

What controls iron and phosphorus solubility in wet deposition? (Nutrient-solubility)

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- **Introduction and motivation**

Iron and phosphorus are important nutrients for marine ecosystems. A major source of iron and phosphorus in the open ocean is from atmospheric deposition. In order to evaluate the impact of atmospheric depositions of iron and phosphorus on the ocean ecosystems and thus the climate, global models need to be able to estimate the flux of bioavailable iron and phosphorus from the atmosphere to the ocean. Therefore, it is essential to know what controls the solubility of these elements, which are poorly understood.

Although there are numerous reports on aerosol Fe solubility (Shi et al., 2012) and some reports of aerosol phosphorus solubility (e.g., Nenes et al., 2011), there are limited data available in literature on iron and phosphorus solubility in rainwater. Theodosi et al. (2010) reported iron solubility in wet deposition in the Eastern Mediterranean. A traditional filtration method using 200 nm pore size filters were used in Theodosi et al. (2010). This filtration method may include nanoparticle Fe, which are shown to be present in wet deposition (Shi et al., 2009), so potentially overestimate the soluble Fe in atmospheric deposition. Therefore, we intend to investigate the effect of the nanoparticles in estimating the solubility of Fe in this study.

Fe and P are potentially related geochemically. We also aim to investigate whether and how the solubility of Fe and P are related.

- **Scientific objectives**

The aim of this work is to understand the factors controlling amount of the soluble (<20nm) and dissolved (<200nm) Fe and/or P in rainwater deposited to the oceans. The specific objectives are:

- (1) To understand the fundamental parameters and processes controlling the concentration and partition of labile, soluble and dissolved Fe and P in dust from rainwater; the parameters to be examined include pH, mass of dust per litre of rainwater; concentrations of ionic species such as sulfate, nitrate, ammonium, Ca²⁺, K⁺ and water soluble organic carbon;
- (2) To clarify how Fe interact with P and trace metals in rainwater and affect their solubilities;
- (3) To quantify the soluble, dissolved and total Fe and P deposition fluxes in Crete

- **Reason for choosing station**

Crete island is in the middle of eastern Mediterranean which is a phosphorus limited ocean. It is an ideal location to study iron and phosphorus from atmospheric deposition because it receives both Saharan dust from Africa and pollution from Europe. Therefore, it provides the unique opportunity to sample Saharan dust, anthropogenic particles, as well as their mixtures. This is essential to better understand the factors controlling iron and phosphorus solubility in atmospheric depositions.

- **Method and experimental set-up**

A commercial dry and wet deposition sampler is used collect both dry and wet deposition samples until July 2014). The dry deposition samples will be collected every two weeks. The wet deposition samples will be collected on event basis. The samples will be size separated to <20nm (defined as soluble fraction) and <200nm (defined as dissolved fraction). The filters, tubes and sample bottles

are thoroughly washed using trace metal clean methods. The remaining samples are filtered and the particulate matter on the filter digested with concentrated acids. All the solution samples will be analyzed with ICP-MS. A separate rainwater sample will also be collected for IC analysis of anions, cations, P and selected water soluble organic carbon.

The soluble and dissolved Fe concentrations in the rainwater will be compared with pH dependent ferrihydrite solubility. The fractional solubility (dissolved to total; and soluble to total) of Fe and P will also be calculated and compared with each other. The data on trace elements and the solubility data will also be compared with dry and wet deposition ionic composition and water soluble organic carbon composition.

Eventually, we will calculate the deposition fluxes of different species of Fe, P, and trace metals in the dry and wet depositions.

- **Preliminary results and conclusions**

Since the last visit, a total of 5 rainwater samples and 6 dry deposition samples were collected and analysed with ICPMS (See table). Fe and Mn in both dissolved and total fractions are usually above limit of detection and thus reportable. Fe, Mn and Ni solubility in rainwater is much higher than in the dry deposition samples.

Rain solubility = dissolved/total*100				
	Mn	Fe	Ni	Cu
Rain 1	5.1	10.7		
Rain 2	73.5	8.9	79.9	
Rain 3	54.9	23.9		39.4
Rain 4	77.9	3.5	69.7	42.4
Rain 5	76.4	11.7	87.2	
Dry deposition solubility= dissolved/total*100				
	Mn	Fe	Ni	Cu
Dry 1	6.3	1.6	12.1	21.6
Dry 2	27.0	1.5	20.1	39.0
Dry 3	30.0	2.0	38.6	55.2
Dry 4	21.0	1.8	23.4	47.5
Dry 5	17.2	3.0	6.2	30.9
Dry 6	27.7	2.2	18.0	38.2

Ni, Cu, As, Cd and Pb are sometimes below limits of detection in rainwater and As, Cd and Pb in dry deposition samples. Therefore, we have tested the potential sources of contamination by running different steps of the sampling and filtration. Different blank samples were collected and analyzed with ICP-MS during this visit. The ICP-MS data illustrated a few potential sources of contamination, which have been eliminated or substantially reduced using more rigorous and frequent acid washing of the sampling funnels, filters and filtration units and improved sample handling.

We also compared the trace element concentrations in blank filtrates using different methods:

- (1) 200nm pore size polycarbonate filter and glass filtration unit
- (2) 200nm pore size PES filters within vivaspin filtration unit (using swing out centrifuge)
- (3) 20nm pore size Teflon syringe filter and syringe filtration
- (4) 3 kDa pore size PES filters within vivaspin filtration unit (using swing out centrifuge)

Blank levels of trace metals in the Vivaspin filtrates have relatively large variations, which leads to relatively high limit of detection. This may be due to contamination of the filters during transport (from Birmingham to Crete) or centrifuge filtration. On the other hand, filtrates in blank samples

with acid washed polycarbonate filters and syringe filters gave lower and more consistent concentrations of trace metals, which lowered the limit of detection. Therefore, we decided not to use the vivaspin and using glass filtration unit and syringe filters.

- **Outcome and future studies**

The sampling will continue until end of July 2014 and we aim to run the same experiment for longer term so that we could monitor the deposition flux of soluble, dissolved and total trace elements.

The next step will be to collect more blank samples using the optimized methodology. These samples will be analyzed to produce reportable detection limits and blank levels of trace metals and P.

Then, the field sampling campaign will continue. We expect to collect ~20 more dry deposition and ~40 wet deposition samples in the next 8 months. The samples will be analysed every two months to avoid long-term storage of the samples.

- **References**

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