

## ***Interactive comment on “A system in balance? – Implications of deep vertical mixing for the nitrogen budget in the northern Red Sea, including the Gulf of Aqaba (Eilat)” by C. Häse et al.***

**C. Häse et al.**

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General statement:

We acknowledge the constructive comments of all three reviewers. The comments indicated that we need to clarify the aim and the general thread of the manuscript, which will be considered in the revised version of the manuscript. Thus, before replying to the referee’s comments in detail, we would like to start with a short summary of our study:

The motivation of the present study was to identify the cause for the higher nitrate deficit in the northern Red Sea compared to the Gulf of Aqaba where it is almost zero. The explanation that we found to be most plausible points to the ‘geochemist’s view’ that

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nitrate is the proximate, and phosphate is the ultimate limiting nutrient for productivity in the system (for details see below). Thus, the main objectives of the manuscript are 1) to elucidate our explanation, 2) to demonstrate that our field data support the 'geochemist's view', and 3) to point out the implications for the protection of the coral reefs in the area..

We admit that the title could be misleading regarding the fact that we compare the northern Red Sea proper and the Gulf of Aqaba. We will change it to "A system in balance? - Implications of the hydrodynamic regime for the nitrogen budget in the Gulf of Aqaba (Eilat) in comparison to the northern Red Sea". The term 'system in balance' refers to the balance between nitrogen losses and nitrogen inputs in relation to phosphate with respect to the 'Redfield' stoichiometry. The question mark in the title should indicate that further investigations are needed to thoroughly corroborate the explanation that we derive here from indirect measures, i.e. nutrient and oxygen concentrations instead of directly determining nitrogen fixation and denitrification rates.

It was criticised by the reviewers that the relationship between the nitrate deficit and iron was not made clear in the manuscript. This relationship includes that the nitrate deficit is a possible consequence of iron limitation of the nitrogen fixation process in the ocean or at least parts of it. However, because of high dust depositions, this can be excluded for the entire area of the Red Sea (see also comment by S. Naqvi). This implies that both the existing positive nitrate deficit in the northern Red Sea and the fact that the nitrate deficit did almost disappear in the Gulf of Aqaba cannot be related to iron concentrations. Hence, there must be another process involved causing the difference in the nitrate deficit between the two adjacent water bodies.

The central question of the present study is what could be the cause for the higher nitrate deficit in the northern Red Sea? Iron can be excluded, and there is no evidence for different atmospheric inputs of N or P into the two water bodies. The other options could be the result of in- and outflow of water masses, and the balance of internal nutrient cycles. The current pattern in the area was such that surface waters from the

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northern Red Sea entered the gulf which was compensated by an opposite flux of deep waters over the sill (Manasrah et al. 2004), resembling the overall pattern throughout most of the year. By the inflow of nutrient-depleted surface waters from the northern Red Sea, the gulf imported a slight nitrate deficit that did not exceed  $0.6 \text{ mmol/m}^3$  at the time of our observations. On the other hand, by the outflow of nutrient-rich deep waters through the Straits of Tiran the gulf exported a somewhat higher nitrate deficit of up to  $1.5 \text{ mmol/m}^3$ . It is obvious that this pattern alone cannot explain the higher nitrate deficit of up to  $6.5 \text{ mmol/m}^3$  in the northern Red Sea. Therefore, we conclude that the difference in the nitrate deficit between the two water bodies must be related to the balance of internal nutrient cycles. The variability in the nitrate deficit of deep waters at the different stations within the northern Red Sea covered the range  $1.8 - 6.5 \text{ mmol/m}^3$  at relatively constant phosphate concentrations of  $0.9 \pm 0.1 \text{ mM}$ . Therefore, we are convinced that the observed difference in the nitrate deficit is related to the nitrogen cycle. Comparing the rate of the input processes into the two water bodies suggests that nitrogen fixation should be rather higher in the northern Red Sea than in the gulf. First, the nitrate deficit in surface waters is more pronounced in the Red Sea proper than in the gulf (Fig. 4). Second, *Trichodesmium* do not tolerate deep vertical mixing, which occurs regularly in the gulf. This led us to the conclusion that the observed difference in the nitrate deficit is controlled by the intensity of the nitrogen loss process rather than that of the input process.

This leads us to the other critical question that was raised by the reviewers, i.e. how the nitrate deficit is related to the ultimate and proximate limiting nutrient for primary production. A positive nitrate deficit implies that nitrogen is lacking in relation to phosphate compared to the phytoplankton demand. This indicates that nitrogen is the nutrient in short supply, i.e. limiting the phytoplankton production in the sense of Liebig's law. According to the 'geochemist's view', nitrogen on the long term follows the corresponding level of phosphate in the system because of regulating feedback mechanisms in the nitrogen cycle, which are lacking in the phosphorus cycle. Whether nitrogen becomes limiting for phytoplankton production or not, depends on the actual balance between in-

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put and loss processes. The model study by Tyrrell (1999) demonstrated that in marine systems phosphate concentrations determine generally the overall level of productivity despite a positive nitrate deficit that persisted on the long term (HNLC regions were not considered). He further demonstrated that the PLN and the ULN do not have to be the same, even in a system in steady state. If we consider nitrogen to be the limiting nutrient in a way without connection to the overall phosphate level, what would the nitrate deficit of almost zero in the Gulf of Aqaba indicate then? That phosphate concentrations met by chance the nitrate concentrations in Redfield stoichiometry, and this in two adjacent water bodies that reveal a remarkable difference in the overall nutrient inventory? The fact that this difference was in the same order of magnitude for both nutrients (factor 3) clearly indicates that the nutrient stoichiometry in the entire system is ruled by internal nutrient cycling, and not by external supply. Hence, the most plausible explanation for our observations was that the nitrate deficit was reduced in the Gulf of Aqaba to almost zero as a consequence of reduced benthic denitrification rates (regarded here as the main loss process with respect to N), which implied also a smaller ‘niche’ for nitrogen fixers. The view that the nitrate deficit is related to the imbalance between nitrogen input and nitrogen losses is not new. However, the fact that the nitrate deficit (1) varied remarkably at an almost constant phosphate concentration within the same water body (northern Red Sea), and (2) almost disappeared in an adjacent water body with a generally lower inventory of both nutrients (Gulf of Aqaba), supports the view that nitrogen behaved like a proximate limiting nutrient (PLN), whereas phosphate as the ultimate limiting nutrient (ULN) determined the overall level of productivity. In this sense, our data support the ‘geochemist’s view’.

In our manuscript we proposed that benthic denitrification rates in the Gulf of Aqaba were ‘suppressed’ by high oxygen concentrations due to deep convective mixing. In addition, the nitrate deficit in the water column was highly correlated with the water-column nitrate content (total oxidized nitrogen). This suggests that the availability of nitrate controls benthic denitrification, which is in accordance with recent publications (e.g. Sigman et al. 2003, Tanaka et al. 2004). This new aspect will be included in the

revised manuscript.

The continuous emission of hundreds of tons of nutrients into shallow waters at the northern end of the Gulf of Aqaba by a fish farm represents a critical threat to the gulf with respect to eutrophication, especially to the coral reefs (Bongiorni et al. 2003, Erez et al. 2005, Lazar et al. 2005). Rough calculations suggest that the nutrient emissions by the fish farm had not yet affected the nutrient inventories of the entire gulf at the time of the 'Meteor' cruise. However, there is an urgent need to further investigate the development of nutrient inventories in the area. That is the reason why we want to keep this issue in our manuscript.

#### 1. Detailed reply to Referee S. Naqvi

With respect to the difference between the 'Meteor' data and our other data from a three-year study, we checked carefully possible reasons, and revised our entire data set. We can exclude a systematic error for just the samples of the Red Sea proper, and in addition have evidence that the observed pattern was not artificial: 1) We emphasize that if there was an error in the nutrient measurements, it had affected all samples considered in the manuscript. All water samples collected during the Meteor 44/2 cruise in the Gulf of Aqaba and in the Red Sea proper were analyzed for nitrate, nitrite, and phosphate after the cruise (only dissolved oxygen was measured on board). The samples were transported and stored altogether under the same conditions, and were run on the FIA by a single operator (MAQ) within one week (first week of April 1999) using the same standards. The samples were analyzed in the order of collection, which means station-wise, whereas the stations did repeatedly alternate between the Gulf of Aqaba, and the Red Sea proper. 2) Reconsideration of our long-term data series revealed that the 'Meteor' data are consistent with the data collected at station I during the years 1997 and 1998. The discrepancy refers to the majority of the data collected during 1999, mostly after the 'Meteor' cruise. There is recent evidence for an increasing nutrient release to the Gulf of Aqaba by a fish farm that could explain the observed increase in the deep-water nutrient concentrations during the year 1999

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(Erez et al. 2005, Lazar et al. 2005). For the above-mentioned reasons, we are convinced that the differences between the Red Sea proper and the Gulf of Aqaba observed during the 'Meteor' cruise are 'real'.

The biggest concern of S. Naqvi was that our data seem to be inconsistent with previous measurements in the region (Grasshoff, 1969; and GEOSECS data from station 405). These studies reported on excess phosphate in surface waters, together with N:P ratios higher than the classical Redfield ratio, which was ascribed to nitrogen fixation. There are limited nutrient data available from the area, especially from the northern Red Sea. H. Weikert from the University of Hamburg, Germany, kindly provided nutrient data collected in June 1979, October 1980, and March 1981 during Meseda cruises 2 and 3, and data from the Meteor 5/5 cruise in August 1987 (only south of 20° N). All these data confirm the presence of a negative nitrate deficit (excess N) in deep waters of the Red Sea proper. However, they also reveal remarkable changes within a relatively short time period of about 3.5 years. The average nitrate deficit of deep waters declined from -1.1 mmol/m<sup>3</sup> in December 1977 (GEOSECS, 20-27° N) and -1.2 mmol/m<sup>3</sup> in June 1979 to -2.1 mmol/m<sup>3</sup> in October 1980 (Meseda 2, 24° N) down to -4.6 mmol/m<sup>3</sup> in March 1981 (Meseda 3, 22-26° N). In August 1987, an average value of -2.8 mmol/m<sup>3</sup> was observed in the southern Red Sea (Meteor 5/5, 15-20° N). Note, that a change in the nitrate deficit of -1 mmol/m<sup>3</sup> in a 1000-m deep water column would require a time period of about 43 years, based on the assumption that it was the result of changes in nitrogen fixation only, and by applying the "geochemical" estimate for the nitrogen fixation rate in the Red Sea of 0.74 Tg N per year (Naqvi et al. 1986). The nitrate deficit in the Red Sea seems to be subject to higher fluctuations than previously assumed. We agree with S. Naqvi that the positive nitrate deficit we observed in the northern Red Sea cannot only be the result of physical mixing of water masses because of a mismatch with any possible combination of the end members. One possibility is that a positive nitrate deficit had been present in the northern Red Sea also in former times, but by chance was missed to be sampled during the few occasions of previous cruises. This would imply a physical separation of the deep water masses

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somewhere between station X of the present study, and station 405 of the GEOSECS cruise for a time period of decades. However, the question remains open how this separation could persist on the long term. Alternatively, the discrepancy between our results and previous data could be explained by a temporal shift in the nutrient stoichiometry in the entire area. S. Naqvi invoked the increase in atmospheric nitrogen deposition to explain the postulated shift. We agree that the mechanism he proposed could lower a N:P ratio that is higher than the classical Redfield ratio of 16. However, it is not clear how an increase in atmospheric nitrogen deposition could result in a N:P ratio less than the Redfield ratio, i.e. a positive nitrate deficit. The proposed decrease in the N:P ratio should end as soon as the level of the Redfield ratio is reached. Other possible explanations for the proposed change from a negative to a positive nitrate deficit in deep waters could be an increase in denitrification rates in the area, or higher phosphate depositions that may result from increased mining activities. However, the first hypothesis is not supported by the oxygen data (see comments by S. Naqvi), and in the second scenario higher phosphate depositions to surface waters should, on the other hand, fuel nitrogen fixation resulting in an even more negative nitrate deficit in deep waters according to the proposed mechanism. We agree that the proposed shift is an important issue that needs clarification. The mechanisms and the reasons behind are not yet identified. However, the implications of such a shift for the conclusions we draw from the comparison of the two water bodies can only be resolved by further investigations in the area.

With respect to the way of calculating the AOU and the nitrate deficit, we want to emphasize that we did calculate the AOU and the nitrate deficit for each sampling depth. Mathematically, it does not matter whether one applies first the multiplication and subtraction, or first the summing up, as long as the depth intervals are consistent. Applying the respective equation for calculating the AOU and the nitrate deficit to the depth-integrated measures gives exactly the same result as depth-integrating the measures calculated from single depths.

Specific comments:

Page 385, lines 17-19: will be restricted to the Red Sea, otherwise see general statement.

Page 386, lines 16-18: see general statement.

Page 392: The aim of the section 4.4 on the preformed nutrients was to indicate that the N:P stoichiometry in the overall system is close to the classical Redfield ratio.

The other specific comments on pages 385, 387, 390, and 392 are accepted and gratefully acknowledged.

2. Detailed reply to Anonymous Referee #2

General comments: see general statement.

Title, Abstract and Introduction:

The title will be change, see general statement. The abstract and introduction will be rewritten to make the structure of the manuscript more clear.

Minor comments: The missing reference of Gruber & Sarmiento 1997 will be added to the list.

Study site: We will change figure 1 to give an extended overview over the study area.

Method:

3.1: The data from the three years time-series provide background information about the system. Originally, they were mentioned to explain the general discrepancy between the Meteor and the time series' data. This issue was clarified above; see reply to comments by S. Naqvi.

The mixing depths were not used for calculations. Because they have to be derived from other measures, we mentioned the way of their determination in the methods. This was to support the section in the results, where the difference in the mixing regime

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between the two water bodies is described.

Minor comments: accepted. We did measure the macro-nutrients nitrate, nitrite, and phosphate.

3.2: The equation on page 391, line 3 will be shifted to the methods.

Minor comments: Total oxidized nitrogen refers to the sum of the oxidized species of dissolved nitrogen salts, i.e. nitrate plus nitrite concentrations. This definition will be added to the method's section 3.2, together with the explanation why we did include nitrite in the calculations: Dissolved nitrite concentrations in the water column of the gulf were most likely the result of nitrite excretion by phytoplankton (Al-Qutob et al. 2002). This applied also to the stratification period, during which the gulf resembled the northern Red Sea. This implies that the nitrite had 'passed' already the step of nitrate uptake by phytoplankton. Although quantitatively of minor importance, we considered it in the calculation to avoid an artificial deviation in the nitrate deficit from the respective stoichiometry of phytoplankton demands.

Results:

4.1: The surface waters in the northern Red Sea are usually depleted in nitrate. This was observed also during the previous cruises to the area that are mentioned above (reply to the comments by S. Naqvi). In section 2, we described in detail that this is related to the prevailing surface current in the Red Sea. On the way north, dissolved nutrients are stripped out of the surface layer by phytoplankton uptake. Nitrogen inputs into the system are nitrogen fixation, atmospheric depositions, and the northward transport of seston by the surface current.

The higher variance in the nitrate deficit in the northern Red Sea reflected a larger horizontal heterogeneity within the investigated area. This heterogeneity was mostly caused by the exchange of water masses with the gulfs of Suez and Aqaba, and by water circulation patterns in combination with the described benthic-pelagic coupling

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(see section 5.2, p. 394, line 24 ff.). The investigated area has open boundaries to the south, however, the extension of figure 1 will clarify that the Red Sea itself is an almost enclosed basin, separated in the south from the Gulf of Aden by another shallow sill.

4.3: The vertical oxygen distribution in Fig. 4 shows the overall pattern in the investigated area. In the northern Red Sea, the oxygen minimum zone was generally more pronounced than in the gulf. In both water bodies, it indicates oxygen utilization rather than lateral transport of water masses from the north. Especially in the gulf, this zone would be eroded during deep mixing events, resulting in a better oxygenation of the water column.

The oxygen minimum zone in the northern Red Sea is not related to that of the Arabian Sea. Surface waters are flowing into the Red Sea from the Gulf of Aden over the sill at Bab-el-Mandeb (Sofianos et al. 2002, see section 2 in the manuscript), which is with 140 m almost as shallow as the productive zone.

By the respective paragraph we intend to describe the vertical distribution of the nitrate deficit and the oxygen concentrations. Figure 4 should demonstrate that there was a relationship between nitrate deficit and oxygen concentrations not only for the values integrated over the water-column, but also for the majority of single data points. The relationship was such that the nitrate deficit in the overall vertical pattern inversely reflected the oxygen concentrations. At saturating oxygen concentrations, as they did occur in the upper layer of the water column, the nitrate deficit was minimal in both water bodies. This upper layer corresponded to the productive zone in the stratified northern Red Sea, and to the mixed layer in the gulf where the mixing depths exceeded the productive zone.

The regression line in Figure 5 was kept as a dashed line beyond the data of the gulf. This should indicate that the linearity originated from the data collected in the gulf. On the other hand the relationship was statistically significant for the entire data set with 82 % of the variance explained. This supports our hypothesis of a general relationship

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between AOU and nitrate deficit in the system. Possible reasons for the deviations from the line in the northern Red Sea are discussed in section 5 (page 395, line 5ff.).

4.4: The constant stoichiometric ratio of 16:1:138 for N:P:O will be mentioned in the introduction.

Discussion:

The first sentence will be omitted.

The point here is that the signature of benthic denitrification is more obvious in the water column of a steep and narrow basin, such as both the Red Sea and the Gulf of Aqaba. This will be clarified in the text.

5.1: The cited publications report on counts of *Trichodesmium* cells and colonies in the area. To the best of our knowledge, nitrogen fixation rates were not yet determined in the Red Sea and the Gulf of Aqaba. It is well documented in the literature that *Trichodesmium* does prefer a stratified water column over a mixed one (see references on page 393, line 24 ff.). The rate of nitrogen fixation in both systems is not limited by the availability of iron (see general statement above).

Subsequent remineralisation means that the *Trichodesmium* cells will be decomposed by microbial activity after the bloom. This takes place in deeper water layers, and leads to a recycling of particulate-bound nutrients into the dissolved pool. In addition, this can be also partly mediated by grazing. Because *Trichodesmium* cells usually reveal higher N:P ratios than non-diazotroph phytoplankton cells, the remineralisation of *Trichodesmium* cells will result in a higher N:P ratio in the dissolved nutrient pool.

5.2: The vertical profiles are from different stations with different mixing depths. Therefore, a mean of all profiles is not appropriate. The examples in Figure 4 are representative.

Figure 1 indicates that the distribution of the stations comprises a latitudinal and a longitudinal transect in the northern Red Sea. Due to political restrictions in the region,

we were not allowed to sample in the Straits directly, or at locations further to the east.

5.3: In the literature, iron limitation of nitrogen fixation was invoked to explain the nitrate deficit in the ocean (e.g. Falkowski 1997, Wu et al. 2000). From our study it can be inferred that there must be a different process involved that was responsible for the positive nitrate deficit of up to 5 mmol/m<sup>3</sup> in the northern Red Sea. The separate paragraph on iron limitation was added to emphasize that also in other oceanic regions iron may not be the sole factor to be considered, which could be of general relevance to biogeochemical studies.

5.4: Phosphate mining takes place in the entire area. Higher phosphate depositions should be reflected in higher surface concentrations in the gulf, which was not observed in the present study.

Concerning the issue of protecting the coral reefs against eutrophication see the general statement above. Coral reefs exist in oligotrophic regions, where mostly nitrogen is assumed to be the nutrient that limits productivity.

Technical corrections:

Legend figure 5: accepted.

Figures 5 and 6: The sentence indicating station numbers will be moved to the legend of table 2, and referred to in the legend of figs. 5 and 6.

### 3. Detailed reply to Referee T. Oguz

1): Based on the available data, it seems rather speculative to provide quantitative estimates for the fluxes under consideration. By the following calculations, we try to provide a feeling for the order of magnitude of the different fluxes. Estimates based on the present nitrate deficit in the water column would require the time period in which the nitrate deficit was built up. Such information is lacking at present. Nevertheless, we try to derive a rough estimate for the average annual denitrification rate in the northern Red Sea, based on the difference in the nitrate deficit between the data collected at

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station X during our cruise, and the GEOSECS data collected at station 405 in 1977. However, this approach can only be applied under the precondition that the nitrate deficit in the northern Red Sea underwent a temporal change during that time period (see reply to comments by S. Naqvi). The observed difference in the water-column nitrate deficit would roughly amount to a change in the order of  $6.5 \text{ mol/m}^2$  within 22 years. This would correspond to a nitrogen loss rate in the range of  $0.3 \text{ mol m}^{-2} \text{ y}^{-1}$ , assuming that the change in the nitrate deficit was entirely due to changes in the benthic denitrification rate. This estimate is at the lower end of the range of  $0.25 - 1.2 \text{ mol m}^{-2} \text{ y}^{-1}$  recently reported for continental shelf sediments (Vance-Harris and Ingall 2005). Naqvi et al. (1986) reported a geochemical estimate for nitrogen fixation of  $0.74 \text{ Tg N y}^{-1}$  in the entire Red Sea ( $\sim 450,000 \text{ km}^2$ ). This corresponds to an average nitrogen fixation rate of  $0.12 \text{ mol N m}^{-2} \text{ y}^{-1}$ . Hence, nitrogen fixation alone could not support the denitrification rate proposed above. By applying a C:N stoichiometry of 4:5 for denitrification (Vance-Harris and Ingall 2005, Li et al. 2006) we can estimate that  $0.24 \text{ mol m}^{-2} \text{ y}^{-1}$  of organic carbon would have to be consumed in order to meet the benthic denitrification rate of  $0.3 \text{ mol m}^{-2} \text{ y}^{-1}$ . Erez et al. (2005) reported a primary production rate of  $80 \text{ g C m}^{-2} \text{ y}^{-1}$  for the gulf during the time of our observations. Applying this value to the northern Red Sea would correspond to a carbon fixation rate of  $6.7 \text{ mol m}^{-2} \text{ y}^{-1}$ . Thus, benthic denitrification could be supported by overall primary production based on the assumption that 3.6 % of the carbon fixed are utilized by benthic denitrification.

2): This is related to the much shorter water renewal time, which is mentioned for both water bodies in section 2. See also general statement.

3): The difference in the subsurface nitrate structure can potentially be related to differences in primary production in the two water bodies. However, it seems much more likely that it is related to the hydrodynamic regime in the overall system. We propose that the deep vertical mixing and the flow pattern of water masses determine the overall structure in the water column. The gulf receives nutrient-depleted surface waters,

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and exports deeper waters with somewhat higher nutrient concentrations. Considering the short residence time of the water, the overall nutrient inventory in the gulf should be lower than in the northern Red Sea. In addition, deep vertical mixing occurs regularly in the gulf, which is responsible for the generally less pronounced gradients in the water column.

4): Accepted, our data restrict the conclusion to the Red Sea, see also general statement above. However, the geochemist's view represents a concept that is either applicable in general or not. It is not restricted to the case that nitrate is the PLN, and phosphate is the ULN. For example, in many freshwater systems phosphate is the PLN and the ULN at the same time.

References to be added to the manuscript:

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