Short residence time for iron in surface seawater impacted by atmospheric dry deposition from Saharan dust events

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[1]   Measurements of dissolved (DFe) and total iron (TFe) in the upper water column are presented from the German SOLAS (Surface Ocean - Lower Atmosphere Study) cruise (M55), along a west to east transect at 10°N, in the equatorial Atlantic in October/November 2002. Aerosol samples were collected simultaneously during this time and are used to estimate an iron flux to the surface waters. Resulting flux estimates combined with iron inventories in the near surface waters reveal extremely short *fractional mean* residence times (6–62 days) for total (dissolved and particulate) iron in waters directly under the path of Saharan dust plumes. These results suggest that individual dust storms can supply a significant amount of the present iron upper water column inventory which is subsequent rapidly removed by aggregation and sinking.   INDEX TERMS: 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4801 Oceanography: Biological and Chemical: Aerosols (0305); 4825 Oceanography: Biological and Chemical: Geochemistry; 4875 Oceanography: Biological and Chemical: Trace elements. **Citation:** Croot, P. L., P. Streu, and A. R. Baker (2004), Short residence time for iron in surface seawater impacted by atmospheric dry deposition from Saharan dust events, *Geophys. Res. Lett.*, *31*, L23S08, doi:10.1029/2004GL020153.

1. Introduction

[2]   Iron (Fe) plays a key role in ocean productivity as it is known to be a limiting factor in many large parts of the global ocean [*Boyd*, 2004]. The low concentrations of DFe found in surface seawater [*Johnson et al.*, 1997] are a product of the low solubility [*Liu and Millero*, 2002] of the thermodynamically favoured redox state, Fe(III), which rapidly forms, or is scavenged by, colloidal and particulate phases. The dissolved forms of Fe are dominated by complexation with organic ligands [*Rue and Bruland*, 1995] which increase the overall solubility and are thought to be more bioavailable [*Anderson and Morel*, 1982] to phytoplankton. Thus it is of great importance to determine the sources and fluxes of Fe to the remote ocean and to understand the biogeochemical processes occurring in the exchange between atmosphere/river and ocean.

[3]   Atmospheric deposition of iron [*Duce et al.*, 1991; *Jickells*, 1999] may represent the dominant source to the open ocean, as mineral dust typically has a composition similar to continental crust (~4.3% Fe w/w) [*Wedepohl*, 1995]. Dust inputs are episodic and occur by either wet or dry deposition resulting in a typical surface enrichment of surface Fe concentrations [*Bruland et al.*, 1994]. The North Atlantic Ocean receives some of the largest dust inputs of the major oceans due to its proximity to the major dust source regions of arid North Africa [*Prospero*, 1996] with major storms tending to occur in the winter and spring [*Goudie*, 1983]. There is no single or continuous source of 'Saharan' dust but rather several source regions with differing chemistries [*Bergametti et al.*, 1989]. The direction of the dust flux follows a seasonal cycle, associated with the seasonal migration of the Intertropical Convergence Zone (ITCZ) [*Moulin et al.*, 1997], with the zone of maximum dust transport from the African coast moving from 5°N in winter to 20°N in summer.

[4]   The supply of Saharan dust strongly influences the particulate fluxes in deep waters of trace metals close to the African coast [*Kremling and Streu*, 1993]. The supply of Fe to North Atlantic surface waters is now thought to be responsible for stimulating N_2 fixation in the cental gyre and thus acting to ameliorate the effects of nitrogen limitation on the overall phytoplankton community [*Michaels et al.*, 1996]. Though recently evidence has been presented for the possibility of phosphorus limitation [*Wu et al.*, 2000] or phosphorus co-limitation with Fe [*Mills et al.*, 2004] of N_2 fixation. The role of Fe in N_2 fixation during the present work is discussed in a companion paper [*Voss et al.*, 2004].

[5]   In the present work we examined the vertical distribution, speciation, inventory and atmospheric sources of Fe in near surface seawater across the Equatorial Atlantic at 10°N as part of the German SOLAS programme. One of the aims of SOLAS is to understand the influence of atmospheric deposition on biogeochemistry in the ocean; Fe is a key element in this regard because of its influence on phytoplankton productivity and in particular N_2 fixation. In this paper we focus on the relationships between estimated dry depositional fluxes of Fe and the residence time for iron.

2. Methodology

2.1. Sampling

[6]   Samples were collected during the German SOLAS cruise, Meteor 55 (M55 Curacao – Douala), from 13 October–16 November 2002 on board the German research vessel *F.S. Meteor*. The cruise track was predominantly along a west-east transect from 60°W to 10°W at 10–11°N (shown in Figure 1). Analytical work was carried out in an over-pressurized class 100 clean air van on loan from the University of Bremen.

2.2. Sampling of Surface Waters

[7]   Seawater samples were obtained using modified Teflon coated PVC General Oceanics (Miami, FL, USA)

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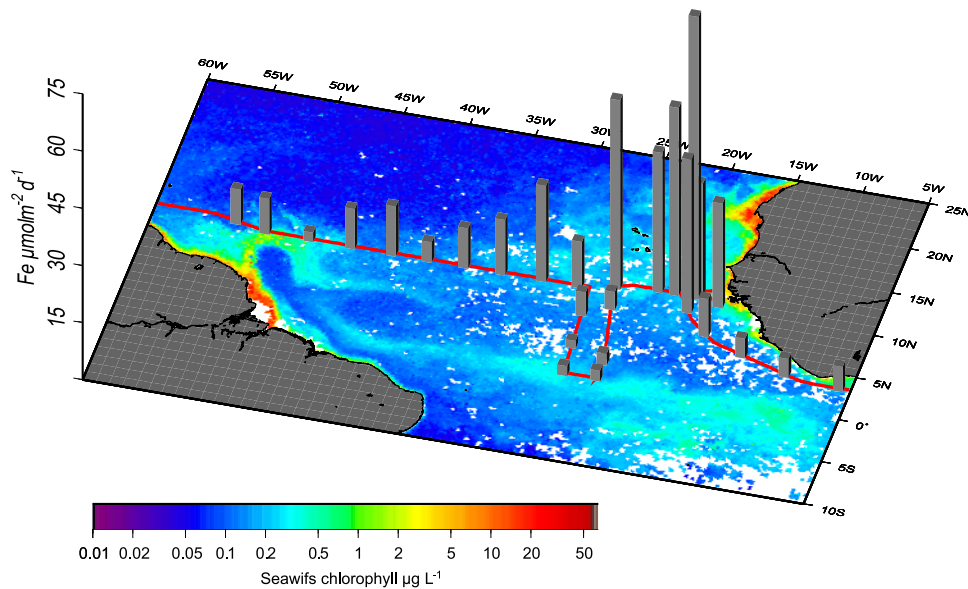[2]School of Environmental Sciences, University of East Anglia, Norwich, UK.

Figure 1. Estimated Atmospheric Iron flux (3D bars) for each day during the course of M55, superimposed on a composite Seawifs chlorophyll image using data from the duration of the cruise (Processed with Seadas software [*Baith et al.*, 2001]). The ship track is also shown in red.

GoFlo (8 L) bottles on a trace metal clean hydrowire using established protocols [*Bruland et al.*, 1979]. Samples were drawn into 1 L trace metal clean low density polyethylene bottles for later analysis in the laboratory. Filtered samples were collected using slight N_2 overpressure and filtration through 0.2 μm filter cartridges (Sartorius).

2.3. Seawater Iron Measurements

[8] Samples were analyzed in the laboratory by graphite furnace atomic absorption (ETAAS: Perkin-Elmer Model 4100 ZL) after pre-concentration by simultaneous dithio-carbamate-freon extraction, from seawater (100–250 g) [*Danielsson et al.*, 1978]. Analytical figures of merit for the analysis can be found in the online supplementary materials[1]. Water column inventories of DFe and TFe were estimated using the trapezoidal rule over the upper 200 m of the water column; this region includes not only the mixed layer but the region of the thermocline and the area where convective mixing occurs.

2.4. Aerosol Sampling

[9] Aerosol samples were collected with a high volume (1 m^3 min^{-1}) sampler (Graseby-Anderson), between 62.3°W and 1.6°W. Wind direction was continually monitored and the sampler was turned off if there was any risk of contamination by exhaust from the ship's stack. The sample collection period was ~23 hours, and the sampler was fitted with a cascade impactor head containing cellulose substrates (Whatman 41) in order to achieve size fractionation of the aerosol particles. Results here are reported for a coarse/fine size split of 1 μm, as this differentiates between mechanically generated (coarse) particles and particles created by gas-to-particle conversion processes [*Raes et al.*, 2000].

[10] Soluble major ions were extracted from aerosol samples (one quarter of each filter suspended in 25 mL ultrapure water) using ultrasonic agitation for 1 hour. The supernatant was then filtered (0.2 μm, cellulose acetate filter) and major ions (including Ca^{2+}) were analysed by ion chromatography (Dionex DX600/DX320). Analytical and procedural blanks for Ca were all undetectable (<0.7 nmol m^{-3}). Concentrations in extracts were converted into atmospheric concentrations by calculating the total quantity of Ca on each filter and dividing by the known volume of air filtered for each sample. The seasalt Ca component (and hence the non-seasalt component, nss Ca) was calculated using Na as the reference species for aerosol sea spray content. Uncertainties quoted for atmospheric concentrations (and deposition fluxes) have been calculated from standard deviations of replicate analyses and propagated for each stage of data analysis by standard error propagation methods. Deposition fluxes for nss Ca were calculated using deposition velocities of 0.1 cm s^{-1} and 2.0 cm s^{-1} for the fine and coarse aerosol fractions respectively [*Duce et al.*, 1991]. Because deposition velocities are rather poorly known, the derived deposition fluxes are subject to an inherent uncertainty of around a factor of 3 [*Duce et al.*, 1991].

[11] The daily Ca flux was used as a proxy for the Fe dust flux by conversion using a Fe:Ca (0.97 mol:mol) value based on typical crustal abundances [*Wedepohl*, 1995]. The Fe:Ca value used in the present study may slightly over estimate the true iron flux as air mass back trajectories and K/Ca ratios in the aerosol indicated the Northern (Fe:Ca = 0.65 ± 0.21) and Central Sahara (Fe:Ca = 1.03 ± 0.23) as the potential source region for the dust [*Chiapello et al.*, 1997].

2.5. Residence Times

[12] Residence times for iron at each station were estimated with the preceding 24 hour flux estimate using a single box model [*Sarthou et al.*, 2003; *Stumm and Morgan*,

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[1]Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2004GL020153.
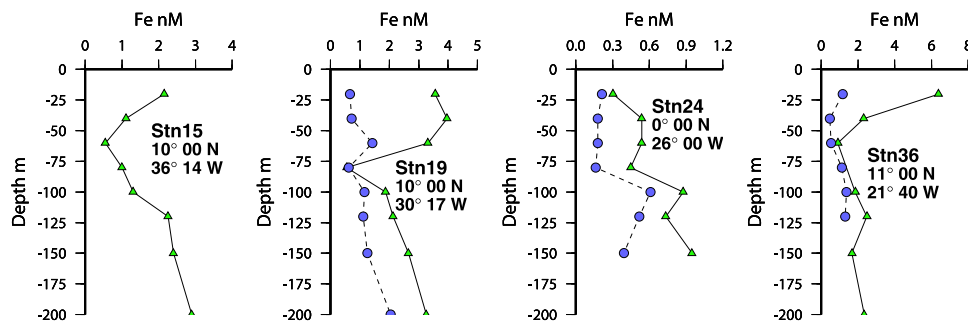
Figure 2. Vertical profiles from selected stations during M55 showing effects of atmospheric iron deposition. (Green – total, blue – dissolved).

1981], assuming a constant Fe inventory. Here we estimate a fractional mean residence time, τ_i, from the equation, $\tau_i = \frac{M}{J_i}$, where M is the inventory and J_i the dry atmospheric flux. The variability in τ_i, is derived from the uncertainty in the deposition velocity (300%). We note that the episodic nature of dust events implies a non-steady state input of iron and can increase iron inventories for some time; related to the deposition history of the water parcel. While such events invalidate the assumptions inherent in the model, a more comprehensive approach would require longer term studies. Using this approach we estimate a residence time for the iron deposited by dry deposition during the previous day – this provides a time scale, or response time, with which to examine the kinetics of other processes that affect iron cycling. The *overall* mean residence time for iron (τ) is then related to the sum of all the fluxes (ΣJ_i), including upwelling and wet deposition, and is given by $\frac{1}{\tau} = \frac{1}{\tau_1} + \ldots + \frac{1}{\tau_n}$.

3. Results and Discussion

3.1. Water Column Distribution of Iron

[13] Typical water column distributions of Fe from four representative stations occupied during this study are shown in Figure 2. Mixed layer depths were typically 20–30 m deep across the transect along 10°N, deepening to around 50 m at the equator. The key feature is the strong surface enrichments seen in the active mixed layer at stations 19 and 36 resulting from recent dry deposition of Fe (no rain). Station 15 also shows surface enrichment probably from a mix of dry and wet deposition as this station was occupied during rain squalls associated with the ITCZ [*Croot et al.*, 2004]. These stations contrast strongly with the much lower DFe and TFe concentrations found at the equator (station 24), which was outside the influence of the Saharan dust plume. A key feature of all of the profiles was a distinct minimum in TFe just under the base of the mixed layer, possibly indicating a zone of greatest scavenging. Previous work on Fe in the equatorial Atlantic have shown similar results, showing elevated surface Fe concentrations, from mostly north-south transects across the Saharan dust plume [*Bowie et al.*, 2002; *Sarthou et al.*, 2003; *Vink and Measures*, 2001].

3.2. Estimated Atmospheric Deposition of Iron

[14] Dry deposition fluxes of Fe are shown in Figure 1. Fluxes ranged from 2–74 µmol Fe m^{-2} d^{-1} with the highest fluxes found close to the African coast and the lowest fluxes at the equator. The data are consistent with MODIS satellite observations during this time, which show the passage of a dust storm that passed the Meteor on October 25–26 and a major dust storm between Nov 4 to 7 (data not shown). Our results are daily flux estimates and not directly comparable to modelled annual fluxes but our values do agree with the overall pattern of dust deposition as predicted in other studies [*Mahowald et al.*, 1999; *Tegen and Fung*, 1994].

3.3. Iron Inventories

[15] Inventories of total and dissolved Fe in the upper 200 m are shown in Figure 3 and are available also as supporting material. Values for total iron ranged from 113 µmol Fe m^{-2} at the Equator, to >400 µmol Fe m^{-2} at stations close to the African coast. DFe inventories were 54 ± 12 % of the TFe present, which was mostly colloidal iron (Croot, unpublished data). Comparison of the Fe inventories with the flux estimates revealed a significant logarithmic relationship (Figure 3: Fe$_{int}$ = 120.4*log$_N$(Fe flux) + 76.8; R = 0.855) – perhaps indicating a rapid removal of particulate Fe at high deposition rates.

3.4. Residence Times

[16] *Mean fractional* residence times for TFe were remarkably short ranging from 6 (range 2–12 days)– 62 (range 21–186) days, with the shortest times associated with high dust flux. Use of the mixed layer alone (20–50 m) would reduce these times by a factor of 4–10. These values are similar to estimates for the Sargasso Sea of ~18 days [*Jickells*, 1999] and considerably shorter than the residence time estimates for Fe in the global ocean of ~100 years [*Bruland et al.*, 1994]. Estimates for the residence time of
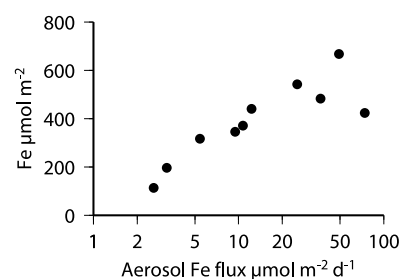

Figure 3. Relationship between estimated aerosol flux for the proceeding 23 hours and the vertically integrated iron inventory for each station during M55.

DFe are critically dependent on the estimation of the aerosol Fe solubility (here taken as 1% [*Johansen et al.*, 2000; *Spokes and Jickells*, 1996]. Our values indicate a residence time of between 280 (range 86–840) days and 10.5 (range 3–5–31.6) years, significantly longer than estimates for the Sargasso Sea of 214–291 days [*Jickells*, 1999]. Our values are probably overestimates as in regions of high deposition the surface seawater is essentially saturated with respect to truly DFe and the principal factor affecting DFe is the rate of transformation into particulate material via biological or abiotic processes [*Johnson et al.*, 1997]. Significant wet deposition with higher iron solubilities, a process not considered here, would also act to reduce the overall residence time for DFe.

[17] Our results here clearly show that in regions of high dust deposition, particulate Fe has a very short residence time in the upper water column with implications for dissolution and scavenging processes. Further work is required to examine Fe residence times in the critical interface between the atmosphere and ocean which all aerosol particles must cross – the sea surface microlayer.

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