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

C. Aghnatios\textsuperscript{1}, R. Losno\textsuperscript{1,2}, and F. Dulac\textsuperscript{3,1}

\textsuperscript{1}Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR7583 CNRS, University Paris 7 Denis Diderot, University Paris-Est Créteil, Paris, France
\textsuperscript{2}Institut de Physique du Globe de Paris (IPGP), Sorbonne Paris Cité University Paris 7 Denis Diderot, UMR7154 CNRS, 75005 Paris, France
\textsuperscript{3}Laboratoire des Sciences du Climat et de l'Environnement (LSCE), UMR8212 CEA-CNRS-UVSQ-CEA Saclay 701, 91191 Gif-sur-Yvette Cedex, France

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Correspondence to: R. Losno (losno@ipgp.fr)
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Abstract

A soil sample collected in a desert aerosol source area near Douz (South Tunisia) was sieved at 20 µm in order to extract the fraction similar to an aerosol generated by wind and used to seed mesocosms during the DUNE experiment. In the present work, this “aerosol-like” fine dust was sequentially leached by short contacts with water at pHs decreasing from 7 to 1. These pHs are representative of various environmental wet conditions, the lowest of which could be reached during cloud conditions. The evolution of the solubility from the highest to the lowest pHs provides information on the necessary strength for the solubilisation of a given element and its lability. The behaviour of the elemental fractional solubility is sorted into two groups: (i) Ca, Sr, Ba, Mn, P constitute group 1, with a solubility between 23 % and 70 % and with a maximum solubility at pH 3; (ii) whereas in group 2 (Al, Fe), the solubility is less than 2 % with 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, which gives phosphorus an unexpected high lability.

1 Introduction

The DUNE experiment (Guieu et al., 2010, 2014) used the finest fraction of an alluvial soil present in South Tunisia (33.452° N, 9.335° E), a region known to provide the western Mediterranean with mineral dust aerosol (Bergametti et al., 1989). This fraction was considered as a model of true atmospheric Saharan dust and was used to seed mesocosms in order to observe the influence of Saharan dust input on the Mediterranean Sea (Guieu et al., 2010). This soil fraction was a mixture of quartz, calcite and clays (Desboeufs et al., 2014). Knowledge of elemental solubility is a key point to assess the impact of atmospheric deposition and then the impact of particle material added into a mesocosm. The word “solubility” covers many different significances 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.

Basically, solubility experiments are carried out using ultra pure water or freshly collected surface sea water (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), linking the dissolution of an element to its binding and its mineralogical form in the solid. We report here the results of an experiment based on the successive leaching of small masses of particles used for the DUNE experiment. Processed \((P, R1, R2)\) and non-processed \((Q)\) dust were used to seed the large mesocosm (Desboeufs et al., 2014). These leaching tests were performed on \(Q\) sample 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 pH and cloud polluted droplets at low pH.

2 Experimental protocol

All of the 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).

Approximately 10 mg of the fine fraction of the soil described in Guieu et al. (2010) was deposited on a 47 mm diameter and 0.2 µm porosity polycarbonate membrane in a polycarbonate filtration device (Nalgene™). One hundred millilitres of leaching solu-
tion was then poured onto the filter, was gently stirred by hand and was left for one minute. The vacuum was applied to the filtration unit until all of the solution passed through, which takes approximately 20 s. Ten millilitres was set aside for pH determination and 60 mL was stored in a polyethylene bottle with the pH decreased to 1 with ultra pure nitric acid (Merck, Suprapur™ grade). Twelve successive leaching steps were applied to the same filter with increased acidity solutions. 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 \(\sim 6.5\)), the following three used a 10\(^{-5}\) M acid solution (pH 5), followed by three steps with 10\(^{-3}\) M acid solution (pH 3) and finally, three steps with 10\(^{-1}\) M acid 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), P (213.628). The instrument was calibrated on each line using standard solutions and was checked five times with the certified reference material SLRS-4 (NRC, Canada). The recovery rate (RR%) was found to be between 97 % and 120 % for the certified elements Ca, Sr, Ba, Mn, Fe and Al. Nevertheless, relative standard deviations for the five SLRS-4 measurements were less than 5 %, except for P which reached 10 %. The detection limit (DL) 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 element present in 10 mg of soil. The DL was 0.002 % for Ca, 0.01 % for Al and Fe, 0.04 % for Mn, 0.2 % for Sr, 0.8 % for Ba and 2 % for P.

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).

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

Finally, solubility is expressed as the amount of dissolved element found in a given leaching batch divided by the total amount of element initially present in the soil mass used for the experiment. A cumulative dissolution was also calculated as the sum of the successive batch dissolution experiments performed until the given one.

3 Results and discussion

The elemental composition of the soil is given in Table 1 and is expressed as oxide, except for calcium which is associated with carbonate, and Sr and Ba which are present at trace levels. The average and standard deviation results of the four replicates, including the measured pHs, are given in the Supplement Table.

Large amounts of calcite are found in the sample (Desboeufs et al., 2014) and the amount of calcium carbonate well explains the ignition loss by its transformation into calcium oxide and carbon dioxide exhaust. The South Tunisian source region is known to produce calcium-rich dust (Bergametti, 1989; Avila et al., 2007) due to carbonated lithology of soils in this region (Claquin et al., 1999). The calcium index of dust shows high calcite concentrations in the dust originating from Tunisia, northern and central Algeria, and Morocco, and low concentrations 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:

\[
\text{CaCO}_3 + \text{H}^+ = \text{HCO}_3^- + \text{Ca}^{2+} \text{ at pH } > 6
\]
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 decreases to 6.7 for the “pH5” leaching solution; with “pH3”, 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 is observed for the first leaching process (Fig. 1a), enforcing the hypothesis that calcium was mainly present as calcium carbonate in the solid. The most acidic solution, “pH1”, was measured at pH 1.1.

A first dissolution pattern is displayed in Fig. 1a. For Ca, Sr and P, the solubility is approximately 5% for the first leaching batch at pH 8 and continuously decreases until the first pH 3 leaching solution, for which it increases up to 30% for Ca. After that, the solubility decreases again except during the first leaching with a solution at pH 1. The pattern is the same for Ba and Mn but with a solubility three times lower than the other elements at each step, except at pH 1 for which the solubilities of all the elements have the same order of magnitude. Gleyzes et al. (2002) point out that the sensitivity of carbonate dissolution to an acid reagent, which occurs at pH 5 and below, is completed during 5 h at pH 5 (Filgueiras et al., 2002). With our experiments, pH 5 was not reached by the leaching solution called “pH5” because of the alkalinity of the soil, which overcomes the unbuffered acidity of the leaching solution. The solution called “pH3” was the first one that was acidic enough to dissolve carbonates. Mn, Sr, Ba and P seem here 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 sea water and fresh water, which can explain the presence of this element in the carbonate fraction of the soil. We define cumulative solubility as the sum of all the solubilities measured in the previous and given batch. If we plot phosphorus cumulative dissolution as a function of calcium cumulative dissolution, a straight line with a slope of 0.86 is obtained by less-squares regression.
(Fig. 2a). This suggests a linked dissolution of calcium and phosphorus for all of the batches and therefore, provides strong evidence for the association of phosphorus with calcium carbonate in the same solid phases.

Fujiwara (1964) found manganese as single Mn$^{2+}$ ions randomly distributed in natural calcium carbonate lattices. In Fig. 2b, we can observe the same manganese behaviour as phosphorus but with a linear regression slope equal to 0.27. Values obtained for the pH 1 leaching step are excluded from the regression because they are above the line. We can conclude that a part of manganese is closely associated with calcium carbonate and released with calcium for pHs lower than or equal to three. At pH 1, other solid phases are releasing manganese which is no longer related to calcium carbonate.

Aluminium and iron belong to a second group. The dissolution of both of these elements was very low until pH 3, where it reached 0.2 % and increased again at pH 1 up to 1 % for aluminium and 0.4 % for iron (Fig. 1b). Filgueras et al. (2002) report the effect of acid leaching on exchangeable and sorbed metals, pointing out the absorbing properties of carbonates. Gleyzes et al. (2002) highlight some dissolution of silicate at low pH but both works conclude that acid leaching does not dissolve oxides. Part of soluble aluminium and iron could be released by carbonate at pH 3 and by silicate at pH 1 and 3, including clays, but excluding oxides as also mentioned by Journet et al. (2008).

At a given pH, a strong decrease is always observed from the first to the third leaching experiment (labelled in order as a, b and c). We can therefore assume that there is a finite stock of elements that can be dissolved at each tested pH and then we can add dissolution percentages measured for each repeated pH. We can also calculate a cumulative solubility for each pH which represents what would be rapidly dissolved at the given pH. The cumulative dissolutions of Al, Fe, Mn and P are displayed in Fig. 3. We can compare the solubility found here with that estimated and calculated in sea water for the DUNE mesocosm experiments, where the same soil fraction was used but after processing with synthetic cloud-like water in order to reproduce condensation-evaporation processes on dust particles during atmospheric transport (Wuttig et al., 2013). They find a similar solubility to that observed here at pH 3 for manganese and
iron (respectively 21 % and 0.25 % vs. 27 to 41 %, and up to 0.12 %) as well as aluminium (0.4 % vs. approximately 1 %). Because Wuttig et al. (2013) have used cloud-processed dust, the solubility similarities obtained from unprocessed dust at pH 3 in water and with cloud-processed dust in sea water let us assume that the acidic conditions encountered during the laboratory cloud processing have been recorded in the dust until it was used to seed the mesocosms and controlled the solubility levels in seawater.

Phosphorus appears here to be much more labile than observed on average for an atmospheric deposition over Corsica (Bergametti et al., 1992), the solubility of which was found to be very low for natural dust and high for anthropogenic aerosol. This is probably due to the calcium carbonate enriched with phosphorus present in the soil used for the DUNE experiment. If we assume that 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 iron behaviour is more complex, its 0.25 % cumulated solubility at pH 3 may represent its fraction associated with carbonates that is either sorbed or included in the lattice, like manganese.

4 Conclusions

The fine fraction of the particular soil from southern Tunisia used in this study has been shown to be representative of mineral dust aerosol transported and deposited in the North-western Mediterranean region, especially in the spring season (Guieu et al., 2010). The observed solubility of various elements from this soil at pH 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 biogeochemistry, appear to have a fraction associated with carbonates that can be dissolved without invoking strong acidic conditions. This yields an unexpected high liability to mineral dust-contained phosphorus (50–55 % at pH = 3 for our sample), and
claims for apportioning the carbonate fraction and its composition in modelling aeolian dust transport and deposition of trace elements to the surface ocean.

In regions impacted 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 weathering strength of rain/cloud water. The weaker solubilisation of trace metals and metalloids by a less acidic atmospheric water can be compensated by the release of carbonate which appears as a potential source of bioavailable nutrients.

Supplementary material related to this article is available online at http://www.biogeosciences-discuss.net/11/2623/2014/bgd-11-2623-2014-supplement.pdf.

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References


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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).

<table>
<thead>
<tr>
<th>Composition</th>
<th>±</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>33.0 % 0.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.9 % 0.4</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.3 % 0.3</td>
</tr>
<tr>
<td>MnO₂</td>
<td>0.055 % 0.002</td>
</tr>
<tr>
<td>MgO</td>
<td>3.5 % 0.1</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>49 % 2</td>
</tr>
<tr>
<td>Na₂O</td>
<td>&lt; 1 % –</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.72 % 0.05</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.54 % 0.01</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.10 % 0.01</td>
</tr>
<tr>
<td>Sr</td>
<td>360 ppm 27</td>
</tr>
<tr>
<td>Ba</td>
<td>270 ppm 14</td>
</tr>
</tbody>
</table>
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**Fig. 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.

Corresponding measured pHs for batches “pH7”, “pH5”, “pH3” and “pH1” are respectively 8, 6.7, 3 and 1.1.
Fig. 2. Cumulated solubility of P (A) and Mn (B) as function of the cumulated solubility of Ca. The plotted line is a least-squares linear regression. The three orange points left for Mn are not included in the regression and were obtained at pH 1.
Fig. 3. Cumulative solubility for P, Mn (left scale), Fe and Al (right scale), The vertical segments are the standard deviation of the four replicates.