Input and cycling of iron in the Gulf of Aqaba, Red Sea

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The Gulf of Aqaba, northern Red Sea, is an ideal natural laboratory for studying the impact of atmospheric dry deposition of iron to the ocean surface. We have measured atmospheric iron deposition weekly for 18 months, and dissolved and total dissolvable iron concentrations in the stratified summer (August) and well-mixed winter (March) water column. Concentrations of dissolved and total dissolvable iron remain roughly constant with depth in March. In August, there is a strong surface enrichment of iron. The accumulation of iron at the surface during the rain-free summer can be simulated by a one-dimensional model including atmospheric iron flux and estimates of iron scavenging, biological uptake and dissolution. An overall dissolution of 2% of dry deposited aerosol iron produces the best fit to the observations. A residence time of half a year for dissolved iron in surface waters with respect to scavenging is calculated for this region.


1. Introduction

The deposition and partial dissolution of mineral dust represents a major source of many bioactive trace metals and nutrients to the ocean. Iron has received the most attention because in many remote regions of the ocean dust deposition represents the major input of this important micronutrient [Duce and Tindale, 1991; Fung et al., 2000; Moore et al., 2002]. The atmospheric deposition rate of iron to the ocean surface varies over three orders of magnitude, from minimum values in the remote Pacific and Southern Ocean to maximum values near desert source regions [Duce and Tindale, 1991; Fung et al., 2000].

The total deposition of iron consists of wet and dry deposition. Recent work suggests precipitation scavenging may be responsible for as much as 30% of total iron deposition to the ocean [Gao et al., 2003]. The fraction of iron that dissolves in both wet and dry deposition is conventionally referred to as the solubility, a term we retain here for consistency with the literature. This solubility is poorly constrained. These values are critical to understanding the biogeochemical fate of iron that falls on the surface of the ocean. For example, a recent model of iron supply and demand in the upper ocean [Moore et al., 2002] found that using a global value of 2% solubility, small phytoplankton growth in 50% of the world ocean would be limited by iron, whereas if solubility is 10%, small phytoplankton growth is limited by iron in only 26% of the ocean.

The Gulf of Aqaba, Red Sea, is an ideal natural laboratory in which to study the process of atmospheric iron deposition to the ocean. The dust inputs are high, other inputs are minimal, and the system is oligotrophic and presumably not limited by iron, all factors that maximize the signal of aeolian deposition in the ocean.

The Gulf of Aqaba is the northeastern extension of the Red Sea, bordered by Israel, Jordan, Egypt and Saudi Arabia. It is a deep, narrow, semiclosed basin surrounded by desert. The Gulf receives large dust inputs from the Sahara and adjacent deserts. Precipitation and runoff are close to zero and benthic sources of iron are minimized by the steep shelf and intense summertime stratification. Exchange of seawater between the Gulf and the Red Sea proper occurs only across a 250-m sill at the southern end (the Straights of Tiran). During the summer the Gulf is thermally stratified, with mixed layer depths of about 20 m. Cooling in winter breaks down stratification and deep overturning occurs between November and April. Winter mixing can reach depths as great as 860 m during exceptionally cold winters [Genin et al., 1995], though typically convective mixing reaches depths of 300–400 m. The Gulf is oligotrophic, with maximum chlorophyll a concentrations of ~0.75 mg m⁻³ in spring at the onset of stratification and minimum concentrations of ~0.25 mg m⁻³ in midsummer [Labiosa et al., 2003]. The majority of the phytoplankton species are ultraphytoplankton (<8 μm). The cyanobacteria, Synechococcus and Prochlorococcus, dominate in the spring and summer, respectively, and eucaryotic species are more abundant during winter mixing [Lindell and Post, 1995]. Trichodesmium spp have been observed in the Gulf, and in some years contribute up to 35% of the primary productivity at the surface [Post et al., 2002]. However, colony abundance is not as great as observed in other
oligotrophic seas, such as the Caribbean and Sargasso and
Trichodesmium spp are not observed every year and at all
seasons [Post et al., 2002].

[6] Given that the Gulf of Aqaba is a semi-enclosed basin
surrounded by desert, we expected a priori that iron supply
from atmospheric deposition would be sufficient to meet the
demands of the phytoplankton community, including the
nitrogen-fixing species. Iron-replete regions of the ocean are
generally phosphorous-limited [Wu et al., 2000], and the
low concentrations of soluble reactive phosphorous in the
Gulf (0.003–0.07 μmol L⁻¹ in surface waters, Israeli
National Monitoring of the Gulf of Eilat, www.iui-eilat.ac.il, and this work) would suggest this system is also
phosphorus-limited. However, the Gulf of Aqaba lacks
continental shelf in the traditional sense, and receives
virtually no runoff, both factors that could limit the supply
of nonatmospheric iron. It is also possible that the solubility
of the aerosol iron deposited in the Gulf is anomalously low,
owing to a combination of short atmospheric residence
times and little wet deposition. To our knowledge dissolved
iron had never been measured in the Gulf of Aqaba, so the
ture iron status of this area was not known. More broadly,
we have combined a time series of aerosol measurements
with water column measurements of dissolved and dissolv-
ble iron in order to better understand the input and cycling
of iron in an oligotrophic system with large inputs of iron by
dry deposition.

2. Methods

2.1. Water Sample Collection

[7] Samples were collected from the Israeli side of the
Gulf on 19–20 August 2003 and from both the Israeli and
the Jordanian sides on 22–25 March 2004. Samples for iron
were collected from a small fiberglass boat using all-plastic
5L GO-Flo bottles deployed on non-metallic line. The GO-
Flo bottles were cleaned prior to deployment by soaking them in 1% hydrochloric acid and rinsing with ultra pure
water and then with sample water. In August 2003 all
samples were collected using the GO-Flos. In March 2004
surface samples were collected through acid-cleaned plastic
tubing (C-flex) using a peristaltic pump. Immediately after
collection, samples for dissolved iron were filtered from the
GO-Flo bottles through in-line acid-cleaned 0.2-μm capsule
filters with Supor membrane (Pall acropak). In August the
filtration was driven by filtered, compressed air, and in
March a peristaltic pump was used. Samples were collected
in acid cleaned (1 day in dilute micro detergent, at least
1 week in 3N HCl, and at least 1 week in 2N HNO₃) low-
density polyethylene bottles. Samples were stored frozen
and in the dark until analysis (~1 week later in 2003 and
7 weeks later in 2004).

2.2. Aerosol Collection

[8] Aerosol samples were collected using a Total Sus-
pended Particle (TSP) High Volume Sampler (HVS) placed
on a roof at the Interuniversity Institute of Marine Sciences
(IIMS) in Eilat, a few meters off the northwest coast of the
Gulf of Aqaba (29.52°N, 34.92°E). The HVS is designed to
have four filter cartridges connected to separate flowmeters
thus collecting four filter samples simultaneously. The
airflow path of the HVS and filter holders are made of all
plastic to minimize contamination with respect to the
measurement of trace metals. Samples were taken at least
once a week over a 24 hour period with an air flow of 2.4–
2.7 m² h⁻¹ between 20 August 2003 and 21 November
2004. Total suspended particles are collected on preweighed
acid washed 47-mm polycarbonate membrane filters. The
filters are weighted again after collection and stored frozen
in polystyrene Petri dishes inside plastic bags until further
analysis.

[9] Aerosol concentrations were converted to fluxes by
calculating a dry deposition velocity for each sampling date
using a particle deposition model based on measured
particle size distributions and local meteorological condi-
tions. See Y. Chen et al. (Estimates of atmospheric dry
deposition and associated input of nutrients to Gulf of
Aqaba seawater, submitted to Journal of Geophysical
Research, 2006) (hereinafter referred to as Chen et al.,
submitted manuscript, 2006) for details.

2.3. Analytical Methods

[10] Samples for iron were thawed at room temperature
and acidified with 4 mL 6N ultrapure HCl per L, 12–
14 hours prior to analysis. Iron (III) was determined by
flow injection analysis with chemiluminescence detection
[Johnson et al., 2003; Obata et al., 1993]. The method was
modified to include inline buffering of the sample to pH 3.3
with sodium acetate buffer just prior to loading onto the
column. The blank associated with this step and with
sample acidification was determined by analyzing acidified
ultra-pure water (18.2 MΩ). The precision of the measure-
ment was ~10% based on repeated measurement of a
single sample on different days. The accuracy of the method
was assessed by analyzing standard reference seawater
(NASS-5, National Research Council, Canada); a value of
3.8 ± 0.3 nmol L⁻¹ was determined, compared to the
certified value of 3.7 ± 0.6 nmol L⁻¹. We were concerned
that Fe(III) in the samples may have been reduced to Fe(II)
during the 14-hour acidification and subsequently not
adsorbed to the 8-hydroxyquinoline column [Lohan et al.,
2005]. We therefore tested 10 samples by analyzing them
before and 30 min after adding 10 μM H₂O₂. As there was
no trend toward higher values after H₂O₂ addition, we
concluded that 14 hours was not long enough to produce
iron reduction in these samples, and therefore did not add
H₂O₂ to the remaining samples.

[11] One aerosol filter for each sampling period was used
for bulk digestion and total iron analysis. A strong-acid
(HF-HNO₃) microwave digestion procedure in Teflon
bombs was used following Chen and Siegfert [2004]. Sam-
ple were digested along with blanks and standards and the
atmospheric concentrations were then calculated using the
mass of the extraction solution, the concentration of the
element and the volume of the air sampled. Iron
concentrations were determined by Inductively Coupled
Plasma Optical Emission Spectroscopy (ICP-OES) in a
matrix of 2% HNO₃.

[12] Samples for nutrient analysis were collected concur-
rently with iron samples and filtered through 0.45-μm
filters. Nitrite, nitrate and soluble reactive phosphorus (SRP) were analyzed using colorimetric methods described by Grasshoff et al. [1999], and modified for a Flow Injection Autoanalyzer (FIA, Lachat Instruments Model QuickChem 8000). SRP was preconcentrated by a factor of about 20 using the magnesium coprecipitation (MAGIC) method [Karl and Tien, 1992], followed by measurement using the FIA. The FIA was fully automated and peak areas were calibrated using standards prepared in low nutrient filtered seawater over a range of 0–10 μmol L⁻¹. The precision of these methods is 0.05 μmol L⁻¹ for NO₂ and NO₃, and 0.01 μmol L⁻¹ for SRP.

3. Results

Atmospheric iron deposition rates varied between 1.5 and 116 μmol m⁻² d⁻¹, with a mean (September 2003 to September 2004) of 10 μmol m⁻² d⁻¹. Total iron content of the aerosol varied between 0.5 and 6.7%, with a mean of 1.9%. Water soluble iron concentrations ranged between 0.06 and 1 nmol m⁻³ with a mean value of 0.5 nmol m⁻³ corresponding to 2–54 nmol mg⁻¹ of aerosol sample [Chen et al., 2006]. Iron fluxes showed considerable short-term variability about the mean (Figure 1). A single anomalously large (6 times the standard deviation) flux was measured on 10 May 2004. We believe this sample is in fact representative of a large flux event, and is not a methodological artifact, for three reasons. (1) Aerosol optical depth (AOD) data from SeaWiFS and MODIS between 1999 and 2004 shows a slight peak in AOD in the second quarter (April, May, June): The average AOD for the entire 6-year period is 0.134; the average second quarter AOD is 0.153. There are no valid MODIS or SeaWiFS satellite data available for the Gulf of Aqaba on 10 May 2004, but the MODIS record shows another very high dust day later that month, and the 2003 record for both satellites shows multiple high dust events in the spring and summer months (R. Labiosa, personal communication, 2005). (2) The total aerosol mass measured on that day was more than 3 times greater than the next highest day, ruling out iron contamination. (3) Observations at the IIMS indicate there was a pronounced “haze” visible during the whole week of 10 May 2004 (A. Post, personal communication, 2004).

Profiles at Station A (29.46°N, 34.93°E, 700 m deep) in the north central Gulf (see Figure 2) show large differences in vertical structure between August and March (Figure 3). In August, the water column is thermally stratified, with a mixed layer of ~20 m. During winter, and into March, the water column is deeply mixed, in 2004 to a depth of ~450 m. In August, both dissolved and total iron show a pronounced surface maximum, approaching minimum and constant values of ~1 nmol L⁻¹ (dissolved) and 4 nmol L⁻¹ (total) below 40 m (Figure 3). In March, dissolved iron concentrations are about 1 nmol L⁻¹ throughout the water column, and total iron, though more variable, is between 3–7.5 nmol L⁻¹ with no surface maximum. Macronutrient concentrations show roughly the opposite trend, with low surface concentrations, near the detection limit, (0.15 μmol L⁻¹ nitrate + nitrite) observed in August, and higher concentrations in March (1.2 μmol L⁻¹) (Figure 3). Similar results are seen for SRP (0.03 and 0.07 μmol L⁻¹ in August and March, respectively) and Si (1.0 and 1.1 μmol L⁻¹ in August and March, respectively) in surface waters. In both August and March, macronutrient concentrations increase below the mixed layer, whereas iron concentrations do not. In August, nitrate is uniformly low to almost 100 m below the base of the mixed layer.

4. Discussion

Converting measured metal concentrations in air to fluxes to the sea surface involves estimating the rate of iron-bearing particle deposition. We use a particle size dependent deposition model to estimate this velocity and assume that iron is uniformly distributed among different aerosol sizes (size fractionated iron concentrations are not available). Iron, however, generally occurs in the coarse (>5 μm) aerosol fraction [Duce et al., 1991] and the coarse particles make up about 60% of the particle volume at our site. These coarse particles largely determine the total dry deposition velocity (Chen et al., submitted manuscript, 2006). Accord-
Figure 2. Concentration of dissolved and total dissolvable iron in the surface waters of the northern Gulf of Aqaba in August 2003 and March 2004. The location of Station A is indicated by the open circle in Figure 2a.

Figure 3. Profiles of dissolved Fe, total dissolvable Fe, nitrate, density, temperature, and salinity in August 2003 and March 2004 at Station A (29.46°N, 34.93°E) in the Gulf of Aqaba. Also shown are results from a one-dimensional model initialized in March and run until August. In this run, which includes complexation by an organic ligand present at a constant concentration of 0.6 nM with a conditional stability constant of $1.2 \times 10^{13}$ M$^{-1}$ [Archer and Johnson, 2000], the scavenging rate for dissolved iron, $K_{Fe}$, was constant with depth and equal to 0.01 yr$^{-1}$ and the fraction of aerosol iron solubilized in the surface was 2%. The time-varying iron input time series was used to force the model. See text for details.
ingly, our calculated iron fluxes are relatively insensitive to the assumption of uniform distribution.

[17] Our estimates of atmospheric iron deposition rate in the Gulf of Aqaba confirm that this is indeed a region with an exceptionally large input of iron from dust. The total dust deposition rate, 28 g m\(^{-2}\) yr\(^{-1}\), agrees well with the value for this region predicted by a recent compilation of three observation-based models (10–20 g m\(^{-2}\) yr\(^{-1}\)) [Jickells et al., 2005], making it one of the highest dust deposition rate areas on Earth. The annual iron deposition rate, 10 µmol m\(^{-2}\) d\(^{-1}\), is about 4 times greater than the annual iron input rate to the Sargasso Sea [Jickells, 1999], and about 10 times greater than that to the Hawaiian island of Oahu [Prospero et al., 1989].

[18] Our measurements of dissolved iron in the Gulf waters confirm our initial hypothesis that iron concentrations would be high and nonlimiting. Indeed, in both August and March, mixed layer dissolved iron concentrations were in excess of 1 nmol L\(^{-1}\), significantly higher than the half saturation constant for growth with respect to iron [Blain et al., 2002; Coale et al., 2003]. In contrast, soluble reactive phosphorus and dissolved inorganic nitrogen concentrations in August are 2–40 nmol L\(^{-1}\) and 40–75 nmol L\(^{-1}\), respectively, potentially low enough for single limitation by either macro nutrient or colimitation [Thingstad et al., 2005; Zohary and Roberts, 1998].

[19] These dissolved iron concentrations are higher than the theoretical solubility limit for iron in seawater (~0.08 ± 0.03 nmol L\(^{-1}\) [Millero, 1998; Wu et al., 2001]). Such supersaturated iron concentrations in the <0.2-µm fraction could be maintained either by the presence of colloidal iron or through complexation by organic ligands. Alternatively, iron may be rapidly released from particles (by thermal dissolution or photolysis) and then scavenged toward a solubility limit. It is of course possible that despite the high concentration of dissolved iron, concentrations of biologically available iron are low. However, we conducted trace-metal clean incubation experiments in November 2004 and did not find enhanced growth when iron was added, indicating that ambient dissolved iron concentrations are not limiting (Z. Chase, unpublished data, 2004).

[20] The dissolved iron concentrations observed in surface waters of the Gulf of Aqaba are significantly higher than seen in the open ocean globally [Johnson et al., 1997]. However, our August and March data are lower than previously reported for surface waters of the northern Gulf of Aqaba (15.6 nmol L\(^{-1}\)) and the northern Red Sea (15–23 nmol L\(^{-1}\)) for samples collected in February 1999 [Shridah et al., 2004]. Our surface water dissolved iron concentrations in August are similar to what was observed in October in the Mediterranean, a nearby semienclosed basin, while concentrations in March are higher than the <0.13 nmol L\(^{-1}\) observed in the Mediterranean in February [Sarthou and Jeandel, 2001]. Our March surface water concentrations are similar to those observed in the Arabian Sea in January and April (mean 1.0 nmol L\(^{-1}\)), but the high concentrations we observed in August were not observed in the Arabian Sea, even after the SW Monsoon [Measures and Vink, 1999].

[21] Although dissolved iron concentrations are high throughout the year we observed substantial spatial variability in surface water concentrations (Figure 2). It is not clear what is driving the spatial variability in iron concentrations in the Gulf, which is most pronounced for total dissolved iron. Specifically, very high concentrations of total dissolved iron were measured at the northern-most stations, on the Israeli side of the Gulf (Figure 2). These sites are adjacent to the commercial center of the town of Eilat, as well as a fish farm operation. These are both potential sources of particulate iron. Another possibility is that there is a strong gradient in aeolian iron supply. The predominant wind direction is from the north, and some large mineral particles may be blown from the land immediately to the north, and deposited on the ocean within a short distance. Finally, there may be a benthic source of iron at these sites, as they are shallow sites where the bottom is sand, and not coral.

[22] In addition to spatial variability, there are marked seasonal differences in the distribution of dissolved and total iron in the northern Gulf of Aqaba, with high surface concentrations in August and lower, more uniform concentrations in March. A similar seasonal cycle has been observed in the Mediterranean [Sarthou and Jeandel, 2001]. The higher surface water iron concentrations observed in August cannot be due to greater dust input at that time; there is no significant seasonal trend in aerosol loads in Eilat, and in both 2004 and 2005 anomalously large aerosol loadings (threefold greater than average) were observed in spring (May and April, respectively, Figure 1 and Chen et al. (submitted manuscript, 2006)). We suggest the higher surface concentrations in August are due to (1) shoaling of the mixed layer and (2) limited biological iron removal due to macronutrients-limited productivity. That is, iron is able to accumulate throughout the summer in a shallow, isolated surface layer, with minimal removal by biological production.

4.1. A Simple Model

[23] We have used a simple one dimensional model to quantify what we know about the behavior of iron in this system. We assume that the only input of iron to the system is from aerosols in the form of dry deposition. Precipitation is virtually nonexistent in the summer as typically there is no rainfall between April and September in Eilat (average rainfall, occurring mainly in the winter, is only 3 cm yr\(^{-1}\) [Morcos, 1970]). Likewise there is practically no runoff. The fact that the Gulf is a rift valley, with very steep sides and a sandy bottom suggests inputs of iron from benthic sources will be minimal. Although this has not been confirmed directly, several lines of evidence suggest benthic sources are indeed minimal. First, profiles even within 1 km of the shore consistently show a surface and not a near-bottom maximum in iron. This is in contrast to the California [Chase et al., 2005b] and Oregon [Chase et al., 2005a, 2002] margins, where benthic sources are significant, and profiles consistently show a near-bottom maximum in iron concentration. Second, elevated concentrations are found at the most shoreward sites, but beyond that, concentrations are very uniform and there is little evidence of a gradient in iron concentration from the margins to the
center of the Gulf (e.g., Figure 2). As discussed above, there is some suggestion of a north to south gradient in iron at the northern end of the Gulf (Figure 2), but not an east-west gradient, suggesting the N-S gradient is related to local anthropogenic inputs from the cities of Eilat and Aqaba. We further assume no advective inputs or losses of iron. One of the outcomes of the modeling exercise is to show that this assumption is probably not valid.

[24] Because we are using data from August 2003 and March 2004, in order to calculate a seasonal change we need to assume that these months are representative of the respective seasons and that there is no interannual variability in the atmospheric iron flux. An analysis of MODIS and SeaWiFS aerosol optical depth data from 1999–2004 found interannual variability in summer values to be less than 10% (R. Labiosa, personal communication, 2005). Aerosol concentrations have been measured and fluxes estimated in Eilat for two summer seasons, 2004 and 2005 (Chen et al., submitted manuscript, 2006). The two years were very similar in terms of mean March–August aerosol flux (34 and 36 mg m\(^{-2}\) d\(^{-1}\) in 2004 and 2005, respectively) as well as the minimum (8 and 9 mg m\(^{-2}\) d\(^{-1}\)) and maximum (264 and 230 mg m\(^{-2}\) d\(^{-1}\)) recorded fluxes. Furthermore, in both years there was one high flux event significantly above the average; in 2004 it was on 10 May, and in 2005, 7 April. Finally, we have compared the March through September results of the real-time Navy Aerosol Analysis and Prediction System (NAAPS) for 2003 and 2004 (Naval Research Laboratory, Aerosol plot generator, 2004, http://www.nrlmry.navy.mil/flambe/plotgen/index.htm). Both years have almost the same average aerosol optical depth over this period (0.26 and 0.29 in 2003 and 2004, respectively). In summary, although a longer aerosol time series and/or coincident aerosol and ocean sampling is certainly preferable, from the above considerations we expect iron aerosol fluxes are relatively stable year to year in this region.

[25] With these assumptions, our hypothesis is that the summertime progression of dissolved iron concentrations in the Gulf of Aqaba can be explained as the balance between aerosol input and dissolution, vertical mixing, abiotic scavenging and biological uptake as presented by equations (1)–(5),

\[
\frac{d \text{Fe}(z)}{dt} = \frac{\partial}{\partial z} K_v \frac{\partial \text{Fe}(z)}{\partial z} + J_T(z)\alpha - Q \times P(z) \times e^{-K_v[\text{Fe'}(z)]}
\]

(1)

where

\[
\frac{\partial}{\partial z} K_v \frac{\partial \text{Fe}(0)}{\partial z} = 0,
\]

(2)

\[
J_T(0) = 13 \mu\text{mol m}^{-2}\text{d}^{-1} \text{or } = f(\text{time}),
\]

(3)

\[
\frac{\partial}{\partial z} K_v \frac{\partial \text{Fe}(600)}{\partial z} = 0,
\]

(4)

\[
J_T(z \neq 0) = 0.
\]

(5)

[26] The first term on the right-hand side of equation (1) represents vertical diffusivity, where \(K_v\), the eddy diffusivity coefficient, was estimated to be \(10^{-3} \text{ m}^2 \text{s}^{-1}\), on the basis of modeling the temperature profiles, as shown below. The next term is the product of total aerosol iron deposition \(J_T\) and iron aerosol solubility \(\alpha\). We used two formulations for \(J_T\). In one, a constant iron flux was applied between 1 March and 1 September, equal to the measured average flux over this period in 2004 (13 \(\mu\text{mol m}^{-2}\text{d}^{-1}\)). We also tested a formulation where the iron input varied as a function of time, based on the 2004 measurements (Figure 1). In the model all of the dissolution occurs within the surface layer (equations (3) and (5)). Aerosol solubility was treated as a free parameter. The next term represents iron loss through biological uptake, and is the product of the primary production \(P\), an average cellular Fe:C ratio \(Q\) and the ratio of export production to total production \(e\). Because we might expect Fe:C ratios to be elevated in this environment with high dissolved iron, we set \(Q\) equal to 20 \(\mu\text{mol:mol}\), a value that has been observed in phytoplankton cultures supplied with abundant iron [Maldonado and Price, 1996; Sunda and Huntsman, 1995]. \(P\) was taken as the average summertime primary productivity in the Gulf (17 mmol C m\(^{-2}\) d\(^{-1}\); based on unpublished \(^{15}\text{C}\) incubation data from 1999–2002 (David Illuz, personal communication, 2004)). We have assumed a constant primary production rate in the upper 100 m, and zero productivity below this depth. In the absence of direct measurement of new and regenerated production in this system we used an upper limit of 0.3 for the ratio of export production to total production \(e\) in this warm oligotrophic system [Laws et al., 2000]. The last term in equation (1) represents loss due to abiotic scavenging, which is formulated two different ways after Archer and Johnson [2000]. In one formulation, we assume no complexation by an organic ligand, and scavenging is proportional to dissolved iron concentration \(\text{Fe}(z) - \text{Fe'}(z)\) in equation (1)). We also tested the formulation that includes complexation of iron by an organic ligand having a concentration of 0.6 nmol L\(^{-1}\) and a conditional stability constant of 1.2 \(\times 10^{13}\) M\(^{-1}\). These parameter values were chosen to match those used by Archer and Johnson [2000]. In this case only the uncomplexed iron \(\text{Fe'}(z)\) is available to be scavenged. In both cases scavenging rate constants were varied tenfold around values optimized by Archer and Johnson [2000].

[27] The model is initialized with the March 2004 profiles. We modeled the temperature and salinity profiles using a similar approach by adding a heating (salt) term to the uppermost layer equivalent to the total heating (salinity increase) observed at the surface between March and August and mixing that input vertically by eddy diffusivity. The best fit to the temperature data was obtained with a \(K_v\) of \(10^{-3}\) m\(^2\) s\(^{-1}\) (Figure 3). Lower values, such as the canonical \(10^{-4}\) m\(^2\) s\(^{-1}\) [Munk, 1966] or the \(10^{-2}\) m\(^2\) s\(^{-1}\) observed in deliberate trace experiments [Laws et al., 2003], produce temperatures at depth that are significantly too low in August. \(K_v\) was also calculated from the vertical velocity field generated by a three-dimensional primitive equation model of the Gulf of Aqaba; over the whole summer, in the upper 200 m the value of \(K_v\) is \(3.5 \times 10^{-3}\)
m$^2$ s$^{-1}$ (R. Labiosa, personal communication, 2005). A similar value of $2.5 \times 10^{-3}$ m$^2$ s$^{-1}$ was calculated on the basis of nitrate profiles and consideration of nitrate uptake kinetics [Badran et al., 2005]. Convective mixing is also important in the Gulf. However, convective processes dominate during the winter season (December–April), whereas eddy diffusion dominates the mixing in the summer (May through November) [Badran et al., 2005], which is what we are interested in modeling. The relatively large diffusion coefficient required in this model may result in part from the fact that we have not included convection; an earlier one-dimensional model reproduced temperature profiles throughout the year with a convective scheme forced by local meteorological conditions and much weaker diffusion ($K_v = 10^{-6}$ m$^2$s$^{-1}$) [Wolf-Vecht et al., 1992].

[28] The August salinity profile is not fit by a simple mixing model using $K_v = 10^{-3}$ m$^2$s$^{-1}$; there is clearly an intrusion of lower-salinity water centered around 100 m (Figure 3). A salinity minimum at about 100 m is regularly observed during the summer in the northern Gulf of Aqaba [Wolf-Vecht et al., 1992; A. Rivlin, personal communication, 2005]. As suggested by Wolf-Vecht et al. [1992] the only possible source of this low salinity water is from the Red Sea proper, across the Straights of Tiran.

[29] The model also does a poor job of reproducing dissolved iron concentrations beneath the surface in August. As we discuss in section 4.2, a solubility of 2% produces a good fit to the surface iron data in August using a variety of different model formulations. However, none of these formulations reproduces the profile below the surface (for example, see output in Figure 3). We believe the most likely explanation for this discrepancy is that there is an advective input of low iron water into the Gulf, associated with the clearly visible intrusion of lower salinity water at about 100 m. There are other possible explanations. First, iron loss terms may be elevated in the region of discrepancy, between 5 and 70 m. For example, if we increase the biological export term ($Q \times F \times e$) by a factor of 250–300 between 5 and 70 m the iron profile is reproduced reasonably well. However, such a large increase in biological removal of iron is difficult to justify, given an already generous choice of $Q$ and $e$, unless productivity in this depth range was anomalously high in 2003. We need to increase the scavenging term a thousandfold, relative to the surface, between 30 and 70 m in order to reproduce the observed profile. Such an extreme increase in the scavenging term at this depth is difficult to justify. Second, if mixing is reduced by an order of magnitude, setting $K_v$ to $10^{-4}$ m$^2$s$^{-1}$, the iron distribution in August is well reproduced (with a slightly higher solubility of 2.5%), because the iron is retained in the surface layer. However, as explained above, with such slow mixing the sub-surface water column is too cold in August relative to observations. Finally, a large dust event just prior to our sampling in August 2003 (i.e., prior to the period of aerosol flux measurement) cannot account for the observed iron vertical profile, unless average fluxes of the rest of the summer were anomalously low, because excess iron still accumulates throughout the summer. However, as discussed above, the NAAPS results suggest 2003 and 2004 had similar total summer aerosol loads, and a more detailed examination of the 2003 summer NAAPS model shows quite constant values, with one 4-sigma dust event in late May and nothing anomalous in August.

[30] We have not included a remineralization term in the model. Doing so, for example following the formulation of Johnson et al. [1997], based on carbon flux, has little impact on the outcome, and produces a worse fit to the data, since it acts as a subsurface iron source, when the model is lacking an iron sink.

[31] We have not attempted to model total dissolvable iron, because of the operational nature of the measurement and because we don’t know the size distribution of total iron, which affects its sinking rate and the extent to which it acts like a solute or like a solid. Features such as the “spike” in dissolved iron near 50 m in March (Figure 2) are difficult to account for in the simple model used to describe dissolved iron. Furthermore, there is clearly strong spatial variability in total dissolvable iron (Figure 2), which suggests there may be local sources of aerosol or nonaerosol particulate Fe. In principle, such sources could affect dissolved iron distributions as well through dissolution, and there is some indication of elevated concentrations of dissolved iron associated with elevated concentrations of dissolved iron in surface waters (Figure 2). The dynamic range for dissolved iron is much smaller than for total iron, suggesting minimum impact of local sources on the dissolved iron distributions. Variable inputs (or outputs such as scavenging intensity) would need to be considered and quantified in a more complete model of iron cycling in the Gulf.

[32] In summary, we have used a simple model to represent a hypothesis about what controls the evolution of dissolved iron concentrations over the summer in the northern Gulf of Aqaba. This model, which includes only aerosol deposition, diffusive mixing and loss due to scavenging and biological uptake, can reproduce surface dissolved iron concentrations in August, but does a poor job of reproducing the dissolved iron profile beneath the surface. The most likely explanation is that iron concentrations within the Gulf are influenced, at least during the summer of 2003, by the advection of low-iron water at a depth of 30–70 m. While this simple model works reasonably well during the summer, a model of the entire annual cycle would need to account for convective mixing during the winter.

4.2. Iron Solubility and Residence Times

[33] One of the goals of the modeling exercise was to constrain the value of the solubility of aerosol iron, by determining which value gives the best fit to the data. Because the subsurface iron profile was not well fit by the model, we focus on the aerosol solubility necessary to account for the observed seasonal accumulation of iron in the surface layer. A solubility of 2% was found to produce the best fit, irrespective of the exact parameterization of iron scavenging, and across a range of reasonable values of the iron scavenging rate constant (Table 1). This result holds whether a constant summer iron flux or a time-varying
Table 1. Results of Model Runs Used to Determine the Best Fit for the Solubility of Dry Deposited Iron

<table>
<thead>
<tr>
<th>Scavenging Rate, yr⁻¹</th>
<th>Best Fit, Solubility, %</th>
<th>Best Fit, Model-Data, nM</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Constant Dust, No Ligand</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00032</td>
<td>2</td>
<td>0.56</td>
</tr>
<tr>
<td>0.0016</td>
<td>2</td>
<td>0.53</td>
</tr>
<tr>
<td>0.008</td>
<td>2</td>
<td>0.40</td>
</tr>
<tr>
<td>0.016</td>
<td>5</td>
<td>12.39</td>
</tr>
<tr>
<td><strong>Variable Dust, No Ligand</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00032</td>
<td>2</td>
<td>0.02</td>
</tr>
<tr>
<td>0.0016</td>
<td>2</td>
<td>−0.01</td>
</tr>
<tr>
<td>0.008</td>
<td>2</td>
<td>−0.17</td>
</tr>
<tr>
<td>0.016</td>
<td>5</td>
<td>10.91</td>
</tr>
<tr>
<td><strong>Constant Dust, Ligand</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.002</td>
<td>2</td>
<td>0.52</td>
</tr>
<tr>
<td>0.01</td>
<td>2</td>
<td>0.36</td>
</tr>
<tr>
<td>0.05</td>
<td>5</td>
<td>−0.38</td>
</tr>
<tr>
<td>0.01</td>
<td>5</td>
<td>12.66</td>
</tr>
<tr>
<td><strong>Variable Dust, Ligand</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.002</td>
<td>2</td>
<td>−0.02</td>
</tr>
<tr>
<td>0.01</td>
<td>2</td>
<td>−0.21</td>
</tr>
<tr>
<td>0.05</td>
<td>2.5</td>
<td>0.64</td>
</tr>
<tr>
<td>0.01</td>
<td>5</td>
<td>11.24</td>
</tr>
</tbody>
</table>

The one-dimensional model was run in a configuration with no complexation by organic ligands, and in a configuration that included scavenging by an organic ligand having a concentration of 0.6 nmol L⁻¹ and a conditional stability constant of 1.2 × 10¹³. Both configurations were run with two different time series of iron inputs. In the “variable dust” run, iron inputs were based on the time series of measured aerosol load and estimated total iron flux in 2004. In the “constant dust” model, the average experimentally determined iron inputs was used, but the flux was evenly distributed throughout the period modeled. The solubility giving the best fit to surface dissolved iron data in August was determined for a range of values of the scavenging rate constant (midpoint values were those determined by Archer and Johnson [2000] as being the best fit to global iron measurements). The fit assuming the fraction of iron that dissolves is 5% is also indicated.

summer iron flux is used (Figure 4). A recent review of aerosol iron solubility [Jickells and Spokes, 2001] concluded that over aerosol iron solubility is probably less than or equal to 2%, reflecting a large fraction of dry deposition with low solubility (<0.1%) and a lower fraction of wet deposition with high solubility (~5%). Our estimated total solubility is thus similar to recent estimates of overall iron solubility, but because the deposition is entirely dry in this region, it suggests the fraction of dry deposition that dissolves in this region is at the high end of previous estimates for other regions.

[34] Chen et al. [2006] have directly measured the solubility of iron in aerosol samples collected at our study site. Using a 30-min leach in filtered seawater with a particulate concentration of 60 mg L⁻¹ in the leaching jar, they find on average 0.3% solubility for iron. While consistent with other laboratory estimates of aerosol solubility in seawater (as reviewed by Jickells and Spokes [2001]), such a low solubility is not consistent with the observed surface water enrichment in August. Total iron fluxes would have to be sixfold higher than estimated from measurements for the measured surface iron concentrations to be consistent with a solubility as low as 0.3%. The difference may reflect additional solubilization that occurs when aerosols reside in the real surface ocean for an extended period of time. Alternatively, the low solubility measured experimentally may be due to the relatively high particulate concentration (60 mg L⁻¹) used. Bonnet and Guieu [2004] found an inverse power law relationship between the percent of iron dissolved from natural and anthropogenic aerosol samples over 7 days and the concentration of aerosol particles in the leaching jar, with greater iron solubility at lower particle concentrations. Applying this power law relationship to the experimental concentration of 60 mg L⁻¹ used by Chen et al. [2006] predicts solubilities of 0.015% and 0.3% for natural and anthropogenic particles, respectively. The fact that the measured solubility at 60 mg L⁻¹ shows better agreement with the anthropogenic than with the natural (Saharan) aerosol may reflect either a preponderance of anthropogenic aerosol in the Gulf of Aqaba, differences in the solubility of natural aerosol in these two regions, differences between a 30-min and a 7-day leach or the difference between a soil sample and an aerosol sample.

[35] Assuming 2% of the aerosol iron dissolves, we can divide the “annual” average iron inventory (Table 2) by the annual dissolved iron flux (2% × total iron flux) to calculate the residence time of dissolved iron with respect to aerosol deposition. A similar calculation can be made for total iron, using the total iron flux. These estimates (Table 3) have uncertainty associated with estimating the annual inventory from two seasons, from the calculation of iron deposition...
rate, and, for dissolved iron, from the estimated solubility. Such uncertainty is generally present in all estimates of iron residence time.

We find a dissolved iron residence time of about half a year near the surface, which is far shorter than the residence time of iron in the ocean as a whole [Bruland et al., 1994], but similar to a recent estimate of iron residence time in surface waters of the North Pacific [Boyle et al., 2005]. Our results are also largely consistent with estimates of dissolved iron residence time in the upper 100 m of the Sargasso Sea, which Jickells [1999] estimated to be 253 days. Residence times for total iron are about tenfold shorter than for dissolved iron, varying from weeks at the surface to almost a year within the upper 500 m (Table 3). These short residence times are consistent with results from the Sargasso Sea (18 days in the upper 100 m [Jickells, 1999]) and from the equatorial Atlantic (6–62 days in the upper 200 m [Croot et al., 2004]).

### 4.3. A Global Context

The relationship between the local rate of aerosol deposition and the iron inventory in the underlying water column is of interest because it should give an indication of whether iron solubility limits the amount of dissolved iron that can accumulate in the water column. In their global compilation, Johnson et al. [1997] found a weak relationship between aeolian iron flux and the 0- to 500-m integrated dissolved iron inventory. The data could be fit with either a linear or a power law relationship. These two equations make very different predictions about the integrated iron inventories expected at locations where the aeolian iron fluxes are greater than those included in the 1997 data set. The annual aeolian iron flux in the Gulf of Aqaba is almost 2 orders of magnitude greater than the greatest flux in the Johnson et al. [1997] compilation. Plotting the Gulf of Aqaba annually averaged data together with the two curves fit to the Johnson et al. [1997] data shows clearly that the new data agree better with the power law than with the linear relationship (Figure 5). This asymptotic relationship implies that there is a solu-

### Table 2. Vertically Integrated Inventory of Dissolved and Total Iron in March 2004 and August 2003, and an “Annual” Average Consisting of the March–August Average

<table>
<thead>
<tr>
<th>Depth, m</th>
<th>March</th>
<th>August</th>
<th>“Annual” Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dissolved Inventory</td>
<td>Total Inventory</td>
<td>Dissolved Inventory</td>
</tr>
<tr>
<td>0–50</td>
<td>26 ± 5</td>
<td>99 ± 40</td>
<td>117 ± ...</td>
</tr>
<tr>
<td>0–100</td>
<td>79 ± 10</td>
<td>305 ± 103</td>
<td>175 ± ...</td>
</tr>
<tr>
<td>0–200</td>
<td>186 ± 9</td>
<td>659 ± 76</td>
<td>259 ± ...</td>
</tr>
<tr>
<td>0–300</td>
<td>270 ± 38</td>
<td>917 ± 165</td>
<td>335 ± ...</td>
</tr>
<tr>
<td>0–500</td>
<td>461 ± 83</td>
<td>1587 ± 341</td>
<td>486 ± ...</td>
</tr>
</tbody>
</table>

*Units are µmol m$^{-2}$. In March, the average and 1 standard deviation from profiles at three different locations are indicated. A single profile from station A was used in August. Inventories were calculated by trapezoidal integration.

### Table 3. Residence Time of Total Iron and Dissolved Iron in the Gulf of Aqaba With Respect to Aerosol Deposition, as a Function of Integration Depth

<table>
<thead>
<tr>
<th>Depth, m</th>
<th>Residence Time Total Iron, days</th>
<th>Residence Time Dissolved Iron, years</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–50</td>
<td>7.4–29.4</td>
<td>0.4–1.5</td>
</tr>
<tr>
<td>0–100</td>
<td>17.2–68.7</td>
<td>0.7–2.7</td>
</tr>
<tr>
<td>0–200</td>
<td>34.0–136.1</td>
<td>1.2–4.8</td>
</tr>
<tr>
<td>0–300</td>
<td>49.8–199.3</td>
<td>1.6–6.5</td>
</tr>
<tr>
<td>0–500</td>
<td>88.6–354.6</td>
<td>2.6–10.2</td>
</tr>
</tbody>
</table>

*Annual average inventories were divided by estimated annual iron input from dust. A solubility of 2% was used in estimating the input of dissolved iron. The range of values reflects an estimated twofold uncertainty in deposition velocity.

![Figure 5. Relationship between the atmospheric deposition of dissolved iron to the sea surface and the dissolved iron concentration integrated from the surface to 500 m. The two curves are fits to the data compiled by Johnson et al. [1997]. See that reference for details of the data used in the compilation. The square shows the data for the Gulf of Aqaba. The range of iron flux represents the September 2003 to September 2004 measured iron input from dust multiplied by a fraction from 1 to 3% to account for dissolution, and including a twofold uncertainty in depositional velocity. The integrated iron inventory is the average of inventories for August 2003 and March 2004 and the range is the associated standard deviation (Table 1).
bility control on dissolved iron concentrations. As aeolian input increases, the amount of dissolved iron in the water column does not increase continuously, but rather approaches a limit dictated by the solubility of iron in seawater.

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