Biogeosciences Discussions

Dissolution of atmospheric cobalt and zinc in seawater

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Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

| ◀ | ▶ |
| ◀ | ▶ |

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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C.-E. Thuróczy et al.

Abstract

Atmospheric dust inputs to the open ocean are major source of trace metals bioavailable for the phytoplankton after their dissolution in seawater. Among them, cobalt (Co) and zinc (Zn) are essential for the growth and for the distribution of major phytoplankton taxon such as coccolithophorids and diatoms. The solubility in seawater of Co and Zn present in atmospheric dusts was studied using an open-flow reactor with and without light irradiation. The analyses of cobalt and Zinc were conducted using voltammetric methods and the global elemental composition of dust determined by ICP-AES. This study highlights the role of the dust origin in revealing the solubility characteristics. Higher dust solubility was found for zinc as compared to cobalt. Cobalt in anthropogenic particles is much more soluble in seawater than in natural particles after 2 h of dissolution. Zinc showed opposite solubilities, higher in natural particles than in anthropogenics. This work is a contribution to ongoing studies which focus on the impact of atmospheric inputs of trace metals onto the primary production.

1 Introduction

Atmospheric inputs of dust to the open ocean are major source of metals and nutrients (Duce and Tindale, 1991; Jickells et al., 2005). River inputs and upwelling can also be a major source of trace metals to the surface ocean (Johnson et al., 1997). The atmospheric source to the open ocean is due to the wind erosion of the lands surfaces, but also to direct emission by the anthropogenic activities (industry, agriculture, transportation). The dissolution of these particles in the upper layer of the ocean can vary with their origin, their elementary composition and the possible transformation which can occur in acid clouds of the atmosphere and/or by UV irradiation. Bioavailable trace metals can regulate the growth of the phytoplankton influencing the primary production and the carbon cycle (Sunda and Huntsman, 1995). The nutritive metals contained in dust are available for phytoplankton after their dissolution in seawater. Among these

micro-nutrients, cobalt (Co) and zinc (Zn) are still poorly studied despite their potential key role in phytoplankton physiology and productivity. For instance the distribution of dissolved Co and Zn in seawater shows nutrient-like profile (such as phosphate and silicate; Saito and Moffett, 2002). Furthermore the growth rate of coccolithophorids, like
5 *Emiliana huxleyi*, and cyanobacteria, like *Prochlorococcus* and *Synechococcus*, can be primarily limited by the low Co concentrations (Sunda and Huntsman, 1995; Saito et al., 2002). In contrast Zn would be primarily requested for the growth of diatoms, rather than Co (Sunda and Huntsman, 1995). Both Zn and Co play important roles in the physiology of the phytoplankton (Frausto da Silva and Williams, 1994) like in the
10 DNA replication (e.g., Zn-fingers), in enzyme activations (e.g., carboxylic anhydrase; Vallee and Auld, 1990) and in the structure of vitamins (for instance Co is the co-factor in the B_{12} vitamin; Kobayashi and Shimizu, 1999). Thus, soluble Co and Zn inputs to the surface ocean can impact the growth, some metabolic processes, the structure of the phytoplankton assemblage and the carbon flux at the atmosphere-ocean inter-
15 face. However the solubility and the biogeochemical impact of these trace metals is still poorly described or virtually unknown.

The dissolution of trace metals could depend on the origin of the particles, on their size, on the type of deposition (dry or wet) and on the pH of the rains (Desboeufs and Losno, 2001; Bonnet and Guieu, 2004; Journet et al., 2008). For instance metals con-
20 tained in carbonated dusts are more easily dissolved in the water than those present in alumino-silicate particles due to different binding strength of the metal to the mould (Desboeufs et al., 2005). So far studies on the dissolution of trace metals have been mainly focusing on iron and have been performed in enclosed systems (Bonnet and Guieu, 2004). Such enclosed experiments have shown that there is a possible satu-
25 ration of dissolved metal in the water (Bonnet and Guieu, 2004) that does not mimic the processes taking place in the surface ocean. Furthermore most of the experiments were done in pure water, and next with different pH to simulate the rains (Desboeufs, 2001), which doesn't fit with the chemical dynamics of the surface ocean. This work aims to determine the solubility of Co and Zn contained in atmospheric dusts from

Dissolution of atmospheric cobalt and zinc in seawater

C.-E. Thuróczy et al.

different origins in the upper layer of the ocean using an open-flow reactor, natural seawater inflow, and the effect of photochemical processes on the dissolution of these trace metals.

2 Material and methods

2.1 Particles sampling

Two types of particles for aerosol simulation were considered here. One is the fine fraction ($<20\,\mu m$, sieved from bulk) of a crustal soil originated from Cape Verde Islands (a loess similar to Saharan soil) for simulation of natural mineral aerosol. The second was a coal dust collected with electrostatic filters in a French power plant (le Havre) for simulation of an anthropogenic aerosol. An example of the differences in morphology between these natural and anthropogenic particles is reported in Fig. 1. It showed small-size particles with a regular and spherical structure for the coal dust and a heterogeneous structure for the natural soil.

2.2 Experimental device

The dissolution experiments of trace metals in seawater was performed using an open-flow reactor to avoid saturation effects, in order to mimic the natural processes which occur in the upper ocean with or without light irradiation. It was constituted of a constant volume pump, a reaction chamber ended by a 47 mm membrane filter (Whatman polycarbonate $0.4\,\mu m$, acid cleaned) and an exhaust tubing (Desboeufs, 2001; Velay, 2006). This reactor allowed a permanent non-stationary system by dint of a continuous flow of seawater on the particles which prevents from saturation of the dissolved phase. The reactor and all the tubings were PTFE material and acid cleaned. The irradiation device consisted of a 125 W high-pressure Xenon bow-lamp which recreates the solar spectrum (Model 125 W MSR) but with some blue-UV enrichment. The

light was brought through an optical fiber to the reactor. The actinic flux in the blue-close UV measured from H_2O_2 decomposition was 10 to 20 times higher than the natural irradiation found with a bright weather (Velay, 2006). The seawater used for these experiments was collected in a HNLC area during the KEOPS cruise aboard RV *Marion-Dufresne* in 2005 (Blain et al., 2007) with ultra-clean conditions using a kevlar wire and GO-FLO bottles. Twenty liters were filtered on board using 0.2 μm Sartorius Sartobran cartridge and stored in ultra-clean Nalgene bottles (LDPE) in the dark.

For both particle types Zn and Co dissolution experiments were conducted under light irradiation, but a couple of experiments were performed in the dark for Co disso-lution.

Around 20 mg of solid phase was weighted and put at the bottom of the reactor under a magnetic stick stirrer. The experiment started when the seawater reached the reactor and was followed during 2 h with a continuous seawater flow. Samples were collected in acid cleaned LDPE Nalgene bottles (60 mL) at the outlet of the reactor. Sampling frequency was every 2 min during the first 20 min of the experiment, after which samples were taken at 30, 45, 60, 90 and 120 min. They were immediately acidified to pH 2 with Suprapur HCl (Merck) and stored at room temperature in the dark before being analyzed by voltammetry. All the experiments were done in an ISO3 clean room, under an ISO1 laminar flow hood.

2.3 Determination of the dust elementary composition

The elementary composition of the dust samples was determined by ICP-AES (Type Optima 3000, Perkin-Elmer) after their mineralization. The mineralization of 60 to 80 mg of particles was performed in ultra-clean Teflon bottles using 2 mL hydrochlo-ric acid 30%, 2 mL of hydrofluoro acid 40% and 2 mL of 65% nitric acid (Normapur™ from Prolabo). The digestion was performed at 50 °C for one day under a fume hood. Then, the acids were left for evaporation at 150 °C. 2 mL of 65% nitric acid were added at 50 °C and the bottles closed for a day. This last sample was diluted in 60 mL of milli-Q™ water in a clean room. The samples were then diluted 10 to 15 times to ad-

just the concentration to the ICP-AES requirements. Blanks samples were prepared without particles using the same protocol used for the dust mineralization to test the cleanliness of the protocol.

2.4 Determination of the dissolution rates of trace metals in seawater

Dissolved Zn and Co concentrations were determined in seawater by Anodic and Cathodic Stripping Voltammetry, respectively (ASV and CSV). The voltammetric equipment consisted of a μAutolab potentiostat (Type III, Ecochemie) connected to a hanging mercury drop electrode (model VA 663 from Metrohm). The mercury drop size was approximately $0.52\,mm^2$. The reference electrode was double-junction, Ag/AgCl, 3 M KCl, with a salt bridge filled with 3 M KCl and a glassy carbon counter-electrode. Samples were stirred with a PTFE Teflon stirrer (2500 rpm). Each equilibrated sample was poured into the voltammetric measurement cell and analyzed following the procedures indicated in Table 1. The samples were brought back to pH 8.2 before analyzing using a 1.5 M borate buffer prepared in 0.4 M NaOH solution. Zn was complexed by APDC (Ammonium Pyrrolidine Dithio Carbamate; Ellwood and van den Berg, 2000). A 0.0013 M stock was prepared in Q-NH_3 0.1%. The final concentration in the sample was $60\,\mu$M. The Co was complexed by nioxime (1,2-cyclohexanedione dioxime; Ellwood and van den Berg, 2001). A first 0.1 M stock was prepared in 0.2 M NaOH and a second one ($40\,\mu$M) was prepared by diluting the first one. The final concentration in the sample was 800 nM.

The voltammetric analyses were calibrated against the NASS-4 certified seawater (calibrated by both "Inductively Coupled Plasma-Mass Spectrometry" and "Graphite Furnace Atomic Absorption Spectrometry"). The concentrations of Co and Zn determined by voltammetry were of the same order (Co: 0.26±0.02 nM, n=3; Zn: 1.69±0.29 nM, n=3) as the certified values (Co: 0.15±0.02 nM; Zn: 1.75±0.27 nM). However, the Co concentration found by voltammetry was slightly higher.

The detection limits were estimated from the standard deviation of replicated analyses with the lowest concentration possible; it was found to be 0.019 nM for Co, close

to those reported by Westerbrink et al. (1990), and 0.142 nM for Zn. The background concentrations measured by voltammetry in the seawater used for the dissolution experiments were 0.049±0.02 nM (n=4) for Co and 0.845±0.1 nM (n=3) for Zn.

3 Results

3.1 Elementary composition of the particles

The elementary composition of the dusts did not vary significantly between natural and anthropogenic dust for Co, but anthropogenic dust was enriched in Zn (Table 2). Consequently the elementary ratio [Co]/[Zn] was much higher in the natural dusts (1.75) compared to coal dusts (0.29) (Table 2).

3.2 Dissolution from dust in seawater

Co and Zn concentrations were measured by voltammetry for each of the kinetic experiment sample. From these measured concentrations, the dissolution rate of X can be computed by the following equation:

$$DR_X = F([X]_{out} - [X]_{in}) + V d[X]_{out}/dt \tag{1}$$

Where DR_X is the dissolution rate of the element X, F the flow rate, $[X]_{in}$ and $[X]_{out}$ the respective dissolved concentrations at the input and the output of the dissolution reactor, V the volume of the dissolution cell and t the time. For discrete sampling, the last term of this equation can be approximated by:

$$V d[X]_{out}/dt = V([X]_{out(i+1)} - [X]_{out(i)})/(t_{i+1} - t_i) \tag{2}$$

Except for the first sample where DR is calculated by: $DR = V([X]_{out} - [X]_{in})/t0$, where $t0$ is the duration of the dissolution cell filling.

The dissolution rate can be expressed as a relative dissolution rate (RDR$_X$ %) with:

$$\text{RDR}_X\% = \text{DR}_X/m_X \tag{3}$$

Where m_X is the amount of element X introduced as part of the dust in the dissolution chamber. Figures 2 and 4 show the dissolution rate as function of time for Co and Zn in the anthropogenic and natural dust.

3.3 Cobalt in seawater

The dissolution rate of anthropogenic Co varied from 0.06%/min at the beginning of the dissolution experiment and fell back to 0.002%/min after 2 h (Fig. 2). Sensible differences were observed between illuminated and dark. A quite different behavior was observed for natural Co. Despite a similar elemental proportion of Co in coal and natural dust, the Co dissolution rate at the beginning was ten times lower in loess (0.007%/min) than in coal dust. But the dissolution rate decreased a bit during the first 30 min, and then increased again after one hour to reach 0.003%/min at the end. The irradiation seemed to produce a noticeable effect at the beginning of the experience by increasing the dissolution rate but both irradiated and dark experiments gave the same dissolution rate at the end of the experiment. However the Co concentrations obtained with the loess were in the same range than the concentration already detected in the seawater, introducing bias in the precision of the calculated dissolution rate as shown with the large uncertainty intervals plotted on Fig. 2. The dissolution rate measured with the open flow reactor can be integrated over the experience time giving cumulative solubility (Fig. 3). This solubility was much higher for the anthropogenic Co (0.8% after 2 h) than for the natural one (0.14% after 2 h). For anthropogenic Co, no differences between irradiated and dark were seen. But for the natural Co, irradiations seemed to speed up the dissolution rate during the first 30 min and then did not affect the dissolution of Co anymore. But the dissolution processes did not stop and may continue after the 2 h of experiment. For anthropogenic Co, the second part of the cumulative dissolution followed the square root shape encountered in continuous

weathering experiments driven by diffusion processes (Wollast, 1967, Fig. 4). Extrapolation of the square root line up to 100% of the Co dissolution (Table 4) gave a time of 3659 d (10 yr) for the anthropogenic particles.

3.4 Zinc in seawater

The Zn composition for both dusts was very different (Table 3) with 10 time more in anthropogenic than in natural. The dissolution rate shape was also different for both dust types. The anthropogenic Zn dissolution started with a rate of about 0.3–0.4%/min and then decreased during the first 30 min. Despite a small increase at 30 min for anthropogenic Zn, the dissolution rate remained low (∼0.02%/min). But for the natural Zn, the dissolution rate increased more and remained at 0.2%/min after 2 h of experiment. Expressed as absolute dissolution rate rather than relative (%), both dissolution rates were similar, respectively 0.04 and 0.06 nmol/min.

At the end of the experiment, natural Zn was more soluble (16%) than anthropogenic (5%) but available quantity was greater for anthropogenic (12 nmol) than natural (5 nmol). Figure 6 represents the cumulative relative dissolution of Zn as function of the time and Fig. 7 as function of the square root of the time and the second part of this plot, for longer times, showed a linear relationship with the anthropogenic dust, but not with the natural one. The extrapolation of the straight line gave a time of 552 h (23 d) for a total dissolution of Zinc from the anthropogenic particles (Table 4).

4 Discussion

4.1 Solubility features of Co and Zn from dust in seawater

The dissolution experiments in open-flow reactor showed significant differences between the natural soil (loess) and the anthropogenic dusts (coal dusts): anthropogenic dusts are much more enriched with Zn compared to natural soils (Table 2), but after

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀ | ▶

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

2 h, the relative amount released is 5% compared to 16% of natural (Table 3). On the contrary natural soils have slightly more Co than anthropogenic dusts (Table 2) but they release less of it after 2 h of exposure to seawater (e.g., 0.14% for the loess against 0.8% for the coal dust; Table 3). This is in similar to what found Sedwick

5 et al. (2007) for iron, with Saharan air containing a relatively high loading of aerosol iron (27.8 nmol Fe m^{-3}) that has a low fractional solubility (0.44%), and north American air containing a relatively low concentration of aerosol iron (0.5 nmol Fe m^{-3}) that has a high fractional solubility (19%). Differences in the morphology of the dust can account for some of these dissolution features. Indeed based on solubility rates of spher-

10 ical particles (using the Stokes-Einstein equation), the small spherical particles of coal dust should be more soluble than the particles of the loess (e.g., bigger and complexed shapes; Fig. 1), provided the dissolution is proportional to the particles size. This would be the case indeed for Co; but not for Zn (Table 3). Differences in mineralogy could also account for the observed dissolution features. For instance the coal dusts were mainly

15 constituted of spheres smaller than 1 μm with a fraction easily exchangeable (75%) and a carbonated structure (<15%) (Guieu et al., 1997; Velay, 2006). The trace metals could thus be weakly bound to this mould. In the coal dusts, the refractory Zn phase could represent only <15% of the total structure (Guieu et al., 1997; Velay, 2006). Thus, the Zn contained in coal dusts could have quickly dissolved in aqueous solution

20 (Fig. 3). In opposite, particles from the natural soils were constituted of quartz, clay, feldspath and pyroxene, in which alumino-silicated mould represents 90% of the whole structure (Ausset, 1996; Ausset et al., 1999; Velay, 2006) and the metals would have been strongly bound in such mineral particles preventing from a quick dissolution of the metals, such as it has been observed for Co and Zn at the beginning of the dissolution

25 experiments (Figs. 2 and 3). It has been suggested that the dissolution of the loess from Cape Verde takes place within two main steps (Desboeufs, 2001): the first one is the dissolution of the most soluble phase by complexation processes. The second one would be the dissolution of the less soluble phases (e.g., silicate phase), which produces a residual layer between the silicate phase and the aqueous solution. At pH

of seawater (of about 8–8.2) the hydroxide ions OH⁻ in seawater would hydrolyze the silicated mould, leading to the second stage of the dissolution reaction. Two dissolution steps of Zn were indeed clearly distinguished for the loess (Fig. 3): a first one just at the beginning of the experiment and a second one starting after 10 min and which appeared to continue beyond 120 min. The increase of Zn and Co solubility after 120 min suggested that the metals were not totally dissolved yet from the loess, and thus that the second step of loess dissolution is probably a slow process. The square root shape obtained after 1 h of dissolution indicates a continuous and stable weathering process for Co and Zn in the anthropogenic particles.

4.2 Atmospheric input of cobalt and zinc to surface oceanic waters and its potential biogeochemical impacts

Atmospheric inputs to the surface ocean generally occur during sporadic events. Among them, Saharan events are major source of dust for the North Atlantic Ocean (Guieu et al., 2002a, b). Dusts from Cape Verde can be transported during such events and then deposited on the surface Atlantic Ocean (Jickells et al., 2005). Assuming an atmospheric inputs to surface waters ranging between 0.002 to 0.1 mg/L of seawater (according to Bonnet and Guieu, 2004) and a mixed layer of 50 m, the Co and Zn atmospheric inputs to surface waters were then calculated by using the dissolution values obtained in this study (Table 5).

The dissolved Co and Zn in seawater from the loess are given as the percentage of dissolved metal to the initial solid composition (e.g., elementary composition, Table 2). The iron inputs by Saharan dust estimated in Milli-Q enclosed water systems (0.07 to 1 nM Fe; Bonnet and Guieu, 2004) are larger than Co and Zn inputs calculated here for the loess for two strengths of atmospheric event (Table 5). Additionally Co concentrations in the surface Atlantic layer (0–50 m) would vary between 20 and 30 pM (Saito and Moffett, 2002, 2001) and Zn between 170 and 320 pM (Ellwood and van den Berg, 2000). The Co inputs to the mixed layer calculated here (e.g., 0.01 to 0.50 pM) would thus be negligible compare to the concentrations found in the North Atlantic, as

well as for the Zn inputs (0.43 to 25.06 pM). Dusts from Cape Verde may thus not be a major source of Co and Zn to the North Atlantic.

Atmospheric inputs of dissolved Co to the surface water calculated for a strong dust event (0.5 pM, Table 5) are as high as the inorganic Co′ cellular requirement of a cal-cifying phytoplankton species like *E. huxleyi* (e.g., Km~0.6 pM; Sunda and Huntsman, 1995; Xu et al., 2007). Similarly dissolved Zn inputs from the loess (0.43 to 25.06 pM; Table 3) are 4 to 250 times higher than the half-saturation constant of inorganic Zn′ for siliceous species like *T. oceanica* (e.g., Km~0.1 pM; Sunda and Huntsman, 1995). Therefore, such atmospheric inputs of Co and Zn have the potential to alleviate growth limitation of *E. huxleyi* and *T. oceanica*, respectively, providing the dissolved metal frac-tion is entirely bioavailable. However these estimates were based on dissolution from loess of Cape Verde that may represent insignificant atmospheric inputs of Co and Zn to the North Atlantic. Complementary studies, especially focusing onto the Saharan events which represent 26% of the total dust input to the global surface ocean (Jick-ells et al., 2005) would thus help to further understand the impact of the atmospheric metals inputs on the oceanic phytoplankton.

The anthropogenic input to the surface ocean is much more difficult to assess since few or no data is available. However, Sholkovitz et al. (2009) estimated the annual apportionment of soluble iron from anthropogenic aerosol source to be from 70 to 85% of the total aerosol input (natural and anthropogenic) near Bermuda and Ireland. In regions with high natural dust input like near Izana and Barbados, it was about 12% (Sholkovitz et al., 2009). Using the solubility of Co and Zn from the coal dust in seawa-ter and its elementary composition obtained in this study (Tables 2 and 3), and using 12% of the total dust concentration in the mixed layer for weak and strong dust event (Table 5), the Co and Zn inputs to the mixed layer (e.g., 0.01–0.35 pM for Co; 0.14–6.83 pM for Zn) may be even lower than the input from natural dusts (e.g., 0.01–0.50 pM for Co; 0.43–25.1 pM for Zn). However a better estimate of the flux of anthropogenic aerosol to the surface ocean is required to further estimate these anthropogenic inputs. For instance anthropogenic fluxes from the east coast of the United States and from

⏮ | ⏭

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Western Europe to the North Atlantic Ocean would be required.

5   Conclusions

This study shows some dissolution processes at the atmosphere-ocean interface of two trace metals hardly studied. Co and Zn play key roles in the functioning of the metabolism of the coccolithophorids and diatoms, respectively. The originality of this work was the use of an open-flow reactor, which simulates the phenomenon occurring at the interface atmosphere-ocean, in order to evaluate the solubility of these two trace metals with the time after the dust deposition at the surface water. However, the experiments described here only investigate the beginning of the dissolution process, especially for natural dusts were no extrapolation is possible after the experiment time. Such study had never been performed before. This work also helps to determinate the percentage of dissolved metal from the dusts in seawater, and therefore to evaluate the atmospheric inputs to the sea surface during a dust event. The results showed clear differences between the natural soil and the anthropogenic dusts. The small spherical and carbonated particles of coal dust released quickly but less Zn in seawater than the natural soils from Cape Verde with an alumino-silicated mould; while the opposite trend was observed for Co.

This work can be pursued with the study of other trace metals important for the marine biology, but also with other dusts (such as Saharan dusts) and with longer dissolution experiment in open-flow reactor which is difficult because large volumes of seawater are needed.

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Dissolution of atmospheric cobalt and zinc in seawater

C.-E. Thuróczy et al.

Table 1. Voltammetric procedures for Zn and Co determinations.

		Zn	Co
	Method	Square wave	Differential pulse
Preteatment	Purge time (s)	300	300
	Conditionning potential (V)	−1.2	−0.7
	Duration (s)	120	180
	Deposition potential (V)	−1	−1
	Duration (s)	1	1
	Equilibration time (s)	10	10
Measurement	Frequency Hz	50	/
	Modulation time	/	0.01
	Interval time	/	0.1
Potentials (V)	Initial	−1.15	−0.7
	End	−0.75	−1.3
	Step	0.003	0.0048–0.0096
	Amplitude	0.01995	0.04995
	Standby	0	0

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 2. Elementary composition in Co and Zn of the natural and anthropogenic dust samples as determined by ICP-AES (μg/g or ppm) and ratio [Co]/[Zn].

Type of dust	[Co] (μg/g)	[Zn] (μg/g)	[Co]/[Zn] (weight)	[Co]/[Zn] (molar)
Natural	182	104	1.75	1.97
Anthropogenic	212	744	0.29	0.32

Table 3. Total dissolved metal from the dust after 2 h in seawater expressed as percentage.

	Cobalt (%)	Zinc (%)
Coal dust in the dark	0.73±0.06	N.D.
Coal dust with light irradiation	0.78±0.06	5.2±0.2
Loess in the dark	0.14±0.06	N.D.
Loess with light irradiation	0.14±0.06	16±1

Table 4. Extrapolation of the straight correlation between the dissolution of Co (Top) and Zn (bottom) as function of the square root of the time. 100% means total dissolution of the metal in seawater.

% Dissolved Co	Extrapolated time (h)	Extrapolated time (d)
10%	840	35
25%	5400	230
50%	22000	920
75%	49000	2200
100%	88000	3700
% Dissolved Zn	Extrapolated time (h)	Extrapolated time (d)
10%	6	0.3
25%	36	1.5
50%	140	6
75%	310	13
100%	550	23

Table 5. Dissolved cobalt and zinc inputs to a mixed layer (50 m) induced by a weak and a strong atmospheric event.

Atmospheric event magnitude	Weak	Strong
Final concentration of Saharan dust in a mixed layer* (mg/L)	0.002	0.1
Cobalt dissolution from the loess with light (%)	0.14	0.14
Zinc dissolution from the loess with light (%)	16.0	16.0
Cobalt input to the mixed layer (pM)	0.01	0.50
Zinc input to the mixed layer (pM)	0.43	25.06

* Values of Bonnet and Guieu (2004)
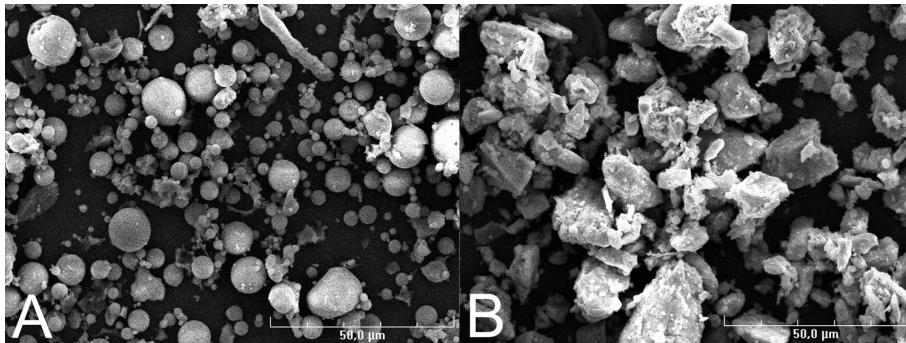
Fig. 1. SEM (Scanning Electron Microscopy) pictures of coal dust **(A)** and of loess from Cape Verde **(B)**. Pictures obtained with the collaboration of the Electronic Microscopy Group, Université de Bretagne Occidentale, Brest, France.
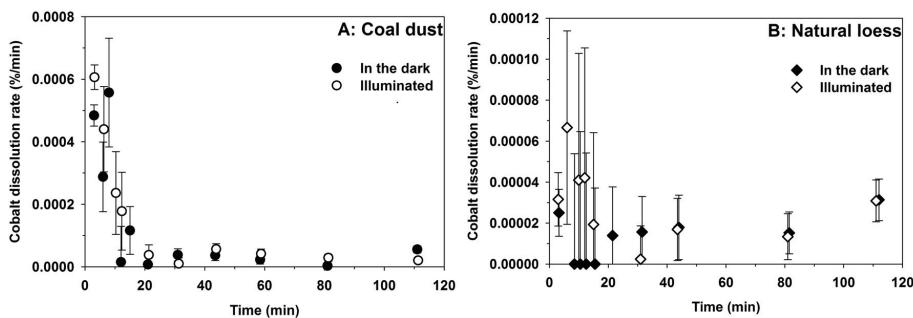
Fig. 2. Dissolution rates of cobalt (%/min) for anthropogenic **(A)** and natural **(B)** dust expressed as function of time.
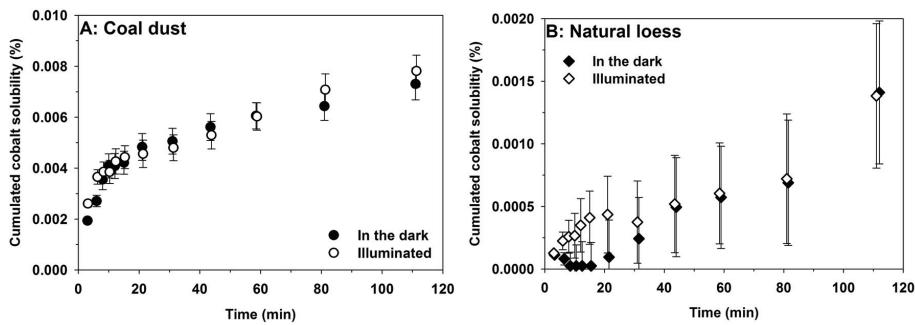
Fig. 3. Cumulated solubility of cobalt (%) as a function of time of the experiment, for anthropogenic **(A)** and natural dusts **(B)**.
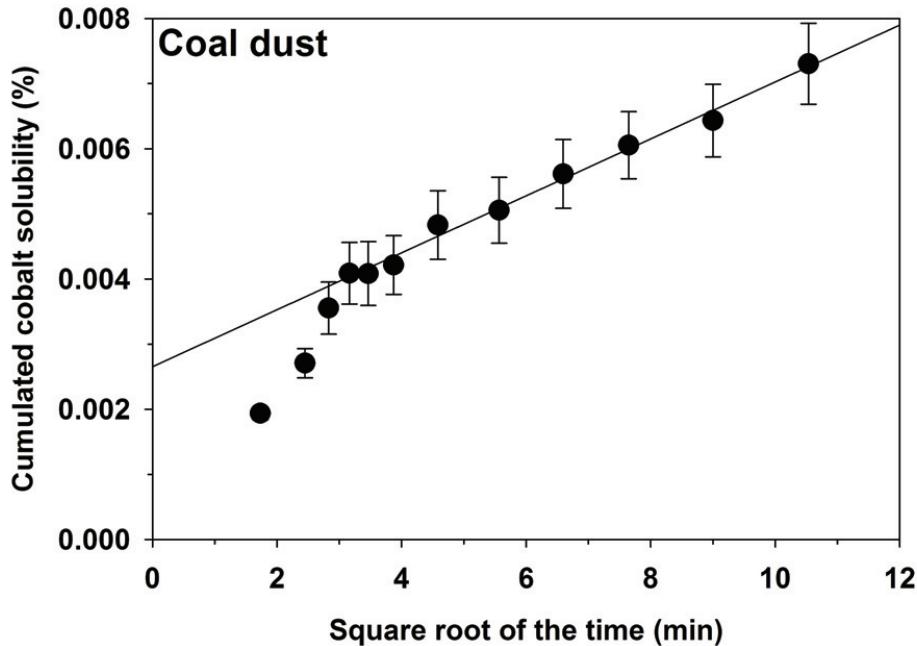
Fig. 4. Cumulated solubility of cobalt (%) as function of square root of the time. ($y=4.372\times10^{-4}\,x+2.653\times10^{-3}$, $R^2=0.991$).
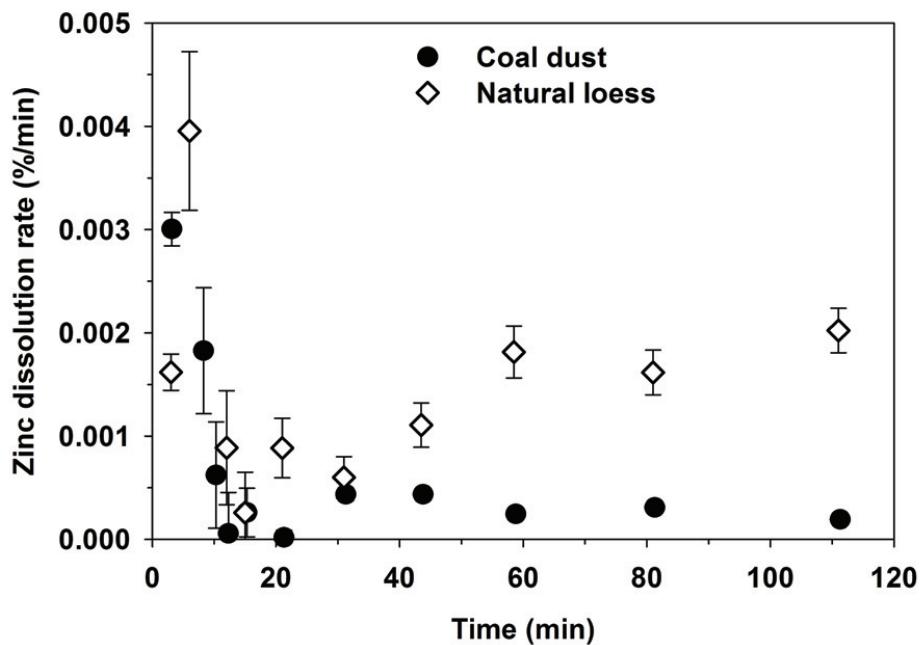
Fig. 5. Dissolution rates of zinc (%/min) for anthropogenic and natural dust as function of time.
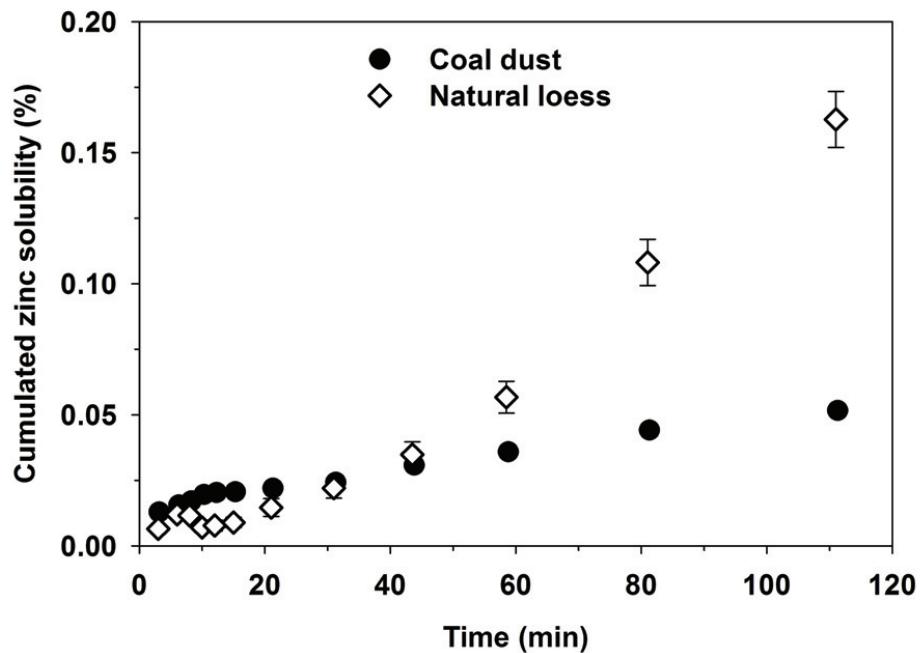
Fig. 6. Cumulated solubility of zinc (%) for anthropogenic and natural dust as a function of time.
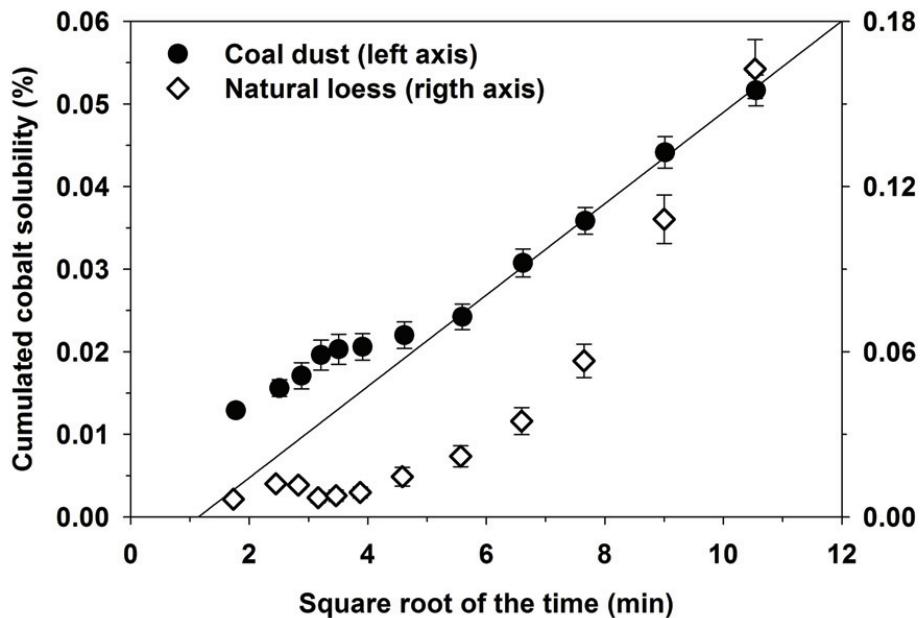
Fig. 7. Cumulated solubility of zinc (%) as function of the square root of time. ($y = 5.531 \times 10^{-3}\, x - 6.316 \times 10^{-3}$, $R^2 = 0.998$).