

A REGENERATION MODEL TO ESTIMATE ADDITION FLUXES AND REMOVAL CONSTANTS OF TRACE METALS IN SEAWATER

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ABSTRACT

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A model is presented for flux evaluation of trace metals in situ. For the practically feasible simplified model, mere estimation of metals in various dissolved states (e.g. Cr(III) and Cr(VI)) and in particulate phase, in a single vertical profile at least, together with temperature, salinity, O_2 , titration alkalinity (TA), Ca^{2+} , NO_3^- , HPO_4^{2-} and H_4SiO_4 parameters enable evaluation of the amount of metal removed in situ, to a first approximation. From the evaluated net metal removed (M_R), estimation could be made for removal constants, i.e. removal times (t), residence times (τ) and removal rate constants (ψ), not only for the average ocean but also for the oxygen-minimum zone. Besides, M_R can be used to calculate t , τ and ψ of various species of the metal concerned, that are not yet available. The present model evaluates t , τ and ψ for total chromium from a single station, which are consistent with the reported values, and shows that chromium is removed with fast-settling particulate matter. This study also reveals that t , τ and ψ values of 0.001 years, 7 years and $0.150 y^{-1}$, respectively, for Cr(III) in the oxygen-minimum zone and 0.006 y, 211 y and $0.005 y^{-1}$ in the marine environment, respectively.

INTRODUCTION

Addition or depletion of a metal to or from seawater needs to be quantified for an understanding of the various fluxes and cycling of the same in a marine environment. Although this is a difficult task, it is essential to give insight into the intricate chemical processes. Though Brewer and Spencer (1975) mentioned the significance of physico-chemical and nutrient parameters for understanding the biogeochemical processes, no quantitative model for the evaluation of trace metal fluxes from those parameters has yet been established. Despite these facts, the possible practical approach must be used to evaluate the fluxes, which can be deduced from measurements in controlled-tank experiments (Santschi et al., 1980, 1983; Amdurer et al., 1983), by sediment trap experiments (Spencer et al., 1978; Brewer et al., 1981; Martin and Knauer, 1983a,b) or by indirect evaluation as has been proposed in the present study. The estimated net removal of a metal in situ leads to the evaluation of removal constants such as removal time (t), residence time (τ), and removal rate constants (ψ).

The present paper discusses a practically feasible, simple model which,

through the evaluation of the extent of decomposition and dissolution of organic and biologically precipitable materials, eventually yields the total metal added to the water column in situ. The net removal of the metal, in situ, can be obtained by the knowledge of the total metal added, increase in adsorbed metal concentration on suspended matter and by the amount of metal diffused. The regeneration model proposed here is of significance since it evaluates additional fluxes and removal constants in situ, and does not need the evaluation of rates of either river input to or sedimentation in the ocean for any metal in question.

THE MODEL

Basis

In seawater the total amount of trace metal, M_T , will be the sum of its respective amounts in the various phases present. The possible phases in seawater include dissolved, living organisms, undecomposed organic matter, skeletal remains, faecal matter, inorganic precipitates/particles, etc. For h number of phases, M_T can be written as

$$M_T = \sum_{i=1}^h A_i M_i \quad (1)$$

where A_i = amount of the i -th phase in seawater, M_i = trace metal concentration in the i -th phase.

To find the metal fluxes and pathways in seawater, the enhanced concentration of the metal (M_A) in seawater has to be calculated. This addition is governed by regeneration (reg) and dissolution (dis) processes in the sea. Thus

$$M_A = \left[\sum_{i=1}^h A_i^r M_i^r \right]_{\text{reg/dis}} + M_{\text{up}} \quad (2)$$

The superscript r indicates the removal from respective phases and addition to seawater. M_{up} is the vertical flux of metals from the sediments. Similarly, the metal removed from seawater after its addition can be written as

$$M_r = \left[\sum_{i=1}^h A_i^a M_i \right]_{\text{ads}} \quad (3)$$

Superscript a denotes addition onto a compartment and removal from seawater. M_r is the metal removed from the quantity added, M_A . In spite of the presence of zooplankton (Urrere and Knauer, 1981; Knauer and Martin, 1983) in the deep sea, adsorption onto particles that are removed at a faster rate from the water column is significant. Adsorption of metal ions onto particles is shown to be the main mechanism for the removal of the same from seawater (Murray and Brewer, 1977; Turekian, 1977; Li, 1981; Kumar,

1983). Knowledge of surface characteristics of an organic/inorganic particle and its charge site concentration might enable the quantification of associated metal.

For z number of particles in seawater, the total adsorbed metal will be

$$M_{\text{ads}} = \sum_{b=1}^z \beta_b M_{\text{SW}} [S]_b \quad (4)$$

where β and S are for particle b . Stumm et al. (1976), Murray and Brewer (1977), Balistrieri and Murray (1981) and Hunter and Liss (1982) discussed the electrostatic and adsorption aspects of inorganic oxides and minerals. Balistrieri et al. (1981) demonstrated more binding capacity for organic particles rather than inorganic particles, through surface $-\text{OH}$ and $-\text{COOH}$ groups. β values should be found experimentally for metal adsorption onto various particles that are possibly present in seawater (Jedwab, 1980) as carried out by Franklin and Morse (1982, 1983), Hunt and Fitzgerald (1983) and Shanbhag and Morse (1983).

From the above equations (2 and 3) the amount of net metal removed, M_{R} , can be written as

$$M_{\text{R}} (\text{mol dm}^{-3}) = M_{\text{A}} - M_{\text{r}} - M_{\text{d}} \quad (5)$$

M_{d} is the metal concentration removed, in situ, due to vertical and horizontal advection and diffusional processes. The extent of M_{d} depends on the sign of advection and diffusion coefficients and the magnitude of their gradients. M_{R} enables us to evaluate t , τ and ψ for the metal M . Having an average concentration of a specific species of metal M or its average total concentration in the length of the water column under consideration (M_{SW}), t is defined as the time needed to remove M_{SW} from 1 dm vertical length of the seawater column. t can be evaluated from the average residence time of particulate matter (τ_{p} , years) in the ocean, M_{SW} and M_{R} as

$$t (\text{years}) = \frac{M_{\text{SW}}}{M_{\text{R}}} \tau_{\text{p}} \quad (6)$$

For the oxygen-minimum zone, M_{SW} and M_{R} are the average values in that zone. Since t is for 1 dm vertical length of the water column, the residence time of M in the entire water column is given by

$$\tau (\text{years}) = t H / 1 \text{ y dm dm}^{-1} \quad (7)$$

where H = height of the water column (38 000 dm for the average ocean). The removal rate constant is given by

$$\psi (\text{y}^{-1}) = 1/\tau \quad (8)$$

Practical approach

Based on manganese data, Martin and Knauer (1983a) mentioned that living cells concentrate metal ions to a lesser extent than the detrital phases, and questioned the utility of trace element levels in plankton. Nevertheless, the role of biota in metal cycling is well documented (Bowen, 1966, 1979; Brewer, 1975; Moore and Boström, 1978; Collier and Edmond, 1983; Knauer and Martin, 1983). The inclusion of a metal ion in a particular carrier phase might depend on its aquatic chemistry. However, the study of trace metal levels in planktonic organisms together with other carrier phases would help in evaluating possible fluxes in seawater.

For the evaluation of M_A , eq. 2 can be simplified to

$$M_A = M_{\text{ox}} + M_{\text{dis}} \quad (9)$$

$M_{\text{ox}} = M_A$ due to oxidation of organic matter; $M_{\text{dis}} = M_A$ due to dissolution of mineral phases either in situ and/or migrated upward from sediments ($= M_{\text{dis in situ}} + M_{\text{up}}$). Oxygen, nitrate, silicate, phosphate, titration alkalinity (TA) and calcium data would enable the estimation of the extent of oxidation of organic matter (O_2 and/or NO_3^-), dissolution of silicate (H_4SiO_4), apatites (HPO_4^{2-}) and carbonates (Ca^{2+} and/or TA) in seawater. If B moles of organic/inorganic carrier phase (B_{cp}) contains C moles of metal (C_M), then each mole of the respective carrier phase (CP) will have C_M/B_{cp} moles of the metal. B_{cp} and C_M can be calculated from the equations

$$B_{\text{cp}} (\text{mol}) = \frac{1 \text{ g of CP}}{\text{Mol. weight of CP}} \quad (10)$$

and

$$C_M (\text{mol}) = \frac{M \text{ in 1 g of CP}}{\text{Mol. weight of M}} \quad (11)$$

Consequently, all concentrations are expressed in this paper in the molar (M) scale. Redfield et al. (1963) gave the general stoichiometric composition of plankton in seawater as $((\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} \text{H}_3\text{PO}_4)$. Since this represents all the major constituent elements that are essential for the formation of simple organic matter, this formula might represent a stoichiometric organic molecule. Using these stoichiometric ratios of plankton composition, Broecker (1974) derived two conservative parameters (NO and PO) to trace different water masses in the ocean. Alternatively, in estimating the amount of organic matter oxidized, Chen (1978) used the same formula and mentioned that the number of moles of organic matter oxidized can be estimated from $\Delta\text{NO}_3/16$. Hence, in the present attempt the composition of 1 mole of organic matter is represented by the formula $[(\text{CH}_2\text{O})_a (\text{NH}_3)_c (\text{H}_3\text{PO}_4)]$

TABLE I

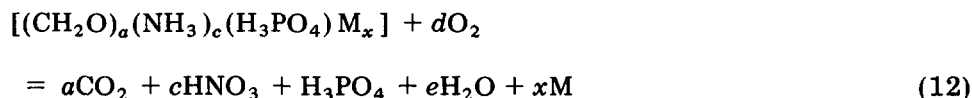
Observed (Cranston, 1983) and calculated added chromium concentrations, in situ

Depth (m)	Cr(III) obs. (nM)	Cr(tot) obs. (nM)	Cr(part) obs. (nM)	Cr(ox) calc. (nM)	Cr(SiO ₄) calc. (nM)	Cr(PO ₄) calc. (nM)	Cr _A calc. (nM)
1	0.03	1.74	0.10	-0.39	-0.04	-0.001	-0.43
10	0.15	1.69	0.01	-0.47	-0.02	-0.001	-0.49
25	0.14	1.61	0.04	-0.61	-0.02	0.000	-0.62
50	0.26	1.70	0.06	-0.26	-0.04	-0.002	-0.30
75	0.37	1.58	0.12	-0.09	-0.03	-0.001	-0.13
100	0.02	1.96	0.15	0.20	-0.02	-0.001	0.17
200	0.06	1.64	0.08	2.10	-0.01	0.000	2.11
300	0.04	1.69	0.06	3.28	-0.01	0.001	3.27
400	0.06	1.77	0.05	5.51	0.11	0.000	5.61
600	0.01	2.03	0.08	7.38	0.28	0.000	7.66
800	0.01	2.29	0.08	7.80	0.44	-0.001	8.24
1000	0.01	2.38	0.07	7.85	0.56	-0.001	8.41
1200	0.09	2.28	0.02	7.76	0.68	0.000	8.43
1500	0.01	2.62	0.01	7.56	0.87	-0.001	8.42
2000	0.01	2.93	0.01	6.82	1.06	0.000	7.88
2500	0.01	2.67	0.01	6.30	1.12	0.000	7.42
3000	0.06	2.90	0.01	5.88	1.17	0.001	7.05
3100	0.01	3.03	0.01	5.83	1.18	0.001	7.01

M_x], which incorporates the metal in question. On the other hand, molecular formulae of the inorganic phases can be the respective mineral phases commonly found in seawater (i.e. opal (SiO₂) for silicates; fluoroapatite (Ca₅(PO₄)₃F) for phosphates and calcite (CaCO₃) for carbonates). As per these formulae, the molecular weights calculated can be used in eq. 10.

Estimation of organic matter oxidized (OMO)

As will be shown later in this study (Table I), biota play an important role in the biogeochemical cycles of elements in seawater. Since there may be regional variations in biogeochemical relationships (AOU: H₄SiO₄: NO₃⁻: HPO₄²⁻), the same should be established, before using these values in the present model, for any specified region. Stoichiometrically these ratios are assumed to be the same in plankton and seawater. Thus a general reaction for the oxidative decomposition of a single molecule of organic matter can be written as



Computations of preformed nutrients (subscripted as pre) and AOU (apparent oxygen utilization) facilitate the OMO calculation based on coefficients in eq. 12. d moles of oxygen decompose 1 mole of organic matter and, hence

$$\text{OMO} = \text{AOU}/d \quad (13)$$

where OMO and AOU are expressed in mol dm^{-3} . Also, OMO can be found from eq. 14:

$$\text{OMO} = \frac{(\text{NO}_3^-(\text{in situ}) - \text{NO}_3^-(\text{surf})) - \text{NO}_3^-(\text{pre})}{c} \quad (14)$$

or after salinity correction (Chen, 1978)

$$\text{OMO} = \frac{1}{c} \left[(\text{NO}_3^-(\text{in situ}) - \text{NO}_3^-(\text{surf})) \frac{S(\text{in situ})}{S(\text{surf})} - \text{NO}_3^-(\text{pre}) \right]$$

where S is salinity and subscript surf refers to surface. The trace metal released to seawater (M_{ox}) can be quantified by using its concentration in 1 mole of organic matter (M_{plank}) as

$$M_{\text{ox}} = M_{\text{plank}}(\text{OMO}) \quad (15)$$

Estimation of mineral dissolved

The extent of opal (SiO_2) dissolution can be found from

$$\text{H}_4\text{SiO}_4(\text{dis in situ}) = \text{H}_4\text{SiO}_4(\text{in situ}) - \text{H}_4\text{SiO}_4(\text{pre}) - \text{H}_4\text{SiO}_4(\text{ox}) \quad (16)$$

Also, silicate mineral dissolved at the seawater—sediment boundary layer migrates upwards. Thus, $\text{H}_4\text{SiO}_4(\text{dis})$ will be

$$\text{H}_4\text{SiO}_4(\text{dis}) = \text{H}_4\text{SiO}_4(\text{dis in situ}) + \text{H}_4\text{SiO}_4(\text{up}) \quad (17)$$

where $\text{H}_4\text{SiO}_4(\text{dis in situ})$ = silicate dissolved in situ, $\text{H}_4\text{SiO}_4(\text{up})$ = silicate migrated upwards.

The metal added to seawater due to the dissolution of opal is

$$M_{\text{H}_4\text{SiO}_4} = \text{H}_4\text{SiO}_4(\text{dis}) M_{\text{opal}} \quad (18)$$

M_{opal} is the concentration of M per mole of opal. Similarly, the upward migrated phosphate from sediments due to dissolution of minerals such as apatite (or phosphatic debris; Suess, 1981) is

$$\text{HPO}_4^{2-}(\text{dis}) = \text{HPO}_4^{2-}(\text{in situ}) - \text{HPO}_4^{2-}(\text{pre}) - \text{HPO}_4^{2-}(\text{ox}) \quad (19)$$

and the metal released due to the dissolution is

$$M_{\text{HPO}_4^{2-}} = \text{HPO}_4^{2-}(\text{dis}) M_{\text{apatite}} \quad (20)$$

The calcium carbonate dissolved is found (Chen, 1978) either by using calcium values

$$\Delta\text{Ca or Ca}_{(\text{dis})} = (\text{Ca}_{(\text{in situ})} - \text{Ca}_{(\text{surf})}) \frac{S_{(\text{in situ})}}{S_{(\text{surf})}} \quad (21)$$

with salinity correction or from titration alkalinity (TA) and nitrate values as

$$\text{Ca}_{(\text{dis})} = 0.5 \Delta\text{TA} + 0.53125 \Delta\text{NO}_3^- \quad (22)$$

where ΔTA and ΔNO_3^- are found as for ΔCa in eq. 21. Hence

$$M_{\text{CO}_3} = \text{Ca}_{(\text{dis})} M_{\text{CaCO}_3} \quad (23)$$

The concentrations of M_{plank} , M_{opal} , M_{apatite} and M_{CaCO_3} can be evaluated from the data of Bowen (1966, 1979), Martin and Knauer (1973), Boström et al. (1974), Moore and Boström (1978), and Kastner (1981).

M_A due to decomposition and dissolution processes (eqs. 12–23) is now written as

$$M_A = M_{\text{ox}} + M_{\text{H}_4\text{SiO}_4} + M_{\text{HPO}_4} + M_{\text{CO}_3} \quad (24)$$

The incorporation of a trace metal into the organic or mineral phases considered in surface layers, results in its regeneration along with its carrier phases in the deep sea. Lerman and Lal (1977) have mathematically demonstrated that the dissolution of particles in the deep sea depends on the abundance, size and the rates of dissolution. Further, for a particle with constant dissolution rate, dissolution might decrease with depth due to the solution losses of smaller particles (Lerman and Lal, 1977). These mineral phases are significant carriers of metals to the deep sea (Murray and Brewer, 1977; Collier and Edmond, 1983; Martin and Knauer, 1983a). The increase in metal concentrations with depth due to these processes and also correlation of this increase with NO_3^- , H_4SiO_4 , HPO_4^{2-} and/or TA (Campbell, 1983; Quinby Hunt and Turekian, 1983, and references therein) manifests their association with a particular phase whether organic or inorganic.

M_A (eq. 24) and computed M_d , through physico-chemical parameters (Brewer and Spencer, 1975), enable the determination of M_R (eq. 5) since M_r could be the concentration of metal in particulate matter in situ. However, it could be admitted that the results of this model are valid for the period of data collection, and are vulnerable to variations in productivity. Due to general changes in productivity with season and the geographical location, it would be necessary to set variability limits for any given region. Hence, the evaluation of this model during lowest and highest production times should set the variable limits on removal rates and constants in the specific area.

A CASE STUDY

To test the model, data on Cr(III), Cr(tot), Cr(part) and other parameters from Cascadia Basin for a single station (station 5 from Cranston, 1983) have been used. The oxidation state of chromium, Cr(III) or Cr(VI), strongly depends on biological and geological factors (Cranston, 1983; Kumar and Reddy, 1985). Though the thermodynamic study shows more stability for Cr as CrO_4^{2-} than Cr(III)-surface complexation with suspended matter in seawater (Kumar and Reddy, 1985), the slow oxidation of Cr(III) to Cr(VI) (Shroeder and Lee, 1975) makes Cr(III) available for adsorption. Cranston (1983) found a significant relationship for chromium with silicate and phosphate. An increase in Cr(tot) with depth has been noticed and attributed to the dissolution of opal in the marginal sediments of the Cascadia Basin (Cranston, 1983). The occurrence of this feature is confirmed after consideration of vertical and horizontal advective and diffusive processes (Cranston, 1983). Since this flux is actually balanced in the basin, the present model is used in the evaluation of in situ fluxes and removal constants.

The biochemical relationship found for Cranston's (1983) data for this station by atoms is

$$\text{AOU}:\text{SiO}_4:\text{NO}_3:\text{PO}_4 = 264:32:16:1$$

and the preformed nutrients are $\text{H}_4\text{SiO}_4 = 14.4 \mu\text{M}$, $\text{NO}_3^- = 11.4 \mu\text{M}$ and $\text{HPO}_4^{2-} = 0.96 \mu\text{M}$. Using eqs. 12–20, the amount of chromium added to seawater is found (eq. 24). Moore and Boström (1978) found no variations of trace metal content in plankton with geographical location or with different taxa. On this basis, and since no data were available for the metal content in carrier phases of Cascadia basin, these were obtained from the literature. For evaluation, chromium concentrations obtained for various carrier phases are: plankton, 0.0048% (dry weight; Boström et al., 1974; Moore and Boström, 1978); opal, 8.3 ppm (Kastner, 1981; Cranston, 1983); apatite, 0.85 ppm (Bowen, 1966). For use in eq. 10, molecular formulae considered for these phases are organic matter = $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4$; opal = SiO_2 ; apatite = $\text{Ca}_5(\text{PO}_4)_3\text{F}$, as discussed earlier. The omission of calcium carbonate dissolution from eq. 24 may not affect the model results since the depth at the present station does not exceed 3200 m, wherein CaCO_3 dissolution occurs significantly at about 3500 m (Lerman and Lal, 1977).

It is evident from Fig. 1 that Cr(tot) increases with increase in depth, while Cr(part) shows high concentration between 50 and 1200 m, with slightly lower concentration above 400 m. The high concentration of Cr(part) near 100 m might be due to greater abundance of abiotic and biotic matter in the surface layer of the ocean and the consequent increase in the surface charge concentration. However, the increase in Cr(part) between 400 and 1200 m is due to a comparatively larger availability of Cr in seawater, which is due to regeneration of organic matter and the presence of

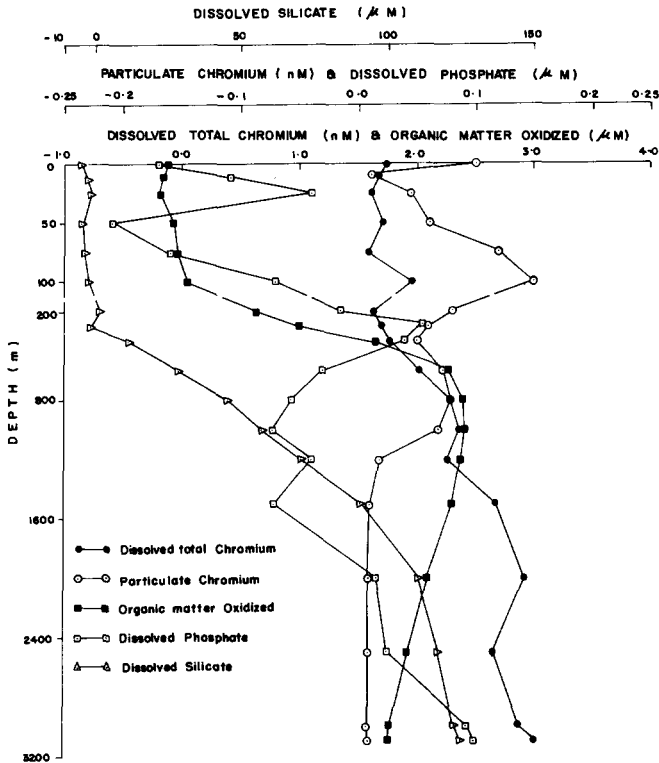


Fig. 1. Profiles of chromium concentrations observed (at station 5; Cranston, 1983) and the dissolved mineral matter computed as per the present model for the same station.

possible mineral phases. Nevertheless, the gradual increase in $\text{Cr}(\text{tot})$ with depth is ascribed to dissolution processes in the deep sea (Cranston, 1983). In agreement with this, Cranston (1983) observed linear relationships for Cr with phosphate and silicate concentrations.

To evaluate the fluxes of Cr from the carrier phases, the extent of dissolution and decomposition of these phases has been calculated as per eqs. 13, 14, 16 and 19. The oxidation of organic matter starts around 200 m depth and reaches a maximum value at about 800 m with a slight decrease downwards (Fig. 1). Figure 1 reveals that dissolution of opal appears around 200 m and increases with depth. This might be due either to diatom shells or to upward migration from the sediments (Edmond et al., 1979; Cranston, 1983). It is obvious from Fig. 1 that, compared to the oxidation of organic matter and opal dissolution, the apatite dissolved is less significant. In concurrence with Fig. 1, added chromium due to dissolution of apatite is insignificant compared to that of opal and organic matter decomposition (Table I). Table I lists the observed values of Cranston (1983) together with those calculated by using the present model. As can be seen from Table I, Cr_A is 2–3 times greater than the observed dissolved $\text{Cr}(\text{tot})$ value. The difference

TABLE II

Removal times (t and τ , y) and rates (ψ , y^{-1}) of chromium estimated from the present model

Ocean/ zone	Chromium species	Parameter	τ_p (y)	
			0.260	
Ocean (average)	Total inorganic	t	0.158 (0.192) ^a	6.2
		τ	6×10^3 (5×10^3) ^d (6×10^3) ^b	2.4×10^5
		ψ	1.6×10^{-4} (2×10^{-4}) ^d	4.2×10^{-6}
	Cr(III)	t	0.006	0.218
		τ	211 (192) ^d	8.2×10^3
		ψ	0.005 (0.005) ^d	1.2×10^{-4}
Oxygen minimum zone	Total inorganic	t	0.065	2.91
		τ	589 (740) ^c	2.6×10^4
		ψ	0.002	3.8×10^{-5}
	Cr(III)	t	7.4×10^{-4}	0.033
		τ	7.0	297
		ψ	0.150	0.003

^aAmdurer et al. (1983); ^bBrewer (1975); ^cMurray et al. (1983); ^dCalculated values for the Cascadia basin using the present model (32 000 dm).

between Cr_A and $Cr(\text{tot})$ should give a Cr_R value, and if this Cr_R is adsorbed onto the suspended particulate matter in seawater, the same should have been reflected in $Cr(\text{part})$ values, which is not the case (Table I). This suggests the removal of Cr_R by the fast-settling suspended matter, but not onto the suspended particulate matter. Here, Cr_R is calculated by subtracting $Cr(\text{part})$ from Cr_A , since Cr_d is balanced by vertical flux from the sediments. By averaging Cr_R , $Cr(\text{III})$ and $Cr(\text{tot})$ from surface to bottom, the removal constants are evaluated using eq. 6 and the results are shown in Table II. For this evaluation, average particulate matter residence times of 0.26 y (based on sinking rates of a fast-settling variety of particulate matter (Honjo and Roman, 1978; Lorenzen et al., 1983; Takahashi and Honjo, 1983)), that agree with the 0.365 y of Brewer et al. (1981), and 10 y (Bacon and Anderson, 1982) are used. This is done by assuming a bimodal distribution, so that the representative values of τ_p for large and small particles in seawater would be 0.26 and 10 y, respectively. Equation 6 with 0.26 y particulate matter residence time (Lorenzen et al., 1983) shows excellent agreement with the reported values of t of Amdurer et al. (1983) for oceans and of Murray et al. (1983) in the oxygen-minimum zone for inorganic total chromium (Table II). Also, the τ value of 6×10^3 y is consistent with the reported values of Brewer (1975) and that calculated based on sedimentation rates, 4.3×10^3 y (Li, 1982). Table II also reveals that $Cr(\text{III})$ in the

oxygen-minimum zone (600–1500 m) is rapidly removed, i.e. $t \approx 0.001$ y where much of the organic matter is expected to decompose, due to its adsorptive tendency and Cr(III) increasing in stability with reduction in oxygen concentration (Kumar and Reddy, 1985). In general, Cr(III) has a τ value of 7 y and a ψ value of 0.150 y^{-1} in the oxygen-minimum zone, whereas it has a t value of 0.006 y, τ of 211 y and ψ of 0.005 y^{-1} in the ocean (Table II). The use of τ_p of Bacon and Anderson (1982) yielded very high values of removal times and rates and departs much from the reported values (Table II). This suggests that the chromium present in seawater might be removed by the particulate matter with $\tau_p \approx 0.26$ y. The average residence times of particulate matter in the ocean are variable due to the large spectrum of the particles present, their nature and their respective settling velocities. However, the removal of few elements like Cr may be made possible by the fast-settling organic (Lorenzen et al., 1983), faecal (Honjo and Roman, 1978) and other skeletal matter (Takahashi and Honjo, 1983), which not only scavenge the metals directly but also metal-coated particulate matter from the water column, during the sinking process. Further, this could be augmented by the observation of Broecker et al. (1973), which states that 97% of the upwelled phosphorus to the surface layer will be removed by the fast-settling particulate matter within a span 30 times less than that which will be removed by downwelling water.

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