Application of Vertical Advection-Diffusion Model for Studying CO₂ & O₂ Profiles in Central Arabian Sea

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The vertical advection-diffusion model proposed by Craig has been applied to the study of CO₂ and O₂ profiles in central Arabian Sea. Distributions of total CO₂ and O₂ are explained better by expressions involving exponential rates than those based on constant production rates.

Kumar and Singbal¹ have used the stoichiometric model of Redfield et al.² to assess the contributions of preformed and dissolved carbonates to total CO₂ contents in waters of central Arabian Sea. This model does not take into explicit consideration the role of physical processes such as mixing and advection. This lacuna however has been rectified in more recent studies on Pacific waters³⁻¹¹, which have made possible the characterisation of seawater on the basis of a vertical advection-diffusion model and data on consumption or production of non-conservative parameters. In the present paper similar computations have been described in the case of a selected oceanographic station in central Arabian Sea.

Methods

St 2358 (lat. 15° 01'N; long. 60° 27'E) occupied by *R V Gaveshni* during 103 cruise (Feb. 1982) in central Arabian Sea was chosen in the present paper for detailed computations based on Craig's vertical advection-diffusion model. Analytical methods adopted for the determination of salinity, total alkalinity, *pH* and dissolved oxygen were same as detailed earlier^{1,12}.

Craig's model assumes that boundary conditions are kept constant by external forces. It also assumes that only vertical advection and diffusion are the effective processes in intermediate waters. Horizontal processes are considered negligible and both eddy diffusion coefficients and vertical velocity are assumed to be constant.

The details of the model and equations are given elsewhere^{6,7}. Summary of the equations employed in the computations is given below.

The steady state distribution of a conservative parameter C is given by

$$C = Co + (Cm - Co) \times f(Z) \qquad \dots (1)$$

where

$$f(Z) = \frac{e[Z/(K_Z/V_Z)]^{-1}}{e[Zm/(K_Z/V_Z)]^{-1}} \qquad ... (2)$$

Cm and Co are concentrations of C at 2 boundaries (m and o), Z is depth in meters, K_Z the eddy diffusion coefficient and V_Z the vertical velocity.

The different rate expressions can be written as:

Constant production rate—Expression for constant production rate, applicable to non-conservative properties is

$$C = Co + (Cm - Co) \times f(Z)$$

$$+ \frac{R}{V_{\alpha}} [Z - Zm \times f(Z)] \qquad ... (3)$$

where R denotes in situ production or consumption rate⁷

Linear rate—If rate R is considered a linear function of depth Z of the form

$$R = Ro + S \times Z \qquad ... (4)$$

one can write

$$C = Co + (Cm - Co) \times f(Z)$$

$$+ \left[\frac{S + Ro(K_Z/V_Z)}{V_Z} \right] \times [Z - Zm \times f(Z)]$$

$$+ \frac{R}{2 V_Z} [Z^2 - Zm^2 \times f(Z)] \qquad \dots (5)$$

Exponential rate—If rate R is an exponential function of depth Z as

$$R = Ro \times e^{(\alpha \times Z)} \qquad ... (6)$$

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one can write7

$$C = Co + (Cm - Co) \times f(Z)$$

$$+ \left[\frac{(Ro + V_Z)}{[1 + \alpha(K_Z/V_Z)]} \right] \times [(1 - e^{(\alpha \times Z)})]$$

$$- [1 + e^{(\alpha \times Zm)} \times f(Z)] \qquad \dots (7)$$

The oxidative ratio is defined as

$$\Delta C/\Delta O = \left[\frac{R_{TCO_2} - 0.5 R_{TA}}{R_{O_2}} \right] \qquad ... (8)$$

where R_{TCO_2} , R_{TA} and R_{O_2} are production rates of CO_2 , total alkalinity and O_2 respectively.

Results and Discussion

Craig's model demands, as seen from Eq.(1), that potential temperature (θ) should vary linearly with salinity (S) in the depth interval under study. Data from st.2358 fulfil this requirement since θ varies linearly with S in the depth range 500-4000 m (Fig.1).

Data for θ and S were fitted to the Eq.(1) using non-linear square iterative procedure based on Gauss method. The 'best' values for θ and S correspond respectively to K_Z/V_Z values of 885 and 853 m. The average value of 869 m has been used in the present calculations. The standard deviations (σ) for θ and S are 0.05° C and 0.008×10^{-3} respectively. The experimental and calculated profiles of these parameters are given in Fig.1.

One can now use the equations given above to compute vertical distribution and rate laws to give oxidative ratios as $R_{\rm CO_2}/R_{\rm O_2}$. Fig. 2 shows the nonlinear plots of TCO₂ and O₂ against θ , indicating oxygen consumption and carbon dioxide production.

Constant production rate—A value of 869 m for (K_2/V_2) is used in Eq.(3) to fit observed data O_2 , TCO_2 and TA. The results are given in Table 1. The oxidative ratio calculated from these values is -0.424, which is 6.3% higher than the value (-0.399) obtained earlier using the model of Redfield et al.² and 10.4% higher than the theoretical slope (-0.384). Fig.3 shows the vertical profiles of O_2 and CO_2 along with the values calculated by this model. It is seen that the calculated values deviate systematically from the observed data.

Linear rate—Linear least-square regression procedure was used to fit the measured O_2 profile by applying Eq.(5) with (S/V_Z) and Ro/V_Z) as adjustable parameters. The computed rate of oxygen production is given in Table 1. Satisfactory agreement between experimental and calculated values is restricted to the bottom waters.

Exponential rate—It has been demonstrated^{9,10} that the exponential law can accurately represent O₂

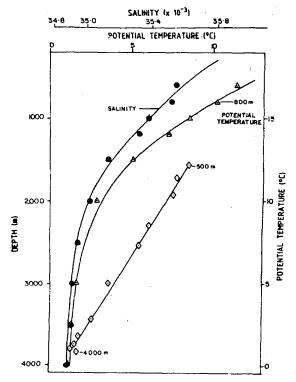


Fig. 1 -- Vertical profiles of potential temperature and salinity of st 2358 [Values calculated on Craig's model are joined by straight line]

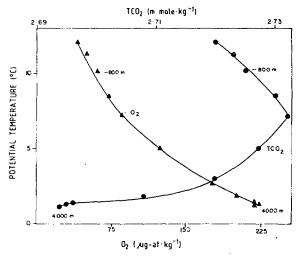


Fig. 2—Total CO₂ and O₂ as functions of potential temperature in seawater at st 2358

profiles in the sea. The present data were accordingly fitted to Eq. (7) and the results are summarized in Table 1. The calculated values of O_2 and CO_2 are in better agreement with experimental data than when constant production rate law is used (Fig. 3).

The agreement for TCO₂ still can be better if one uses TCO₂ values which are corrected for salinity and

Table 1-Production Rates Calculated by Vertical Advection-Diffusion Model

| Calculated rate | Standard deviation | Oxidative ratio |
|--|--|--|
| | Constant production rate | |
| $R_{O_2} V_Z = -(6.25 \pm 0.48)10^{-5}$ | 0.01 mg-at. kg ⁻¹ | -0.424 |
| $\mathbf{R}_{1\text{CO}_2}/V_Z = (2.91 \pm 0.20)10^{-5}$ | 0.01 m mol. kg ⁻¹ | |
| $R_{TA}/V_Z = (0.52 \pm 0.07)10^{-5}$ | 0.003 m eq.kg ⁻¹ | |
| | Linear rate | |
| $R_{O_2}/V_Z = (1.82 \pm 0.72) \times 10^{-5} - (5.47 \pm 0.49) \times 10^{-8} \times Z$ | 0.008 | |
| | Exponential rate | |
| $R_{O_2} V_Z = \frac{-(1.82 \pm 0.29)10^{-8}}{e^{(0.864 \pm 0.10) \times Z}}$ | × 0.006 mg - at kg - 1 | at 1000 m = -0.494 |
| $R_{CO_2}/V_Z = \frac{(1.35 \pm 0.36)10^{-5}}{e^{(0.53) \pm 0.19) \times 2}}$ | - | at 1200 m = -0.453 at 2000 m = -0.365 |
| $R_{1A}/V_Z = (0.82 \pm 0.52)10^{-5}$ | 0.003 m eq. kg ⁻¹ | at 3000 m $= -0.270$ |
| - | Exponential rate used when TCO ₂ is corrected for alkalinity and salinity (TCO ₂) | |
| $R_{TCO_2}V_Z = (0.86 \pm 0.13)10^{-5} \circ e^{(0.848 \pm 0.193) \times Z}$ | | at 800 m = -0.390 at 3000 m = -0.447 |

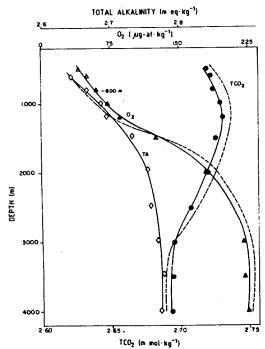


Fig. 3 Vertical profiles of O₂, TCO₂ and TA at st 2358 [----values based on constant production rate law and ————— values based on exponential rate law]

alkalinity as described elsewhere¹. In this case, the oxidative ratios obtained (-0.39 at 800 m depth and -0.477 at 3000 m depth) are in better agreement with the calculated values. The values are given in terms of rate in Table 1.

The calculated oxidative ratios obtained by exponential law vary with depth (Table 1), presumably because the exponents obtained in the computations are not equal as required for constancy of oxidative ratio.

In the foregoing account, an attempt has been made to obtain oxidative ratios which are acceptable within analytical errors and the limitations of the model. It would appear that the vertical advection-diffusion model can be applied with relatively greater accuracy at water depth exceeding 4000 m.

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