Inventory of released inorganic carbon from organic matter remineralization in the deeper Arabian Sea

Axel Hupe,1,2 Helmuth Thomas,3 Venugopalan Ittekkot,4 and Ralf Lendt1

Abstract. An attempt is made to quantify the biological carbon pump in Arabian Sea subsurface waters by estimating the total concentrations of remineralized dissolved inorganic carbon (DICrem) and its water column inventory. The influence of different sets of $\Delta$AOU/$\Delta$ACorg ratios, which are either constant or variable with depth, on the estimate is assessed. Throughout the water column the horizontally mapped DICrem concentrations increase northward due to enlarged export fluxes of organic matter and subsequently enhanced remineralization processes as well as to the accumulation of remineralization products along the trajectory path of the water masses ventilating the Arabian Sea from the southern Indian Ocean. The choice of the remineralization ratios generates significant differences in the DICrem concentrations at specific depth horizons. The DICrem inventory of the Arabian Sea between 500 and 4500 m in the years 1995–1997 amounts to ~39–44 Gt C depending on the applied remineralization ratios.

1. Introduction

The monsoon-forced nutrient supply to the mixed layer by coastal upwelling in the summer and vertical convection in the winter is the prime factor responsible for the high rates of primary and new production in the Arabian Sea [e.g., Smith et al., 1998; Morrison et al., 1998; Brink et al., 1998; Bhattachiri et al., 1996; Brock et al., 1991]. Part of the produced organic matter is exported to the deep Arabian Sea, where most of it is remineralized to dissolved inorganic carbon (DIC), nitrate, and phosphate. As the biologically fixed DIC in the exported organic matter is replenished from the atmospheric CO2 reservoir, the DIC released within the interior of the ocean reflects, in general, the drawdown of atmospheric CO2 via the biological carbon pump. For upwelling areas such as the Arabian Sea, showing a CO2 supersaturation with respect to the atmosphere [e.g., Goyet et al., 1998; Körtzinger et al., 1997; Sarma et al., 1998; R. Lendt et al., The response of the near-surface carbonate system of the northwestern Arabian Sea to the SW monsoon and related biological forcing, submitted to Journal of Geophysical Research, 2000], this in turn means that the oceanic gross release of CO2 to the atmosphere is reduced and should thus be understood as an oceanic net uptake. Many efforts have been made to estimate the total concentrations of remineralized DIC (DICrem) within the Arabian Sea [Goyet et al., 1999; Sabine et al., 1999; George et al., 1994; Millero et al., 1998; Kumar et al., 1990; Mintrop et al., 1999; Takahashi et al., 1985]; however, no values of its oceanic inventory are currently available to quantify the biological pump in this area.

DICrem is commonly assessed by converting the biological changes in the concentrations of nutrients or apparent oxygen utilization (AOU) into the release of DIC using the Redfield ratios, which reflect the stoichiometric composition of particulate organic matter [Redfield et al., 1963]. Here we determine the DICrem inventory of the Arabian Sea at the time of the surveys (1995–1997) between 500 and 4500 m with reference to different sets of stoichiometric ratios. In order to investigate the impact of the remineralization ratios on DICrem we compare DICrem estimates relying on depth-dependent ratios obtained from an extended data set using the technique of Hupe and Karstensen [2000] with DICrem estimates employing constant ratios of Redfield et al. [1963] and Anderson and Sarmiento [1994].

2. Data

For the inventory estimates we use temperature, salinity, and oxygen data of the following cruises in the Arabian Sea in 1995 and 1997 (Figure 1): German R/V Meteor World Ocean Circulation Experiment (WOCE) cruises M32/1 and M32/4; U.S. R/V Thomas G. Thompson Joint Global Ocean Flux Study (JGOF) cruises TTN/043, TTN/045, TTN/049, TTN/053, and TTN/054; German JGOF expeditions M31/3 and M32/3; and R/V Sonne cruise SO119. To fill the data gap in the eastern Arabian Sea (>65øE), we incorporated selected data of the analyzed mean fields of the World Ocean Atlas 1998 (asterisks) extracted from the Web site http://www.nodc.noaa.gov/OC5/data_woa.html. In addition, we use nutrient, DIC, and alkalinity data from M32/4 and U.S. JGOF cruises to recalculate the remineralization ratios. The precision of hydrochemical tracers involved in the DICrem calculations from respective cruises is summarized in Table 1. Although the uncertainty of the field data is given here on a per-mass basis, in the further context, volumetric units are used because of the integration routines. Estimates above 500 m were omitted, as the situation became too complex owing to the strong monsoon reversal in the Arabian Sea.

3. Approach

Recently, Hupe and Karstensen [2000] have applied a linear inverse mixing model, the extended optimum multiparameter (OMP) analysis [Karstensen and Tomczak, 1998; Karstensen,
to observational hydrographic, nutrient, and carbon data in order to derive a new set of $\Delta C_{org}/\Delta N/\Delta P/-\Delta O_2$ remineralization ratios for Arabian Sea subsurface waters between 550 and 4500 m. In summary, the model predicts the mixing fractions of predefined source waters, the time- and space-integrated amount of biogeochemical changes in oxygen, nutrient, and inorganic carbon properties due to remineralization processes, and the nitrate deficit due to denitrification. Additionally, the effects of calcium carbonate dissolution and anthropogenic CO$_2$, which decouple the DIC concentrations from biological nutrient and oxygen changes, are accounted for. The main advantage of this method is that it takes into account mixing of water masses by all processes such as diapycnal mixing which, in turn, plays a vital role in the northern Indian Ocean [Anderson and Sarmiento, 1994; Tomczak and Godfrey, 1994]. The main disadvantage is that the estimated biological changes in oxygen, nutrients, and DIC cannot be taken as total concentrations because the presumed source-water types are already mixtures of other water masses and do not represent preformed concentrations of the biogeochemical tracers. Consequently, the OMP results are restricted to be relative values with respect to the source-water definitions and are applicable only in terms of ratios of particulate organic matter remineralization. For clarification, if the source-water types would be defined further away from the investigation area ("upstream"), the values of the time- and space-integrated biological changes increase while the remineralization ratios should be still the same.

To improve the results of this study, data of the cruises TTN/043, TTN/045, TTN/053, and TTN/054 were incorporated additionally in the OMP analysis to reassess the remineralization ratios. As listed in Table 1, at least one of the required tracers (temperature, salinity, oxygen, nitrate, silicate, phosphate, DIC, and alkalinity) is missing in the data sets of the remaining cruises. The OMP analysis is thus not applicable to these data sets. Figure 2 shows the mean $-\Delta O_2/\Delta C_{org}$ ratios versus depth, as well as the standard deviations (error bars)

Table 1. Precision of Hydrochemical Data Involved in the DIC$_{rem}$ Calculations of This Study

<table>
<thead>
<tr>
<th>Cruises</th>
<th>DIC</th>
<th>TA</th>
<th>$O_2$</th>
<th>Si(OH)$_4$</th>
<th>PO$_4^{3-}$</th>
<th>NO$_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTN</td>
<td>±1.2$^b$</td>
<td>±3.2$^b$</td>
<td>±0.05$^a$</td>
<td>±0.3$^d$</td>
<td>±0.01$^d$</td>
<td>±0.1$^d$</td>
</tr>
<tr>
<td>M32/4</td>
<td>±2</td>
<td>±5</td>
<td>±0.1</td>
<td>±0.5</td>
<td>±0.1</td>
<td>±0.1</td>
</tr>
<tr>
<td>M32/1</td>
<td>na</td>
<td>na</td>
<td>±0.1</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>M32/3</td>
<td>...</td>
<td>...</td>
<td>±0.1$^e$</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>M31/3</td>
<td>...</td>
<td>...</td>
<td>±0.2</td>
<td>na</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>SO119</td>
<td>...</td>
<td>...</td>
<td>±0.1</td>
<td>na</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>WOA1998</td>
<td>na</td>
<td>na</td>
<td>±?</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

$^a$Hydrochemical data given in $\mu$mol kg$^{-1}$; na, not available; ellipsis dots, data available but not used in this approach.

$^b$From Millero et al. [1998].

$^c$From Morrison et al. [1999].

$^d$Approximately ±0.2% of full-scale ranges for nutrients (data available at http://usjgofs.whoi.edu/jg/dir/jgofs/arabian/).

$^e$From H. Thomas et al. DIC/NO$_3$ relationship as a tool for the determination of denitrification, (submitted to Deep Sea Research, 1999).
obtained by adding 100 times random noise on source-water types and observational data simultaneously (for details, see Hupe and Karstensen [2000]). These ratios reflect the biological oxygen consumption related to the released DIC during organic matter remineralization relative to the predefined source-water types. Note that the model-based ACorg values used for the ratios are not equal to the total concentrations (DICrem), the determination of which is the objective of this manuscript. The -\(\Delta O_2/ACorg\) ratios confirm the depth-dependent trend of remineralization suggested by Hupe and Karstensen [2000] and reveal mean values of 1.56 ± 0.16 at 500-1200 m, 1.49 ± 0.11 at 1200-2000 m, and 1.35 ± 0.12 below 2000 m. These values, subdivided into three depth ranges, are denoted hereinafter as HK00.

As a first approximation, an observed DIC concentration (DICobs) in the interior of the ocean is made up of the fractions of individual water masses having a definite physical (mixing, solubility) and biogeochemical (remineralization, CaCO\(_3\) dissolution) history:

\[
DIC_{obs} = \sum_{j=1}^{n} k_j (DIC_{pref} + DIC_{rem} + DIC_{CaCO3})
\]

where
- \(k_j\) mixing coefficient of source water \(j\) with \(\Sigma k_j = 1\);
- \(n\) number of source waters;
- DIC\(_{pref}\) preformed DIC determined by preformed alkalinity and air-sea interaction;
- DIC\(_{rem}\) DIC release due to remineralization of organic matter;
- DIC\(_{CaCO3}\) DIC release due to dissolution of CaCO\(_3\).

In order to convert the relative \(\Delta C_{org}\) values to total concentrations of DIC\(_{rem}\), we apply a tight correlation between the oxygen consumption -\(\Delta O_2\) yielded by the OMP analysis and the AOU (Figure 3):

\[
AOU = 1.149(-\Delta O_2) + 129.61 \quad (r^2 = 0.97).
\]

This relationship may be expected because -\(\Delta O_2\) corresponds to a source-water-related AOU. The standard error of the estimates averages only ±4.3 \(\mu\)mol kg\(^{-1}\) or 1.7% related to the mean AOU value. The total amount of remineralized DIC can only be assessed indirectly via the substitution of -\(\Delta O_2\) in the -\(\Delta O_2/ACorg\) ratio with AOU. Hence the knowledge of the remineralization ratios is crucial in calculating DIC\(_{rem}\). We assume that the -\(\Delta O_2/ACorg\) ratios as well as the -\(\Delta O_2/AOU\) correlation hold true for data that could not be analyzed with the OMP model. For comparison we calculated the DIC\(_{rem}\) concentrations using the constant -\(\Delta O_2/ACorg\) ratios of Anderson and Sarmiento [1994] (Figure 2, stars) and the classical Redfield ratio [Redfield et al., 1963] (Figure 2, dashed line), abbreviated hereinafter as AS94 and RKR63, respectively. All -\(\Delta O_2/ACorg\) remineralization ratios involved in the DIC\(_{rem}\) inventory estimates of this study are summarized in Table 2.

We start the inventory estimates by interpolating AOU onto 15 standard depths (500:100:1000, 1250:250:2000, and 2500:500:4500 m; adopted from HK00) and calculate DIC\(_{rem}\) on those depths with reference to the HK00, AS94, and RKR63 remineralization ratios of -\(\Delta O_2/ACorg\). The values of each of the 15 depth levels are projected onto a 1° grid to the horizontal area of the Arabian Sea using an objective mapping technique. DIC\(_{rem}\) was mapped over an area from 0° to 25°N and 50° to 80°E according to Somasundar et al. [1990]. For a better characterization the investigation area is divided into a northern (17°-25°N), a central (9°-17°N), and a southern (0°-9°N) latitude belt. In succession, each gridded DIC\(_{rem}\) value is then multiplied by the volume of water between adjacent standard depths, i.e., within a 100-m slab between the 500- and 600-m levels. These values are subsequently summed up to generate first the inventories of the latitude belts and finally to the total DIC\(_{rem}\) inventory in the Arabian Sea between 500 and 4500 m. For the calculations of the 1° x 1° arrays we applied the TerrainBase 5-min global bathymetry/topography (data available at ftp://ncardata.ucar.edu/datasets/ds759.2/index.html) using every twelfth value.

### 4. Results and Discussion

#### 4.1. Distribution of DIC\(_{rem}\)

The results of the DIC\(_{rem}\) estimates using three sets of variable and constant remineralization ratios with depth are depicted in Figures 4–6. Figures 4a–4c show horizontally averaged profiles in the northern, central and southern latitude belts, respectively, in the Arabian Sea. Following the vertical distribution of AOU, the maximum concentrations of DIC\(_{rem}\) (160–220 \(\mu\)mol L\(^{-1}\)) are reached at intermediate depths in all latitude belts, whatever remineralization ratio is involved. To-
Figure 4. Horizontally averaged remineralized dissolved inorganic carbon (DIC<sub>rem</sub>) profiles using the remineralization ratios of Hupe and Karsten [2000] (HK00), AS94, and RKR63 in three latitude belts: (a) 17°-25°N, (b) 9°-17°N, and (c) 0°-9°N.

Figure 5. Horizontally mapped DIC<sub>rem</sub> concentrations (μmol L<sup>-1</sup>) at 600 m using the remineralization ratios of (a) HK00, (b) AS94, and (c) RKR63.

ward the deep sea the values are generally decreasing to 110–135 μmol L<sup>-1</sup> DIC<sub>rem</sub>. However, the results depend significantly on the chosen set of −ΔO<sub>2</sub>/ΔC<sub>org</sub> ratios. Throughout the water column the highest values are generated by the RKR63 ratios. The lowest limit of the DIC<sub>rem</sub> concentrations is supplied by the HK00 ratios above 2000 m and by the AS94 configuration below this depth. As expected, the DIC<sub>rem</sub> profiles using HK00 are not as smooth as AS94 and RKR63 profiles, owing to the step change of ratios at 1200 and 2000 m. Possibly, the −ΔO<sub>2</sub>/ΔC<sub>org</sub> ratios at intermediate depth and the deep sea are somewhat too high or too low, respectively.

To emphasize regional aspects of organic matter remineralization, the objectively analyzed DIC<sub>rem</sub> concentrations are plotted for the depths of 600 and 3000 m (Figures 5 and 6). DIC<sub>rem</sub> increases independently of the applied remineraliza-
Figure 6. Horizontally mapped DICrem concentrations (µmol L⁻¹) at 3000 m using the remineralization ratios of (a) HK00, (b) AS94, and (c) RKR63.

The estimated DICrem inventories of the Arabian Sea between 500 and 4500 m for the three latitude belts are summarized in Table 3. At the time of the surveys (1995-1997) the investigation area contains a total inventory of 39.5 Gt C from organic matter remineralization employing the depth-dependent HK00 ratios. Applying the constant ratios of AS94 reveals an inventory of almost the same magnitude because the differences resulting from both sets of ratios are cancelled out by vertically integrating the mapped DICrem concentrations. This is because the AS94 ratios reveal higher values at inter-
mediate waters, whereas the HK00 values are higher in the deep sea below 2000 m (Figure 4). Thus the vanishing of the differences is principally ascribed to the choice of the vertical integral. The highest inventory estimate of ~44 Gt C is supplied by the RKR63 ratio. It is very difficult to evaluate a reasonable estimate of the potential errors associated with the calculated inventories. Although some error contributions are difficult to assess (i.e., errors generated from the mapping routines and area calculations of the arrays), we believe that the variability in the DIC$_{rem}$ inventories is caused mainly by uncertainties of the stoichiometric ratios and the AOU. We performed a sensitivity study for the HK00 $-\Delta O_2/\Delta C_{org}$ ratios with the standard deviations (Table 2) and an error for the AOU concentrations of $\pm 5 \, \mu$mol kg$^{-1}$. The latter consists of errors of the inventories are of the order of at least 10%.

Recently, Pahlow and Riebesell [2000] estimated DIC$_{rem}$ inventory for the North Pacific between 500 and 3000 m of ~300 Gt C by using the AS94 $-\Delta O_2/\Delta C_{org}$ ratio of 1.45. Like the Arabian Sea, this area is a major denitrification site with a thick oxygen minimum zone at intermediate depth [e.g., Broecker and Peng, 1982; Boulahdid and Minster, 1989]. If one would adjust the fifteenfold greater area of the North Pacific ($75 \times 10^6 \, m^2$) to the dimensions of the Arabian Sea for the same depth interval ($5 \times 10^6 \, m^2$), the resulting inventory of 20 Gt C would be considerably lower than the estimate of ~30 Gt C for the Arabian Sea at the same depth range using the HK00 ratios. Potentially, the Arabian Sea contains more DIC$_{rem}$, owing to enhanced export fluxes of organic matter in the highly productive northern part, especially if one considers that the DIC$_{rem}$ concentrations derived from AS94 are higher than the HK00 values at depths above 2000 m.

The inventories of the three latitude belts vary greatly, owing to the different volumes of these regions. The southern part contains roughly 50% of the total DIC$_{rem}$ inventory. This is because more than 50% of the volume in the investigation area is located in the region between 0° and 9°N and is not due to a more effective biological pump in this latitude belt. To get a better representation of the regions where DIC$_{rem}$ is accumulated, we look at the specific inventories, which are calculated by dividing the inventories by the surface area of the respective latitude belt. The distributions of the specific inventory for the depth range 500–3000 m are shown in Figure 7. Here the most productive areas in the northern Arabian Sea clearly reveal the highest values. Employing the HK00 ratios, we see that the specific inventory of DIC$_{rem}$ increases from ~370 mol C m$^{-2}$ at the equator to almost 440 mol C m$^{-2}$ in the northernmost Arabian Sea. While the specific inventories derived from HK00 and AS94 are similar (Table 3), the values produced by RKR63 are up to 50 mol C m$^{-2}$ higher. An illustration of the specific inventories down to 4500 m is omitted because of the data scarcity at this depth.

Two recent studies have exploited DIC$_{rem}$ as an essential parameter while assessing anthropogenic CO$_2$ in the water column of the Arabian Sea [Goyet et al., 1999; Sabine et al., 1999]. Sabine et al. [1999] used the AS94 $-\Delta O_2/\Delta C_{org}$ ratio, which is considered in the present study for comparison (Table 3). The corresponding DIC$_{rem}$ inventories should thus be comparable, although Sabine et al. [1999] did not explicitly report on those values. Goyet et al. [1999] used a $-\Delta O_2/\Delta C_{org}$ ratio which was a mean value of RKR63 and AS94. The corresponding DIC$_{rem}$ inventories should thus lie between the latter ones (Table 3). A comparison of specific inventories of DIC$_{rem}$ and anthropogenic CO$_2$ in the three latitude belts of the Arabian Sea is illustrated in Figure 8. The specific anthropogenic CO$_2$ inventories for the year 1996 were extracted from a recent global study by Thomas et al. [2001], providing 18.7, 19, and 22.4 mol C m$^{-2}$ for the northern, central, and southern Arabian Sea, respectively. Thomas et al. [2001] have developed a method for anthropogenic CO$_2$ quantification which is independent of remineralization ratios. Figure 8 shows that the anthropogenic CO$_2$ inventory is only ~5% of the DIC$_{rem}$ inventory between 500 and 4500 m. Keep in mind that if the upper 500 m were considered, the DIC$_{rem}$ inventories would be even larger. Interestingly, the distributions of the specific inventories of DIC$_{rem}$ and anthropogenic CO$_2$ reveal contrast-
ing patterns. The specific DIC\(_{\text{rem}}\) inventories increase northward because of the higher biological production in the north. In contrast, anthropogenic CO\(_2\) shows the highest inventories in the southern Arabian Sea since the deeper Arabian Sea is largely ventilated from the south. The younger, more recently ventilated waters which contain higher anthropogenic CO\(_2\) concentrations are thus found in the southern Arabian Sea.

5. Summary and Conclusions

The current study has focused on a first assessment of the DIC\(_{\text{rem}}\) inventory in the Arabian Sea. DIC\(_{\text{rem}}\) concentrations have been obtained with reference to different –\(\Delta Q/\Delta C\text{org}\) remineralization ratios and AOU. The DIC\(_{\text{rem}}\) water column inventories at the times of the surveys (1995–1997) have been estimated in order to quantify the biological carbon pump in the Arabian Sea between 500 and 4500 m. The scope of this study is to investigate the differences of the estimates resulting from applying variable (HK00) and constant (AS94 and RKR63) –\(\Delta Q/\Delta C\text{org}\) ratios with depth. We find a significant impact of the different sets of ratios on the DIC\(_{\text{rem}}\) concentrations at specific depth horizons. The highest concentrations throughout the water column are achieved by using the classical Redfield ratio. The depth-dependent HK00 ratios lead to lower DIC\(_{\text{rem}}\) values compared with the AS94 ratio above 2000 m and vice versa in the deep ocean below this depth. By vertically integrating the calculated DIC\(_{\text{rem}}\) concentrations, the opposing influences of the involved remineralization ratios in intermediate and deep waters (partly) cancelled out due to the actual choice of the depth integral. The Arabian Sea stores most of the anthropogenic CO\(_2\) is accumulated, the DIC\(_{\text{rem}}\) values diverge up to 40 \(\mu\)mol L\(^{-1}\) depending on the applied ratio. As the DIC\(_{\text{rem}}\) concentrations are subtracted from the observed DIC, whatever method is applied to estimate the amount of anthropogenic CO\(_2\), the differences stemming from the remineralization ratios have to be reflected in the calculated anthropogenic CO\(_2\) [e.g., Wanninkhof et al., 1999]. A ratio-based difference of 40 \(\mu\)mol L\(^{-1}\) is even higher than the anthropogenic CO\(_2\) concentration itself in the Arabian Sea at intermediate depth [Sabine et al., 1999; Goyet et al., 1999; Thomas et al., 2001]. Thus more studies have to be carried out to estimate more reliable global remineralization ratios to reduce the uncertainties associated with these ratios in many fields of biological and chemical oceanography.

The depth-dependent remineralization ratios should have an even greater impact on estimating the budget of DIC\(_{\text{rem}}\) by accounting for the water mass ages to calculate the residence times of the remineralization products in the deeper Arabian Sea. The preferential remineralization of nutrients with depth, also proposed by many other studies [e.g., Shaffer, 1996; Shaffer et al., 1999; Thomas et al., 1999], should lead to a more efficient biological carbon pump compared with a constant remineralization of carbon and nutrients. The water mass ages in the Arabian Sea could be assessed by combining OMP analysis with a mixing analysis of the transient tracer CFCs [Karstensen and Tomczak, 1998]. However, this technique is not applicable here because CFCs are missing in the current data set except for M32/4.

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References


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