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ZINC PARTITIONING IN MEDITERRANEAN RAINWATER

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Abstract. Eleven rainwater samples were collected in the Western Mediterranean region in clean conditions in order to study the partitioning of zinc between soluble and insoluble forms. The pH of the rainwater sampled ranges between 4 and 7; the high values of pH resulting from the neutralization of acidic species by the calcium carbonate present in desertic dusts. The soluble zinc ranged between 15 and 99% of the total zinc; the higher percentage are observed for the lower pH, and the lower percentage for the higher pH. This variable solubility can be explained by an adsorption-desorption equilibrium which is highly sensitive to the value of pH in rainwater.

Introduction

It is now clear that atmospheric inputs of trace metals to terrestrial and marine environments are dominated by wet-deposition processes, particularly in the mid-latitudes regions [Galloway et al., 1982]. Because the availability of trace metals to the marine and terrestrial ecosystems varies highly with their physico-chemical form [Moore et al., 1984; Maring and Duce, 1987; Hardy and Creclius, 1981], it is important to identify the parameters which control the phase-changes in rainwaters. One of the most significant interactions is the partitioning between dissolved and particulate phases. Only few data exists on trace elements partitioning in rainwater, though many studies have discussed the processes controlling the partitioning of trace elements in aquatic environments [Stumm W. and Morgan J.J., 1981; Eisenreich S.J., 1981]. From these studies, it is likely that heavy metals may be present in dissolved, colloidal or particulate fractions, may be included in minerals, may form labile or non labile complexes [Benjamin and Leckie, 1981]. The transfer of trace metal species from the solid to the liquid phase can result from various physico-chemical ways. First, when the trace metal is included in a mineral lattice, the exchange of cations can occur between the lattices and some other cations existing in solution. Obviously, this process will be strongly dependent on the physico-chemical properties of the particles (type of mineral lattice, particle size...). This type of solubilization will be mainly controlled by the kinetic of extraction. Second, if the trace metal is

present as salt, its solubilization will be highly controlled by pH and common ion effects. Finally, trace metal species can also be adsorbed on particulate or colloidal matter. There is a rapid exchange of cations (usually H^+) or a desorption by complexation. In the latter case, an equilibrium between soluble and insoluble phases is attained, with the activity of the insoluble phase dependent on both the amount of insoluble metal and the number of available sites for adsorption. The ionic strength and especially pH will control these adsorption-desorption processes.

To our knowledge, this paper presents the first data on the partitioning of zinc in carefully collected individual rainwater samples characterized by a wide range of pH. The partitioning of Zn in rainwater is discussed, attention being focused on the variability of soluble/insoluble ratio in relation with changes in pH.

Sampling and analytical procedures

The samples were taken from our sampling station at Capo Cavallo (42°31 N, 8°40 E) on the Northwestern coast of Corsica Island. This site is located 300 m above sea-level and about 700 m distant from the shore line. It is exposed 80% of the time to marine air-masses from Southwest to Northeast. Moreover, the closest pollution sources originating from the city of Calvi are distant from 20 km. Rainwater samples were collected by using ultra-clean procedures during two field experiments in March-April 1986 and October-November 1987 (table 1). Each rain event was collected separately by using a single-use polyethylene collector of 452 cm² aperture. Immediately after the end of the rain, the insoluble matter was separated from the liquid phase by filtration on Nuclepore 0.4 µm filter. This operation was made in a filtering hood. The liquid phase was weighted and separated into three aliquots: 10 ml were used for immediate determinations of pH and conductivity; about 50 ml were acidified with HNO₃ Prolabo Normatom and stored in a teflon flask for trace metals analyses; the last aliquot was used for determination of major ions. These analyses were performed by ionic chromatography, colorimetric methods, and flame atomic absorption spectrometry. HCO₃⁻ was determined by using slightly modified Gran's titration. These analyses allowed us to establish the ionic balance; the mean ratio between cations and anions for these eleven rains was 0.94 ± 0.07 . The trace elements analyses were performed by X-Ray Fluorescence Spectrometry for the insoluble fraction [Losno et al., 1987] and by flameless

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TABLE 1. Conditions for the rain collection and associated pH.
a) Total of major insoluble elements in oxide form.

Sample	Date	Time	Volume (l)	pH	Total mineral a) charge of insoluble material (mg.l ⁻¹)
P1	03/22/86	10 A.M.	0.033	4.03	1.3
P2	04/07/86	10 A.M.	0.395	6.88	17
P3	04/08/86	3 P.M.	0.493	6.55	9
P4	04/08/86	5 P.M.	0.214	5.76	3
P5	04/08/86	10 A.M.	0.382	4.61	0.3
P6	04/09/86	12 P.M.	0.218	4.39	0.5
P7	10/22/87	10 A.M.	0.107	6.30	12
P8	10/22/87	10 A.M.	0.030	6.08	24
P9	10/29/87	11 A.M.	0.116	5.84	6
P10	10/29/87	2 P.M.	0.286	4.94	2.5
P11	10/29/87	4 P.M.	0.187	4.63	1

atomic absorption spectrometry for the dissolved fraction.

Source regions of zinc in mediterranean rainwaters

The pH values for the eleven individual rains collected were found to vary between 4 and 7 (table 1). For each rain sample, three-dimensional backward trajectories of the air-masses [Martin et al., 1987] arriving at the 700 hPa barometric level show also a strong relationship between pH and the geographic origin of the air-masses. Rain associated with air masses coming from African regions exhibit higher values of pH (between 5.8 and 6.9) than those resulting from an European origin. These variations of pH for Mediterranean rainwaters in relation with the origin of the associated air masses are not unexpected. Löye-Pilot et al. [1986] have underlined such a variability: these high values of pH, which are systematically associated with African dust transport episodes, result from the balancing of the background acidity (H₂SO₄, HNO₃) by the high contents of calcium carbonate present in the Saharan dust. The acidic species are mainly linked to anthropogenic emissions in the Medi-

terranean rainwater. The non marine sulfate represents about 90% of the total sulfate for the collected "Saharan rains" and nitrate and non marine sulfate exhibit similar concentrations for rains associated to European or Saharan air masses (table 2).

This can be easily explained by the frontal character of Saharan dust advection over the Western Mediterranean region [Prodi et al., 1979; Bergametti et al., in press, 1988]. The trajectories for the Saharan rains collected confirm these studies. We can observe a strong difference in the origin of the air masses in relation with their final barometric level. The trajectories ending in the lower layer (925 hPa) show an European origin, while the upper levels (700 or 500 hPa) indicate air masses coming from African area. A mixing occurs between detritic alkaline air masses from North Africa and polluted air masses containing sulfuric and nitric acids, zinc and other pollutants. The total zinc concentrations observed in the Mediterranean rainwater confirm this feature; based on the measured aluminium concentrations in rainwater and the crustal abundances of zinc [Mason, 1966], it can be calculated that less than 10% of total zinc is of terrigenous origin in our rain samples,

TABLE 2. Concentrations for soluble and insoluble zinc and an estimate of the contribution in crustal zinc. (Values in $\mu\text{mol.l}^{-1}$, accuracy 6% for insoluble and 8% for soluble zinc, 10% for non marine sulfate and 5% for nitrates.

Sample	Soluble zinc	Insoluble zinc	Total zinc	Crustal zinc	non marine sulfate	nitrate
P1	2.42	0.039	2.5	0.0014	115	97
P2	0.07	0.325	0.40	0.0228	130	33
P3	0.04	0.123	0.16	0.0126	18	3.5
P4	0.20	0.017	0.22	0.0055	21	7
P5	0.40	<0.004	0.40	0.0004	21	9
P6	0.24	0.051	0.29	0.0002	52	13
P7	1.22	0.377	1.6	0.0166	82	55
P8	0.11	0.256	0.37	0.0393	103	63
P9	0.29	0.069	0.37	0.0127	32	23
P10	0.11	0.012	0.11	0.0054	42	24
P11	0.13	0.008	0.14	0.0019	24	15

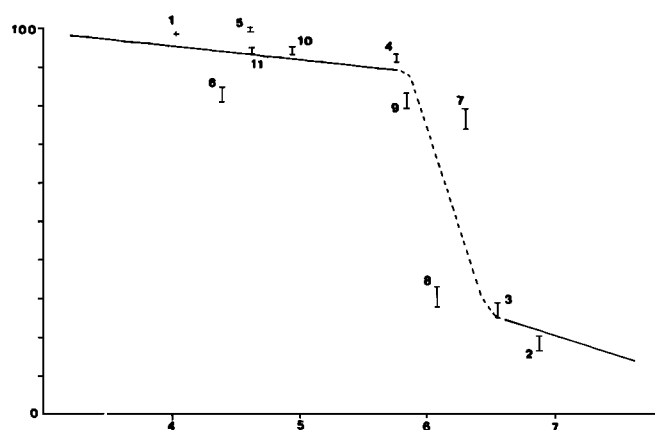


Fig. 1. Percentage of soluble zinc in Mediterranean rainwater as a function of pH.

whatever the origin of the air masses (table 2). Consequently, it can be concluded in view of the previous discussion, that the zinc present in the Mediterranean rainwater results strongly from anthropogenic emissions, even in the case of "Saharan rains".

Solubility of zinc

Figure 1 reports the variations of the percentage of soluble Zn as a function of rainwater pH. We observe that most of zinc is soluble in the rains which have a pH lower than 5.5. An abrupt decrease appears in zinc solubility for the higher pH.

One hypothesis to explain our data is a kinetic control of the extraction of zinc from the crystalline lattice. This hypothesis can be ruled out since it cannot explain the abrupt change in the Zn solubility for a narrow pH range and, as mentioned above, the zinc contained in our rain samples was not included in detritic soil minerals.

As previously indicated, a second possibility to explain the zinc behaviour in our rain samples is the formation of insoluble salts. The ionic species able to form insoluble salts with zinc are the hydroxides (OH^-) which form $\text{Zn}(\text{OH})_2$, the phosphates (PO_4^{3-}) which form $\text{Zn}_3(\text{PO}_4)_2$ and the carbonates (CO_3^{2-}) which form ZnCO_3 [Joussot-Dubien, 1962; Seiqueira, 1988]. Taking into account the low ionic strength of our rains, we assume equivalence between concentration and activity. Using the acidity constants for CO_2 and H_3PO_4 , the measured concentrations of HCO_3^- , phosphorus and pH values, it is possible to calculate the ionic products $[\text{Zn}^{2+}][\text{CO}_3^{2-}]$, $[\text{Zn}^{2+}][\text{OH}^-]^2$ and $[\text{Zn}^{2+}]^3[\text{PO}_4^{3-}]^2$. We observe (table 3) that all these ionic products are significantly lower than the solubility products of these salts. It appears therefore that the changes in zinc solubility do not result from the formation of insoluble salts.

On the other hand, the curve obtained for zinc solubilization (figure 1) is typical of a desorption-adsorption equilibrium. This process has been proposed by White and Driscoll [1987] to explain the partition of zinc in a lacustrine system. The percentage of soluble zinc is about 80-100% for rainwater with pH lower than 5.5 and only 20% for rainwater with pH greater than 6.5. This curve of a neutralization type, with a strong decrease of the percentage of dissolved zinc around pH = 6.2, is similar to those obtained from a theoretical [Davis and Leckie, 1978] or experimental [Jenne, 1968; Schultz et al., 1987] point of view for zinc adsorption on hydrated oxides. The similitude between the transition pH of our rains and laboratory experiments [Schultz et al., 1987], suggests that complexing agents, such as organic ligands, have only a little influence on the zinc partitioning in these rainwater samples. The greater mass of insoluble matter in non acidic rains contributes to a greater number of absorption sites, and enhances probably the pH dependence of the zinc solubility. However, this influence of the number of adsorption sites on zinc solubility can only appear in the range of the pH transition from 5.5 to 6.5.

Table 3. Solubility of zinc salts.

Sample	Activity of anions			Ionic Products		
	$[\text{OH}^-]$	$[\text{PO}_4^{3-}]$	$[\text{CO}_3^{2-}]$	$[\text{Zn}^{2+}][\text{OH}^-]^2$	$[\text{Zn}^{2+}]^3[\text{PO}_4^{3-}]^2$	$[\text{Zn}^{2+}][\text{CO}_3^{2-}]$
P1	1.1E-10	---	< 1E-10	2.8E-26	---	---
P2	7.6E-8	1.0E-7	4.7E-8	4.1E-22	3.5E-36	3.3E-15
P3	3.6E-8	2.1E-8	7.3E-9	5.6E-23	3.9E-38	3.3E-16
P4	5.8E-9	1.5E-9	2.9E-10	6.6E-24	1.8E-38	5.8E-17
P5	4.1E-10	2.4E-12	< 1E-10	6.6E-26	3.7E-43	---
P6	2.5E-10	8.8E-13	< 1E-10	1.5E-26	1.1E-44	---
P7	2.0E-8	4.3E-14	1.1E-8	4.8E-22	3.4E-45	1.4E-14
P8	1.2E-8	3.6E-14	---	1.6E-23	1.7E-48	---
P9	6.9E-9	---	9.7E-10	1.4E-23	---	2.9E-16
P10	8.7E-10	< 1E-17	< 1E-10	8.4E-26	< 1.3E-55	---
P11	4.3E-10	< 1E-17	< 1E-10	2.3E-26	< 1.3E-55	---

Published value of the solubility products (Joussot-Dubien, 1962):

5.5E-16 9.1E-33 7.1E-11
to 2.7E-17

Conclusion

Although the present data set is limited to eleven rainwater samples, our results strongly suggest that the zinc solubility in atmospheric precipitations is controlled by adsorption-desorption processes on existing particles; such processes are largely dependent on the rainwater pH. It should be pointed out that, in our samples, the insoluble zinc is labile, easily mobilized by fast chemical reactions. It can be therefore assumed that the fate of the soluble and insoluble zinc will be largely dependent on the type of natural environment where this element will be deposited. Taking into account the diversity of terrestrial ecosystems, it will be difficult, in this case, to propose a uniform biogeochemical impact for the deposited zinc. On the contrary, in seawater, where the ionic strength is close to 0.3, pH near to 8 and mineral and organic ligands are abundant, it is probable that most of the wet deposited zinc will be soluble in surface seawater whatever the pH of precipitations. Consequently, most of the atmospheric flux of zinc to the ocean is likely to be biologically available.

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