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## Appendix A: Calculation of change in $pH_T$ due to $CO_2$ gas exchange between headspace and seawater sample in a bottle.

Initial pH<sub>T</sub> and TCO<sub>2</sub> values (pH<sub>T,i</sub> and TCO<sub>2,i</sub>) in the seawater samples without CO<sub>2</sub> gas exchange were chosen arbitrarily so as to reproduce the variety of seawater conditions that were observed during cruise MR02-K06. Then, initial  $pCO_2$  and TA values in the seawater ( $pCO_{2,i}^{SW}$  and TA<sub>i</sub>) were calculated from pH<sub>T,i</sub> and TCO<sub>2,i</sub> using the equilibrium relations for carbonates (DOE, 1994). The initial  $pCO_2$  in the headspace of the sealed bottle ( $pCO_{2,i}^{HS}$ ) was chosen from the values between 350 µatm (uncontaminated atmosphere) and 1000 µatm (room air). The final  $pCO_2$  in the headspace ( $pCO_{2,i}^{HS}$ ) was assumed to be close to  $pCO_{2,i}^{SW}$ . From the initial and final  $pCO_2$  values in the headspace, the change in the number of micromoles of CO<sub>2</sub> ( $\Delta n_{CO2}$ ) in the headspace with a volume of  $V^{HS}$  was calculated with the following equation of state (Eq. A.1), assuming that CO<sub>2</sub> behaved as an ideal gas:

$$\Delta n_{\rm CO_2} = \frac{\left(p \rm CO_{2,f}^{\rm HS} - p \rm CO_{2,i}^{\rm HS}\right) f_{\rm p} \cdot V^{\rm HS} f_{\rm V}}{RT} \quad . \tag{A.1}$$

Variables in Eq. A.1 that have not been defined are as follows:

$f_{\rm p}$	: Factor to convert pressure unit (101325 Pa atm <sup><math>-1</math></sup> ).
$V^{\rm HS}$	: Volume of the headspace in a bottle $(2 \text{ cm}^3)$ .
$f_{\rm V}$	: Factor to convert volume unit $(10^{-6} \text{ m}^3 \text{ cm}^{-3})$ .
R	: Gas constant (8.31451 J $mol^{-1} K^{-1}$ ).
Т	: Temperature in K.

The change in TCO<sub>2</sub> in the seawater sample (in  $\mu$ mol kg<sup>-1</sup>) was calculated with the following equation:

$$\Delta \text{TCO}_2 = \text{TCO}_{2,f} - \text{TCO}_{2,i} = -\frac{\Delta n_{\text{CO}_2}}{\rho V^{\text{SW}}} \quad , \tag{A.2}$$

where  $\rho$  and  $V^{SW}$  are the sample density (in kg dm<sup>-3</sup>) and volume (0.250 dm<sup>3</sup>), respectively. Then, the perturbed pH<sub>T</sub> was calculated from the equilibrium relationship for carbonates from perturbed TCO<sub>2,f</sub> and initial TA<sub>i</sub>, which does not change during CO<sub>2</sub> gas exchange.

## Appendix B: Calculation of the $pH_T$ change derived from the addition of saturated HgCl<sub>2</sub> solution.

The  $Hg^{2+}$  ion reacts with various inorganic ligands to form metal complexes. The stability constants of major  $Hg^{2+}$  complexes are given in Table B.1 (Stumm and Morgan, 1996). The formation of complexes with hydroxide and carbonate affects TA (Eq. B.1) and TCO<sub>2</sub> (Eq. B.2) in seawater and hence perturbs  $pH_{T}$ .

Table B.1 Stability constants for various Hg<sup>2+</sup> complexes<sup>a</sup>.

Ligands Complexes	OH⁻	Cl <sup>-</sup>	CO3 <sup>2-</sup>	$SO_4^{2-}$
HgL	10.6	7.2	16.1	2.5
$HgL_2$	21.8	14.0		3.6
$HgL_3$		15.1		
$HgL_4$		15.4		
HgOHL		18.1		

<sup>a</sup> Constants are given by the logarithms of the overall formation constants,  $\beta$ , at 25 °C and an ionic strength of zero. The stability constants were corrected to an ionic strength of 0.7 mol kg<sup>-1</sup> with activity coefficients (-log  $\gamma$ ) of 0.146 and 0.584 for charges of ±1 and ±2, respectively.

$$TA^{mix} = [HCO_3^{-}] + 2[CO_3^{2-}] + [B(OH)_4^{-}] + [OH^{-}] - [H^{+}]_F - [HSO_4^{-}] + [Hg(OH)^{+}] + 2[Hg(OH)_2] + [Hg(OH)Cl] + 2[Hg(CO_3)]$$
(B.1)

$$TCO_2^{mix} = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}] + [Hg(CO_3)]$$
 (B.2)

The basic algorithm for calculating the  $pH_T$  change caused by the addition of saturated HgCl<sub>2</sub> solution involves correcting for the consumption of hydroxide and carbonate ions caused by the formation of Hg complexes in the calculation of  $pH_T$  from TCO<sub>2</sub> and TA.

To use the stability constants in Table B.1, which are given at an ionic strength  $I = 0 \mod \text{kg}^{-1}$ , we corrected for the activity coefficient to obtain the constants at the ionic strength of seawater (0.7 mol kg<sup>-1</sup>). The thermodynamic stability constant  $\beta$  of complex HgL<sub>x</sub> is expressed by Eq. B.3:

$$\beta_{\text{HgL}_{x}} = \frac{a_{\text{HgL}_{x}}}{a_{\text{Hg}}a_{\text{L}}^{x}} = \frac{[\text{HgL}_{x}^{2-x\nu}](m^{0})^{x}}{[\text{Hg}^{2+}][\text{L}^{\nu-}]^{x}} \cdot \frac{\gamma_{\text{HgL}_{x}}}{\gamma_{\text{Hg}}\gamma_{\text{L}}^{x}}$$
(B.3)

Variables in Eq. B.3 are as follows:

$a_{\mathrm{M}}$	: Activity	of an ion	M (dim	nensionless).
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- [M] : Concentration of an ion M in mol  $kg^{-1}$
- $m^0$  : Standard value of concentration (1 mol kg<sup>-1</sup>).
- $\gamma_{M}$  : Activity coefficient of ion M (dimensionless).

Eq. B.3 can be rearranged to Eq. B.4 to give the stability constant  $X_{HgLx}$ :

$$\log X_{\text{HgL}_{X}} = \log \left( \frac{[\text{HgL}_{X}^{2-xv}](m^{0})^{x}}{[\text{Hg}^{2+}][\text{L}^{v-}]^{x}} \right)$$

$$= \log \beta_{\text{HgL}_{X}} - \log \gamma_{\text{HgL}_{X}} + \log \gamma_{\text{Hg}} + x \cdot \log \gamma_{\text{L}}$$
(B.4)

The values of log  $\beta_{\text{HgLx}}$  in Eq. B.4 are given in Table B.1. The values of  $-\log \gamma$  in Eq. B.4 are substituted by 0.584 or 0.146 depending on the charge of the ionic species (Stumm and Morgan, 1996). For example, log  $X_{\text{HgLx}}$  for  $\text{HgCl}_4^{2-}$  is calculated as follows:  $\log \beta_{\text{HgCl4}} = 15.4$ ;  $-\log \gamma_{\text{HgCl4}} = 0.584$ ;  $+\log \gamma_{\text{Hg}} = -0.584$ ;  $+\log \gamma_{\text{Hg$ 

We used the following procedure to calculate the pH<sub>T</sub> in seawater that contained HgCl<sub>2</sub>:

a) First, TA was calculated from  $pH_T$ , TCO<sub>2</sub>, temperature and salinity measured for seawater obtained in the equatorial Pacific Ocean during the cruise MR02-K06 with the dissociation constants for carbonic acid reported by Lueker et al. (2000). Because the samples were diluted with saturated HgCl<sub>2</sub> solution by the ratio of volume  $V^{SW}$ :  $V^{Hg}$ , the diluted values of TCO<sub>2</sub> (TCO<sub>2</sub><sup>mix</sup>), TA (TA<sup>mix</sup>) and salinity ( $S^{mix}$ ) were calculated with the following equations:

$$TCO_2^{mix} = TCO_2 \cdot V^{SW} / (V^{SW} + V^{Hg}),$$
  

$$TA^{mix} = TA \cdot V^{SW} / (V^{SW} + V^{Hg}),$$
  

$$S^{mix} = S \cdot V^{SW} / (V^{SW} + V^{Hg}).$$

- b) The effect of dilution on  $pH_T$  was then calculated by iterative methods from  $TCO_2^{mix}$  and  $TA^{mix}$  to give  $pH_T^{mix}$  after the addition of HgCl<sub>2</sub> solution without considering the effect of Hg<sup>2+</sup> complexes.
- c) Concentrations of hydroxide ion  $[OH^-]$  and carbonate ion  $[CO_3^{2-}]$  were calculated from  $pH_T^{mix}$  and  $TCO_2^{mix}$ . The concentrations of chloride and sulphate ions were calculated from salinity  $S^{mix}$  (DOE, 1994).

d) The concentration of each Hg<sup>2+</sup> complex was calculated from Eqs. B.5 and B.6, using the result of procedure c):

$$[HgL_{x}^{2-xv}] = X_{HgLx} [Hg^{2+}] [L^{v-}]^{x}, \qquad (B.5)$$

$$C_{\rm Hg} = [{\rm Hg}^{2^+}] + \Sigma [{\rm HgL}_{\rm x}^{2-{\rm xv}}] = [{\rm Hg}^{2^+}] (1 + \Sigma X_{\rm HgLx} [{\rm L}^{\rm v-}]^{\rm x}).$$
(B.6)

- e) Perturbations of TA by HgOH<sup>+</sup>, Hg(OH)<sub>2</sub>, Hg(OH)Cl and HgCO<sub>3</sub> from TA<sup>mix</sup> in Eq. B.1 were calculated to give a corrected TA value, TA'. This procedure corresponds to the correction for the consumption of OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> caused by HgCl<sub>2</sub> addition.
- f) The concentration of HgCO<sub>3</sub> was subtracted from  $TCO_2^{mix}$  in Eq. B.2 to give a corrected  $TCO_2$  value,  $TCO_2'$ . This procedure corresponds to the correction for the consumption of  $CO_3^{2^-}$ .
- g) A corrected pH<sub>T</sub> value, pH<sub>T</sub>', was calculated from TCO<sub>2</sub>' and TA' by the same method described in procedure b).
- h) If the difference between pH<sub>T</sub>' and pH<sub>T</sub><sup>mix</sup> was larger than 0.00001, pH<sub>T</sub><sup>mix</sup> was substituted by pH<sub>T</sub>'. Then procedures c) through h) were repeated. The value of pH<sub>T</sub>' converged after two or three iterations.

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