



Iron redox speciation in atmospheric rainwater : method and application in Guadeloupe rainwater.

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Iron may be a limiting nutrient in oceanic region for primary productivity. It is well known that atmospheric deposition is the main source of iron in open ocean. However, its bio-availability depends on the soluble form concentration in natural waters. Because Fe(II) is more soluble and bio-available to phytoplankton than Fe(III), measurement of ferric species in atmospheric waters seems to be potentially important to evaluate available iron flux.

A method to measure Fe(II) based on the formation of the complex between Fe(II) and ferrozine (FZ)(Stookey, 1970) coupled with Atomic Absorption Spectrometry has been developed and adapted to atmospheric water measurement. Then, rainwater of Guadeloupe has been analysed in may 2005 to estimated total atmospheric iron flux and iron redox speciation.

Complexation of Fe(II) by ferrozine (FZ) is the method usually adopted to study redox speciation of iron in seawater and freshwater (Siefert et al, 1999; Willey et al, 2000; Zhang et al, 2001; Kieber et al, 2001). A pre-concentration step on a C18 Sep-Pak cartridge is used to improve sensitivity and detection limit of the method (King et al, 1991; Yi et al, 1992; Sedlak et al, 1997; Zhuang et al, 2001). Analyses are performed by Atomic Absorption Spectrometry (Sofitikis et al, 2004). The method is characterized by detection limits of 0.3 en ppb for Iron(II) and 0.2 en ppb for Iron(III) with sampling volume of 30 mL.

The recovery efficiency of Fe(II) on Sep-pak was carried out in three different matrix (acidified MilliQ, synthetic rainwater and rainwater collected next to Paris). The recovery of Fe(II) is dependent on pH with an optimal Fe(II) recovery superior to 95% between pH 2 and 2,3. The step of acidification to pH 2 of the sample implies that the

pre-concentration on the Sep-pak cartridge cannot be carried out on line of the rain sampling. This is the reason why, the stability of samples have been tested. Results show that sample acidification has to be performed in the 10 minutes after collect and the acidified sample can be stored less than one hour before passing through the cartridge. The results demonstrate the method is well suited for Fe(II) determination in atmospheric water.

Experiments achieved in may 2005 shows that total deposition fluxes of iron acid leachable fraction in Guadeloupe vary between $7 \pm 2 \mu\text{g.m}^{-2}.\text{d}^{-1}$ and $256 \pm 2 \mu\text{g.m}^{-2}.\text{d}^{-1}$. Furthermore, four filtered rainwater events were collected and passed through the open column to separate Fe(II) and Fe(III). Total iron varies between 24 ± 2 and 212 ± 2 nM. Fe(II) represents a significant fraction of the total iron in any sample collected in Guadeloupe. Average Fe(II) contribution is about $88 \pm 12\%$ of the total iron.