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Published in:
Journal of Phycology

DOI:
[10.1111/j.0022-3646.2003.03-023.x](https://doi.org/10.1111/j.0022-3646.2003.03-023.x)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2003

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Visser, F., Gerringa, L. J. A., Gaast, S. J. V. D., Baar, H. J. W. D., & Timmermans, K. R. (2003). The Role of the Reactivity and Content of Iron of Aerosol Dust on Growth Rates of Two Antarctic Diatom Species. *Journal of Phycology*, 39(6), 1085-1094. <https://doi.org/10.1111/j.0022-3646.2003.03-023.x>

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THE ROLE OF THE REACTIVITY AND CONTENT OF IRON OF AEROSOL DUST ON GROWTH RATES OF TWO ANTARCTIC DIATOM SPECIES¹

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The atmosphere is widely recognized as a major source of Fe in the form of iron-containing dust. This study provides the first experiments in which the impact of dust on the growth rates of single species of Antarctic diatoms was assessed under laboratory conditions. The dust was among others characterized by x-ray powder diffraction analysis, analysis of total and amorphous Fe content, and dissolution rates of Fe in seawater. The amount of bioavailable Fe from the dust was determined, not via the complicated chemistry of Fe in seawater but by using diatoms as bioindicators for available Fe. Cultures of two large diatom species, *Actinocyclus* sp. and *Thalassiosira* sp., were amended with potential dust aerosols from two dust-supplying regions, Namibia and Mauritania, and responses on growth rates were monitored. Apart from a difference in total Fe content, a difference in crystallinity existed in the Fe minerals of both dust types. The fraction of amorphous Fe was reflected in a higher reactivity/dissolution of Fe in seawater. The increase in growth rate upon dust addition was positively related with the amount of amorphous Fe in the dust and with the dissolution rate of Fe in seawater. However, compared with equal FeCl₃ concentrations, the dissolved Fe from the dust was not completely available for the diatoms. Interestingly, the diatoms used only a small part of the dissolved Fe, demonstrating the importance of algae as bioindicators.

Key index words: bioavailability; bioindicators; diatoms; dust; Fe limitation; iron

Abbreviations: AAS, atomic absorption spectrometry; Fe_{diss}, dissolved Fe; HNLC, high nutrient low chl; XRD, x-ray powder diffraction

In the subarctic and equatorial Pacific Ocean and the Southern Ocean, together comprising over 20% of total oceanic surface waters, algal biomass remains low despite high major nutrient concentrations (Martin et al. 1994, Price et al. 1994, Boyd 2002). There is ample evidence that in parts of these high nutrient low chl (HNLC) regions, phytoplankton growth is limited by iron (and light) (Nelson and Smith 1991, Sunda and Huntsman 1997). Iron is a cofactor for many enzymes; it has a major impact on the rate of light utilization by

phytoplankton cells and therefore primary production (Raven 1990, Geider and LaRoche 1994).

Several iron-enrichment data sets from HNLC regions, involving either bottle experiments or meso-scale enrichments, showed an increase in biomass, primary production, and growth rates, especially of large diatoms, by a factor of 2–4 (de Baar et al. 1995, Coale et al. 1996, Boyd et al. 2000, Timmermans et al. 2001b). Because of the low solubility of iron in oxygen-rich seawater, the concentration of dissolved iron (Fe_{diss}, operationally defined as the fraction passing a filter with a pore size of 0.2 µm) in the remote HNLC regions is very low: 0.02 nM (Fitzwater et al. 2000, Liu and Millero 2002). In coastal waters, the concentration of Fe_{diss} can be 1–100 nM from riverine input and coastal run-off (Chester 1990).

Despite the low concentration of Fe_{diss}, algal blooms do occur in the Antarctic HNLC regions (de Baar et al. 1995). More generally, because nutrient-rich upwelling waters contain very little iron (Martin 1992), one of the ways the phytoplankton in the HNLC regions can obtain this essential element is from dissolution of iron-rich atmospheric dust (Duce 1986, Martin et al. 1989b, Donaghay et al. 1991, Young et al. 1991, Boyd et al. 2000, Hoppema et al. 2003). Levels of Fe_{diss} above 1 nM can be found in surface waters after a major wet deposition of dust aerosols during a rainstorm (de Baar and de Jong 2001, Hanson et al. 2001). Evaluation of a number of blooms in HNLC regions showed that they took place 6–7 days after daytime wet aerosol dust deposition (Saydam and Polat 1999).

Iron can be present in atmospheric dust in different forms: 1) as amorphous iron-(hydr)oxides, 2) as crystalline iron-(hydr)oxides, and 3) as one of the structural elements of crystalline minerals. Because of its low thermodynamic stability and high specific surface area, the amorphous iron-(hydr)oxide has a higher chemical reactivity than that from the other two fractions. Fe will dissolve more easily in seawater from the amorphous iron-(hydr)oxides (Zhuang et al. 1992, Kuma and Matsunaga 1995). This is therefore assumed to be the most important source of bioavailable iron, where “bioavailable,” defined in the strict sense of the word, is that fraction of the total iron concentration that causes a biological effect (on the diatoms).

Several factors will determine the impact of dust deposition on the growth rates of the phytoplankton. Not only the amount of dust, but also the type of dust is important. The iron content of the dust and the reactivity of it differ greatly between types from different source regions (Duce et al. 1991, Saydam

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and Senyuva 2002). During atmospheric transport to the ocean surface, the dust is exposed to different conditions influencing the solubility and therefore probably also bioavailability of its iron-(hydr)oxides present. UV light will reduce the insoluble iron(III)-oxides by photochemical reactions, and as a result of cycling through clouds, the aerosols are repeatedly exposed to a range of pH values from 2 to 5. Low pH values markedly increase the solubility of the iron-oxides (from 0.2% at pH 8.0 to 70% at rainwater pH 4; Spokes and Jickells 1996). Dust aerosols either fall out (dry deposition) or rain out (wet deposition) into the oceans. For wet deposition in rainwater (pH 4–7), about 14% of the iron from the aerosols enters into solution, whereas the dissolution of dry-deposited aerosols is deemed negligible (Duce et al. 1991). Therefore, the iron supplied to the ocean, especially daytime wet deposition of aerosol dust, is expected to influence phytoplankton growth (Saydam and Senyuva 2002).

The chemistry of iron in seawater is complex. Iron entering the water as dust is upon partial dissolution quickly oxidized to colloids. Of the remaining Fe_{diss} , >99% is complexed by organic ligands (Gledhill and van de Berg 1994, Rue and Bruland 1995). It has been demonstrated that organic complexation of Fe will influence availability for phytoplankton (Barbeau et al. 1996, Hutchins et al. 1999, Timmermans et al. 2001b). Thus, the biogeochemical reactivity of Fe entering the ocean from the atmosphere depends not only on their speciation before deposition but also after mixing with seawater (Jickells and Spokes 2001). Because of the complicated chemistry (including the kinetic aspects), it is still uncertain which part of the iron pool in seawater is being used by the phytoplankton (Gerringa et al. 2000). The bioavailable sources are assumed to be dissolved inorganic Fe(III) and Fe(II). Part of the dissolved organically complexed Fe(III) is probably also available for biota (Hutchins et al. 1999, Sunda 2001, Nishioka et al. 2001).

The stimulative effects of aerosol dust on phytoplankton growth has been observed in opportunistic studies in the field (DiTullio and Laws 1991, Young et al. 1991, Boyd et al. 1998, Bishop et al. 2002) and during deckboard experiments (Martin et al. 1991). To the best of our knowledge, no experiments have been conducted amending single species algal incubations with aerosol dust under fully controlled laboratory conditions. Here, we report the effects of physico-chemically characterized dust on the growth rates of ecologically relevant open oceanic phytoplankton diatom species. We provide the first experiments in which algal biology is linked directly to the chemistry of iron in dust. Specifically, our first aim was to determine the impact of dust deposition on the growth rates of large Antarctic diatoms. The growth rate responses were then related to relevant aspects of the physico-chemical composition of the dust. The second goal proceeded from the difficulties in defining the bioavailable fraction because of the complicated chemistry of Fe_{diss} in seawater. Therefore, it is logical to determine

the effect of iron addition on diatom growth, instead of measuring the presumably bioavailable iron pool itself (Timmermans et al. 2001b). The approach was to relate the effects of dust addition to the effects of FeCl_3 additions on growth rates of the diatoms (the classical Monod-type of response; Monod 1950). The choice of the potential dust aerosols was made based on the fact that the Sahara (Mauritania) and the South African desert (Namibia) belong to the world's largest sources of dust (Goudie and Middleton 2001, Dupont and Wyputta 2003). The dust from Mauritania represents relatively Fe-poor dust with a low content of amorphous material; the dust from Namibia represents relatively Fe-rich dust with a high content of amorphous minerals. The dust was characterized with x-ray powder diffraction (XRD), the specific surface area was determined to indicate the content of amorphous material (Van der Gaast 1991), and the amorphous Fe fraction was determined with ascorbate extraction (Kostska and Luther 1994). The reactivity of Fe from the dust was determined by dissolution experiments under anoxic conditions with ascorbic acid and in seawater (Postma 1993).

MATERIALS AND METHODS

Diatom growth experiments. Two large, centric, Antarctic diatom isolates, *Actinocyclus* sp. (diameter, 140 μm ; single cells) and *Thalassiosira* sp. (diameter, 70 μm ; chain-forming individual cells interconnected through a thin thread), were obtained from cultures present at the Royal Netherlands Institute for Sea Research. Originally, the species were isolated from the Atlantic Sector of the Southern Ocean. Both species had been grown for several months in filtered (0.2 μm) Antarctic seawater, collected south of the Polar Front (HNLC region) during expedition ANT XVIII/2 with the R.V. *Polarstern* in November 2000. This seawater contains low concentrations of Fe (0.067 nM) but high concentrations of the major nutrients nitrate (26.1 μM), phosphate (1.82 μM), and silicate (24.5 μM).

Square polycarbonate incubation bottles (125 mL) were cleaned before use by soaking in analytical grade 1 N HCl for 24 h and rinsing three times with Milli-Q water (Millipore, Molsheim, France). Subsequently, the bottles were sterilized using boiling Milli-Q. All manipulations were performed on a laminar flow bench, using sterilized trace-metal clean materials (Timmermans et al. 2001a).

Series of growth experiments were set up by amending unialgal incubations in 125 mL of Antarctic seawater with increasing amounts of Fe_{diss} ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution in Milli-Q) or various amounts of dust (Table 1). Incubations without FeCl_3 or dust addition served as controls (blanks). Initial concentrations of phytoplankton cells were approximately 1 cell $\cdot \text{mL}^{-1}$ for *Actinocyclus* and 5–10 cells $\cdot \text{mL}^{-1}$ for *Thalassiosira*. All incubations were kept at a temperature of 2–4°C, and light (16:8-h light:dark cycle) was provided by cool white fluorescence tubes (100 $\mu\text{mol photons} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$). One milligram of dust provided to the diatoms in the incubations (surface area of the incubation bottles, 25 cm^2) represents a high input compared with estimations made for the oceans; it corresponds to the amount of dust that phytoplankton receives per month in the North Atlantic and per year in the South Pacific and South Atlantic (estimated 4.0 $\text{g} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$ and 0.4 $\text{g} \cdot \text{m}^{-2} \cdot \text{y}^{-1}$, respectively; Duce et al. 1991). The incubations were sampled two to three times per week, and individual cells were counted using 5-mL settling chambers and a Zeiss Axiovert 25 inverted

TABLE 1. Growth rates of *Actinocyclus* sp. and *Thalassiosira* sp. in incubations to which dust was added.

Addition	Growth rate	Bio-available [Fe] ^a (nM)	Measured total Fe _{diss} ^b (nM)	Calculated growth rate ^c
<i>Actinocyclus</i> sp.				
Blank	0.1	x	0.067	x
1 mg Maur	0.25 ± 0.02	0.5	1.7	0.29
5 mg Maur	0.21 ± 0.02	0.36	5.8	0.32
1 mg Nam	0.41 ± 0.03	x	12.8	μ _{max}
5 mg Nam	0.43 ± 0.03	x	44.2	μ _{max}
<i>Thalassiosira</i> sp.				
Blank	0.38	x	0.067	x
1 mg Maur	0.25 ± 0.01	0.035	1.7	0.53
5 mg Maur	0.28 ± 0.02	0.04	5.8	μ _{max}
1 mg Nam	0.40 ± 0.01	0.12	12.8	μ _{max}
5 mg Nam	0.45 ± 0.03	0.32	44.2	μ _{max}

^aThe amount of bioavailable Fe these incubations contain according to Fig. 1. An 'x' indicates the value cannot be determined by this approach.

^bTotal Fe_{diss} measured in the incubations.

^cGrowth rates that would be expected according to these Fe_{diss} values, calculated with Eq. (1).

Nam, dust from Namibia; Maur, dust from Mauritania. *Actinocyclus*, μ_{max} = 0.33 · d⁻¹; *Thalassiosira*: μ_{max} = 0.54 · d⁻¹.

microscope (Zeiss, Jena, Germany). Growth response in relation to availability of iron was determined by modeling the growth rates from the incubations with FeCl₃

$$\mu = \frac{\mu_{\max} \times [\text{Fe}]}{K_m + [\text{Fe}]} \quad (1)$$

(after Monod 1950) using a least-square fit. Here, μ is the daily growth rate (d⁻¹), μ_{max} is the maximum growth rate of the diatoms under these conditions, and K_m is the half-saturation value for growth (in nM of Fe_{diss}). In a novel methodology, we first determined the response of the diatoms to FeCl₃ additions (Monod curve). Next, the growth rates that resulted from additions of Namibian or Mauritanian dust were projected on the Monod curve, and the corresponding amount of bioavailable Fe could be estimated.

Dust characterization: mineral composition and surface area. The experiments were carried out using two types of potential dust material: silty clay loam (approximately 95% of particles <20 μm in diameter) from a dry riverbed in Namibia (Sossuvlei, 24.74 S; 15.29 E) and sand (approximately 90% of grains 100–2000 μm in diameter) from Mauritania (Tidra, 19.35 N; 16.25 W). This latter dust was sieved dry over polyvinyl chloride sieves, and the fraction less than 63 μm was used in the experiments. These two dust source regions are arid and semi-arid and well-recognized as important dust sources (Jickells and Spokes 2001). The dust samples used in this study may deviate in physicochemical properties from dust entering the Southern Ocean, for example, from Patagonian or Australian sources. For the Southern Ocean, there is a striking paucity of data for both dust fluxes and the properties of the dust (Jickells and Spokes 2001).

The specific surface area of the two dust samples was measured with a Micromeritics Tristar 3000 (Norcross, GA, USA), based on the principle of N₂ adsorption to a known amount of dust particles. Both dust samples were further analyzed by XRD to determine their mineral composition, applying Cu Kα radiation (λ = 1.5418 Å). Before analysis the samples were Ca exchanged and after that dried at 60°C. Nonoriented specimens were prepared pressing an amount of this material in a depression in a metal plate. For details on instrumentation and methodology, see Van der Gaast (1991).

Analyses of Fe content. The amorphous Fe content of the dust was determined by extraction using an ascorbate

mixture at pH 8.0 for 24 h (Kotska and Luther 1994). Crystalline Fe was determined using dithionite at pH 4.8 (Canfield 1988, Kotska and Luther 1994). After leaching, the samples (triplicate) were centrifuged. The supernatant was filtered over a 0.2-μm Gelman (Ann Arbor, MI, USA) Acrodisc filter. Total Fe was determined by acid digestion in a microwave bomb for 2.5 h. For this, 0.1 g of dust was placed in a Teflon tube and 6 mL HCl, 2 mL HNO₃, and 2 mL HF (all Suprapur quality) (Merck, Darmstadt, Germany) were added. After cooling, the samples were transferred quantitatively to 50-mL receivers with 30 mL saturated Suprapur boric acid and filled up to 50 mL with Milli-Q.

Dissolution of Fe in seawater and reactivity of the dust. Dissolution of the particles in seawater and the concentration of Fe_{diss} in the incubations was determined by adding 1 and 5 mg of dust to 125 mL of Antarctic seawater. After 24 h, aliquots were filtered over a 0.2-μm Gelman Acrodisc filter.

The rate of reductive dissolution of the two dust samples was determined using ascorbic acid as reductant (Postma 1993, Larsen and Postma 2001). The experiments were carried out using excess ascorbic acid, so the dissolution rate was independent of the concentration of the reductant (Postma 1993). Dust was placed in a freshly prepared 10-mM ascorbic acid solution (pH 3) in a 250-mL reaction vessel at room temperature (Namibia, 0.5 g in 250 mL; Mauritania, 1.5 g in 150 mL). Purified and water-saturated N₂ was continuously passed through the vessel to maintain anoxic conditions, and the suspension was stirred continuously to prevent the particles from settling. The pH was kept constant by adding concentrated Merck (Darmstadt, Germany) Suprapur HCl (Postma 1993). In time series, aliquots (duplicates, approximately 10 mL) were filtered over a 0.2-μm Gelman Acrodisc filter.

An assemblage of Fe-(hydr)oxides with variable mineralogy and reactivity can be considered to represent a reactive continuum described by a distribution function g(k, t). This function defines the population density of grains with reaction rate k at time t. Based on the gamma distributions of the reactivities of these grains, the amount of solid mass, m (μmol · g⁻¹), remaining in a sample at time t (s) can be described by Eq. (2), where the mass at time 0 is m₀ (Boudreau and Ruddick 1991):

$$\frac{m}{m_0} = \left(\frac{a}{a+t} \right)^v \quad (2)$$

where parameter $a(s)$ indicates the average lifetime of the reactive components in the mixture and v is a dimensionless parameter solely related to the shape of the gamma distribution curve (Roden and Wetzel 2002, van der Zee 2002). The parameters a and v are determined by a least-square fit of Eq. (2) to the values of m/m_0 . When solution composition is kept constant, the general rate equation for the dissolution kinetics of a polydisperse sample of crystals (Christofferson and Christofferson 1976) can be described by Eq. (3) (Postma 1993):

$$\frac{J}{m_0} = \frac{v}{a} \left(\frac{m}{m_0} \right)^{1+\frac{1}{v}} \quad (3)$$

The term v/a in Eq. (3) can be interpreted as the apparent rate constant for a mixture. The exponent $(1 + 1/v)$ provides an indication of the degree of heterogeneity in reactivity of the oxides undergoing reduction (Roden and Wetzel 2002, van der Zee 2002). The data from the reactive continuum were modeled in Eq. (3) using a least-square fit.

All materials used (bottles, filters, etc.) were cleaned before use by soaking them 1 day in analytical grade 6 N HCl, followed by 1 week in analytical grade 1 N HCl and triple rinsing with Milli-Q water. New materials were first immersed in a detergent bath (Laviton) for 1 week and rinsed twice with Milli-Q water (Ecolab, St. Paul, MN, USA). Only synthetic material was used (plastics). Samples for the determination of Fe_{diss} were filtered and acidified to pH 2 with Suprapur HCl. Fe_{diss} was measured by flame atomic absorption spectrometry and by flow injection (de Jong et al. 1998) depending on the Fe concentrations.

RESULTS

Diatom growth experiments: growth in relation to FeCl_3 . The growth curves from the FeCl_3 addition experiments yielded a μ_{max} of $0.54 \cdot \text{d}^{-1}$ and a $K_m (\text{Fe}_{\text{diss}})$ of 0.04 nM for *Thalassiosira* and a μ_{max} of $0.33 \cdot \text{d}^{-1}$ and a $K_m (\text{Fe}_{\text{diss}})$ of 0.2 nM for *Actinocyclus* (Fig. 1). At a concentration of 0.07 nM Fe in the Antarctic seawater, *Thalassiosira* will grow relatively faster than *Actinocyclus*: $0.7 \times \mu_{\text{max}}$ for *Thalassiosira* compared with $0.3 \times \mu_{\text{max}}$ for *Actinocyclus*.

Impact of dust additions. Addition of each dust sample induced enhanced growth rates. *Actinocyclus* showed an especially marked response (Table 1). The dust from Namibia had a higher impact on the growth rates of both diatom species than the dust from Mauritania. For *Actinocyclus*, addition of 1 or 5 mg of dust from Namibia resulted in a rise of the growth rate by a factor 4, compared with the incubation without dust addition (blank). The addition of the same amounts of Mauritanian dust resulted in a rise of the growth rate by a factor of 2–2.5. For *Thalassiosira*, addition of 1 or 5 mg of dust from Mauritania seemed to inhibit cell growth, and adding the dust from Namibia only resulted in a rise of the growth rate by a factor of about 1.2. For *Actinocyclus*, addition of 1 mg of dust from Mauritania resulted in a higher growth rate than the addition of 5 mg of this dust. Adding a larger amount of dust probably results in enhanced readsorption of Fe to the dust particles (Chester et al. 1993, Zhuang and Duce 1993), leading to a lower fraction of bioavailable Fe.

Bioavailable Fe. The growth rates of the diatoms in the incubations to which dust had been added (Fig. 1) were lower than would be expected according to the

FIG. 1. Growth curves of (a) *Actinocyclus* sp. and (b) *Thalassiosira* sp. in response to additions of FeCl_3 (also see Table 1). The data points (o) are fitted to the Monod function (Eq. 1). Growth rates in response to addition of dust are indicated as follows: $\blacklozenge$ and $\bullet$, 1 and 5 mg, respectively, dust from Mauritania; $\blacktriangle$ and $\blacksquare$, 1 and 5 mg, respectively, dust from Namibia. The cross-points of the dotted lines, originating from the observed growth rates in response to dust addition, with x-axis indicate the amount of bioavailable Fe_{diss} present in the incubations (one example per species).

concentrations of Fe_{diss} measured in these incubations (Table 1). For example, the incubation to which 5 mg of dust from Mauritania was added had a $[\text{Fe}_{\text{diss}}]$ of 5.8 nM. According to the Monod curve (response to FeCl_3) for *Actinocyclus*, the species should reach a growth rate of $0.32 \cdot \text{d}^{-1}$ at this value (Fig. 1). The *Actinocyclus* cells in the incubation, however, only reached a growth rate of $0.21 \cdot \text{d}^{-1}$ (Table 1), using only approximately 6% of the Fe_{diss} . Apparently, $[\text{Fe}_{\text{diss}}]$ is not a good measure for bioavailable Fe present in the incubations to which dust had been added. A comparison of the results based on the FeCl_3

incubations and the incubations to which dust had been added (Fig. 1) indicate that *Actinocyclus* uses about 6%–30% of the Fe_{diss} pool and *Thalassiosira* only 0.7%–2%, depending on the amount of dust added (Table 1).

Mineralogical composition of the dust samples and the reactivity of Fe: mineralogical composition and surface area. The XRD pattern of the dust from Namibia showed large amounts of amorphous material, quartz, clay minerals, and calcite and minor amounts

of feldspar and carbonates (Fig. 2a). This dust was derived from a riverbed where fine particles were trapped by the overlaying water or as a crust during dry periods. Weathering therefore will be predominantly chemical, resulting in material of small grain size and high amounts of amorphous material. The pattern of the dust from Mauritania showed large amounts of quartz, feldspar, amphibole, and halite (NaCl), a rather small amount of amorphous material, and minor amounts of clay minerals and some

FIG. 2. XRD patterns showing the mineral composition of the dust from (a) Namibia and (b) Mauritania. Peaks represent crystalline minerals, and the areas under the curves indicate the presence of amorphous material. C, chlorite; M, mica; Q, quartz; Ca, calcite; F, feldspars; A, amphibole; G, gypsum; An, anhydrite; H, halite; Carb, Mg-Ca carbonates; hk0, nondiagnostic reflection of clay minerals.

gypsum (Fig. 2b). Weathering here will be predominantly mechanical by wind. The fine material will be blown out as dust. Salts are typical for desert material. They precipitate when water evaporates. Both dust samples contain mica with a rather high Fe content (this can be seen from the ratio of the (M001)/(M002) peaks ≈ 3 ; Fig. 2, a and b). The chlorite probably also contains some Fe but less than the mica. Both minerals are present in higher amounts in the dust from Namibia than in that from Mauritania. The dust from Namibia has a surface area of $30.4 \text{ m}^2 \cdot \text{g}^{-1}$, which is almost six times higher than the surface area of the dust from Mauritania, $5.4 \text{ m}^2 \cdot \text{g}^{-1}$.

Some 5.7% of the dust from Namibia consists of Fe, and this corresponded well with the values of 5%–7% measured for the abundance of Fe in the earth's crust (Taylor 1964) (Table 2). The lower value of 1.84% (total Fe) of the Mauritanian dust was caused by relatively high amounts of quartz and feldspars. As can be expected according to the results from the incubations of the diatoms, the dust from Namibia contained not only three times more total Fe than the dust from Mauritania, but the amorphous Fe fraction was almost seven times higher (Table 2).

Reactivity. The reactivity of a material is dependant on the mineralogy, crystallinity, and surface area of the particles (Postma 1993). During reductive dissolution, the dust from Namibia released 3.5–4 times more Fe per gram of dust than that of Mauritania (Fig. 3a). The reactive continuum (Fig. 3b) showed that the reactivity of the samples was highest for the dust from Namibia. During the entire experiment, the remaining fraction of Fe-(hydr)oxides (m/m_0) was lowest in the dust from Namibia. Although the difference between the reactivities of the two dust types seemed to be rather small, it is important as the dust from Namibia contained more Fe. A small difference in reactivity will result in a higher release of Fe.

Normally, dithionite extractable Fe is used as the expression of m_0 . In this experiment, however, the value of m_0 was given by the amount of total Fe, as the amount that dissolved during reductive dissolution was higher than the dithionite extractable Fe (Table 2). Postma (1993) showed that it is possible to quantitatively compare the reactivity of different materials, using Eq. (3). For the dust from Namibia the average lifetime of the reactive components $a = 10010.2 \text{ s}$ and $v = 0.031$. For the Mauritania dust $a = 15125 \text{ s}$ and $v = 0.037$. Reductive dissolution of both dust

FIG. 3. (a) The amount of Fe released ($\mu\text{M} \cdot \text{g}^{-1}$) during the dissolution of dust from Namibia and Mauritania related to time (h). (b) Reactive continuum of both dust samples; the lines represent the fraction of undissolved Fe (m/m_0) during the course of the experiment (time in h).

samples can now be described by the following rate equations:

$$\text{Namibia: } J/m_0 = 3.05 \times 10^{-6} (m/m_0)^{33.7} \quad (4)$$

$$\text{Mauritania: } J/m_0 = 2.23 \times 10^{-6} (m/m_0)^{30.7} \quad (5)$$

TABLE 2. Amorphous, crystalline and total Fe content of the dust samples from Namibia and Mauritania.

	Namibia		Mauritania		Ratio N/M
	$\mu\text{mol} \cdot \text{g}^{-1}$	Weight % of dust	$\mu\text{mol} \cdot \text{g}^{-1}$	Weight % of dust	
Amorphous Fe	11.2	0.06	1.65	0.01	6.8
Crystalline Fe	45.6	0.26	10.4	0.06	4.7
Total Fe	1024	5.7	330	1.84	3.1

N/M is the ratio of the values obtained for both dust samples, respectively, Namibia/Mauritania.

TABLE 3. Concentrations of dissolved Fe in incubations to which dust was added (in absence of diatoms).

Addition	[Fe _{diss}] (nM)	Amount released ($\mu\text{M} \cdot \text{g}^{-1}$)	% of amorphous Fe
1 mg Maur	1.7	0.43	25
5 mg Maur	5.8	0.29	17
1 mg Nam	12.8	3.20	29
5 mg Nam	44.2	2.21	20

Indicated are the amounts of Fe released per gram of dust and the percentage of amorphous Fe with respect to the total Fe content, present in the incubated dust. Nam, dust from Namibia; Maur, dust from Mauritania.

The exponents 33.7 and 30.7 are characteristic for the reactivity of the Fe-(hydr)oxides. The apparent rate constant, v/a , depends on solution composition, which was the same for the reductive dissolution of both dust samples. Comparison of the two rate equations therefore showed a dissolution rate, J (normalized to total amount of Fe), that is highest for the dust from Namibia, which is consistent with the findings from the reactive continuum.

Release of Fe in seawater. From the Namibian dust, 7.5 times more Fe dissolved into the Antarctic seawater than that from Mauritania (Table 3). This ratio was almost twice as high as the ratio found in the reductive dissolution experiment (Fig. 3a) and corresponded to the ratio of 6.8 found between the amounts of amorphous Fe in the dust (Table 2).

Addition of a five times higher amount of dust (Namibian or Mauritanian) did not result in a five times higher concentration of Fe_{diss}. This was probably caused by the enhanced (re)absorption to the surface of the dust particles as their number increases (Spokes and Jickells 1996). Interestingly, the percentage of the amorphous Fe fraction that dissolved did not differ between the two dust types. The values for the dust from Namibia were a little higher, confirming the higher reactivity of this dust as previously described.

DISCUSSION

This study shows that it is possible to simulate the process of dissolution of dust (mimicking a wet deposition event) and the resulting reaction of the phytoplankton in laboratory incubations. More importantly, our study demonstrates that it is differences in the reactivity of the iron and not in the iron content of the dust that determined the responses of the diatoms. The general stimulating effect of atmospheric dust on phytoplankton has been demonstrated in opportunistic field studies (DiTullio and Laws 1991, Young et al. 1991, Boyd et al. 1998, Bishop et al. 2002) and deck incubations (Martin et al. 1991), but our study is the first to make the causal relation for single phytoplankton species under laboratory conditions. Our results support the field observations that atmospheric dust can induce diatom growth in Fe-limited

media (Saydam and Polat 1999). Both Antarctic diatom species showed enhanced growth rates in response to the addition of dust samples and will benefit from dust storms when the Fe_{diss} concentration of the seawater can reach values above 1 nM (de Baar and de Jong 2001). By characterizing the dust that was added, the relation between dust composition and the impact of the dust on the growth rates of the diatoms could be determined.

The results show a clear relation between the amorphous Fe content and reactivity of the dust type and the impact of the dust on diatom growth. The impact on the growth rates of both diatom species was higher after dissolution of the dust from Namibia than after dissolution of the dust from Mauritania. The results from the physicochemical analyses of the dust corroborate these findings: The silty clay loam from Namibia has a higher specific surface area, contains more amorphous Fe, and has a higher reactivity than the sand from Mauritania. The amount of Fe that dissolved from the dust particles in seawater is 7.5 times higher for the dust from Namibia. This value corresponds well with the ratio of 7 found between the amounts of amorphous Fe of the dust samples. The percentage of amorphous Fe that dissolved from the grains is almost equal in both dust samples, about 23%. Apparently, the amount of Fe that will dissolve after (dry) deposition of these dust samples in seawater is largely governed by the size of the amorphous Fe fraction, altered to some extent by the overall reactivity of the material. These characteristics of the dust particles will therefore also determine the impact of (dry) dust deposition on the growth rates of phytoplankton, as was shown by the higher impact of the dust from Namibia in the incubations of the diatoms. This is consistent with the finding of Kuma and Matsunaga (1995), that the availability of colloidal Fe was related to the thermodynamic stability and kinetic lability of the colloidal ferric oxide phases, which they had offered to different phytoplankton species.

Characterization of the dust, however, still does not determine the bioavailability of the Fe_{diss}. Our study shows that only a fraction of the Fe_{diss} is bioavailable, and phytoplankton (diatoms) as bioindicator can determine this fraction. It is shown that the impact of the dust addition differs between the two diatom species. *Thalassiosira* seems to be limited less by the low concentration of Fe_{diss} in the Antarctic seawater than *Actinocyclus*. As a result, the impact of the dust additions on the growth rate of *Thalassiosira* is small. It is possible that both species have adapted different strategies to cope with the Fe limitation of the Antarctic seawater. Generally, smaller phytoplankton species have lower iron requirements (Sunda and Huntsman 1997), also consistent with the allometric relationship for surface-to-volume ratio. From our experiments it appears that *Thalassiosira* is able to grow relatively fast at low concentrations of Fe_{diss} but cannot benefit from the aerosol addition, whereas *Actinocyclus* normally grows rather slowly and is able to increase its growth

rate dramatically after a dust storm. Field verification is necessary, however, for latter assumptions.

Because it is presently not feasible to determine the bioavailable Fe_{diss} fraction using chemical methods, the diatoms were used as bioindicators. Only the input, Fe_{diss} in the seawater, plus Fe_{diss} from the dust, and the output, diatom growth, were known. By comparing these growth rates from incubations to which dust had been added to the standard (μ - Fe as FeCl_3) curve of the species, the amount of bioavailable Fe in the incubations to which dust had been added could be estimated. Applying this method, it was shown that the concentration of Fe_{diss} was not a good measure for bioavailable Fe: the diatoms only used a small part of this Fe fraction. The discrepancy between the amounts of bioavailable Fe in the incubations with the FeCl_3 solution and the incubations with Fe derived from the dust samples might be explained by the presence of ligands and colloids. The dust probably provides the seawater with Fe bound in these two forms and both will (negatively) affect the bioavailability of Fe_{diss} in the seawater. Assuming a difference in availability of the different Fe forms, not all colloidal Fe or Fe bound to ligands may be available for the diatoms (Anderson and Morel 1982, Kuma and Matsunaga 1995, Nishioka and Takeda 2000).

The method that we applied, using a Monod growth curve to assess the bioavailable Fe from dust, should only be used with appropriate caution. Strictly speaking, one of the basic assumption for proper use of the Monod function, steady state, might not be fulfilled. Because of the dissolution of Fe from the dust, the chemistry of Fe can be expected to be out of equilibrium. Moreover, the diatoms will affect Fe_{diss} concentrations during their growth. On the other hand, ligands and colloids originating from the dust may have created more or less constant Fe levels, if the (buffered) dissociation is in balance with the biological uptake. Because at present there is no better way of describing the Fe kinetics and the biological response of the phytoplankton, we applied the Monod function, but we are aware of the underlying restrictions and assumptions. The results should be regarded as integration over time, indicating the overall response of phytoplankton to dust addition.

The amount of 1 mg of dust added to incubations is comparable with the amount of Fe the phytoplankton can receive monthly in the North Atlantic and annually in the Southern Atlantic and Southern Pacific (Duce et al. 1991). The rise in phytoplankton growth rate by a factor of 2–4 upon Fe-enrichment experiments in HNLC regions resulted in blooms (de Baar et al. 1995, Boyd et al. 2000). Both the desert dust from Mauritania and the dry riverbed dust from Namibia could therefore induce a bloom of phytoplankton in the field because the growth rate of *Actinocyclus* rises by a factor of 2.5–4 after addition of the two types of dust. *Thalassiosira* does almost reach its maximum growth rate on addition of dust from Namibia, but the increase in growth rate is only about 20%. It is therefore

unlikely that deposition of this dust would cause a bloom of this species. For *Actinocyclus*, addition of 1 or 5 mg of dust from Namibia resulted in a growth rate that was higher than the maximum growth rate. This could indicate that the dust from Namibia adds important compounds to the Antarctic seawater, in addition to Fe alone for this species.

Desert origin dust has often been named a possible Fe source for phytoplankton in HNLC regions (Duce et al. 1991, Saydam and Senyuva 2002). Dust derived from dry riverbeds is a source that has not been assessed thoroughly yet (Martin et al. 1989b) but seems potent in inducing blooms. In general, the impact of both dust types on the growth rates of the phytoplankton will probably be higher in the field due to smaller particle sizes, atmospheric transport, exposure to UV light, repeated freeze drying of the dust, and deposition in (acid) rainwater (Spokes and Jickells 1996). This can be assumed to result in a higher reactivity of the aerosols. The results of this study must therefore be regarded as a minimum response.

In summary, we have demonstrated the use of open ocean marine diatoms as bioindicators of bioavailable iron originating from atmospheric dust. Depending on the physicochemical characteristics of the dust, phytoplankton growth is stimulated. The dust samples from different source regions differ in reactivity and iron content. These differences are clearly reflected in the response of the diatoms. Fe_{diss} measurements could not have indicated this response. The impact of (dry) dust deposition on the growth rates of large diatoms seems to be largely determined by the amorphous Fe fraction of the dust and the reactivity of the material. Using these parameters, it is possible to compare dust from different source regions in terms of impact on growth rates. Atmospheric transport is likely to increase this impact (Spokes and Jickells 1996), rendering our results as a minimum response. Knowing the percentage of Fe that is bioavailable for the phytoplankton makes it possible to calculate the growth rates of the phytoplankton in large areas of the oceans as a result of dust storms. By combining these data, it will be possible to calculate changes in, for example, phytoplankton standing stock as a result of changes in patterns of dust deposition and thus estimate effects on global biogeochemical cycles.

This study is a research project that F. V. carried out during the final year of the study Marine Biology at the University of Amsterdam. We thank Peter Croot (IfM, Kiel, Germany), who collected the dust from Namibia during his holidays, and Martin de Jong (Alterra, Texel), who collected the dust sample from Mauritania. Discussions with Eric Epping (Royal NIOZ) improved the interpretation of our data. Further, many thanks to Patrick Laan (Royal NIOZ), who was an indispensable help with the flame atomic absorption spectrometry and measured the flow-injection samples, and Claar van der Zee (Laboratory of Chemical Oceanography, Universite Libre de Bruxelles), who responded quickly to our many e-mails with questions about the Fe-reactivity experiments. We thank Winfried Gieskes from the Rijksuniversiteit Groningen for being the examiner during the research project and the coworkers from

- the Marine Chemistry and Geology (MCG) department at Royal NIOZ for their enthusiastic support. We acknowledge the support of from the European Commission's Marine Science and Technology Programme under contract EVK2-1999-00227 (IRONAGES, "Iron Resources and Oceanic Nutrients—Advancement of Global Environment Simulations").
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