion aerosols albeit not explored in this study, in increasing Fe (II) concentrations in dust deposited in the Sierra Nevada cannot be denied as combustion aerosols, has high Fe (II) content compared to low Fe (II) in soil [Luo *et al.*, 2008]. In fact, Guieu *et al.* [2005] showed that forest fires in Europe increased the concentration of iron in the surface waters of the Ligurian Sea. The sampling location in the Sierra Nevada perhaps receives about less than 5% of total Fe [see Luo *et al.*, 2008, Figure 4c] and about 20–40% of soluble Fe from combustion sources [see Luo *et al.*, 2008, Figure 7d]. A recent study however has indicated that aeolian dust compared to combustion aerosols is the major source of total soluble iron deposited in the Sierra Nevada [see Ito, 2015, Figure 2d]. Furthermore, the back trajectory analyses for two of the collection dates (24 July and 30 August) suggest that the source of dust in the Sierra Nevada is indeed the region in North Africa where the sampling of soil had taken place (Figures 3a and 3b). The trajectory analysis also sheds light on the arrival of air masses for those remaining days (Figure S1). The arrivals were generally either from Morocco in North Africa or Portugal and minimal contact with land in a few cases (07 August and 17 October). The Lidar-derived vertical profile of atmospheric boundary layer in Granada, Spain, also shows that dust transport occurred at altitude above 3000 m (Figure 3c) during 21 July 2008, which is similar to results reported in Mladenov *et al.*'s [2010] study. In fact, instances of remarkably high rates of Saharan dust transport to oligotrophic lakes in the Sierra Nevada have been shown by previous studies [e.g.; Morales-Baquero *et al.*, 2006; Pulido-Villena *et al.*, 2006; Mladenov *et al.*, 2008, 2011].

The dust arriving in the Sierra Nevada Mountains is highly enriched in Fe (II) relative to the fine fraction that is emitted by the source region, and the average enrichment ratio is approximately 15. The higher concentration of Fe (II) in parent soil is consistent with results from dust sources in Southern Africa [e.g., Bhattachan *et al.*, 2015]: sediments (i.e., parent soil) from the Makgadikgadi and Etosha salt pans and interdunes from the southern Kalahari were found to be richer in Fe (II) than their fine fraction ( $<45\ \mu\text{m}$ ). The analysis of Saharan dust also showed that particles greater than  $50\ \mu\text{m}$  were rich in quartz with larger grain size richer in iron [Kandler *et al.*, 2009]. There have been only a limited number of studies that have determined the dust enrichment in soluble iron (Fe (II)). For example, the relative Fe (II) proportion increased from  $<1\%$  in Chinese loess to 4% in collection sites over an urban area and up to 50% in marine dust aerosols sampled in the central Pacific Ocean after being transported for approximately 1000 km [Zhuang *et al.*, 1992]. We found that Fe (II) solubility in dust sourced from North Africa that is deposited in the Sierra Nevada is about 0.9%. The Fe (II) solubility measured in this study is consistent with modeled estimate of change in iron solubility in dust sourced in North Africa ( $<0.5\%$  Fe solubility) and deposited in the Sierra Nevada (0.5–1% Fe solubility) [Ito and Shi, 2016]. A recent study has also shown that submicron dust sourced from North Africa may have already experienced atmospheric processing before leaving the African coast [e.g., Ravelo-Pérez *et al.*, 2016]. Our estimated Fe (II) solubility is also close to the range (between 1 and 6%) for dry deposition [Gao *et al.*, 2003] and comparable to iron solubility found in Saharan dust [Spokes *et al.*, 1994; Bonnet and Guieu, 2004; Baker *et al.*, 2006]. In fact, global ocean biogeochemical models assume iron solubility between 1 and 10% [Fung *et al.*, 2000] and average iron solubility of 4.6% for dry and 17% for wet deposition [Fan *et al.*, 2006]. It is suggested that high variability in iron solubility existing in airborne dust [see Fan *et al.*, 2006, Table 1] likely depends on distance from the dust source and modes of deposition [Gao *et al.*, 2003]. Furthermore, it is reported that the dry deposition accounts for only 20% of total deposition to the oceans [Fan *et al.*, 2006], and the solubility of iron is much lower in dry deposition compared to wet deposition of dust [e.g., Gao *et al.*, 2003; Fan *et al.*, 2006]. Therefore, the extent of enrichment in iron could perhaps be larger if the dust is deposited via wet deposition. However, not only the distance from the dust source but also other factors such as, the duration of transport, grain size, pH, and dust concentration influence the release of iron [Bonnet and Guieu, 2004; Mackie *et al.*, 2005].

Because the coarser sediment fraction does not undergo atmospheric transport, the enrichment in soluble iron is here evaluated by comparing Fe (II) concentrations extracted from dust aerosols ( $<10\ \mu\text{m}$ ) from deposition sites only with Fe (II) in the fine fractions ( $<45\ \mu\text{m}$ ) at the source. Thus, the enrichment ratio is here reported between two different size classes (i.e.,  $<10\ \mu\text{m}$  at sink versus  $<45\ \mu\text{m}$  at source). We believe this to

be a “fair” comparison, as (i) the 45  $\mu\text{m}$  obtained through sieving is made of many tiny aggregates that are likely broken up during the dust production and emission process in the natural environment mainly by production of dust during saltation and induced aeolian abrasion by collision of sand grains [Bullard *et al.*, 2004] and (ii) the Fe (II) content in  $< 45 \mu\text{m}$  fraction is smaller than in the parent soil (Table 2), which suggests that it can be even smaller in the  $< 10 \mu\text{m}$  fraction and the enrichment effect perhaps stronger than the values reported above. Thus, our results provide at least a conservative estimate of the Fe (II) enrichment during atmospheric transport. A geochemical analysis of a fine fraction from the dust source does not appear to be feasible because dry sieving with smaller meshes becomes challenging due to electrostatic forces, the presence of aggregates, and strong interparticle cohesion. Furthermore, it has been found that coarser particles (greater than 10–20  $\mu\text{m}$ ) can also be transported long distances [e.g., McTainsh *et al.*, 1997; Middleton *et al.*, 2001]. In fact, Mladenov *et al.* [2010] also reported a positive and significant relationship between the total iron loadings and particulate materials ( $>0.45 \mu\text{m}$ ) in the dust deposited in the Sierra Nevada. We also showed that effect of extraction time on concentration of Fe (II) is quite large (Table S1); however, it is often argued that a major portion of iron is extracted in the first few minutes. Trapp *et al.* [2010] showed that the concentration of Fe (II) slightly increased as a function of extraction time in acidic conditions.

## 5. Conclusion

In this study, we showed that the dust arriving in the Sierra Nevada Mountains in Spain from North Africa is enriched in Fe (II). However, we acknowledge that we do not quantify the fluxes of iron-in-dust and their effect of iron in dust to lake biogeochemistry in the Sierra Nevada. Because the oligotrophic lakes in the Sierra Nevada are extremely sensitive to dust deposition [Pulido-Villena *et al.*, 2006; Mladenov *et al.*, 2011] and dust can increase primary and bacterial productivity in these lakes [Morales-Baquero *et al.*, 2006; Reche *et al.*, 2009], the inputs of Fe (II) contained in the Saharan dust could promote biological productivity of oligotrophic lakes. It has been shown that there is a positive relationship between lake productivity and iron input [e.g., Vrede and Tranvik, 2006]. Overall, the impact of dust on terrestrial and marine biogeochemistry [Okin *et al.*, 2004; Jickells *et al.*, 2005] may strongly depend on the soluble iron enrichment during the atmospheric transit investigated in this study.

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