Global Biogeochemical Cycles

Supporting Information for

The Biogeochemistry of cobalt in the Mediterranean Sea

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Introduction

This supplementary information contains a text, three figures and three tables. The text provides the details of the equations and the model parameterization used in this study to determine the physical and biogeochemical fluxes. The first figure shows the vertical distribution of particulate ratios of phosphorus, and of cobalt to the lithogenic elements aluminium and titanium in the Mediterranean Sea. The second figure is related to the remineralization paragraph of the manuscript and provides further information supporting the low remineralization rate of cobalt in the Mediterranean Sea. Figure S3 shows the output of the 1D biogeochemical model for remineralization and scavenging of cobalt in the intermediate and deep Mediterranean Sea. Two tables (S1 & S2) provide results of analyses of certified reference materials. The values of primary production rate used in this study and their references are included in a third table (S3).

Text S1.

1D Biogeochemical model

Surface layer (0-200 m depth)

- Local biological uptake rates of cobalt by phytoplankton and bacteria in the surface layer were estimated following Equation (1).

$$\mathbf{FsCo_{uptake} = Co/C * PPR} \quad (1)$$

With $FsCo_{uptake}$: the biological uptake of sCo, Co/C: the mean elemental particulate ratios of biogenic cobalt to organic carbon in the suspended particles, and PPR: the primary production rate (Table S3) [*Moutin and Rimbault*, 2002; *Bosc et al*., 2004; *van de Poll et al*., 2015].

- The biological cobalt pump (or export of biogenic pCo at 200 m, F_{200m} $pCo_{biogenic}$) was estimated following Equation **(2).**

$$\mathbf{Biological\ Co\ pump = F_{200m}\ pCo_{biogenic} = FsCo_{uptake} * CPE} \quad (2)$$

With $FsCo_{uptake}$: the biological uptake of Co, and CPE: the carbon pump efficiency (percentage of the primary production rate reported in Table S3) [*Moutin and Rimbault*, 2002; *Sanchez-Vidal et al., 2005; Speicher et al., 2006*].

- The scavenging Co flux (FCoscav) was considered negligible in this layer.

Intermediate and deep layers (200 m-bottom depths)

- The export flux of biogenic pCo (F_Z $pCo_{biogenic}$) was considered dependent on the depth (z) and it was parameterized using a power law function following Equation (3).

$$\mathbf{F_z\ pCo_{biogenic} = F_{200m}\ pCo_{biogenic} * (z/200)^{\beta}} \quad (3)$$

with β = -0.3 after *Miquel et al*. [2011] who estimated that ~38% of the organic carbon leaving 200 m is remineralized at 1000 m.

- Integration of the remineralization flux ($\int F_Z Co_{remin}$) below 200 m was calculated following Equation (4).

$$\mathbf{\int F_Z Co_{remin} = F_{200m}\ pCo_{biogenic} * (1-(z/200)^{-0.3})} \quad (4)$$

- Integrated scavenging fluxes ($\int FzCo_{scav}$) were estimated equal to 0 at 200 m depth, equal to $\int F_{600m}Co_{remin}$ at 600 m, and equal to $\int F_{1500m}Co_{remin} + \gamma$ at the mean bottom depth (1500 m), with γ equals to 1 $nmol.m^{-2}.d^{-1}$ in the Eastern basin and to 2.6 $nmol.m^{-2}.d^{-1}$ in the Western basin as described in the main text.
  Then, the parameterization of the scavenging flux was estimated by resolving the quadratic Equation (5) of the integrated scavenging fluxes as a function of depth.

$$\mathbf{\int FzCo_{scav} = az^2 + bz + c} \quad (5)$$

With **a**, **b** and **c** equal, respectively, to **7.0 10^{-7}**, **2.1 10^{-3} and -4.5 10^{-1}** in the Western Basin and to **-4 10^{-8}, 1.7 10^{-3} and -3.4 10^{-1}** in the Eastern Basin.

Finally, **$FzCo_{scav}$** was determined as the derivative with depth of the $\int FzCo_{scav}$ function and is a linear function (Equation **(6)).**

$$FzCo_{scav} = 2az + b \quad (6)$$

Physical model

- The vertical diffusion flux of DCo ($FDCo_{zdiff}$) was estimated following Equation **(7).**

$$FDCo_{zdiff} = -Kz * \delta[DCo]/\delta z \quad (7)$$

With Kz: the vertical diffusivity ranging from 0.3 $cm^2.s^{-1}$ in the surface to 10^{-3} $cm^2.s^{-1}$ in the deep sea (after *Wu and Haines* [1998]), and $\delta[DCo]/\delta z$: the vertical DCo gradient that was measured.

- Convection flux of DCo ($FDCo_{convection}$) from the intermediate to the deep sea was estimated following Equation **(8)**.

$$FDCo_{convection} = [DCo]_{IW} * Fw_{convection} \quad (8)$$

Whith $[DCo]_{IW}$: the mean [DCo] in the intermediate waters, and $Fw_{convection}$: the convection rate of deep water masses. $Fw_{convection}$ are equal to 0.04 Sv, 0.3 Sv, and 1.1 Sv in the Cretan Sea, the South Adriatic Sea and in the North Western basins, respectively (After *Roether and Schlitzer* [1991]; *Zervakis et al*. [2004]; *Van Cappellen et al*. [2014] and *Durrieu de Madron et al*. [2013]).

- Upwelling flux of DCo ($FDCo_{upwelling}$) from the deep to the intermediate waters were estimated following Equation **(9)**.

$$FDCo_{upwelling} = [DCo]_{DW} * Fw_{upwelling} \quad (9)$$

Whith $[DCo]_{DW}$: the mean [DCo] in the deep waters, and $Fw_{upwelling}$: the upwelling rates of deep water masses, which are equal to the convection rates (see Equation (**8**)).

- The theoretical DCo concentrations in the Levantine Intermediate waters at the ouflow of the Sicily Channel (DCoLIW-SC) and of the Gibraltar Strait (DCoLIW-GS) were estimated following Equations (**10**) and (**11**), respectively.

$$DCo_{LIW\text{-}SC} = (DCo_{EDW} * Fw_{upwelling} + DCo_{Cretan\ Sea} * Fw_{LIW}) / (Fw_{upwelling} + Fw_{LIW}) \quad (10)$$

$$DCo_{LIW\text{-}GS} = (DCo_{WDW} * Fw_{upwelling} + DCo_{LIW\text{-}SC} * Fw_{LIW}) / (Fw_{upwelling} + Fw_{LIW}) \quad (11)$$

Where DCo_{EDW} and DCo_{WDW} are the mean DCo recorded in Eastern (45.8 pM) and Western (47.4 pM) basins, $DCo_{Cretan\ Sea}$ is the mean DCo recorded in the forming area of LIW (110.6 pM), Fw_{LIW} the advection rate of LIW set to 1.1 Sv [*Lascaratos et al*., 1999; *Van Cappellen et al*., 2014] and $Fw_{upwelling}$ the upwelling of deep waters into the intermediate layer. $Fw_{upwelling}$ is equal to the convection rate of deep water-masses in each basin (see Equation 6).

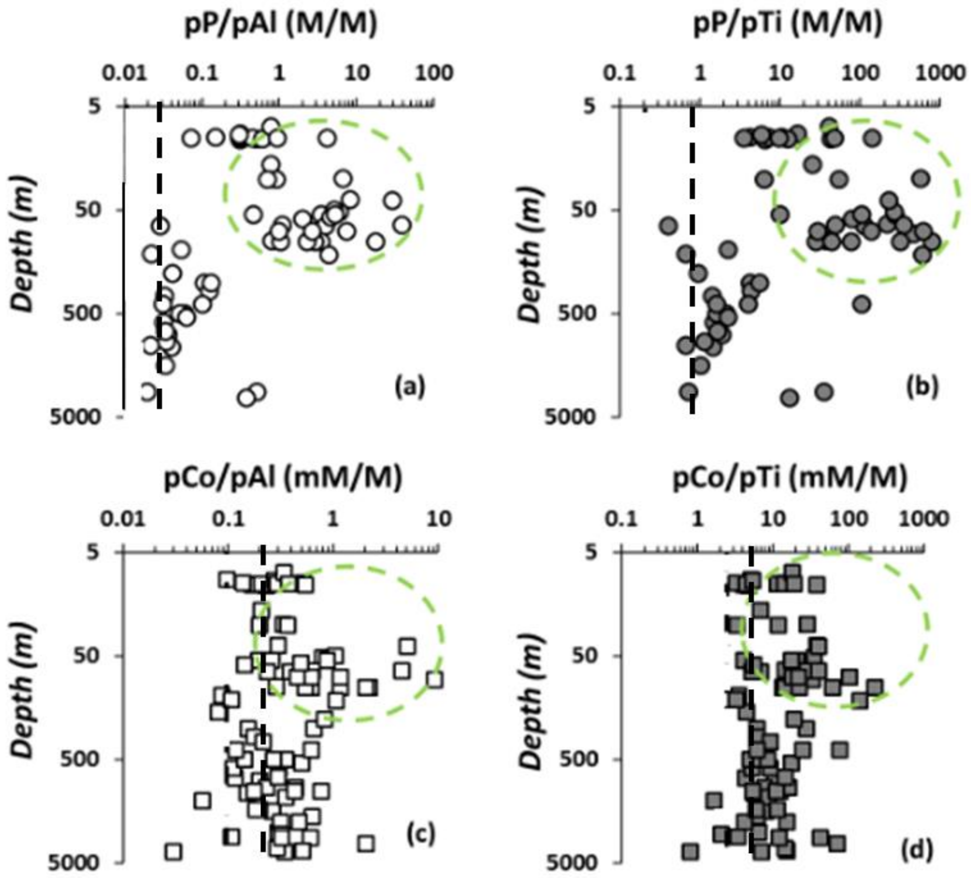

Figure S1. Scatter plots of particulate ratios of phosphorus (pP, **a**&**b**) and of cobalt (pCo **c** & **d**) to aluminium (pAl, **a** & **c**) and titanium (pTi, **b** & **d**) as a function of depth in suspended particles collected along the GEOTRACES-A04 section. Elemental ratio in Mediterranean aerosols [*Gülü et al*., 2000; *Heimbürger et al*., 2010] is indicated in black dashed line. Green dashed circles indicate the data in the productive layer (Chl-a > 0.1 µg.l^{-1}).

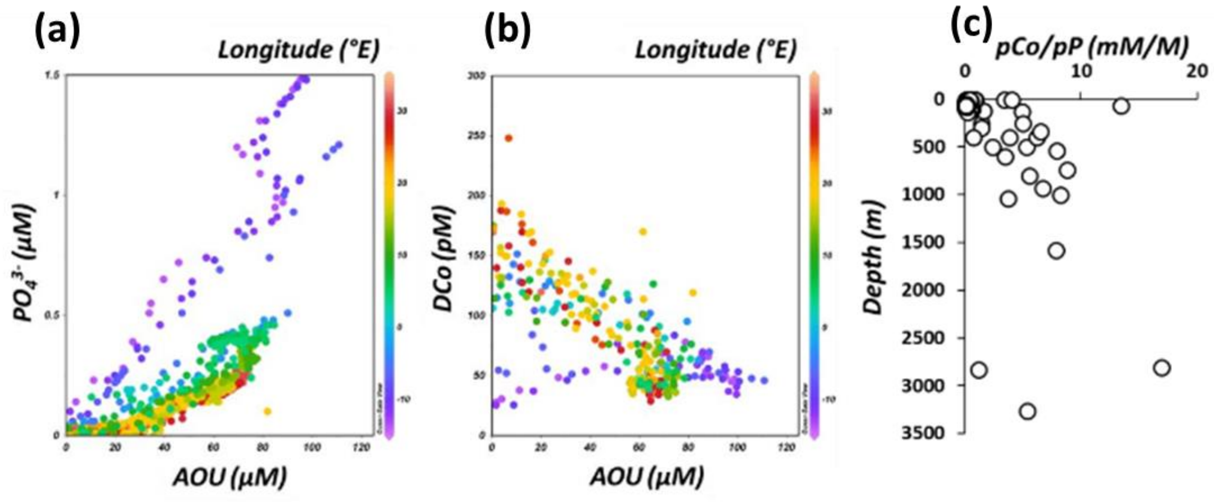

Figure S2. Scatter plots of phosphates (PO4^{3-}, **a**) and DCo **(b)** concentrations against AOU measured along the GEOTRACES-A04 section, colors indicate the longitude. **(c)** Scatter plot of the particulate ratio of cobalt (pCo) to phosphorus (pP) as a function of the depth along the GEOTRACES-A04 section.

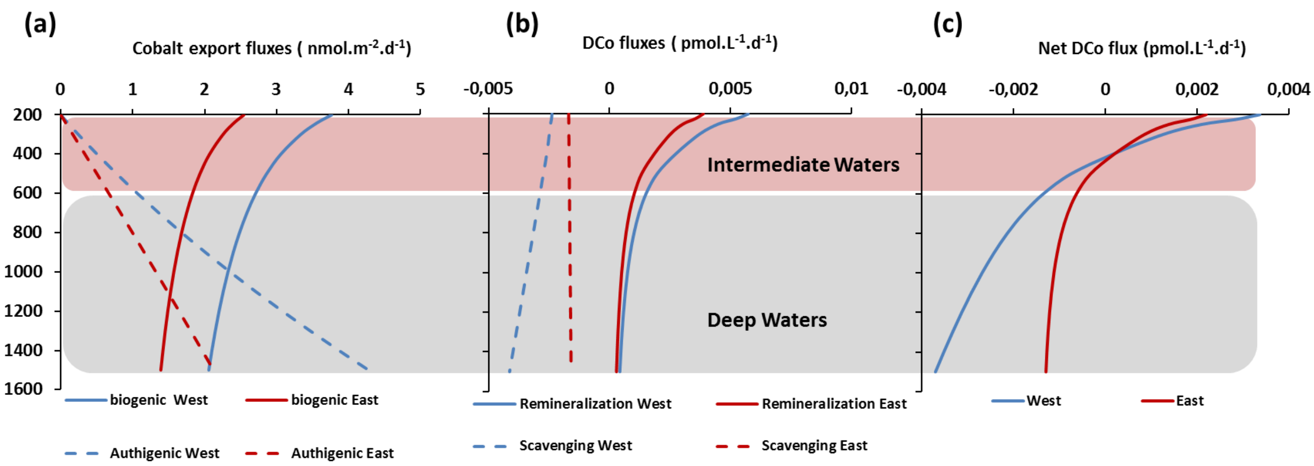

Figure S3. Output of the 1 dimensional biogeochemical model of Co remineralization and scavenging. **(a)** Vertical export fluxes of biogenic and authigenic particulate cobalt. **(b)** Scavenging and remineralization fluxes of DCo in the water-column of the Western basin and the Eastern basin. **(c)** Net biogeochemical DCo flux in the water-column (remineralization + scavenging) in the Eastern and Western Basins.

Sample	DCo measured (pM)	Consensus value
SAFe S	5.1 ± 2.2 (n =25)	4.8 ± 1.2
SAFe D1	42.3 ± 1.4 (n =15)	45.4 ± 4.7
SAFe D2	44.2 ± 1.7 (n =25)	45.7 ± 2.9
GEOTRACES S	29.8 ± 2.0 (n =35)	31.8 ± 1.1
GEOTRACES D	63.2 ± 2.3 (n =25)	65.2 ± 1.2

Table S1. Certified reference material measurement for dissolved cobalt

Total particulate trace elements quality control data						
Element	**Al**	**P**	**Mn**	**Fe**	**Co**	**Ti**
Isotope measured (For ICP-MS)	**27**	**31**	**55**	**56**	**59**	**47**
Certified Reference Material (CRM)—BCR-414						
µg/g after correction for digest blank	**GeoReM**	**GeoReM**	**BCR-Certified**	**BCR-Certified**	**BCR-Indicative**	**BCR-Certified**
BCR 414 value	**2454 ± 803.4**	**12840 ± 4978**	**299 ± 13**	**1850 ± 190**	**105 ± 25**	**105 ± 25**
Mean ± SD	**2393 ± 355.1**	**13837± 1879**	**265 ± 43**	**1745± 279**	**1.43 ± 1.22**	**97.83 ± 14.76**
recovery	**111%**	**108%**	**89%**	**94%**	**85%**	**93%**

Table S2. Certified reference material measurement for particulate trace elements

Sector	*Sub-Basin*	**Primary production $mgC.m^{-2}.d^{-1}$**	**Carbon export $mgC.m^{-2}.d^{-1}$**	**Phytoplankton/bacteria Dominant species**	**Reference**
West	*Alboran Sea*	610[a] 502 ± 243.5[b]	24.2 ± 9.4[b]	Diatoms, Synechoccocus, Prasinophytes, Cryptophytes[c]	[a]Bosc et al., 2004 [b]Sanchez-Vidal et al., 2005 [c]van de Poll et al., 2015
	Central	506.7 ± 243.5[d]	22.0 ± 13.1[d] 81 ± 96[f]	Synechoccocus Chorophytes & Pelagophytes[c]	[d]Moutin and Rimbault, 2002 [c]van de Poll et al., 2015 [f] Miquel et al., 2011
	Tyrrhenian Sea	375[a] 395[d]	7.4[d] 30-178[e]	N.D.	[a]Bosc et al., 2004 [d]Moutin and Rimbault, 2002 [e]Speicher et al., 2006
East	*Ionian Sea*	314[a] 318.1 ± 74.4[d]	11.8 ± 9.0[d]	Prochlorococcus[c]	[a]Bosc et al., 2004 [d]Moutin and Rimbault, 2002
	Levantine Basin	290[a] 210[c] ± 55 250[d]	9.5 ± 7	Prochlorococcus, Synechoccocus & Pelagophytes[c]	[a]Bosc et al., 2004 [d]Moutin and Rimbault, 2002; [c]van de Poll et al., 2015;
	South Aegean Sea	382.6[a]	10.8[e]	Prochlorococcus[c]	[a]Bosc et al., 2004 [c]Moutin and Rimbault, 2002 [e]Speicher et al., 2006

Table S3. Values of primary productivity and carbon export reported in the literature used in this study. Phytoplankton / bacteria dominant species are also indicated.