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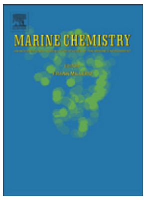

# Aerosol iron deposition to the surface ocean — Modes of iron supply and biological responses

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ABSTRACT

In the last two decades the role of aerosol iron supply to the ocean has received growing attention. Research has mainly focused on three themes — how much iron is supplied to the ocean from dust; where this aerosol iron is deposited (depositional models); and modelling of the biogeochemical impact of iron supply to the ocean in the past, present and future. Here, we investigate the relationship between modes of iron supply (mechanisms, dissolution rate and timescales) to the upper ocean and the subsequent biological responses in the present day. The reported solubility of iron from dust ranges from 0.001–90%, and this variability appears to be linked to both aerosol properties and leaching schemes employed. Consequently, biogeochemical modelling studies have used a wide range of iron dissolution rates (1–12%) and have reported a broad suite of biogeochemical responses. Re-examination of evidence, from ocean observations, of enhanced biological and/or biogeochemical response to aerosol iron supply in the modern ocean suggests that much of it is flawed, and that there are only a few cases in which there is a causative link between dust supply and biological response. The resulting small size of this dataset is due to a wide range of confounding factors including seasonality of environmental factors controlling phytoplankton production (light, silicic acid, phosphate, iron), and the elemental stoichiometry of the aerosols (iron and other nutrients) during dissolution. Thus, the main impact of aerosol iron supply appears to be an initial rapid release of iron, followed by a slow and sustained release of iron during its mixed layer residence time, which may result in small increases in the dissolved iron mixed-layer inventory. The implications of such a mode of iron release from aerosol dust are explored using a simple dust/biota assessment test for both contemporary and paleoceanographic case-studies. We conclude that dust deposition can easily be mistakenly attributed as a primary cause of enhanced biological activity and that, due to the slow dissolution of iron, dust-mediated phytoplankton blooms are probably rare in the modern ocean.

## 1. Introduction

Since the 1990's, there has been a significant transition in the research directions of dust environmental research. Prior to this period, the main focus was on the atmospheric transport of pollutants and geochemical tracers around the globe (e.g. SEAREX, Prospero et al., 1989). However, in 1990 Martin's seminal study brought together the Vostok ice core record (specifically dust, atmospheric carbon dioxide concentrations, and temperature) and his findings on the positive effects of iron-enrichment on phytoplankton growth rates in High Nitrate Low Chlorophyll (HNLC) waters (Martin, 1990). Over the following decade, it became increasingly evident that iron supply plays a pivotal role in setting the productivity of many ocean regions (Coale et al., 1996), and that dust deposition is a major iron supply mechanism to the global ocean (Duce and Tindale, 1991).

This recognition of the important role of dust in supplying iron to the ocean resulted in a proliferation of both dust deposition models (see Mahowald et al., 2007), and of lab-based dust dissolution experiments (e.g. Spokes et al., 1994). The resulting data from both of these approaches were then used in global biogeochemical models to explore the impact of aerosol iron on the ocean carbon cycle in both the present and the geological past (e.g. Moore et al., 2002b; Christian et al., 2002). During the 1990's the increased range of sensors on satellites dramatically increased the power of remote-sensing as a means to investigate both the nature and extent of episodic dust events (Husar et al., 1997) and to compare these with the biological and biogeochemical signatures after such dust events (e.g. Gabric et al., 2002). The availability of such coupled satellite datasets also provided validation for both dust deposition and ocean biogeochemical models.

In the last decade there have been developments in the range of tools that can be employed as proxies for the impact of dust deposition on oceanic biota, such as ship-of-opportunity surveys (Breviere et al., 2006) or profiling floats (Bishop et al., 2002). Over this period, advances also took place in our understanding of the role of iron supply in the biogeochemistry of low-latitude oligotrophic waters where iron-depleted nitrogen-fixing cyanobacteria are present (Falkowski, 1997;

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Sanudo-Wilhelmy et al., 2001). Thus, the impact of dust supply on the oceans could potentially control the supply of iron over a large proportion of the ocean, at both high and low latitudes. There have now been many reports of the stimulation of the pelagic biota following dust supply in both high (Bishop et al., 2002) and low latitude (Lenes et al., 2001) waters.

The field of iron biogeochemistry is rapidly advancing, and recent lab and field studies suggest that there may be additional mechanisms for the longer-term dissolution (i.e. days to weeks) of aerosol iron in the upper ocean (Barbeau et al., 2001; Borer et al., 2005; Kraemer et al., 2005). Furthermore, the environmental cues that set the productivity of nitrogen fixers in the low latitude ocean have been shown to be more complex than previously thought, with a range of factors including iron and phosphate (Mills et al., 2004), dissolved inorganic carbon (Hutchins et al., 2007) and/or the ratio of nitrate to phosphate in the upper ocean (Deutsch et al., 2007). Such new observations on both the longer timescales of pelagic dust dissolution, and on the biological responses to dust supply in oligotrophic waters have yet to be fully integrated into global modelling schemes of the biological effects of dust dissolution into the surface ocean.

In this synthesis we investigate for the modern ocean a) the controls on the dissolution of dust in the upper ocean – from short-term physicochemical versus longer-term microbial and photochemical – and whether either of these modes of control have been adequately mimicked in the lab and subsequently represented in model simulations; and b) the links between dust supply and the consequent biological responses in both low and high latitude waters. Together, this information permits the development of a relatively simple tool, for observationalists, to constrain the likelihood of whether biological events, such as observed episodic phytoplankton blooms, are driven by dust supply to the ocean. Such a tool is offered not as an alternative to dust deposition or ocean biogeochemical models, but to promote a greater understanding of the wide range of factors, and their interplay, that will set the conditions for a dust-mediated response by pelagic biota. Note, consideration of changes in dust supply on longer timescales such as those associated with climate variability in both the present day (years to decades) or geological past (centuries to millennia)) and their impact on the biota are beyond the scope of this study.

## 2. Methods

### 2.1. Dissolution schemes

There has been little agreement about schemes to quantify the magnitude and rates of iron release from dust, and the interpretation of dissolution data has been confounded by a wide range of solubility estimates (e.g. see commentary in Jickells and Spokes, 2001; Mackie et al., 2008). In Section 3.1, the wide variation in methods employed and results obtained are presented and discussed. Briefly, however, the effects of three primary variables have been investigated in many of these studies: pH, dissolution medium, and extraction time (with pH probably the most contentious). Generally the dissolution schemes share common features. Aerosol material (or soil material from dust source regions) is collected and placed in the medium of choice. The majority of reported solubility values were determined using fresh water as a proxy for the initial cloud processing of the dust. The focus of most studies has been to quantify iron released "quickly" (usually arbitrarily defined) so extraction times have typically been short (minutes–hours) for studies at or close to the pH of rainwater or seawater. However, as rates of iron dissolution are slow, there have also been solubility determinations made at low pH. It is argued that at low pH, the extent of iron dissolution is unchanged (i.e. no more of the total iron dissolves at low pH than would dissolve otherwise), but that the rate of dissolution is accelerated. In other words, for convenience, readily measured quantities of iron are released in minutes–days rather than weeks–months.

Additionally, as discussed below, although longer term dissolution processes for dust appear to be important, models that incorporate terms for both short and longer term dissolution of iron are few. An unwelcome outcome of this has been confusion and disagreement over the likely impact of dust on climate-primary production feedbacks for both the past (especially the Last Glacial Maximum (LGM)) and the future (Hand et al., 2004; Tegen et al., 2004a,b; Mahowald et al., 2004).

### 2.2. Assumptions: microbial transformations of dust

In this study, we explore the relationship between microbially-mediated dissolution followed by uptake of aerosol iron in the euphotic zone, and how it impacts the partitioning of exported particulate iron into lithogenic and biogenic components. To do this we use data on microbial iron uptake rates, dust deposition rates into surface waters, and on the downward oceanic flux of particulate iron at two sites where such information exists: BATS (Bermuda Atlantic Time Series), Huang and Conte (accepted), Tian et al. (2008); and FeCycle (SW subantarctic Pacific), Frew et al., 2006). In our calculations we assume that microbes taking up iron use new iron (i.e. that supplied from dust deposition, or from upwelling) relative to regenerated iron (i.e. that recycled within the pelagic foodweb) in a ratio of 0.1:0.9; based on what is to our knowledge the only measurements available — during the FeCycle experiment (Boyd et al., 2005). In addition, reliable estimates of the export of particulate Fe (PFe) were only available from two different depths in the subsurface ocean: 500 m (BATS) and 120 m (FeCycle). We have made a direct comparison of these data and have assumed that most biological remineralisation of the lithogenic iron is insignificant below the euphotic zone i.e. in the absence of light the photochemical/siderophore mediated dissolution of lithogenic iron (Kraemer et al., 2005) is halted. However, also see a recent study by Hansard et al. (in review) that reports significant concentrations of Fe(II) to depths of 1000 m at sites across the North Pacific. One potential causative mechanism for the presence of Fe (II) at depth is reductive dissolution of residual lithogenic Fe within settling biogenic particles (Hansard et al., in review).

### 2.3. Assessment of the dust/biota link

We have developed a simple tool to classify whether given dust storm events warrant further attention as probable, possible or unlikely initiators of phytoplankton blooms in iron-limited waters. In particular, the tool will allow researchers to more quickly identify whether events are unlikely to initiate biological events so that other causative mechanisms can be investigated. It is not a predictive model, but uses a set of simple equations to set upper and lower bounds on variables, about which little is known, associated with the transport and deposition of dust and the consequent biological response. Researchers should then consider the likelihood of a particular set of variables falling within the calculated bounds. We liken the tool to a "spherical cow" (Harte, 1988). The assessment tool runs in a spreadsheet. Copies are available from the corresponding author, to enable users to insert their preferred values for the model parameters.

The equations and parameterisation are presented in the Appendix. The tool has two modules. Briefly, the first calculates the amount of dust deposited per unit area downwind of a dust storm using a simple exponential decay; a "half-decrease distance" (defined as the distance over which half of the transported dust load is lost from atmosphere, Prospero et al., 1989). The second module calculates the cumulative change to the concentration of dissolved iron in the mixed layer, $[\mathrm{Fe}_{\mathrm{Dissolved}}]$, caused by dust deposition, by biological uptake and by downward particulate export flux. A phytoplankton bloom may be initiated if $[\mathrm{Fe}_{\mathrm{Dissolved}}]$ exceeds a given threshold for an assigned time period. The outcome of this assessment is most