



A fine fraction of soil used as an aerosol analogue during the DUNE experiment: sequential solubility in water, decreasing pH step-by-step

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Abstract. A soil sample collected in a desert aerosol source area near Douz (southern Tunisia) was dry-sieved at 20 μm in order to extract the fraction similar to a wind-generated aerosol, and was used to seed mesocosms during the DUNE experiment (a DUst experiment in a low Nutrient, low chlorophyll Ecosystem). In this work, said “aerosol-like” fine dust was sequentially leached by short contacts with water at initial pHs, decreasing from seven to one, representing various wet environmental conditions. For each step, the solubility of a given element is calculated as the amount of its dissolved fraction, relative to its total amount. The evolution of this fractional solubility from the highest to lowest pHs provides information on the chemical strength needed to solubilise a given element and its lability. The behaviour of the elemental solubility was sorted into two groups: (1) Ca, Sr, Ba, Mn, and P, with a solubility between 23 % and 70 %, and a maximum sequential solubility at pH 3; (2) Al and Fe, with a solubility of less than 2 % and the highest release at pH 1. Similar solubility patterns in group 1 for Ca, P, and Mn suggest a possible association of the elements in the same minerals, most probably carbonates.

1 Introduction

The DUNE experiment (Guieu et al., 2010, 2014) used the finest fraction of an alluvial soil collected in southern Tunisia (33.452° N, 9.335° E), a region known to provide the western Mediterranean Basin with mineral dust aerosol (Bergametti et al., 1989). This soil fraction was considered a model of natural atmospheric Saharan dust and was used to seed mesocosms in order to observe the influence of Saharan dust input on the biogeochemistry of the Mediterranean Sea (Guieu et al., 2010). This soil fraction was mainly a mixture of quartz, calcite and clays (Desboeufs et al., 2014). Knowledge of elemental solubility is key to assessing the impact of atmospheric deposition and the impact of particle material added into a mesocosm. The word “solubility” covers many different meanings and different protocols, as explained in Sholkovitz et al. (2012) in the case of iron. In this paper on fractional solubility, we discuss the amount of soluble element divided by the total amount of the element present in the soluble and insoluble phases. The soluble-fraction separation method is described in Sect. 2.

Solubility experiments are generally carried out using ultra-pure water or freshly collected surface seawater (Buck et al., 2013) or a buffered solution at pH 4.7 (Baker et al., 2006). Solubility could also be more than a simple single value; for example, a list of values respectively associated with a set of successive extraction protocols (Gleyze et al.,

2002, Filgueiras et al., 2002). These different values link the dissolution of an element to its binding and its mineralogical form in the solid. Here, we report the results of an experiment based on the successive leaching of small masses of particles used for the DUNE experiment. Cloud processed (used in DUNE-P and DUNE-R) and non-processed (used in DUNE-Q) dust analogues were used to artificially seed large mesocosms (Desboeufs et al., 2014). The cloud-processed dust samples have been put into contact with synthetic cloud water in the laboratory (Guieu et al., 2010). The leaching tests reported here were performed on the non-processed dust analogue, which has not been modified. We performed the leaching using water solutions with increasing acidity in order to measure the lability of the elements in the pristine dust, as well as to investigate the fate and behaviour of such dust in various wet environments, including non-polluted rainwater at high pHs and cloud polluted droplets at low pHs.

2 Experimental protocol

All operations described here took place in an ISO-6 clean room with thoroughly washed labware. Bottles and devices that were in contact with the samples were washed using dish detergent, then soaked for at least one day in a 2 % Decon™ (lab detergent) bath, prepared with osmosed water, carefully rinsed, soaked for one week in 2 % hydrochloric acid in osmosed water, rinsed again with ultra-pure water (Elgapure™), soaked for at least one month in high purity 2 % hydrochloric acid (Meck™, Suprapur™ grade), diluted with ultra-pure water, and finally rinsed with ultra-pure water and left to dry in a laminar flow bench (ISO-1).

The dried collected soil was, first of all, gently crushed and then dry-sieved using nylon meshes. The fraction, which passed through the 20 µm mesh, was mixed in a unique batch and used as a mineral dust aerosol analogue for the DUNE experiments. Details are provided in Guieu et al. (2010). Approximately 10 mg of this dust analogue was deposited on a 47 mm diameter and 0.2 µm porosity polycarbonate membrane in a polycarbonate filtration device (Nalgene™). Leaching solution (100 mL) was then poured onto the filter, gently stirred by hand and left for 1 minute. After this delay, a vacuum was applied to the filtration unit until all of the solution had passed through, which took approximately 20 s more. In all, 10 mL was set aside for pH determination, and 60 mL was stored in a polyethylene bottle, the pH having decreased to 1 with ultra-pure nitric acid (Merck, Suprapur™ grade). Twelve successive leaching steps were applied to the same filter with increasing acidity solutions, following the leaching literature (e.g. Filgueiras et al., 2002; Gleyzes et al., 2002). Nitric acid (Merck, Suprapur) and ultra-pure water were used to prepare the acidic water solutions. The first three leaching steps used simple ultra-pure water (pH ~ 6.5, lower than 7 due to ambient CO₂ dissolution; hereafter referred as “pH 7”), the following three used 10⁻⁵ M acid so-

lution (“pH 5”), followed by three steps with 10⁻³ M acid solution (“pH 3”), and finally, three steps with 10⁻¹ M acidic solution (“pH 1”). Four replicate experiments were carried out with the same conditions.

Analyses were performed by ICP-AES (Perkin Elmer, Optima 3000) with a CETAC ultrasonic nebulisation, as described in Desboeufs et al. (2003) for the elements dissolved in the solution after leaching. The following elements were determined using the atomic emission line (wavelength in brackets, nm): Ca (422.673), Sr (407.771), Ba (455.403), Mn (257.61), Fe (259.94), Al (396.152), and P (213.628). The instrument was calibrated on each line using standard solutions, and was checked five times with the certified reference material (CRM) SLRS-4 (NRC, Canada, certified values reported in Yeghicheyan et al., 2001 or Heimburger et al., 2013). P is not certified in this CRM. An indicative concentration was published in Yeghicheyan et al. (2001), but a more recent value [P]₄ was retrieved from the SLRS-5/SLRS-4 concentration ratio R_P published in Heimburger et al. (2013), and its concentration [P]₅ in SLRS-5 published in Yeghicheyan et al. (2013). These values are respectively equal to $R_P = 1.43 \pm 0.02$ and $[P]_5 = 8.2 \pm 3 \mu\text{g L}^{-1}$. The deduced concentration in SLRS-4 is found to be $[P]_4 = [P]_5 / R_P = 5.7 \pm 2 \mu\text{g L}^{-1}$. The recovery rate was found to be between 97 and 120 % for the certified elements Ca, Sr, Ba, Mn, Fe, and Al, and 96 % for P using the recalculated value [P]₄. P calibration solutions were also checked by measuring a dilution by 10 of a 10 ppm commercial solution (Thermo Elemental ICAP calibration solution) independent of the calibration solutions, and an accuracy of 2 % was found for this check. The relative standard deviations for the five SLRS-4 replicated measurements were less than 5 %, except for P, where it reached 10 %. The analytical detection limit (DL) for one measurement was determined for each element as three times the standard deviation of the analytical blanks, converted into the quantities present in 100 mL of solution, and expressed as the percentage of the element present in 10 mg of soil. Because the final results were an average of four experimental replicates, the detection limit value for a single measurement was divided by the square root of four (two) to take into account the averaging effect. The DL values are reported on the last line in Table 2.

To test the cleanliness of the protocol and evaluate the experimental detection limit of the analyses, we made two blanks by leaching the pristine filters only. All these experimental blanks were below the detection limit so that the experimental detection limit was equal to the analytical detection limit.

Elemental analyses of the soil were performed by X-ray fluorescence (Pan Analytical 2400) after calcination at 1050 °C and lithium tetraborate/metaborate fusion. Major and minor elements were determined using geostandards (BX-N, BE-N, ST-N from SARM, Nancy, France) for calibration. Ba and Sr were measured by ICP-AES after acid

digestion (Desboeufs et al., 2014 for Sr, K. Desboeufs, personal communication, 2011 for Ba).

Finally, the solubility was expressed in a given leaching batch as the amount of element found in the 100 mL of solution, which passed through the filter divided by the total amount of element initially present in the soil mass used for the experiment. This solubility can be called the “relative fractional solubility”. A cumulative solubility was also calculated as the sum of the successive batch dissolution experiments performed up until the given batch. The average results of the four replicates with associated uncertainty are displayed in Table 2. We can see in this table that most of the uncertainty for the dissolution step is due to the DL.

3 Results and discussion

The elemental composition of the soil is given in Table 1 and is expressed as oxides for the major elements, except for calcium, which is associated with carbonate. The last column of the table displays the composition as elements, including Sr and Ba, which are present at trace levels. The median and standard deviation results of the four replicates, including the measured pHs, are given in Table 2.

Large amounts of calcite were found in the sample (Desboeufs et al., 2014) and the amount of calcium carbonate explained the ignition loss well with its transformation into calcium oxide and carbon dioxide exhaust. The southern Tunisian source region is known to produce calcium-rich dust (Bergametti, 1989; Avila et al., 2007) due to the carbonated lithology of the soils in this region (Claquin et al., 1999). High calcite concentrations were measured in the dust originating from Tunisia, northern and central Algeria, and Morocco, and low concentrations occur south of, approximately, 27° N (Kandler et al., 2007).

The pH of each leaching solution was measured at the end of each dissolution batch and exhibits modifications from the original pH because of the alkalinity of the soil. This alkalinity can be attributed to carbonate dissolution:

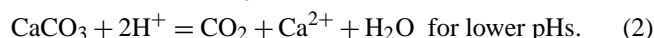
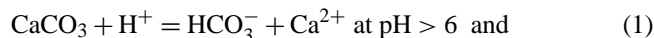
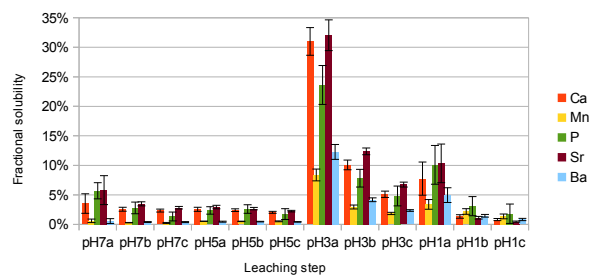
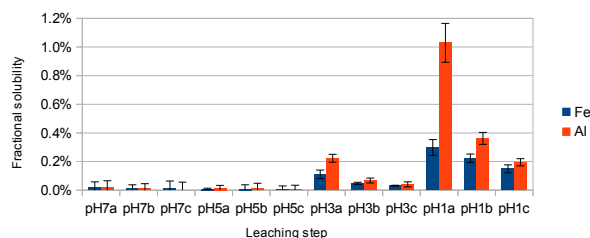


Table 2 summarises the obtained results. For the three successive dissolution experiments with the same leaching solution, no noticeable pH variations were observed. For pure water, the pH was buffered around 8. By increasing the acidity of the leaching solution, the pH decreased to 6.7 for the “pH 5” leaching solution; with the “pH 3” solution, the end of the buffering capacity of the solid was reached with a measured pH equal to 3.0. At this pH of 3, a maximum calcium release was observed for the first leaching process (Fig. 1a), strengthening the hypothesis that calcium was mainly present as calcium carbonate in the solid. The most acidic solution, “pH 1”, was measured at pH 1.1.



a)



b)

Figure 1. Average fractional solubility relative to the initial quantity of element measured for each leaching step from pH7a to pH1c for each group. (a) Ca, Mn, P, Sr, Ba (group 1), (b) Al and Fe (group 2). The segments are the standard deviation of the four replicated experiments. The corresponding measured pHs for batches “pH 7”, “pH 5”, “pH 3”, and “pH 1” are 8, 6.7, 3, and 1.1, respectively.

A first dissolution pattern is displayed in Fig. 1a. For Ca, Sr, and P, the solubility was approximately 5 % for the first leaching batch at pH 8, and it continuously decreased until reaching the first “pH 3” leaching solution, for which it increased up to 30 % for Ca. After this pH, the solubility decreased again, except during the first leaching with a solution at pH 1. The pattern was the same for Ba and Mn, but with a solubility that was three times lower than that for the other elements at each step, except for that at pH 1, for which the solubilities of all displayed elements were of the same order of magnitude. Both Filgueiras et al. (2002) and Gleyzes et al. (2002) pointed out carbonate dissolution with a mild acid reagent, which occurs at pH 5 and below. With our experiments, pH 5 was not reached by the leaching solution labelled “pH 5” because of the alkalinity of the soil, which overcame the unbuffered acidity of the leaching solution. The solution labelled “pH 3” was the first one that was acidic enough to dissolve carbonates. Here, Mn, Sr, Ba, and P seem to be strongly linked to calcium carbonate. This is not surprising for Sr and Ba, which both belong to the same periodic-table column, as Ca. Kitano et al. (1978) found phosphorus uptake by calcium carbonate in seawater and fresh water. Released phosphorus may be one element that has been incorporated into the carbonate during its formation period. Plotting the phosphorus cumulative dissolution as a function of the calcium cumulative dissolution, a

Table 1. Elemental composition of the soil for the major and minor elements. Sr and Ba are from Desboeufs et al. 2014, *Q* sample for Sr, R for Ba). The right column, written in italics, is the elemental composition.

Compound	Composition (as oxide)	+/-	Composition (as element)
SiO ₂	33.0 %	0.7	<i>15.4 %</i>
Al ₂ O ₃	8.9 %	0.4	<i>4.7 %</i>
Fe ₂ O ₃	3.3 %	0.3	<i>2.3 %</i>
MnO ₂	0.055 %	0.002	<i>0.035 %</i>
MgO	3.5 %	0.1	<i>2.1 %</i>
CaCO ₃	49 %	2	<i>19.6 %</i>
Na ₂ O	< 1 %	–	<i>< 1 %</i>
K ₂ O	1.72 %	0.05	<i>1.4 %</i>
TiO ₂	0.54 %	0.01	<i>0.32 %</i>
P ₂ O ₅	0.10 %	0.01	<i>0.044 %</i>
Sr			360 ± 27 ppm
Ba			270 ± 14 ppm

straight line with a slope of 0.86 is obtained by least-squares regression (Fig. 2a). This suggests a linked dissolution of calcium and phosphorus for all batches and therefore provides strong evidence for the association of soluble phosphorus with calcium carbonate in the same solid phases. This type of association between calcium and phosphorus in Saharan dust was reported in Nenes et al. (2011) who found that between 50 and 70 % of phosphorus is associated with calcium using a specific Ca-bond-P extraction method. These authors decided on the presence of apatite, because they never hypothesised an association between calcite and phosphorus, yet the protocol they used extracted calcite as well. However, Nezat et al. (2007) reported that apatite does not dissolve well in silicated soils with 0.1 M nitric acid solution, and a 1 M concentration is necessary to prevent the absorption of P onto aluminium or iron oxides. They also suggested the presence of fluoroapatite in carbonate minerals. The experiments, presented here on calcite-rich soil, revealed the importance of phosphorus associated with carbonate, which followed the same dissolution pattern.

Fujiwara (1964) found manganese as single Mn²⁺ ions randomly distributed in natural calcium carbonate lattices. In Fig. 2b, we can observe the same behaviour for manganese as for phosphorus, but with a linear-regression slope equal to 0.27. The values obtained for the pH 1 leaching step were excluded from the regression because they were above the line. We can conclude that part of manganese was closely associated with calcium carbonate and was released with calcium for pHs higher than or equal to 3. At pH 1, solid phases that were different from calcium carbonate released manganese. Aluminium and iron belong to a second group of elements. Indeed, the dissolution of both these elements was very low (max. 0.2 %) until pH 3, and then it increased up to 1 % for aluminium and 0.4 % for iron at pH 1 (Fig. 1b).

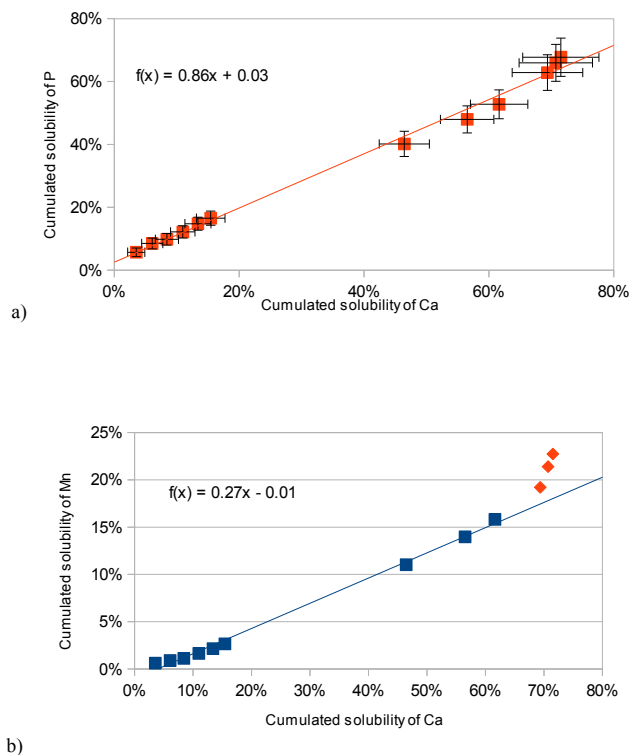


Figure 2. Cumulated solubility of (a) P and (b) Mn as a function of the cumulated solubility of Ca. The plotted line is a least-squares linear regression. The three orange points for Mn are not included in the regression and were obtained at pH 1.

At a given pH, a strong decrease was always observed from the first to the third leaching step (labelled in order as a, b, and c) without a noticeable measured pH variation. We can therefore assume that there is a finite stock of elements that can be dissolved at each tested pH. The dissolution percentages measured for each repeated pH can thus be added. We can also calculate a cumulative solubility for each pH that represents the amount that would be rapidly dissolved at the given pH. The cumulative dissolutions of Al, Fe, Mn, and P are displayed in Fig. 3. Elements belonging to group 1 (Mn, P) are much more soluble than those belonging to group 2 (Al and Fe), and two scales are necessary to display both groups on the same figure.

The very low solubility of Al and Fe at the highest pHs was already observed for the Saharan dust analogue, e.g. for Saharan losses collected in Cape Verde (Desboeufs et al., 1999). The solubility is reported as slightly higher (3 and 1.7 % respectively) by Baker et al. (2006) for Saharan dust collected over the Atlantic. This increase in solubility from pristine soil to aerosol is attributed by Baker et al. (2006) and Desboeufs et al. (2001) to ageing and acid processing in clouds. This behaviour was also observed in our sample, where an acid processing at pH 1 increased the aluminium and iron solubility near to the values proposed by Baker et al. (2006)

Table 2. Final pH and relative fractional solubility of each measured element for each leaching step. The associated uncertainty of the averaged measurements is calculated as three times the standard deviation of the four replicates divided by the square root of 4, the number of replicates. The uncertainty of cumulated dissolution should be calculated as the square root of the sum of the square of all previous dissolution steps.

Sample name	Measured final pH	Ca fraction	Sr fraction	Ba fraction	Mn fraction	Fe fraction	Soluble Al fraction	Soluble P fraction
Averaged fractional solubility values on the 4 experimental replicates								
7a	8.0	4 %	5.8 %	0.6 %	0.6 %	0.02 %	0.02 %	6 %
7b	7.8	3 %	3.5 %	0.4 %	0.3 %	0.01 %	0.01 %	3 %
7c	8.0	2 %	2.8 %	0.4 %	0.2 %	0.01 %	< DL	1 %
5a	6.8	3 %	2.9 %	0.4 %	0.5 %	0.01 %	0.01 %	2 %
5b	6.7	2 %	2.7 %	0.5 %	0.5 %	0.01 %	0.01 %	3 %
5c	6.5	2 %	2.2 %	0.4 %	0.5 %	0.01 %	0.01 %	2 %
3a	3.2	31 %	32 %	12 %	8.4 %	0.11 %	0.22 %	24 %
3b	3.0	10 %	12 %	4.2 %	3.0 %	0.05 %	0.07 %	8 %
3c	3.0	5 %	6.8 %	2.3 %	1.8 %	0.03 %	0.04 %	5 %
1a	1.2	8 %	10 %	5.0 %	3.4 %	0.30 %	1.03 %	10 %
1b	1.1	1 %	1.1 %	1.5 %	2.2 %	0.22 %	0.36 %	3 %
1c	1.1	1 %	0.5 %	0.8 %	1.3 %	0.15 %	0.20 %	2 %
Absolute associated uncertainty								
7a	1.6	2.5 %	3.7 %	0.6 %	0.5 %	0.06 %	0.07 %	2 %
7b	1.2	0.5 %	0.5 %	0.1 %	0.1 %	0.04 %	0.05 %	1 %
7c	1.0	0.4 %	0.3 %	0.1 %	0.1 %	0.08 %	0.09 %	1 %
5a	0.7	0.5 %	0.5 %	0.1 %	0.0 %	0.01 %	0.03 %	1 %
5b	0.4	0.3 %	0.3 %	0.1 %	0.1 %	0.04 %	0.05 %	1 %
5c	0.4	0.2 %	0.2 %	0.1 %	0.1 %	0.04 %	0.04 %	1 %
3a	0.2	3.5 %	3.9 %	1.9 %	1.5 %	0.05 %	0.04 %	5 %
3b	0.3	1.2 %	0.9 %	0.5 %	0.5 %	0.01 %	0.03 %	2 %
3c	0.3	0.8 %	0.6 %	0.2 %	0.3 %	0.00 %	0.03 %	3 %
1a	0.4	4.2 %	4.9 %	1.9 %	1.2 %	0.08 %	0.20 %	5 %
1b	0.4	0.4 %	0.3 %	0.3 %	0.7 %	0.05 %	0.06 %	2 %
1c	0.4	0.3 %	0.1 %	0.3 %	0.6 %	0.04 %	0.04 %	2 %
DL		0.01 %	0.1 %	0.4 %	0.02 %	0.005 %	0.005 %	1 %

for Saharan dust. Filgueras et al. (2002) reported the effect of acid leaching on exchangeable and sorbed metals, pointing out the absorbing properties of carbonates. Gleyzes et al. (2002) highlighted some dissolution of silicate at low pHs, but both works concluded that acid leaching does not dissolve oxides. Journet et al. (2008) showed that clays releases soluble iron at pH 1. For the carbonated dust studied in this paper, we do not have enough data to clearly attribute the origin of the dissolved aluminium and iron to a specific solid phase, but a noticeable solubility increase at pH 3 might attribute a part of soluble aluminium and iron to carbonated phases.

We can compare the solubility found here with that estimated and calculated in seawater during the DUNE mesocosm experiments, where the same soil fraction was used, but only after processing with synthetic cloud-like water to reproduce condensation–evaporation processes on dust particles during atmospheric transport (Wuttig et al., 2013). For manganese, iron, and aluminium, these authors reported sol-

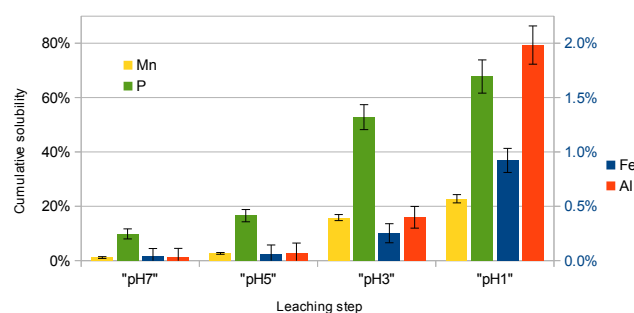


Figure 3. Cumulative solubility for Mn, P (left scale), Fe, and Al (right scale). The vertical segments are the standard deviation of the four replicates.

ubilities that are respectively equal to 27–41, 0.12, and 1 %. In our work, the cumulated solubility of manganese remained low at the highest pHs and increased significantly at pH 3, reaching a value of 16 ± 1.5 % (value \pm uncertainty). An

additional increase of the solubility was observed for the last leaching step at pH 1, with a maximum value of $23 \pm 2\%$. For iron and aluminium, the cumulated solubility remained very low (less than 0.1 %) for the highest pHs. Starting from pH 3, it approached the value observed in the mesocosms where a solubility of $0.25 \pm 0.14\%$ and $0.4 \pm 0.15\%$ was observed for iron and aluminium, respectively. At pH 1, the observed cumulated solubility exceeded the solubilities calculated in the mesocosms. It is important to keep in mind that the calculated solubilities in the mesocosms were marred by a significant uncertainty. The average solubility similarities obtained from unprocessed dust at pH 3 in water (this study) and cloud-processed dust in seawater (Wuttig et al., 2013) indicate that the acidic conditions encountered during the laboratory cloud processing (see Guieu et al., 2010) were recorded in the dust until it was used to seed the mesocosms. This recorded acidity controlled the solubility levels in seawater.

Using aerosols sampled on the SE Mediterranean coast, Herut et al. (1999) measured relative solubilities for P in seawater that were between 10 to 30 % for air masses coming from Africa or Arabia. Ridame and Guieu (2002) measured P solubilities of 2 to 10 % in seawater (after 6 h) and 5 to 20 % in fresh water (after 24 h) for the finest fraction of soil collected in southern Algeria. Izquierdo et al. (2012) measured an average solubility of 11 % in pure water for deposited Saharan dust collected on the NW Mediterranean coast. This solubility could increase up to 50 % if the air masses are influenced by anthropogenic emissions. Bergametti et al. (1992) measured soluble and insoluble phosphorus in rainwater in Corsica. Phosphorus solubility was also low for natural dust and high for anthropogenic aerosols. Nenes et al. (2011) showed a strong increase in P solubility in Saharan dust, from 5–10 % up to 90 % after a 24 h acid processing at pH 2. Here, we find a solubility of 10 % for “pH 7” and 55 % at pH = 3. The “pH 7” solubility value is consistent with the dissolution experiments reported for non-polluted air masses. The rise in solubility in the polluted air masses is similar to those observed here from pH 7 to pH 3. This increase could be caused by the presence of more soluble anthropogenic phosphorus in the collected aerosols, as well as processing of the dust by more acidic conditions. In the leaching experiments reported in this paper, phosphorus does not change, and therefore only acid processing caused the observed increase in solubility.

If we assume that the carbonates are completely dissolved at pH 3, we can see in Fig. 3 that approximately 50 % of phosphorus and 15 % of manganese dissolved at that pH were most likely associated with carbonates in the fine fraction of the investigated soil. Despite the fact that the behaviour of iron is more complex, its 0.25 % cumulated solubility at pH 3 might represent its fraction associated with carbonates, in an undetermined form, that may be either adsorbed or included in the lattice, like manganese.

4 Conclusions

The fine fraction of the carbonate-rich soil from southern Tunisia used in this study has been shown to be representative of mineral dust aerosol transported and deposited in the northwestern Mediterranean region, especially in spring (Guieu et al., 2010). The observed solubility of various elements from this soil, with pHs down to 3, highlights the importance of the carbonate fraction in the dissolution process. Trace elements such as manganese and phosphorus, which are micro-nutrients for marine organisms, appear to have a fraction that is associated with carbonates and that can be dissolved with the typical acidic conditions encountered in cloud water, without invoking extreme acidic conditions. This yields a high lability to mineral dust-contained phosphorus (50–55 % at pH = 3 for our sample), and indicates that the carbonate fraction and its composition should be used to model aeolian dust transport and the associated deposition of nutrients and micro-nutrients onto the surface of the ocean.

In regions affected by mineral dust transport, carbonate dissolution prevents the acidification of rainwater by anthropogenic gases, such as nitric or sulphuric acid (Losno et al., 1991), and therefore decreases the weathering strength of rain/cloud water. The weaker solubilisation of trace metals and phosphorus by a less acidic atmospheric water can be compensated by the release of carbonate, which appears as a potential source of bioavailable nutrients.

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