

CONTRASTING BIOGEOCHEMICAL CYCLES OF COBALT IN THE SURFACE WESTERN ATLANTIC OCEAN

Gabriel Dulaquais*¹, Marie Boye¹, Rob Middag^{2,3}, Stéphanie Owens⁴, Viena Puigcorbe⁵, Ken Buesseler⁴, Pere Masqué^{5,6,7}, Hein de Baar² and Xavier Carton⁸

¹ Laboratoire des Sciences de l'Environnement Marin UMR6539, Institut Universitaire Européen de la Mer, Technopôle Brest Iroise, Place Nicolas Copernic, 29280 Plouzané, France

² Department of Marine Chemistry and Geology, Royal Netherlands Institute for Sea Research, P.O. Box 59, 1790 AB Den Burg, The Netherlands

³ Department of Chemistry, University of Otago, P.O. Box 56, Dunedin 9054, New Zealand

⁴ Woods Hole Oceanographic Institution, Woods Hole, MA 02543-1050, USA

⁵ Institut de Ciència i Tecnologia Ambientals & Department of Physics, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

⁶ Oceans Institute & School of Physics. The University of Western Australia. 35 Stirling Highway, Crawley, WA 6009. Australia.

⁷ School of Natural Sciences and Centre for Marine Ecosystems Research, Edith Cowan University, Joondalup, WA, Australia

⁸ Laboratoire de Physique des Océans, Université de Bretagne Occidentale - UFR Sciences, 6 avenue Le Gorgeu, C.S. 93837, 29238 Brest Cedex 3, France

* corresponding author : G. Dulaquais, LEMAR UMR6539, 29280, FRANCE (gabriel.dulaquais@univ-brest.fr)

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/2014GB004903

Key points:

- The fluxes involved in the surface cycle of dissolved cobalt are assessed in the Western Atlantic Ocean
- The recycling can sustain the biological requirement for cobalt in subtropical domains
- The atmospheric and Amazon inputs affect the cobalt distribution

Abstract

Dissolved cobalt (DCo; $< 0.2\mu\text{m}$; 14 to 93 pM) and the apparent particulate cobalt (PCo; $> 0.2\mu\text{m}$; < 1 to 15 pM) were determined in the upper water-column (< 1000 m) of the Western Atlantic Ocean along the GEOTRACES-A02 section (64°N to 50°S). The lowest DCo concentrations, typical of a nutrient-type distribution were observed in surface waters of the subtropical domains. Strong linear relationships between DCo and phosphate (P) as well as meridional gradients of decreasing DCo from high latitudes were characterized and both linked to the Co biological requirement. External sources such as the Amazon and the atmospheric deposition were found to contribute significantly ($> 10\%$) to the DCo stock of the mixed layer in the equatorial and north subtropical domains. Biotic and abiotic processes as well as the physical terms involved in the biogeochemical cycle of Co were defined and estimated. This allowed establishing the first global budget of DCo for the upper 100 m in the Western Atlantic. The biological DCo uptake flux was the dominant sink along the section, as reflected by the overall nutrient-type behavior of DCo. The regeneration varied widely within the different biogeochemical domains, accounting for 10% of the DCo-uptake rate in the subarctic gyre and for up to 85% in southern subtropical domain. These findings demonstrated that the regeneration is likely the prevailing source of DCo in the surface waters of the Western Atlantic, except in the subpolar domains where physically-driven sources can sustain the DCo biological requirement.

Index terms: Biogeochemical cycles, processes and modeling, Nutrient and nutrient cycling, Trace elements, Descriptive and regional oceanography.

Keywords: Cobalt, Biogeochemistry, Atlantic, Chemical oceanography, GEOTRACES

1 Introduction

Cobalt (Co) is an essential trace nutrient required as the central atom of vitamin B₁₂ (cobalamin) [Bertrand *et al.*, 2007]. Cobalt can also substitute for zinc involved as a co-factor in the carbonic anhydrase and the alkaline phosphatase that are essential for the acquisition of inorganic carbon and dissolved organic phosphorus by phytoplankton, respectively [Lane and Morel, 2000; Gong *et al.*, 2005]. Cobalamin is also used by bacteria and archaea for anaerobic processes such as fermentation or dehalogenation [Swanner *et al.*, 2014 and reference therein]. Moreover cyanobacteria like *Prochlorococcus sp.*, which often dominate the picophytoplankton assemblage and account for a significant proportion of the primary production in oligotrophic regions, have an absolute requirement for Co [Campbell *et al.*, 1994; Sunda and Huntsman, 1995; Saito *et al.*, 2002]. The elemental compositions of

phytoplankton also suggest that Co is an important micronutrient for the coccolithophorids, diatoms and dinoflagellates [*Ho et al.*, 2003].

Previous studies have reported a nutrient-type distribution of dissolved cobalt (DCo) in surface waters of oligotrophic and temperate domains [*Martin et al.*, 1993; *Saito and Moffett*, 2002; *Jakuba et al.*, 2008; *Noble et al.*, 2008], which is related to its biological uptake by cyanobacteria [*Saito et al.*, 2002; *Saito and Moffett*, 2002; *Bown et al.*, 2011]. Other surface distribution patterns have been observed, notably a nearly conservative-type behavior in the Southern Ocean associated with a low biological uptake of DCo by the Antarctic diatoms [*Bown et al.*, 2011].

Previous field studies have reports a correlation between DCo and the macronutrient phosphate (P) in surface waters of different biogeochemical domains, indicative of their proportional biological uptake [*Saito et al.*, 2004; *Noble et al.*, 2008; *Saito et al.*, 2010; *Bown et al.*, 2011]. Those studies also showed that the DCo/P depletion ratio varied between the oceanic domains, potentially reflecting differences in the phytoplankton assemblage and productivity, as well as regional variations in the input of DCo (and/or P). Thus, this comprehensive survey of DCo distributions across oceanic provinces will also increase our understanding of the coupling between DCo and P in the surface waters.

Previous estimates suggested that biological uptake is the prevailing sink of DCo in oligotrophic waters [*Saito et al.*, 2002; *Bown et al.*, 2011]. Indeed, biological uptake can be significantly higher than other removal mechanisms of DCo from surface waters such as co-oxidation with manganese through microbial oxidation [*Moffett and Ho*, 1996; *Saito et al.*, 2004] or export by adsorption (scavenging) on settling particles [*Bown et al.*, 2011]. An indirect estimate suggested that recycling of Co in surface waters due to abiotic processes, microbial loop, cell lysis, and grazing, could sustain up to 70-90% of the DCo biological uptake in the subtropics of the southeastern Atlantic [*Bown et al.*, 2011]. However, the terms that drive the internal cycle of DCo in the upper ocean need to be better assessed, notably the regeneration flux of DCo in surface waters, considering its potential importance in the Co cycle.

Among the external sources, the deposition of dust from the Patagonian and the Sahara deserts has been shown to be an important source of Co in the surface waters of the southwestern Atlantic and the central-northern Atlantic, respectively [*Gaiero et al.*, 2003; *Baker et al.*, 2007]. For example, the relative DCo maximum observed in sub-surface waters of the Sargasso Sea has been related to significant atmospheric Co input during the late summer [*Shelley et al.*, 2012]. In other regions, the atmospheric deposition is likely

negligible, such as the southeastern Atlantic [Bown *et al.*, 2011] and south-central Atlantic [Noble *et al.*, 2012]. However, there are still large uncertainties in estimates of the atmospheric deposition of Co in the surface waters, due to the limited data on the fractional solubility of Co in aerosols and on the elemental compositions of the dust that vary depending on their provenance. By taking into account some of this spatial variability, our study reassesses the atmospheric deposition of Co in the Western Atlantic.

The observation of an inverse linear relationship between DCo and salinity in the northwestern Atlantic [Saito and Moffet, 2002] and the western Equatorial Atlantic [Tovar-Sanchez and Sañudo-Whilhelmy, 2011] suggest that freshwater may be another external source of DCo in the surface Western Atlantic. For instance, the Amazon River represents a significant source of many elements to the western Equatorial Atlantic [Boyle *et al.*, 1982], however its importance to DCo needs to be better constrained. Recent work has also hinted at the importance of lateral advection of water masses enriched in DCo following contact with continental margins in the southeastern Atlantic [Bown *et al.*, 2011] and of the diffusion from intermediate waters in the frontal areas of the Western Atlantic [Dulaquais *et al.*, 2014]. With only a first, tentative budget made for the southeastern Atlantic and the Southern Ocean [Bown *et al.*, 2011], the sources and biogeochemical cycle of Co are still poorly constrained in the surface waters.

Despite these major advances, the oceanic behavior of DCo in the surface waters is still not well understood, with little data on DCo distribution in the global ocean. In this respect, a survey along a large radial in the entire Western Atlantic Ocean was considered to be an ideal scheme to observe the changes in the surface vertical distribution of DCo across contrasting biogeochemical domains. In this study we investigate the meridional distributions of DCo and the apparent particulate cobalt (PCo) in the upper 1000 meters along a section in the Western Atlantic Ocean. Spanning from the East coast of Greenland (64°N) to the Malvinas Plateau (50°S) the radial encountered several biogeochemical domains. Two oligotrophic subtropical areas, the equatorial zone, and the subpolar and subantarctic latitudes in the extremities of the section were crossed. The distribution of Co is discussed in the context of the biogeochemical and physical features of the domains and the external inputs from the atmosphere and the Amazon in order to determine the various sources and sinks of Co. The coupling of Co with the macronutrient P and the potentially significant role of Co regeneration in surface waters of the Western Atlantic are also discussed. By parameterizing

the different processes involved in the Co cycle, a tentative budget for Co in the upper 100 meters is presented on the scale of the individual domains and the Western Atlantic basin.

2 Method

2.1 Cruise track and sampling

Seawater samples were collected during four cruises along the GEOTRACES-A02 section spreading from 64°N to 50°S in the Western Atlantic Ocean that were conducted between 2010 and 2012 (Figure 1). A total of 47 stations with a vertical resolution of 6-10 depths between 9 m and 1000 m were sampled for dissolved cobalt analyses (DCo), and 15 stations for total (unfiltered) cobalt determinations (TCo). The apparent particulate cobalt concentrations (PCo) were calculated by subtraction of DCo from TCo. The complete dataset of cobalt (dissolved, total, and apparent particulate) at all stations is available at the international GEOTRACES datacenter (<http://www.bodc.ac.uk/geotraces/>).

Samples were collected using the TITAN-CTD frame [*de Baar et al.*, 2008] of NIOZ (Netherlands), with 24 ultra-clean sampling bottles of 24.4 L each made of PVDF plastic [*Rijkenberg et al.*, 2014]. The frame was placed in a Class-100 container for sub-sampling [*de Baar et al.*, 2008]. Unfiltered samples were transferred into acid cleaned 250 ml Nalgene[®] LDPE bottles for TCo analyses. The samples for DCo analyses were collected after filtration using 0.2 µm Sartobran[®] 300 (Sartorius) cartridges under pure N₂ pressure (filtered 99.99% N₂, 0.7 atm) in acid cleaned 250 ml or 500 ml Nalgene[®] LDPE bottles. All samples were acidified using ultrapure HCl[®] (Merck, 0.01M) immediately after their collection. Then the acidified samples were stored in double bags in the dark and at ambient temperature, before later analyses in the shore-based laboratory.

2.2 Analytical method for cobalt analyses

2.2.1 Method

Prior to the analyses, the samples were UV-digested [*Saito and Moffett*, 2002; *Shelley et al.*, 2010] for 3 h in acid clean silica tubes using a 600 W high-pressure mercury vapor lamp [*Bown et al.*, 2011; *Dulaquais et al.*, 2014], and left for an equilibration time of 48 h. Dissolved and total cobalt concentrations were determined by Flow-Injection Analysis (FIA) and chemiluminescence detection following the method adapted from *Shelley et al.* [2010], as described in *Bown et al.* [2011] and *Dulaquais et al.* [2014]. The system consists of one 10-

ports injection valve (VICI valves from VALCO instruments) which operates as an autosampler, and of two micro-electronically actuated injection valves (VICI valves from VALCO instruments) to inject the sample and the reagents using Tygon® tubes. The flow injection is provided by a peristaltic pump (205 CA, Watson Marlow).

The reagents are prepared with trace metals quality reagents under a laminar flow hood (ADS Laminaire, ISO 5 class) with ultrapure water (MiliQ, 18.2 mΩ) the day before the analysis and kept at room temperature for an overnight equilibration [Dulaquais *et al.*, 2014].

The sample were buffered online with ammonium acetate (0.3 M, ACS Reagents), and loaded on an IDA-Toyopearl chelating resin to preconcentrate the cobalt contained in each sample. Then a HCl solution (0.1 M, Suprapur® Merck) was injected through the column to elute Co. The eluate was warmed in a 60 °C thermostatic bath. The detection system consists of a photomultiplier detector (Hamamatsu, H9319 Series). The injection valves and the photomultiplier detector are operated on a laptop computer by a modified Labview® 8.4 interface (E. Duvieilbourg and M. Boye, LEMAR). The electrical devices are connected to a modulator of current (ELLIPSEMAX 600, MGE/UPS Systems).

The Co concentrations were calibrated against two calibration lines made with standard additions of cobalt of 0, 12.5, 25, 50, 75 and 100 pM to seawater, and performed before and after each series of 8 or 12 samples. TCo and DCo concentrations are based on triplicate analyses of each sample using the mean peak height of the chemiluminescent signal, and they are corrected with respect to blank analyses. Two to four reagent blanks including the buffer blank were analyzed per series of 8-12 samples at the beginning and at the end of the series, in acidified MilliQ water instead of the sample [Bowie and Lohan, 2009; Bown *et al.*, 2011].

The final standard deviation of the measurement is calculated by propagating the uncertainties on blanks, the calibration curves and the deviation of the triplicate analyses. A t-test was applied to verify that the difference between TCo and DCo is significant to allow reliable estimation of PCo concentration. The standard error on PCo is calculated by combining uncertainties of DCo and TCo measurements ($SD_{PCo} = (SD_{DCo}^2 + SD_{TCo}^2)^{0.5}$).

2.2.2 Analytical performance

The mean reagent blank (based on all blank determinations) was 4.2 ± 2.1 pM of Co in MilliQ (n = 180). The limit of detection of the method estimated as three times the standard deviation of the mean reagent blank was thus 6.3 pM of Co (n = 180). Each series of samples was validated by running samples previously collected during the Sampling and

Analysis of Iron (SAFe) program or the GEOTRACES program, following the same procedure as describe above. The DCo concentrations we measured in the SAFe and GEOTRACES reference-samples were in excellent agreement with the consensus values (Table 1, www.geotraces.org). The analytical precision of the method was determined from repeated analyses of the surface GEOTRACES (GS) reference-sample, yielding an uncertainty of $\pm 3.8\%$ expressed as relative standard deviation on the mean ($n = 15$). Despite our agreement with the consensus values, some new concerns have recently emerged regarding possible losses of DCo due to storage protocol. Some underestimation of DCo could indeed result from storage of non-acidified samples collected in low O_2 and/or high dust environments; this effect should be minor for samples from the South Atlantic and similar regions, but may be more pronounced for North Atlantic samples due to the very high dust loads (Mak Saito, WHOI, personal communication). Additional work should be done to further assess this potential storage artifact, especially when the samples are acidified before storage as we have done for our samples and the GEOTRACES and SAFe reference samples.

2.3 Hydrography

Hydrological parameters (salinity (S), temperature (T), dissolved oxygen (O_2), conductivity, fluorescence and turbidity) were measured using a SBE9+ underwater sensor, a SBE3+ thermometer ($\pm 0.001^\circ\text{C}$), a SBE4 conductivity sensor ($\pm 0.3 \text{ mS}\cdot\text{s}^{-1}$), a SBE43 dissolved oxygen sensor ($\pm 2\%$), a Chelsea Aquatracka MKIII fluorometer ($\pm 0.2\mu\text{g}\cdot\text{l}^{-1}$), and a Wetlabs C-Star transmissiometer ($\pm 0.02\%.\text{C}^{-1}$).

2.4 Macronutrients analysis

Seawater samples for nutrient analysis were collected the ultra-clean sampling bottles (PVDF) describe above and transferred to 125 ml polypropylene bottles. All the nutrients were analyzed onboard by colorimetric methods following the methods of *Murphy and Riley* [1962] for phosphate (PO_4^{3-}), *Strickland and Parsons* [1968] for silicate ($\text{Si}(\text{OH})_4^-$), and *Grasshoff et al.* [1983] for nitrate (NO_3^-) and nitrite (NO_2^-). The detection limits of the methods (3σ after 24 analyses of the same sample) were 18 nM for phosphate, 252 nM for silicate, 190 nM for nitrate, and 3 nM for nitrite [van Ooijen, 2010].

3 Results

3.1 Dynamical features

The different surface physical features along the section are presented on Figure 1. In the North, the section crossed the Sub-Arctic Gyre (SAG) between 64°N and 50°N, where the Labrador Sea Water (LSW) dives to form, with the Arctic Bottom Water, the Western North Atlantic Deep Water (WNADW). In this area, the surface currents (East Greenland Current (EGC) and Labrador Current (LC) induce a mean southward flow. The well oxygenated and dense waters of the subarctic gyre are separated, in the south, by the North Subtropical Front (NSTF) at ~ 45°N from the relatively low-oxygenated, saline and warm waters of the North Atlantic Subtropical Gyre (NASG). The NSTF is characterized by high temperature anomaly (+ 5°C) and by a strong eastward geostrophic current in surface waters (data not shown), likely the North Atlantic Drift [Reid, 1994], known for its important role on climate regulation [Minobe *et al.*, 2010].

In the NASG, low-density waters occur in the top 600 meters due to relatively high salinity and temperature ($S > 35$, $T > 10^{\circ}\text{C}$; Figure 2). However at 15°N and to a lesser extent at 4°N these saline waters were covered by relatively fresh waters (Figure 2, $32.1 < S < 34.9$), originating from the Amazon plume. The waters influenced by the Amazon plume were also characterized by high Si:N ratio (Figure 3c).

Leaving the NASG southwards, the section enters the equatorial area. Here the zonal geostrophic velocities (not shown) indicate the presence of several surface and subsurface jets (Figure 1). The North Equatorial Current (NEC, at 5-10°N), the North Equatorial Counter-Current (NECC, at ~ 3°N; $0.2 \text{ m}\cdot\text{s}^{-1}$), the South Equatorial Current (SEC, at 5-10°S) and the South Equatorial Under-Current (SEUC, at ~5°S, $0.12 \text{ m}\cdot\text{s}^{-1}$ 200 m depth) [Peterson and Stramma, 1991; Stramma and England, 1999] can thus be located. The equatorial domain is bordered by the NEC in the North and by the SEC in the South, both of which were characterized by westward surface geostrophic propagating vectors and similar speed (respectively 0.15 and $0.2 \text{ m}\cdot\text{s}^{-1}$). A mean flow toward the northwest, the north Brazil current (NBC), results from these equatorial surface currents. This equatorial current system supplies eddies to the northern subtropical domain [Oschlies and Garçon; 1998]. Additionally under these surface currents, an oxygen minimum zone (OMZ; $\text{O}_2 < 150 \mu\text{M}$) was also observed between 150 and 600 meters (Figure 2c). Part of this low O_2 -signature was due to the advection of the poorly oxygenated Atlantic Central Waters ($\text{O}_2 < 50 \mu\text{M}$; Noble *et al.*, [2012]), flowing westward from the African shelf across the Atlantic basin.

Southward the section enters into the South Atlantic Subtropical Gyre (SASG). South of the SASG, in addition to strong eddy activity in this area as observed in the geostrophic current field, the Malvinas-Brazil confluence (MBC), an eastward jet resulting from the Brazil current (BC) flowing southward and the Malvinas current (MC) flowing northward, can be located in the Argentine basin at around 40°S (e.g.; at station 6b; geostrophic data not shown). The saline and relatively oxygen-poor waters of the MBC separate the SASG from the Sub-Antarctic Waters (SAW). At depth the Drake Antarctic intermediate waters (D-AAIW) are flowing northward in the southern part of the section.

3.2 Biogeochemical provinces

The different biogeochemical domains characterized along the section (Figure 3) were mostly delineated by the frontal and jet systems described above (Figure 1). The surface waters of the SAG were marked by relatively high phosphate and nitrate concentrations ($\text{NO}_3^- > 10 \mu\text{M}$, data not shown; $\text{PO}_4^{3-} > 0.8 \mu\text{M}$). Furthermore the Chlorophyll *a* levels observed in the southern side of the SAG and lower nutrients concentrations (e.g.; $\text{Chl } a = 1.9 \mu\text{g}\cdot\text{L}^{-1}$, $\text{NO}_3^- < 1\mu\text{M}$, $\text{PO}_4^{3-} < 0.2\mu\text{M}$ at St.#10-49°N, 24 m depth, Figure 3) suggested the occurrence of a phytoplankton bloom. In the upper 100 m of the two subtropical domains the extremely low nutrients concentrations (such as observed in the NASG: $\text{PO}_4^{3-} < 0.5 \mu\text{M}$; $\text{NO}_3^- < 5 \mu\text{M}$, $\text{Si} < 5 \mu\text{M}$) and the sub-surface Chlorophyll *a* values ($\text{Chl } a. < 0.03 \mu\text{g/L}$, Figure 3d) were characteristic of oligotrophic conditions. In these domains, the N/P ratios were generally below the Redfield ratio in the upper 100 m waters (Figure 3b) suggesting that nitrogen might be more limiting than phosphorus. However a greater depletion of nitrogen relative to phosphate was observed in the upper 300 m of the SASG ($\text{N:P} < 10$) compared to the NASG ($\text{N:P} > 25$; Figure 3b; [Dulaquais et al., 2014]) likely due to a greater proportion of N_2 -fixers, such as diazotrophic cyanobacteria, in the NASG than in the SASG [Mather et al., 2008]. In the equatorial area, low nutrients concentrations were observed in the upper-100 m ($\text{NO}_3^- < 0.8 \mu\text{M}$; $\text{PO}_4^{3-} < 0.1 \mu\text{M}$; $\text{Si} < 1.3 \mu\text{M}$), whereas high concentrations of nitrate and phosphate ($\text{NO}_3^- > 34 \mu\text{M}$; $\text{PO}_4^{3-} > 2.3 \mu\text{M}$) and low levels of silicate ($5 \mu\text{M} < \text{Si} < 15 \mu\text{M}$) were recorded at intermediate depths due to the incursion of the Atlantic Central Waters [Dulaquais et al. 2014]. In this area, the Chl-*a* levels were similar to those recorded in the oligotrophic domains. South of the MBC, the influence of the AAIW and upper circumpolar deep waters (UCDW) generated a southward gradient of nutrients in the top-1000 meters layer (Figure 3a) with increasing concentrations southward. Relatively high nutrient

concentrations were generally observed in the top-200 meters depths ($\text{NO}_3^- > 20 \mu\text{M}$; $\text{PO}_4^{3-} > 1.2 \mu\text{M}$; $\text{Si} > 15\mu\text{M}$). In the southern latitudes of the section, the Chl-*a* concentrations $> 0.5 \mu\text{g.L}^{-1}$ and the high levels of nitrite ($\text{NO}_2^- > 0.16 \mu\text{M}$) observed in the upper-100 meters layer, associated with the depletion of silicate levels ($\text{Si} < 1.2 \mu\text{M}$) and the low Si:N ratio (< 0.2) (Figure 3c), hinted at the final stages of a diatom bloom.

3.3 The distributions of cobalt in surface waters of the Western Atlantic

The meridional and vertical distributions of DCo and PCo are presented in the upper 1000 meters along the section in Figure 4. Dissolved cobalt concentrations ranged from 14.7 ± 1.4 to 93.3 ± 3.3 pM along the section and mostly follow a nutrient-like behavior in the upper 1000 meters (Figure 4a). The lowest concentration was observed in surface waters of the SASG (e.g.; at 9 m depth at St.#11b-26°S) whereas the highest were recorded in the OMZ of the equatorial area (e.g.; at St.#15b-9°S at 290 m depth). The vertical distributions of PCo generally exhibited higher concentrations in the subsurface and decreasing concentrations with depth (Figure 4b). PCo concentrations ranged from near undetectable values to 15.2 ± 2.3 pM (e.g.; at St.#5c -50.8°N at 761 m depth). The relative proportion of PCo to TCo (Figure 5a) ranged from less than 5% at several stations in the intermediate waters (250-1000 m) to up to 34 % (at St.#26-25 m depth), with a mean of 12 ± 12 % ($n = 76$), indicating that cobalt was primarily present in the dissolved fraction. Furthermore the relative proportion of PCo co-varied with the Chl *a* distribution (Figures 5a-b).

Distinct vertical distributions of DCo were observed in the surface waters of the different biogeochemical domains (Figures 6). At the highest latitudes of the northern subarctic gyre, high DCo concentrations were measured (about 60 - 70 pM; Figures 4a and 6a). Here the particulate cobalt was howed similar in terms of concentration and vertical distribution to those observed by *Weinstein and Moran* [2004], with relative PCo maxima in the sub-surface (ranging from 5.9 ± 1.0 to 10.4 ± 2.0 pM), and decreasing concentrations with depth (Figure 6f). In the southern side of the SAG, high PCo concentrations were observed in the Chl-*a* maximum (at St.#11; 25 m PCo = 8.2 pM). Lower DCo concentrations were detected in surface waters of this region (Figure 6a) in August 2012 during Leg-4 (e.g., mean $\text{DCo}_{25\text{m}} = 43.2 \pm 1.6$ pM $n = 2$) compared to measurements in samples collected in April 2010 during Leg-1 (e.g.; mean $\text{DCo}_{25\text{m}} = 64.6 \pm 5.4$ pM at 25 m $n = 4$).

D_{Co} was depleted in the surface waters of both subtropical domains and its concentration increased with depth below the nutricline, featuring a nutrient-like distribution (Figures 4a and 6b,d). The concentrations of D_{Co} were slightly lower in the SASG (mean D_{Co}_{f100m} = 24 ± 5 pM) compared to those recorded in the NASG (mean D_{Co}_{f100m} = 33 ± 8 pM). Furthermore the P_{Co} distribution also showed, like D_{Co}, lower concentrations in the subsurface waters of the SASG (< 5 pM; Figure 6i) compared to the NASG (> 5 pM; figure 6g). Additionally relative maxima of D_{Co} were observed at about 10 m depth at a few stations in the NASG (as exemplified for station 26, Figure 6b).

In the equatorial area, the D_{Co} distribution was characterized by low concentrations in the top 100 m (mean D_{Co}_{f100m} = 30 ± 9 pM, n = 44) and a sharp increase between 100 and 250 m (mean D_{Co}_{f100-250m} = 62 ± 13 pM, n = 10), that continued to increase to reach maximum values at about 400 meters depth (mean D_{Co}_{f250-400m} = 73 ± 10 pM, n = 19) (Figures 4 and 6c). These maximum concentrations were the highest values recorded along the section, reaching values up to 93.3 ± 3.3 pM (at 9°S), and strongly correlated with the oxygen depletion ($\Delta D_{Co}/\Delta O_2 = -0.28 \mu M/M$, $R^2 > 0.66$) as reported by *Dulaquais et al.*, [2014]. The distribution of P_{Co} in this equatorial domain was similar to that observed in the other domains, with relatively high concentrations in surface waters (P_{Co} > 5 pM, Figure 6h), reaching a maximum value of 10.2 ± 2.1 pM observed at 10 m at St.#40 (1.15°N).

South of the Brazil-Malvinas confluence, in the subantarctic waters, a surface southward increasing gradient of D_{Co} was observed (Figure 4a), and the vertical distribution of D_{Co} showed nutrient distribution in the upper 200 meters, below which the concentrations were relatively constant. At these latitudes, the highest D_{Co} concentrations were recorded in the core of D-AAIW (100-600 m; Figure 6e).

4 Discussion

With the aim to better constraining the biogeochemical cycle of cobalt in the surface Western Atlantic, regional variability in the D_{Co}:P relationship is discussed and key fluxes, conceptualized in Figure 7, are estimated. We propose an estimate of the regeneration rate of D_{Co} in surface waters due to a combination of abiotic processes, the microbial loop, cell lysis, and grazing. We also evaluate the external inputs of Co from the atmosphere and the Amazon River to the surface Western Atlantic. Surface (100 m) Co budgets are proposed the different biogeochemical domains of the Western Atlantic.

4.1 Internal cycle of dissolved cobalt in the surface Western Atlantic

4.1.1 The dissolved cobalt and phosphate relationship

The vertical distribution of DCo was nutrient-like, akin to the macronutrient phosphate (P) in the oligotrophic and tropical surface waters (Figure 4a). Strong linear correlations between DCo and P have been previously reported in the surface waters of subtropical regions in the South Pacific [Ellwood, 2008], the north-east Pacific [Sunda and Huntsman, 1995], the North Atlantic [Martin *et al.*, 1993] and the Sargasso Sea [Saito and Moffett, 2002, Jakuba *et al.*, 2008], as well as in other oligotrophic systems [Saito and Moffett, 2002; Bown *et al.* 2011], or in upwelling [Saito *et al.*, 2004], in eddies near islands [Noble *et al.*, 2008], and in Antarctic waters of the Ross Sea [Saito *et al.*, 2010]. These correlations suggested that the biological uptake of DCo is proportional to that of P in the surface waters [Jakuba *et al.*, 2008; Noble *et al.*, 2008; Bown *et al.*, 2011]. Along the section sampled here, when all the data are considered, a linear relationship between DCo and P concentrations was also obtained in the surface layer (0-250 m) providing a mean DCo:P slope of $23.1 \mu\text{M M}^{-1}$ ($R^2 > 0.53$, $n = 231$; Figure 8a). However, the slopes of DCo:P correlations varied across the different biogeochemical domains crossed along the section (Figure 8b), with the highest DCo:P slopes observed in the two subtropical domains ($> 50 \mu\text{M.M}^{-1}$). These regional differences in DCo:P could reflect differences in phytoplankton assemblages between the domains, since a wide range of internal Co:P cellular quota have been reported for different phytoplankton species [Ho *et al.*, 2003; Cullen *et al.*, 2003; Tovar-Sanchez *et al.*, 2006; Twining *et al.*, 2011; Twining and Baines, 2013]. Other factors could account for the regional differences in DCo:P ratios, including differences in the surface regeneration rate, external sources, and/or physical processes [Noble *et al.*, 2008].

A mean DCo:P slope of $31.2 \mu\text{M M}^{-1}$ ($R^2 = 0.78$; $n = 28$) was found in the surface Subarctic gyre (Figure 7b), which is similar to the slope previously observed at high latitudes, as exemplified in the Ross Sea (e.g., $37.6 \mu\text{M M}^{-1}$; Saito *et al.* [2010]). The DCo:P slopes did not vary significantly in surface waters of the SAG despite a southward decrease of DCo concentrations (Figure 4a & 8b). Diatoms may dominate the phytoplankton assemblage at the highest latitudes of the SAG [Parsons and Lalli, 1988], whereas coccolithophorids were probably blooming in the southern side of this domain during spring [Okada & McIntyre, 1979; Head *et al.*, 2000; Gregg & Casey, 2007]. Diatoms have a lower cellular Co:P quota ($60\text{-}150 \mu\text{M M}^{-1}$) compared to coccolithophorids ($300\text{-}360 \mu\text{M M}^{-1}$) [Ho *et al.*, 2003; Cullen *et al.*, 2003; Tang and Morel, 2006; Twining *et al.*, 2011] that have an higher biological

requirement for Co [Sunda and Huntsman, 1995]. In turn, it is possible that strong biological uptake of DCo (and P) by blooming coccolithophores could have caused the depletion of DCo observed in the southern section of the SAG. The invariance of the DCo:P slope in this domain suggests that additional processes, such as the lateral advection, may account for the observed correlation. The seasonal decrease of the DCo surface concentrations observed in this area between April 2010 ($\text{DCo}_{\text{upper } 250\text{m}} = 66 \text{ pM}$ at St.# 6- 58.6°N) and August 2012 ($\text{DCo}_{\text{upper } 250\text{m}} = 55.1 \text{ pM}$ at St.#3c-57.2°N, Figure 6a) fits with the observed formation of the shallow pycnocline or thermocline at the end of spring which can promote the coccolithophorid bloom [Head et al., 2000].

At the high latitudes of the southern hemisphere, the lowest DCo:P slope of $21.5 \mu\text{M M}^{-1}$ ($R^2 = 0.79$; $n = 22$; Figure 8b) was observed in the subantarctic waters. This slope might reflect the low Co:P cellular quota of diatoms [Twining et al., 2011] which probably dominate in this area [Ferreira et al., 2013; Browning et al., 2014]. In addition the high productivity of this area [Field, 1998] may have significantly reduced the DCo stock close to the MBC (Figure 4a), in spite of a low Co biological requirement by diatoms [Sunda and Huntsman, 1995]. A southward shift between the surface gradient of DCo and dissolved zinc (DZn) in subantarctic waters [Croot et al., 2011, Middag et al, unpublished data] suggests a southward decrease of DCo uptake by diatoms when DZn becomes non-limiting. Indeed, diatoms are known to preferentially assimilate Zn compared to Co [Sunda and Huntsman, 1995].

The equatorial domain was characterized by a low DCo:P slope of $\sim 27 \mu\text{M M}^{-1}$ ($R^2 > 0.87$; $n = 51$; Figure 8b). It contrasts with the extremely high DCo:P slope ($> 560 \mu\text{M M}^{-1}$) reported at similar latitudes but in the Central Atlantic [Saito and Moffett, 2002]. However it may be difficult to compare these ratios since the latter was obtained with subsurface samples (5 meters depth only), and close to the African coast. In that area, DCo probably accumulated at the subsurface notably due to dust dissolution, which would increase the DCo:P slope. In the western Equatorial region, the plankton assemblage could be dominated by both the cyanobacteria *Richelia intracellularis* and the diatom *Pseudonitzschia* during summer (June-July) [Tovar-Sanchez et al., 2006]. The DCo:P slope recorded in this area ($27.1 \mu\text{M M}^{-1}$) was similar to the cellular Co:P mean quota determined for the bulk of these species ($31 \mu\text{M M}^{-1}$; Tovar-Sanchez et al., [2006]) suggesting that the biological uptake of DCo and P by cyanobacteria and diatoms can drive their concentrations and ratio. The low DCo:P observed

in the surface waters of the Equatorial domain may also be accounted for by vertical diffusion fluxes from intermediate waters of relatively low DCo:P ($23.1 \mu\text{M M}^{-1}$ between 250 and 600 m depths) [Dulaquais *et al.*, 2014].

The highest DCo:P slopes were observed in the subtropical areas (Figure 8b), with the highest mean value being observed in the Sargasso Sea (DCo:P $> 65.8 \mu\text{M M}^{-1}$; $R^2 > 0.65$; $n = 32$; Figure 8b). Combined with the low DCo concentrations recorded (Figure 4a), it suggests strong biological uptake of DCo in the subtropical provinces. The ratios observed in this study were in the same range, although slightly higher, than those previously reported in other oligotrophic regions [Saito and Moffett, 2002; Noble *et al.*, 2008; Jakuba *et al.*, 2008; Bown *et al.*, 2011, Twining and Baines, 2013]. The cyanobacteria *Prochlorococcus sp.* and *Synechococcus sp.*, which dominate the picophytoplankton assemblage in oligotrophic regions, have an absolute cobalt requirement for growth [Saito *et al.*, 2002] and thus assimilate Co leading to the low DCo concentrations recorded in these domains (Figure 4a). Furthermore, the high DCo:P observed in these oligotrophic waters are consistent with the high Co:P cellular ratios reported in phytoplankton bulk dominated by *Prochlorococcus sp.* and *Synechococcus sp.* from the Eastern Atlantic [e.g.; $260 \mu\text{M M}^{-1}$; Tovar-Sanchez *et al.*, 2006].

Significantly lower P concentrations were recorded in the NASG (mean $0.07 \mu\text{M}$) compared to the SASG (mean $0.19 \mu\text{M}$) in the upper 250 m. The alkaline phosphatase activity of the biota could be enhanced at nanomolar concentrations of P [Ji and Sherrell, 2008], as reported in the Sargasso Sea and thus the biological uptake of DCo would also be higher [Sunda and Hunstman, 1995; Jakuba *et al.*, 2008]. Thus it is possible that Co was used more intensely in the NASG, likely contributing to the higher DCo:P there ($65.8 \mu\text{M M}^{-1}$) compared to the SASG ($52.5 \mu\text{M M}^{-1}$). = The higher atmospheric input of Co in the northern hemisphere (Figure 10) also likely caused an accumulation of DCo relative to P in the NASG (Figure 4c) and thus higher DCo:P ratios.

Overall, the regional DCo:P slopes were generally lower than Co:P cellular ratios of the dominant phytoplankton species suggesting that other processes were occurring in addition to biological uptake in surface waters.

4.1.2 Biological uptake and regeneration rate of dissolved cobalt in surface waters as exemplified at the BATS station

The cellular quotas of Co:P reported for the dominant phytoplankton functional groups potentially present in the different biogeochemical domains along the section were significantly higher than the corresponding DCo:P slopes we measured in the surface waters except in the Equatorial region (Figure 8b) [Ho *et al.*, 2003; Cullen *et al.*, 2003; Tang and Morel, 2006; Tovar-Sanchez *et al.*, 2006; Twining *et al.*, 2011; Twining and Baines 2013]. For instance, DCo:P in the upper 250 meters of the Sargasso Sea ($65.8 \mu\text{M M}^{-1}$) was four times lower than the cellular Co:P quota of the predominant cyanobacteria (e.g.; $260 \mu\text{M M}^{-1}$; as reported in a bulk of *Prochlorococcus sp.* and *Synechococcus sp.* in the Eastern Atlantic; Tovar-Sanchez *et al.*, [2006]). Because the apparent biological use of DCo relative to P did not match the cellular quotas, the stoichiometric DCo:P slopes should thus reflect a combination of the several sinks and sources terms, such as regeneration in surface waters, in addition to the biological uptake. Hence, the DCo:P measured in the Sargasso Sea was used to discriminate the terms and to estimate the regeneration rate of DCo. The biological uptake rate of DCo by the cyanobacteria, that presumably dominate the phytoplankton assemblage in these waters, was estimated in the top-100 meters (Table 2). The biomass was derived from the *in situ* Chl-*a* (fluorescence) measurements, and literature values were used for growth rate of cyanobacteria in the Sargasso Sea and their Co/C cellular quota (Equation 1, and references therein). We estimated a Co:C cellular quota of $2.16 \pm 0.7 \mu\text{M M}^{-1}$ for cyanobacteria, which is in agreement, considering the relative error, with the Co:C ratio reported in particulate matter of Sargasso Sea ($1.5 \pm 0.6 \mu\text{M M}^{-1}$; Sherrell and Boyle [1992]) and the Co:C cellular quota of *Synechococcus sp.* ($1.43 \mu\text{M M}^{-1}$; Sunda and Hunstman [1995]) grown in zinc-depleted conditions similarly to surface waters of the Sargasso Sea [Bruland and Frank, 1983]. In our approach, the scavenging process could not be discerned from the biological uptake. The co-variation between the relative proportion of PCo and the Chl *a* concentration we observed in the upper-1000 m along the section (Figure 5) strongly suggests that the transfer of DCo to PCo could be mainly driven by biological processes rather than by scavenging onto particles. Thus, the scavenging rate of DCo ($\text{FDCo}_{\text{scavenging}}$) was assumed negligible in the surface waters. This assumption is further supported by a previous study that also suggests absence of scavenging in the upper waters column of Sargasso Sea [Moffett and Ho, 1996].

$$FDCo_{\text{uptake}} = (Co/C)_{\text{cyano}} * (C/Chl a) * 1/M_C * [Chl a]_{100m} * \mu \quad (1)$$

where $(Co/C)_{\text{cyano}} = 2.16 \mu\text{mol.mol}^{-1}$ using $(Co/P)_{\text{cyano}} = 260 \mu\text{mol mol}^{-1}$ [Tovar-Sanchez et al., 2006] and $(P/C)_{\text{cyano}} = 8.3 \pm 2.6 \text{ mmol mol}^{-1}$ (after the review by Bertilsson et al., [2003]); μ is the growth rate of cyanobacteria in the Sargasso Sea and it is equal to 0.4 d^{-1} [Mann, 2000]; $C/Chl a = 75 \text{ g.g}^{-1}$ [Arrigo et al., 1998]; M_C is the carbon molar mass (12 g mol^{-1}).

These calculations lead to an uptake flux of DCo of $45 \pm 15 \text{ nmol DCo m}^{-2} \text{ d}^{-1}$ by the cyanobacteria at the BATS station (Table 3), which is in agreement with an estimate by Saito et al. [2002] for the upper 100 m of the Sargasso Sea ($30 \pm 12 \text{ nmol DCo m}^{-2} \text{ d}^{-1}$). The apparent slope of DCo versus P ($\Delta DCo/\Delta P_{\text{app}}$) reflects the sum of the fluxes $\sum F$ (sources and sinks) of DCo relative to that of P as in Equation (2):

$$(\Delta DCo/\Delta P)_{\text{app}} = \sum F_{\text{DCo}} / \sum F_P \quad (2)$$

The DCo fluxes were estimated in the top 100 meters at the BATS station (Table 2). The P fluxes were estimated using the same parameterization as for DCo, but using the P concentrations data (Table 2). In the Sargasso Sea, the regeneration rate of P ($FP_{\text{reg.}}$) was determined using a relationship between regeneration and uptake fluxes of P ($FP_{\text{reg.}} = -0.35 * FP_{\text{uptake}}$; McLaughlin et al. [2013]). Then using Equation (2), the regeneration flux of DCo can thus be written as:

$$FCo_{\text{reg}} = [(\Delta DCo/\Delta P)_{\text{app}} * \sum F_P] - [FDCo_{\text{diffusion}} + FDCo_{\text{advection}} + FDCo_{\text{atmosphere}} + FDCo_{\text{uptake}} + FDCo_{\text{scavenging}}] \quad (3)$$

A DCo regeneration rate of $37 \pm 15 \text{ nmol m}^{-2} \text{ d}^{-1}$ was estimated at BATS (Table 2), using the measured DCo/P slope at BATS of $69.2 \mu\text{M M}^{-1}$. This regeneration flux represented about 80% of the Co uptake rate by cyanobacteria (e.g.; $FCo_{\text{reg.}}/FCo_{\text{uptake}} = 0.8$), indicating that most of the biogenic cobalt can be recycled in these surface waters. A different approach resulted in similar estimates of 70-90% regeneration for oligotrophic waters of the southeastern Atlantic [Bown et al., 2011]. From these calculations, we estimate a corresponding turnover of Co in cyanobacteria cell ($\tau_{\text{Co cell}} = FCo_{\text{uptake}}/FCo_{\text{reg.}}$) of 1.3 days at BATS.

In Sargasso Sea, the regeneration rate of P represented only 35% of its biological uptake in these waters (Table 2). The two-fold difference in regeneration rates of P and DCo suggest non-Redfieldian regeneration of P and DCo, and is probably the cause of the mismatch between the DCo:P slope and the Co:P cellular ratio in these waters. These

estimates of biological DCo fluxes are based on estimated Co:C ratio in cyanobacteria; large uncertainty exists on this term, and further determinations will be required to improve such calculation of the bio-assimilation and regeneration rate of DCo. The organic speciation of DCo also needs to be taken into account since it too can impact the bioavailability of DCo [Saito *et al.*, 2002; Bown *et al.*, 2012]. For instance, it has been suggested that *Prochlorococcus sp.* are able to assimilate organically-bounded DCo [Saito *et al.*, 2002], and that cyanobacteria might produce organic binding-DCo ligands in oligotrophic waters [Bown *et al.*, 2012].

4.1.3 Export of cobalt from the surface waters

The export flux of cobalt on settling particles from the surface waters was estimated using the export fluxes of the particulate organic carbon (POC) at 100 meters depth (C_{export} , Equation 4) inferred from $^{234}\text{Th}/^{238}\text{U}$ measurements ($^{234}\text{Th}_{\text{flux}}$) in the water column and the $\text{POC}/^{234}\text{Th}$ ratio measured in large particles $> 53 \mu\text{m}$ (Owens [2014, accepted]; Puigcorb  *et al.*, [in prep.]). The Co:C ratio was found to co-vary in large and total particles ($n = 5$) in the north-western Atlantic (at 35.4°N - 66.5° , and 39.7°N - 69.8°W) during the GEOTRACES-A03 cruise (Phoebe Lam, personal communication). This allows us to use equation 5 and to calculate the export fluxes of Co by the large settling particles ($> 53 \mu\text{m}$) at 100 meters ($\text{FCo}_{\text{export}}$, Equation 6).

$$C_{\text{export}} = ^{234}\text{Th}_{\text{flux}} * (\text{POC}_{>53\mu\text{m}} / ^{234}\text{Th}) \quad (4)$$

$$\text{PCo}_{>53\mu\text{m}} / \text{POC}_{>53\mu\text{m}} = \text{PCo}_{>0.2\mu\text{m}} / \text{POC}_{>1\mu\text{m}} \quad (5)$$

$$\text{FCo}_{\text{export}} = C_{\text{export}} * (\text{PCo}_{>53\mu\text{m}} / \text{POC}_{>53\mu\text{m}}) \quad (6)$$

In the northern hemisphere, the carbon export fluxes were available at date for 14 stations at 100 m depth [Puigcorb  *et al.* in prep], and mean values of the Co:POC ratios were estimated in the SAG, the NASG and the EA (Table 3). In the southern hemisphere, the carbon export fluxes were available at 18 stations at 100 m depth [Owens, 2014] but there was no POC data available in the SASG and the SAW. For these domains, PCo/POC ratios recorded in similar biogeochemical conditions in surface waters (e.g.; T, Chl-*a*, DCo) but in the south-eastern Atlantic [Bown *et al.*, 2011] were used instead (Table 3).

In the Subarctic gyre and the Equatorial area, the PCo/POC ratios were, respectively, equal to 2.1 ± 0.6 and $1.5 \pm 0.4 \mu\text{M M}^{-1}$ at 100 m depth. These values are in excellent agreement with the Co/C cellular quota of coccolithophorids in non-limiting conditions ($1.4 - 3.6 \mu\text{M M}^{-1}$; Sunda and Huntsman, [1995]; Ho *et al.* [2003]) but much higher than those

measured in oceanic diatoms ($0.3 \mu\text{M M}^{-1}$; *Twining et al.* [2011]). At 23°N , the PCo/POC ratio ($6.9 \pm 1.3 \mu\text{M M}^{-1}$) was 3 times higher than the cellular quota of the predominant cyanobacteria ($1.43\text{-}2.16 \mu\text{M M}^{-1}$; *Sunda and Huntsman*, [1995]; *Tovar-Sanchez et al.* [2006]) and than the PCo/POC ratio obtained in particulate material collected with *in situ* pumps in oligotrophic conditions ($1.5 \pm 0.6 \mu\text{M M}^{-1}$; *Sherrell and Boyle* [1992]), suggesting an additional (lithogenic) source of PCo in these waters probably from the atmosphere as shown below. In the SASG, the PCo/POC ratio used ($2.15 \mu\text{M M}^{-1}$; *Bown et al.* [2011]) was in the range of the cellular quota of cyanobacteria [*Sunda and Huntsman*, 1995; *Tovar-Sanchez et al.*, 2006]. South of the Southern Subtropical Front, the PCo/POC ratio of $0.4 \mu\text{M M}^{-1}$ (derived from *Bown et al.* [2011]) was in agreement with the cellular quota of diatoms [*Twining et al.*, 2011] that probably dominate the phytoplankton assemblage in this area [*Browning et al.*, 2014].

The estimated export flux of Co varied within the different biogeochemical domains (Table 3), with the lowest in the SAW ($2.3 \pm 0.5 \text{ nmol m}^{-2} \text{ d}^{-1}$; $n = 6$) and the highest in the NASG ($13 \pm 32 \text{ nmol m}^{-2} \text{ d}^{-1}$; $n = 6$). Interestingly, relatively lower Co export fluxes were estimated in domains with potentially higher particulate sinking rates such as the SAW and the north EA, due to the predominance of diatoms, compared to areas like the NASG that are dominated by cyanobacteria and have nominally lower particulate sinking rates (Table 3). This suggests that the export of Co by particles might not be directly proportional to the primary productivity, and that other parameters should be taken into account such as the biological requirement and uptake of Co by the dominant functional groups that can drive the Co abundance in the exported biogenic particles. This result contrasts with previous assumptions suggesting that the POC export could be rather small in oceanic domains dominated by the pico- and nano-plankton [*Takahashi and Bienfang*, 1983; *Silver et al.*, 1986; *Goldman*, 1988, 1993]. However, it is in line with recent findings showing that *Synechococcus sp.*, *Prochlorococcus sp.* and nano-plankton can represent a significant portion of the POC downward flux especially in the oligotrophic regions, contributing to up to $33 \pm 16\%$ of the POC export flux in the Sargasso Sea [*Lomas and Moran*, 2011]. In turn, the absolute requirement of cyanobacteria for Co associated with the atmospheric deposition, as discussed in the following section, below could account for the enrichment of large particles in Co and, therefore for the high export flux of Co estimated in the NASG.

4.2 External sources of dissolved cobalt in the Western Atlantic

4.2.1 The input by the Amazon

With a mean water flux of $172\,000\text{ m}^3\text{ s}^{-1}$ [Molleri *et al.*, 2010], the Amazon River represents an important source of many elements to the Western equatorial Atlantic [Boyle *et al.*, 1982; Aucour *et al.*, 2003; Seyler and Boaventura, 2003] and its influence has been traced as far as the Caribbean basin [Moore *et al.*, 1986]. In contrast, it has a little impact on regions south of the Equator and east of 47°W [Molleri *et al.*, 2010] due to the direction of its plume. However, retroflexion of the North Brazil Current and the Equatorial countercurrent can transport signatures of the plume southeastwards of its mouth [Molleri *et al.*, 2010].

A strong linear correlation between DCo concentrations and salinity of 32 to 36.5 was found in the plume of the Amazon ($R^2 > 0.97$, $n = 9$; this study; Figure 9a). At the extrapolated zero salinity, the DCo concentration was thus estimated at 287 pM (Figure 9a). This end-member estimate is significantly lower than the DCo concentration of 0.64-1.87 nM reported for the upper Amazon [Seyler and Boaventura 2003]. Similarly, under-estimation of the DCo end-member for a North American estuary has already been reported [Saito and Moffett, 2002]. Transfer from dissolved to particulate fractions through chemical flocculation [Church, 1986; Moffett and Ho, 1996] can explain the difference between the reported and estimated end-members. The Co discharge to the estuary of the Amazon has been shown to predominantly occur as particulate cobalt, representing up to 95% of the total Co discharge [Seyler and Boaventura; 2003]. It is thus conceivable that the increase of the ionic strength across the saline gradient would cause flocculation and particles precipitation that would trap much of the riverine input in the delta sediments [Smoak *et al.*, 2006]. On the other hand, sediments are subjected to constant reworking, such as sediment resuspension and dissolution that would increase the DCo input from the estuary. Additional data are clearly needed across the saline gradient to understand the behavior of DCo in the Amazon plume. Biological drawdown, in addition to such flocculation processes and to the dilution of the plume, can also account for the decrease of DCo along the pathway of the plume. For instance, higher intra-cellular Co-quotas of bacteria growing in the plume of the Amazon were reported compared to those of species growing outside it [Tovar-Sanchez and Sañudo-Wilhelmy, 2011], suggesting higher biological uptake of DCo in the Amazon plume.

In order to estimate the input of DCo from the Amazon to our study region, we used the first order DCo-salinity relationship (Figure 9a; $\Delta\text{DCo}/\Delta\text{S} = -7.5\text{ pM}$). Then we normalized the relationship assuming the Amazon influence is null for $\text{S} \geq 36.5$ (Equation

7), since no plume was observed along the section at S above this value. The Amazon plume was depicted by its low salinities and its relatively high Si:N ratios observed in the mixed layer, consistent with previous observations [Hellweger and Gordon, 2002]. We estimated the concentration of DCo brought by the Amazon (DCo_{Amazon}) and its relative contribution (% DCo_{Amazon} , Figure 9b) to the mean DCo concentration recorded in the mixed layer (DCo_z), according to:

$$DCo_{Amazon} = (S_{obs} - 36.5) * \Delta DCo / \Delta S \quad (7)$$

$$\% DCo_{Amazon} = DCo_{Amazon} / DCo_z * 100 \quad (8)$$

Where S_{obs} is the observed salinity and varies from 32 to 36.5; z varied between 15 and 60 m.

The input of DCo by the Amazon was significant (> 10%) for 10 stations ($DCo_{Amazon} > 10\%$ of DCo_z ; Figure 9b), and varied between 2.2 ± 0.5 pM at 18°N (St.#30) and up to 14.3 ± 2.9 pM at 15°N (St.#32) where it accounted for 51% of the DCo_z . The advection of DCo by the plume of the Amazon River was detectable until 18°N (between St.#18b and 30; Figure 9b), whereas northwards it was considered negligible as it represented less than 10% of the DCo_z . The contribution southwards of the Amazon mouth was also found to be negligible. These estimates suggest that the DCo inputs by the Amazon discharge can be significant in the north-western tropical Atlantic between the Equator and 18°N (Figure 9b).

In fact, the inputs of nutrients by the Amazon River might significantly promote the diazotrophy in the central-western Atlantic, as it has been previously suggested [Subramaniam *et al.*, 2008]. It has been shown that up to 100 % of the cellular metal content (including Co) of the diazotroph *Trichodesmium sp.* growing in the Amazon plume of the central Atlantic may actually originate from the Amazon discharge [Tovar-Sanchez *et al.*, 2006]. These cyanobacteria are producers of B₁₂-vitamin that requires Co as the central atom [Bonnet *et al.*, 2010] and B₁₂ production could be enhanced by input of DCo [Panceza *et al.*, 2008]. The production of B₁₂-vitamin may also promote the development of several other phytoplankton species limited by this vitamin [Bertrand *et al.*, 2007; Bonnet *et al.*, 2010], when iron is not limiting as likely it was the case in these waters [Rijkenberg *et al.*, 2014]. In turn, the input of DCo by the Amazon in the north equatorial area could have ecological implications through an Amazon-DCo-B₁₂ cascade.

4.2.2 The atmospheric contribution

Several sub-surface DCo maxima ($DCo_{10m} > DCo_{25m}$) were observed along the section in the northern hemisphere, especially in the NASG and in the northern equatorial

area (Figures 6b-c). Moreover relative maxima of PCo were generally observed in the upper 50 meters along the transect (Figure 4b). The highest surface concentrations of PCo were recorded in the NASG, representing 10-20% of the TCo in sub-surface, and up to 34% at 26°N (e.g., PCo = 10.3 ± 2.6 pM at 25 m), whereas this fraction only represented generally less than 2% of the TCo concentration below 400 m. These observations suggested a possible atmospheric deposition of PCo in the NASG that produced subsurface DCo maxima after dissolution. In addition anomalies of high DCo:P ratios (up to > 5.4 mM M⁻¹) were observed in the surface waters of the NASG centered at 23°N and the equatorial area (Figure 4c), likely resulting from an accumulation of DCo versus P. Indeed, the Co:P ratio in aerosols is significantly higher than in seawater ($\text{Co:P}_{\text{seawater}} < 10^{-3}$ M.M⁻¹, this study; $\text{Co:P}_{\text{aerosols}} > 10^{-2}$ M.M⁻¹, Reid *et al.*, [2003]). Therefore dissolution of aerosols might have caused these high DCo:P ratio. Additionally the relative accumulation of DCo (versus P) was associated with an enrichment of dissolved aluminum (DAI) [Middag *et al.*, unpublished data] in these surface waters (Figure 4c), further suggesting dust inputs in this region, far away from other potential external sources. Previous observations have shown that dust can be transported from North Africa to the entire tropical Atlantic all year long [Prospero and Lamb, 2003]. Using a modified dust deposition MADCOW model based on DAI as proxy for the dust input [Measures and Brown, 1996; Measures and Vink, 2000; Vink and Measures, 2001; de Jong *et al.*, 2007], and the surface DAI concentrations recorded along the section [Middag *et al.*, unpublished data], we estimated dust deposition rates in the Western Atlantic. Improvements in this model are inclusion of variable mixed layer depth, variable Al solubility of aerosols, and variable DAI residence times. The residence time of DAI in surface waters was assessed from its scavenging flux (Equation 9; see auxiliary material for the parameterizations and coefficients). Dust deposition fluxes ranged from less than 0.20 ± 0.04 g m⁻² y⁻¹ at several stations in the SASG (St.# 7, 8, 9, 10) to up to 5.4 ± 1.1 g m⁻² y⁻¹ at about 8°N (St.#36).

Despite the difficulties and limitations to use DAI as a dust proxy [Dammshäuser *et al.*, 2011], especially due to its removal through biogenic particles [Moran and Moore, 1988; Middag *et al.*, 2009], our estimations are consistent with previous studies showing that the atmospheric input can be 10 times higher in the NASG than in the SASG [Tegen *et al.* 2004; Jickells *et al.* 2005], and with model predictions of dust deposition in the Atlantic Ocean [Ginoux *et al.* 2001 Tegen *et al.* 2004; Mahowald *et al.*, 2005; van Hulst *et al.*, 2013] (see auxiliary material).

$$\text{Dust deposition rate} = \text{DAI} * z * M_{\text{Al}} * (\text{Ab}_{\text{Al}} * S_{\text{Al}} * \tau_{\text{Al}})^{-1} \quad (9)$$

where DAI is the mean dissolved aluminum (Al) concentration in the mixed layer; z is the mixed layer depth; M_{Al} is the molar mass of aluminum; Ab_{Al} is the crustal abundance of Al; S_{Al} is the solubility of Al in aerosols (from Baker et al., 2013); τ_{Al} is the residence time of Al in the mixed layer (see auxiliary material for parameterizations and coefficients).

Considering these estimated rates of dust deposition, and the concentrations of Co in dust ($[\text{Co}]_{\text{dust}}$) that varied from 17 to 170 $\mu\text{g g}^{-1}$ in aerosols of the West Atlantic depending of their origins [Gaiero et al., 2003; Reid et al., 2003; Rudnick and Gao, 2003; Baker et al., 2007; Trapp et al. 2010; Xia & Gao, 2010; Shelley et al., 2012; Rachel Shelley, personal communication] (see auxiliary material), we estimated the atmospheric Co deposition flux ($\text{Flux Co}_{\text{atm}}$) along the section, according to Equation 10:

$$\text{Flux Co}_{\text{atm.}} = \text{Dust deposition rate} * [\text{Co}]_{\text{dust}} \quad (10)$$

The estimates of Co deposition rates varied from 0.9 $\text{nmol.m}^{-2}.\text{d}^{-1}$ in the center of the SASG to up to 17.4 $\text{nmol.m}^{-2}.\text{d}^{-1}$ close to Patagonia (St.#1b) (Figure 10). The strongest deposition of dust was centered on the EA (see auxiliary material), whereas the relatively high atmospheric inputs of Co were located in the temperate latitudes of the northern hemisphere (35°N - 50°N ; mean $\text{Flux Co}_{\text{atm}} = 8 \pm 1 \text{ nmol.m}^{-2}.\text{d}^{-1}$), the northern equatorial area (mean $\text{Flux Co}_{\text{atm}} = 8 \pm 2 \text{ nmol.m}^{-2}.\text{d}^{-1}$) and away from Patagonia in the SAW (mean $\text{Flux Co}_{\text{atm}} = 9 \pm 4 \text{ nmol.m}^{-2}.\text{d}^{-1}$). Much lower Co atmospheric depositions were found in the SASG (mean $\text{Flux Co}_{\text{atm}} = 1.5 \pm 0.5 \text{ nmol.m}^{-2}.\text{d}^{-1}$) and the SAG (mean $\text{Flux Co}_{\text{atm}} = 3 \pm 1 \text{ nmol.m}^{-2}.\text{d}^{-1}$). The high atmospheric deposition of Co in the EA was linked to the high dust deposition, and those estimated in the SAW and at temperate latitudes of the North Atlantic to the Co enrichment of, respectively, the Patagonian aerosols [Gaiero et al., 2003] and the North American aerosols [Rachel Shelley personal communication]. Low Co atmospheric inputs was mainly caused by low dust depositions.

The atmospheric input of soluble Co ($\text{Flux SCo}_{\text{atm.}}$) was then estimated using solubility coefficients of Co from dust, following Equation 11.

$$\text{Flux SCo}_{\text{atm.}} = \text{FCo}_{\text{atm}} * S_{\text{Co}} \quad (11)$$

where S_{Co} is the dissolution coefficient of cobalt from atmospheric particles in seawater and varies from 3% to 15% depending of the origin of the aerosol (see auxiliary material for the coefficients)

The modeled atmospheric deposition of soluble Co showed a different pattern compared to the estimated input of TCo (Figure 10). The highest input of soluble Co was indeed located in the temperate northern Atlantic, where 10 times higher inputs of soluble Co were estimated compared to the SASG (Figure 10). The model also showed a strong asymmetry of the soluble Co inputs between the two hemispheres with higher $F SCo_{atm}$ in the north with the exception of the SAW where inputs from Patagonia are detected (Figure 10).

Despite consistent trends, these estimations have to be taken carefully due to the lack of available data on the different parameters, especially on the solubility of aerosols in seawater. Moreover seasonal differences in the intensity of the dust deposition and in the air masses regimes likely introduce seasonal differences in Co inputs. For instance lower dust deposition can occur during fall than in summer [Prospero and Lamb, 2003]. We compared the accuracy of our estimates in the West Atlantic with the only two direct measurements of the atmospheric inputs of soluble Co available in the literature at date. At the BATS station (31°N), our estimate of soluble Co deposition ($0.7 \text{ nmol m}^{-2} \text{ d}^{-1}$) is in the range of the atmospheric DCo input previously measured during the FeATMISS-1 and FeAST-6 cruises (1.1 (late summer) and $0.1 \text{ nmol (early summer) m}^{-2} \text{ d}^{-1}$, respectively; Figure 10) [Shelley *et al.*, 2012]. At about 8 °N our estimation ($0.7 \text{ nmol m}^{-2} \text{ d}^{-1}$; Figure 10) was in agreement with the atmospheric inputs of soluble Co recorded in this area during fall by Baker *et al.* [2007] ($0.6\text{-}1.1 \text{ nmol m}^{-2} \text{ d}^{-1}$). Overall our estimations strongly suggested that the atmospheric input can be a main external source of DCo in the subtropical and equatorial areas of the northwestern Atlantic. The asymmetry of SCo_{atm} inputs between the two hemispheres may be due to the westward trade winds that are strongest at the Equator and 30°N compared to the south, and to the North American aerosols that can be enriched in Co at temperate latitudes (Rachel Shelley personal communication). The higher inputs of soluble Co in the northern hemisphere can account for the relative accumulation of DCo (versus P) observed in the surface waters of the NASG (Figure 4c). Without the atmospheric input, the concentrations of DCo in the surface waters of the NASG would be similar to those recorded in areas receiving far less atmospheric inputs, such as in the SASG (e.g.; $24 \pm 5 \text{ pM}$) and in another oligotrophic gyres like in the Central Pacific (Noble *et al.* 2008) and the South Central Atlantic [Noble *et al.* 2012]. The biogeochemical implications of the atmospheric source of DCo are discussed in details elsewhere [Dulaquais and Boye in review].

4.3 Residence time of cobalt in the upper 100 meters along the Western Atlantic

The residence time of dissolved (DCo) and particulate (PCo) cobalt in the upper 100 m of the different domains were inferred using the stocks measurements and estimates of

sources and sinks fluxes we estimated (Table 4). It is conceptualized in a simplistic scheme of the Co cycling shown in Figure 7. The particulate export flux of Co (Table 2) was used to estimate the residence time of PCo in surface waters (Equation 12).

$$\tau \text{ PCo} = \text{PCo stock} * \text{Co export rate}^{-1} \quad (12)$$

The residence time of DCo due to biogeochemical processes ($\tau \text{ DCo}_{\text{biogeo}}$, Table 4) was estimated considering the loss of DCo from the upper 100 m due to the export of the biogenic fraction of PCo (Equation 13). For the calculations, we assumed that the atmosphere was the only source of lithogenic PCo and that scavenging do not occurs in the upper 100 meters. In a steady state regime, the export of the biogenic fraction of PCo can then be determined using Equations 14 and 15.

$$\tau \text{ DCo}_{\text{biogeo}} = \text{DCo stock} * \text{Co}_{\text{biotic}} \text{ export rate}^{-1} \quad (13)$$

$$\text{Co}_{\text{biotic}} \text{ export rate} = \text{Co export rate} - \text{Co}_{\text{lithogenic}} \text{ export rate} \quad (14)$$

$$\text{Co}_{\text{lithogenic}} \text{ export rate} = \text{FCo}_{\text{atm}} - \text{FCo}_{\text{sol}} \quad (15)$$

The residence time of DCo due to physical processes ($\tau \text{ DCo}_{\text{phy}}$, Tables 4) was also estimated following Equation 16. The smaller of the two estimations will be considered as the residence time of DCo.

$$\tau \text{ DCo}_{\text{phy}} = \text{DCo stock} * (\text{FDCo}_{\text{advection}} + \text{FDCo}_{\text{diffusion}})^{-1} \quad (16)$$

The residence times of particulate cobalt in the surface waters were generally much lower than those of the dissolved cobalt in the different domains, up to 28 times lower in the SASG (Table 4). Particulate cobalt resided shortly in the two oligotrophic domains ($\tau \text{ PCo} \sim 20$ days), whereas at high latitudes and near the equator, longer PCo residence times were estimated, up to 200 days in the SAG. In this later domain, the residence time of PCo was probably overestimated, as we assumed a steady state, whereas an intensive bloom occurring during our period of sampling (spring) may have increased the PCo stock by the assimilation of DCo. This would result in the apparent high stock of PCo ($\sim 1 \mu\text{mol.m}^{-2}$) that might not be representative of the annual average PCo stock.

The longer residence times of DCo were estimated in the two oligotrophic domains (~ 1.5 years). In these high-regeneration systems, the residence times of DCo were driven by biogeochemical processes rather than by the physical processes ($3 < \tau \text{ DCo}_{\text{phy}} / \tau \text{ DCo}_{\text{biogeo}} < 7$). On the contrary, at high latitudes the physical processes may drive the DCo residence time ($0 < \tau \text{ DCo}_{\text{phy}} / \tau \text{ DCo}_{\text{biogeo}} < 0.06$). Similar low DCo residence times were estimated in the two hemispheres at high latitudes (0.7 year). Advection of DCo enriched waters by the Labrador

Current in the north and by the Malvinas Current in the south and strong seasonal biological Co uptake may explain the short residence time at those high latitudes. On either sides of the Equator we estimated an intermediate residence time of ~ 1 year. Like at the high latitudes, the physics could drive the DCo residence time there, notably due to high DCo input through diffusion caused by sharp vertical DCo gradients and by the Equatorial Current system that increases the diffusivity [Dulaquais *et al.*, 2014]. Furthermore, the organic complexation of DCo in surface waters could slow down its scavenging onto particles [Saito and Moffett, 2001; 2002], further increasing its residence time in surface waters. The abundance of cyanobacteria in oligotrophic waters combined with their capacity to produce DCo organic ligands [Saito *et al.*, 2005] would both account for the longer residence time of DCo estimated in these regions. Determination of the organic complexation of DCo in these waters is required to further confirm this hypothesis.

In the northern subtropical domain, the residence time of DCo is 4 times higher than that previously estimated in the same area (e.g.; 0.32 year; Saito and Moffett [2002]). However it might be difficult to compare both values, since the latter was estimated without taking into account the regeneration process. Indeed, it was calculated as the quotient between the DCo stock and a mean annual new production of carbon at BATS [Jenkins and Goldman, 1985] that relies on a mean particulate Co:C ratio in the Sargasso Sea [Sherrell and Boyle, 1992]. On the other hand, our estimate of the biological transfer time of the DCo stock ($\tau_{\text{DCo}_{\text{bio}}} = \text{DCo}_{\text{stock}} / \text{FDCo}_{\text{uptake}}$) at BATS (0.2 ± 0.1 year; Table 4) is in the range of the previous estimate of Saito and Moffett [2002]. In turn, the regeneration process increases the residence time of DCo in surface waters of Sargasso Sea.

Overall, these first assessments of the residence time of Co showed interesting features in the different domains. Longer PCo residence times were found in areas with shorter residence times of DCo and inversely, suggesting exchange processes between the two fractions. However additional studies will be needed to better constrain these terms.

4.4 Comparative budgets and biogeochemical cycling of cobalt in the surface waters of the Western Atlantic

The Co budgets in the upper-100 m water-layer of each biogeochemical province are presented in Table 5 for PCo and DCo and shown conceptually for the entire Western Atlantic in Figure 11. These budgets represent the state of the system at the time of the observations, hence they only integrate fluxes and processes operating with a timescale that

allows their observations. The aim of this exercise is to compare the characteristics of the different domains and the order of magnitude of the different terms rather than determine absolute values. The budgets are based on the full datasets available during the cruises (chemical, biological, geochemical and hydrographic parameters), but some fluxes had to be estimated using parameters from the literature when cruise data were lacking.

Biological assimilation was the dominant flux in the different biogeochemical domains (Table 5). This is in line with the observations showing an overall nutrient-like distribution of DCo in the surface waters (Figures 4 and 6). The biological uptake flux of DCo was estimated as mentioned above, using Chl-*a* values derived from the *in situ* fluorescence measurements obtained during the cruises and reported values of cellular quotas of Co/C in the phytoplankton species (Table 5) dominating in the different biogeochemical provinces [Sunda and Huntsman, 1995; Ho *et al.*, 2003; Tovar-Sanchez *et al.*, 2006; Twining *et al.*, 2011; Twining and Baines, 2013]. The lowest uptake was estimated for the SAW ($22 \text{ nmol.m}^{-2}.\text{d}^{-1}$) and the highest in the SAG ($106 \text{ nmol.m}^{-2}.\text{d}^{-1}$). In the latter domain a bloom of coccolithophorids was likely occurring during our period of sampling in 2010 as suggested by the relatively high Chl-*a* and PCo levels (Figures 3d and 4b) and potentially accounting for this extremely high uptake rate of DCo. The re-occupation of the SAG at a different season showed a decrease of the DCo stock by $1.4 \text{ } \mu\text{mol m}^{-2}$ ($\sim 25\%$ of DCo stock) between April 2010 (St.#8) and July 2012 (St.#3c) at $57\text{-}58.6^\circ\text{N}$ (Figure 6a). Considering the daily uptake of DCo estimated in the SAG during spring ($106 \text{ nmol m}^{-2} \text{ d}^{-1}$, Table 5), the observed DCo decrease ($1.4 \text{ } \mu\text{mol m}^{-2}$) would correspond to 13 days of biological uptake. This fits with the timescale of a coccolithophorid bloom [Brown and Yoder, 1994], further supporting the idea that the surface DCo depletion observed in summer was related to a coccolithophorid spring bloom. The regeneration rate of DCo in the surface waters (Co_{reg}) was the second most important flux, and represented between 10 and 85% of the Co-uptake flux ($\text{Co}_{\text{uptake}}$; Table 5). The highest regeneration fluxes of DCo were estimated in the subtropical domains ($\text{Co}_{\text{reg}}/\text{Co}_{\text{uptake}} > 0.75$), consistent with the concept of oligotrophic areas being regenerated systems. At the high latitudes, the regeneration fluxes were low ($\text{Co}_{\text{reg}}/\text{Co}_{\text{uptake}} < 0.25$), with the lowest flux estimated in the SAG (10%). The equatorial area was marked by an intermediate regeneration rate, representing about 50% of the Co-uptake flux. Hence, the regeneration can be the dominant internal source of DCo in the surface waters, especially in the subtropical domains.

The removal fluxes of Co by export via settling particles to deeper waters were 5 (in the NASG) to 25 (in the SAG) times lower than the biological uptake of DCo (Table 5),

reinforcing the importance of surface recycling of biogenic Co in oligotrophic surface waters. Among the external sources to the surface waters, the inputs of DCo by the Amazon can be considered significant only in the northern Equatorial area ($> 1 \text{ nmol m}^{-2} \text{ d}^{-1}$), and to a lower extent in the southern side of the NASG. The atmospheric inputs of soluble Co were considered as significant in three areas, the SAW, the EA and the NASG. However, the atmospheric source was relatively small compared to the other fluxes (Table 5), probably because low solubility of aerosols that can limit their impact.

Lateral advection by mesoscale structures can be an important term of the DCo-budget at a local scale [Dulaquais *et al.*, 2014]. These eddies can act either as intensive source or sink of DCo depending on whether they are cyclonic or anticyclonic [Dulaquais *et al.*, 2014]. Nevertheless the lateral input of DCo by these eddies would be negligible at the scale of a basin, such as in the subtropical domains (Table 5). By contrast the advection of DCo-enriched surface waters like from the eastern Atlantic by the Equatorial currents, and from the Amazon plume entrained by the Equatorial Counter-Current, can represent a significant source of DCo at low latitudes (Dulaquais *et al.*, [2014] and Table 5 respectively). Similarly, the lateral transport of DCo-enriched surface waters from high latitudes to DCo-depleted temperate waters by the Labrador Current in the North and by the Malvinas current in the South can also represent important source terms in the DCo surface budgets (Table 5). At frontal systems, turbulence and diffusivity could also account for a significant input of DCo from deep waters into the surface (Dulaquais *et al.*, [2014]; Table 5).

The nearly conservative behavior of DCo observed at high latitudes in the North associated with the high DCo concentrations recorded in these surface waters are in line with the budget estimations that indicated strong inputs of DCo into the surface layer due to lateral advection of DCo-enriched waters from higher latitudes and comparatively low biological uptake (Table 5). It is possible that melting of Arctic ice enriched in DCo (e.g.; $\text{DCo}_{\text{ice}}/\text{DCo}_{\text{seawater}} > 15$; Tovar-Sanchez *et al.*, [2010]), as well as continental shelf enrichment along the surface waters circulation were significant sources of DCo at these high latitudes. Additionally the estimated DCo uptake flux by phytoplankton increased southward from these high latitudes and this is in line with the observations that DCo showed a nearly conservative behavior that gradually changed to a nutrient-like vertical distribution in the southern side of the SAG (Figure 4a). It is conceivable that this seasonal biological removal of DCo would be partially resupplied by regeneration of DCo at the end of summer, and by the mixing from wind-stress turbulence during late fall and winter times. In the subtropics, the nutrient-like P distributions of DCo (Figure 4a) fitted with the high biological uptake and

extremely high regeneration rate (>80%) of DCo estimated for the oligotrophic gyres (Table 5). *Prochlorococcus* and *Synechococcus sp.* dominated the phytoplankton assemblage in those domains, and their high biological requirement for cobalt probably generated the surface DCo depletion. This nutrient-like distribution was recorded at different seasons [Saito and Moffett, 2002], hence it could be a permanent feature of the Co cycle in the oligotrophic systems. However, higher external inputs were detected in the northern gyre, especially due to the dust deposition during the dry season and to the Amazon River discharge during the wet season, and they generated an asymmetry between the two hemispheres (Figures 9b and 10; Table 5). In the Equatorial area, the physical processes can sustain the biological uptake of DCo both sides of the Equator (Table 5). Relatively high vertical diffusion DCo fluxes due to the incursion of DCo-enriched Atlantic Central Waters [Dulaquais et al., 2014] may indeed constitute a substantial source of DCo there (Table 5), in addition to the westward lateral advection of DCo-enriched waters by the Equatorial currents system [Dulaquais et al., 2014]. The inputs by the physical dynamics can actually sustain up to 40 % of the DCo drawdown due to biological uptake on both sides of the Equator.

The global budget (DCo + PCo) at the scale of the Western Atlantic (Table 5) clearly showed that the subtropical domains are acting as sink of Co (~ - 1100 tons of Co/year), especially in the NASG. In contrast, high latitudes and equatorial Atlantic constituted sources of Co into the surface Western Atlantic, balancing the sink determined in the subtropics (~ + 1200 tons of Co/year). This mass balance suggests exchanges between the different domains probably through circulation of intermediate waters and transport by eddies. The MBC and the equatorial current system indeed supply eddies to the south and north subtropics, respectively. These dynamic structures can then supply in DCo the subtropics by advection of enriched surface waters, as well as by vertical advection/diffusion of DCo from intermediate waters wherein concentrations are higher. Like dust events, blooms, and export flux, eddy events can vary seasonally. Thus the seasonal variability within the different domains must be taken into account to understand the biogeochemical cycle of cobalt in the surface Western Atlantic.

5 Conclusions

Significant regional correlations were observed between DCo and P across the different biological domains of the western Atlantic Ocean in part due to differences in the phytoplankton community composition. For instance, the highest DCo:P depletion ratios

recorded in the two subtropical domains were related to an absolute requirement for DCo of the dominant cyanobacteria species whereas the low DCo:P recorded in the subantarctic waters could reflect the low Co requirement of diatoms.

Biological uptake was the main sink of DCo in the surface waters of the western Atlantic, resulting in the overall nutrient-like distribution of DCo. The co-variation of biogenic PCo and Chl-*a* further supports the micro-nutritive behavior of Co. The higher biological assimilation rates of DCo by cyanobacteria at tropical latitudes compared to subpolar and subantarctic domains, can lead to the decreasing gradients of surface DCo observed from the high to the low latitudes along the western Atlantic. Regeneration that includes abiotic processes, microbial loop, cell lysis and grazing was the prevailing internal source of DCo in oligotrophic surface waters, sustaining up to 85% of the biological DCo drawdown. Overall, the internal cycle of DCo was primarily driven by the two processes of biological uptake and regeneration.

The atmospheric input was a significant source of DCo to the northern hemisphere and generated an asymmetry in DCo concentrations between the north and south subtropical domains. The Amazon River accounted for up to 50% of the DCo inventory of the mixed layer in the tropical northwestern Atlantic, but its impact rapidly decreased away from the mouth. Together, these external sources can sustain the higher biological demand of DCo estimated in the northern subtropical gyre compared to the southern gyre.

Advection of DCo-enriched waters from the high latitudes can be source of DCo especially to the subpolar Atlantic, a region characterized by a low Co regeneration rate. Moreover, lateral advection and vertical diffusion can sustain the biological demand of DCo in the Equatorial area.

Constraining the different sources and sinks has also allowed estimation of the DCo residence time in the upper 100 m. Short residence times driven by physical processes were determined at high northern latitudes (~ 0.7 year), whereas residence times were more than two times longer in the regenerated systems of the subtropics (~ 1.5 years).

Tentative budgets of Co in surface waters were assessed and they suggested non-steady state regimes at the scale of each biogeochemical domain. At the scale of the western Atlantic basin, the loss of Co (dissolved plus particulate) in the subtropics could be balanced by the gain at the high latitudes and in the equatorial area. Exchanges and transportation from source regions (high latitudes) to sink regions (subtropics) through dynamic features (surface jets, eddies, circulation at intermediate depths) could balance the Co budget in the Western Atlantic basin.

This study has demonstrated the importance of variability in internal cycling and external sources of DCo across biogeochemical domains to regional and basin-scale Co budgets. This work also provides new keys to the parameterization of cobalt biogeochemistry in marine systems, which can be implemented in future three-dimensional global models of the oceanic cobalt cycle.

Acknowledgement

The complete dataset of cobalt (dissolved, total, and apparent particulate) at all stations is available at the international GEOTRACES datacenter (<http://www.bodc.ac.uk/geotraces/>).

We are indebted to the Captains, Officers and Crew Members of the *R.V. Pelagia* and *R.S.S. James Cook*: without their exceptional support, this large ocean section would not have been possible. We are most grateful to Loes Gerringa and Micha Rijkenberg, the Chief Scientists of the cruises. We warmly thank Jan van Ooijen, K. Bakker, E. van Weerlee, S. Ossebaar for the analyses of nutrients, as well as S. Ober, Martin Laan, Steven van Heuven, S. Asjes and L. Wuis for providing high quality CTD data. We are much grateful to M. Rutgers van der Loeff for providing the particulate carbon data in the west-northern Atlantic, R. Shelley for communication on cobalt concentrations in North Atlantic aerosols and P.J. Lam for communication on cobalt/carbon ratio in the different size class of west-northern Atlantic marine particles. This investigation was supported by the GEOTRACES-GEOSECS revisited in the West Atlantic project coordinated by M. Boye and funded by the French LEFE-CYBER National Program of the Institut National des Sciences de l'Univers (INSU). We also acknowledge the European COST-Action ES801 for funding a Short Term Scientific Mission to G. Dulaquais to join the last cruise of the GEOTRACES-A02 section. The Université de Bretagne Occidentale (UBO) and the Région Bretagne (ARED) are supporting the PhD fellowship of G. Dulaquais. PM was supported in part by a Gladden Visiting Fellowship awarded by the Institute of Advanced Studies at The University of Western Australia. This investigation is a contribution to the international GEOTRACES program.

We warmly thank the two referees Mak Saito and Johann Bown for their comments and constructive remarks.

References

- Antoine, D., J.-M. Andre, & A. Morel (1996), Oceanic primary production, 2, Estimation at global scale from satellite (coastal zone color scanner) chlorophyll, *Global Biogeochemical Cycles*, *10*, 57-69.
- Arrigo, K. R., Worthen, D., Schnell, A., & Lizotte, M. P. (1998). Primary production in Southern Ocean waters. *Journal of Geophysical Research: Oceans (1978–2012)*, *103*(C8), 15587-15600.
- Aucour, A. M., Tao, F. X., Moreira-Turcq, P., Seyler, P., Sheppard, S., & Benedetti, M. F. (2003), The Amazon River: Behaviour of metals (Fe, Al, Mn) and dissolved organic matter in the initial mixing at the Rio Negro/Solimoes confluence. *Chemical geology*, *197*(1), 271-285.
- Baker, A. R., K. Weston, S. D. Kelly, M. Voss, P. Streu & J.N. Cape (2007) Dry and wet deposition of nutrients from the tropical Atlantic atmosphere: Links to primary productivity and nitrogen fixation. *Deep Sea Research part I*, *54*, 1704 - 1720.
- Bertilsson, S., O. Berglund, D. M. Karl, & S. W. Chisholm. (2003), Elemental composition of marine *Prochlorococcus* and *Synechococcus*: implications for the ecological stoichiometry of the sea. *Limnology & Oceanography* *48*, 1721-1731.

- Bertrand, E.M., Saito, M. A., Rose, J. M., Riesselman, C. R., Lohan, M. C., Noble, A. E., Lee, P. A. & DiTullio, G. R. (2007), Vitamin B12 and iron co-limitation of phytoplankton growth in the Ross Sea. *Limnology & Oceanography*, *52*, 1079-1093.
- Bonnet, S., Webb, E. A., Panzeca, C., Karl, D. M., Capone, D. G., & Sañudo-Wilhelmy, S. A. (2010). Vitamin B12 excretion by cultures of the marine cyanobacteria *Crocospaera* and *Synechococcus*. *Limnology & Oceanography*, *55*(5), 1959.
- Bowie, A. R., & M. C. Lohan. (2009), Analysis of iron in seawater, in Practical Guidelines for the Analysis of Seawater, edited by O. Wurl, chap. 12, pp. 235 – 257, Taylor and Francis, Boca Raton, Fla., ISBN:978- 1-4200-7306-5,.
- Bown, J., Boye, M., Baker, A., Duveilbourg, E., Lacan, F., Le Moigne, F., Planchon, F., Speich, S., & Nelson, D. M. (2011), The biogeochemical cycle of dissolved cobalt in the Atlantic and the Southern Ocean south off the coast of South Africa. *Marine Chemistry*, *126*, 193–206, doi:10.1016/j.marchem.2011.03.008, 2011.
- Bown, J., Boye, M., & Nelson, D. M. (2012). New insights on the role of organic speciation in the biogeochemical cycle of dissolved cobalt in the southeastern Atlantic and the Southern Ocean. *Biogeosciences*, *9*, 2719-2736.
- Boyd, P. W., & Newton, P. P., (1999), Does planktonic community structure determine downward particulate organic carbon flux in different oceanic provinces? *Deep-Sea Research part I*, *46*, 63-91.
- Boyle, E. A., Husteded, S. S., & Grant, B. (1982), The chemical mass balance of the Amazon Plume II. Copper, nickel, and cadmium. *Deep Sea Research part A.*, *29*(11), 1355-1364.
- Brown, C. W., & Yoder, J. A. (1994). Coccolithophorid blooms in the global ocean. *Journal of Geophysical Research: Oceans (1978–2012)*, *99*(C4), 7467-7482.
- Browning, T. J., Bouman, H. A., Moore, C. M., Schlosser, C., Tarran, G. A., Woodward, E. M. S., & Henderson, G. M. (2014), Nutrient regimes control phytoplankton ecophysiology in the South Atlantic. *Biogeosciences*, *11*(2), 463-479.
- Campbell, L., H. A. Nolla, & D. Vaultot (1994), The importance of *Prochlorococcus* to community structure in the central North Pacific Ocean, *Limnology & Oceanography*, *39*, 954-961, doi:10.4319/lo.1994.39.4.0954.
- Carpenter, E., Montoya, J.P., Burns, J., Mulholland, M., Subramaniam, A. & Capone, D.G., (1999), Extensive bloom of a N₂ fixing symbiotic association in the tropical Atlantic ocean. *Marine Ecology: Progress Series* *188*, 273–283.
- Charette, M.A. & Moran, S.B., (1999), Rates of particle scavenging and particulate organic carbon export estimated using ²³⁴Th as a tracer in the subtropical and equatorial Atlantic Ocean. *Deep-Sea Research part II*, *46*, 885-906.
- Church, T. M. (1986). Biogeochemical factors influencing the residence time of microconstituents in a large tidal estuary, Delaware Bay. *Marine Chemistry*, *18*(2), 393-406.
- Cullen, J. T., Chase, Z., Coale, K. H., Fitzwater, S. E., & Sherrell, R. M. (2003). Effect of iron limitation on the cadmium to phosphorus ratio of natural phytoplankton assemblages from the Southern Ocean. *Limnology & Oceanography*, *48*, 1079-1087
- Dammshäuser, A., Wagener, T., & Croot, P. L. (2011). Surface water dissolved aluminum and titanium: Tracers for specific time scales of dust deposition to the Atlantic? *Geophysical Research Letters*, *38*(24), doi:10.1029/2011GL049847
- de Baar, H.J.W., K.R. Timmermans, P. Laan, H.H. De Porto, S. Ober, J.J. Blom, M.C. Bakker, J. Schilling, G. Sarthou, M.G. Smit & M. Klunder (2008), Titan: A new facility for ultraclean sampling of trace elements and isotopes in the deep oceans in the international GEOTRACES program. *Marine Chemistry*, *111* (1-2).

- de Jong, J.T.M., Boye, M., Gelado-Caballero, M.D., Timmermans, K.R., Veldhuis, M.J.W., Nolting, R.F., van den Berg, C.M.G. & de Baar, H.J.W., (2007), Inputs of iron, manganese and aluminium to surface waters of the Northeast Atlantic Ocean and the European continental shelf. *Marine Chemistry* 107, 120–142.
- Dulaquais, G., Boye, M., Rijkenberg, M. J. A., & Carton, X. (2014), Physical and remineralization processes govern the cobalt distribution in the deep western Atlantic Ocean. *Biogeosciences*, 11(6), 1561-1580.
- Ellwood, M.J. & C.M.G. van den Berg, (2001), Determination of organic complexation of cobalt in seawater by cathodic stripping voltammetry, *Marine Chemistry*, 75, 33-47.
- Ellwood, M. J. (2008). Wintertime trace metal (Zn, Cu, Ni, Cd, Pb and Co) and nutrient distributions in the subantarctic zone between 40–52 S; 155–160 E. *Marine Chemistry*, 112(1), 107-117.
- Ferreira, A., Stramski, D., Garcia, C. A., Garcia, V. M., Ciotti, A. M., & Mendes, C. R. (2013). Variability in light absorption and scattering of phytoplankton in Patagonian waters: Role of community size structure and pigment composition. *Journal of Geophysical Research: Oceans*, 118(2), 698-714.
- Field, C.B., Behrenfeld, M.J., Randerson, J.T., & Falkowski, P., (1998). Primary production of the biosphere: integrating terrestrial and oceanic components. *Science* 281, 237-240.
- Flatau, M. K., Talley, L., & Niiler, P. P. (2003). The North Atlantic Oscillation, surface current velocities, and SST changes in the subpolar North Atlantic. *Journal of Climate*, 16(14).
- Gaiero, D.M., Probst, J. -L., Depetris, P. J., Bidart, S. M. & Leleyter, L., (2003), Iron and other transition metals in Patagonian riverborne and windborne materials: geochemical control and transport to the southern South Atlantic Ocean. *Geochimica et Cosmochimica Acta*, 67 (19), 3603-3623.
- Ginoux, P., Chin, M., Tegen, I., Prospero, J. M., Holben, B., Dubovik, O., & Lin, S. J. (2001). Sources and distributions of dust aerosols simulated with the GOCART model. *Journal of Geophysical Research: Atmospheres (1984–2012)*, 106(D17), 20255-20273.
- Goldman, J. C., (1988). Spatial and temporal discontinuities of biological processes in pelagic surface waters, in *Toward a theory on biological-physical interactions in the world ocean*, (ed. B. J. Rothschild), pp. 273-296, (Kluwer Academic, Dordrecht).
- Goldman, J. C., (1993), Potential role of large oceanic diatoms in new primary production, *Deep-Sea Research part I*, 40, 159-168.
- Gong, N., Chen, C., Liping, X., Chen, H., Lin, X. & Zhang, R. . (2005), Characterization of a thermostable alkaline phosphatase from a novel species *Thermus yunnanensis* sp. nov. and investigation of its cobalt activation at high temperature, *Biochimica et Biophysica (BBA)-Proteins and Proteomics Acta* , 1750, 103-111
- Grasshoff, K., Ehrhardt, M. & Kremling, K.: *Methods of seawater analysis*. Verlag Chemie GmbH, Weinheim. 419 pp., 1983.
- Gregg, W.W. & Casey, N.W., (2007), Modeling coccolithophores in the global oceans. *Deep-Sea Research part II*, 54, 447-477.
- Head, E. J. H., Harris, L. R., & Campbell, R. W. (2000), Investigations on the ecology of *Calanus* spp. in the Labrador Sea. I. Relationship between the phytoplankton bloom and reproduction and development of *Calanus finmarchicus* in spring. *Marine ecology. Progress series*, 193, 53-73.
- Hellweger, F.L., & Gordon, A.L., (2002), Tracing Amazon River water into the Caribbean Sea. *Journal of Marine Research* 60, 537–549.

- Ho, T. Y., Quigg, A., Finkel, Z. V., Milligan, A. J., Wyman, K., Falkowski, P. G., & Morel, F. M. M. (2003). The elemental composition of some marine phytoplankton. *Journal of Phycology*, 39(6), 1145-1159.
- Honjo, S., Dymond, J., Prell, W. & V. Ittekkot, (1999), Monsoon-controlled export fluxes to the interior of the Arabian Sea. *Deep-Sea Research part II*, 42, 831-870.
- Jakuba, R.W., Moffett, J.W. & Dyrman, S.T. (2008), Evidence for the linked biogeochemical cycling of zinc, cobalt, and phosphorus in the western North Atlantic Ocean. *Global Biogeochemical Cycles*, 22 (4) , doi: 10.1029/2007GB003119.
- Jenkins, W. J., & Goldman, J. C. (1985), Seasonal oxygen cycling and primary production in the Sargasso Sea. *Journal of Marine Research*, 43(2), 465-491.
- Ji, Y. & Sherrell, R.M., (2008), Differential effects of phosphorus limitation on cellular metals in *Chlorella* and *Microcystis*. *Limnology & Oceanography* 53, 1790–1804.
- Jickells, T.S., An, Z.A., Baker, A.R., Bergametti, G., Brooks, N., Boyd, P.W., Duce, R.A., Hunter, K.A., Junji, C., Kawahata, H., Kubilay, N., Andersen, K.K., La Roche, J., Liss, P.S., Mahowald, N., Prospero, J.M., Ridgwell, A.J., Tegen, I. & Torres, R., (2005), Global iron connections between desert dust, ocean biogeochemistry and climate. *Science*, 308, 67–71.
- Karl, D.M., Letelier, R., Hebel, D., Tupas, L., Dore, J., Christian, J. & Winn, C., (1995), Ecosystem changes in the North Pacific subtropical gyre attributed to the 1991-92 El Nino. *Nature* 373, 230-234
- Karl, D. M., Christian, J. R., Dore, J. E., Hebel, D. V., Letelier, R. M., Tupas, L. M., & Winn, C. D., (1996), Seasonal and interannual variability in primary production and particle flux at Station aloha, *Deep-Sea Research part II*, 43, 539-568.
- Lane, T. W., & F. M. M. Morel (2000), Regulation of carbonic anhydrase expression by zinc, cobalt, and carbon dioxide in the marine diatom *Thalassiosira weissflogii*, *Plant Physiology*, 123, 345–352, doi:10.1104/pp.123.1.345.
- Li, F., Ginoux, P., & Ramaswamy, V. (2008). Distribution, transport, and deposition of mineral dust in the Southern Ocean and Antarctica: Contribution of major sources. *Journal of Geophysical Research: Atmospheres (1984–2012)*, 113(D10).
- Lomas, M. W., & Moran, S. B. (2011), Evidence for aggregation and export of cyanobacteria and nano-eukaryotes from the Sargasso Sea euphotic zone. *Biogeosciences*, 8(1).
- Mahowald, N.M., Baker, A.R., Bergametti, G., Brooks, N., Duce, R.A., Jickells, T.D., Kubilay, N., Prospero, J.M. & Tegen, I., (2005), Atmospheric global dust cycle and iron inputs to the ocean. *Global Biogeochemical Cycles* 19, GB4025. doi:10.1029/2004GB002402
- Mann, E. L. (2000), Trace metals and the ecology of marine cyanobacteria, Ph.D. thesis. MIT/WHOI Joint Program in Oceanography.
- Martin, J.H., Gordon, R.M., Fitzwater, S. & Broenkow, W.W., (1989), Vertex — phytoplankton iron studies in the Gulf of Alaska. *Deep-Sea Research part a* 36 (5), 649.
- Martin, J.H., Fitzwater, S.E., Gordon, R.M., Hunter, C.N. & Tanner, S.J., (1993), Iron, primary production and carbon nitrogen flux studies during the JGOFS North-Atlantic Bloom Experiment. *Deep-Sea Research Part I* 40 (1–2), 115-134.
- Mather, R., Reynolds, S., Wolff, G., Williams, R. G., Torres-Valdes, S., Woodward, E. M. S., Landolfi, A., Pan, X., Sanders, R. W., & Achterberg, E. (2008), Phosphorus cycling in the North and South Atlantic Ocean subtropical gyres, *Nature Geosciences*, 1, 439–443.
- McLaughlin K., J. A. Sohm, G.A. Cutter, M.W. Lomas & A. Paytan, (2013), Phosphorus cycling in the Sargasso Sea: Investigation using the oxygen isotopic composition of

- phosphate, enzyme-labeled fluorescence, and turnover times *Global Biogeochemical Cycles*: 27, 1–13, doi:10.1002/gbc.20037, 2013
- Measures, C.I. & Brown, E.T., (1996), Estimating dust input to the Atlantic Ocean using surfacewater Al concentrations. In: Guerzoni, S., Chester, R., (Eds.), *The impact of African Dust across the Mediterranean*, Kluwer, Dordrecht, 389pp.
- Measures, C.I. & Vink, S., (2000), On the use of dissolved aluminium in surface waters to estimate dust deposition to the ocean. *Global Biogeochemical Cycles* 14, 317–327.
- Michaels, A. F. & Knap, A. H., (1996), Overview of the U.S. JGOFS Bermuda Atlantic Time series Study and the Hydrostation S program, *Deep Sea Research part II*, 43,2-3, 157-198.
- Middag, R., H. J. W. de Baar, P. Laan, & K. Bakker (2009), Dissolved aluminium and the silicon cycle in the Arctic Ocean, *Marine Chemistry*, 115, 176–195, doi:10.1016/j.marchem.2009.08.002.
- Minobe, S., Miyashita, M., Kuwano-Yoshida, A., Tokinaga, H., & Xie, S. P. (2010). Atmospheric response to the gulf stream: seasonal variations. *Journal of Climate*, 23(13), 3699-3719.,doi:10.1175/2010JCLI3359.1
- Moffett, J.W. & Ho, J. (1996), Oxidation of cobalt and manganese in seawater via a common microbially catalyzed pathway. *Geochimica and Cosmochimica Acta*, 60 (18), 3415-3424,
- Moller, G.S.F., de M. Novo, E.M.L. & Kampel, M., (2010), Space–time variability of the Amazon River plume based on satellite ocean color. *Cont. Shelf Res.* 30, 342–352
- Moore, W. S., Sarmiento, J. L., & Key, R. M. (1986). Tracing the Amazon component of surface Atlantic water using 228Ra, salinity and silica. *Journal of Geophysical Research: Oceans (1978–2012)*, 91(C2), 2574-2580.
- Moran, S. B., & R. M. Moore (1988), Evidence from mesocosm studies for biological removal of dissolved aluminum from sea water, *Nature*, 335, 706–708, doi:10.1038/335706a0
- Murphy, J. & Riley, J.P (1962), A modified single solution method for the determination of phosphate in natural waters. *Analytica Chim. Acta*, 27, 31-36.
- Newton, P. P., Lampitt, R. S., Jickells, T. D., King, P., & C. Boutle, (1994), Temporal and spatial variability of biogenic particle fluxes during the JGOFS northeast Atlantic process studies at 47°N, 20°W. *Deep-Sea Research part I*, 41, 1617-1642.
- Noble, A. E., Saito, M. A., Maiti, K., & Benitez-Nelson, C. R. (2008), Cobalt, manganese, and iron near the Hawaiian Islands: A potential concentrating mechanism for cobalt within a cyclonic eddy and implications for the hybrid-type trace metals. *Deep-Sea Research part. II*, 55, 1473–1490, doi:10.1016/j.dsr2.2008.02.010.
- Noble, A. E., Lamborg, C. H., Ohnemus, D. C., Lam, P. J., Goepfert, T. J., Measures, C. I., Frame, C. H., Casciotti, K. L., DiTullio, G. R., Jennings, J., & Saito, M. A. (2012), Basin scale inputs of cobalt, iron, and manganese from the Benguela-Angola front to the South Atlantic Ocean. *Limnology & Oceanography*, 57, 989–1010.
- Okada, H., A. McIntyre, (1979), Seasonal distribution of modern coccolithophores in the western North Atlantic Ocean. *Marine Biology*, 54,319–328
- Oschlies, A., & V. Garçon (1998), Eddy-induced enhancement of primary production in a model of the North Atlantic Ocean, *Nature*,394, 266–269.
- Owens, S.A., Pike, S. & K.O. Buesseler (accepted 2014). Thorium-234 as a tracer of particle dynamics and upper ocean export in the Atlantic Ocean. *Deep Sea Research-II*.
- Parsons, T. R., & Lalli, C. M. (1988), Comparative oceanic ecology of the plankton communities of the subarctic Atlantic and Pacific oceans. *Oceanography and Marine Biology, An Annual Review*, 26, 317-359.

- Peterson, R. G., & Stramma, L. (1991), Upper-level circulation in the South Atlantic Ocean. *Progress in Oceanography*, 26, 1–73, doi:10.1016/0079-6611(91)90006-8.
- Peterson, R. G., C. S. Johnson, W. Krauss, & R. E. Davis (1996), Lagrangian Measurements in the Malvinas Current, in *The South Atlantic. Present and past circulation*, edited by G. Wefer et al., pp. 239-247, Springer-Verlag, New York
- Prospero, J.M., Lamb, P.J., (2003), African droughts & dust transport to the Caribbean: climate change implications. *Science* 302, 1024–1027.
- Reid, J.L. (1994), On the total geostrophic circulation of the North Atlantic Ocean: Flow patterns, tracers and transports. *Progress in Oceanography*, 33, 1-92.
- Reid, E. A., Reid, J. S., Meier, M. M., Dunlap, M. R., Cliff, S. S., Broumas, A., Perry, K., & Maring, H. (2003). Characterization of African dust transported to Puerto Rico by individual particle and size segregated bulk analysis. *Journal of Geophysical Research: Atmospheres (1984–2012)*, 108(D19).
- Rijkenberg, M. J., Middag, R., Laan, P., Gerringa, L. J., van Aken, H. M., Schoemann, V., de Jong, J. T. M. & de Baar, H. J. (2014). The Distribution of Dissolved Iron in the West Atlantic Ocean. *PloS one*, 9(6), e101323.
- Rudnick, R. L. & Gao, S., (2003), Composition of the continental crust. In: Rudnick, R. L. (ed.) *The Crust*. Amsterdam: Elsevier, pp. 1-70.
- Saito, M. A. & Moffett, J. W. (2001), Complexation of cobalt by natural organic ligands in the Sargasso Sea as determined by a new high sensitivity electrochemical cobalt speciation method suitable for open ocean work. *Marine Chemistry*, 75, 49–68.
- Saito, M. A. & Moffett, J. W. (2002), Temporal and spatial variability of cobalt in the Atlantic Ocean. *Geochimica Cosmochimica Acta*, 66, 1943–1953.
- Saito, M. A., Moppett, J. W., Chisholm, S. W., & Waterbury, J. B. (2002), Cobalt limitation and uptake in *Prochlorococcus*. *Limnology & Oceanography*, 47(6), 1629-1636.
- Saito, M. A., Moffett, J. W., & DiTullio, G. R. (2004), Cobalt and nickel in the Peru upwelling region: A major flux of labile cobalt utilized as a micronutrient. *Global Biogeochemical Cycles*, 18, GB4030, doi:10.1029/2003GB002216.
- Saito M. A., G. Rocap, & J. W. Moffett (2005), Production of cobalt binding ligands in a *Synechococcus* feature at the Costa Rica Upwelling Dome. *Limnology & Oceanography*, 50, 279–290, doi:10.4319/lo.2005.50.1.0279.
- Saito, M.A. & Goepfert, T.J. (2008), Zinc–cobalt colimitation of *Phaeocystis antarctica*. *Limnology & Oceanography*, 53 (1), 266–275.
- Saito, M. A., Goepfert, T. J., Noble, A. E., Bertrand, E. M., Sedwick, P. N., & DiTullio, G. R. (2010), A seasonal study of dissolved cobalt in the Ross Sea, Antarctica: micronutrient behavior, absence of scavenging, and relationships with Zn, Cd, and P. *Biogeochemistry*, 7, 4059–4082, doi:10.5194/bg-7-4059-2010.
- Seyler, P. & Boaventura, G.R., (2003), Trace elements in the mainstream Amazon River. In: McClain, M.E. (Ed.), *The Biochemistry of the Amazon Basin*. Oxford University Press, Oxford, UK, p.534
- Silver, M. W., Gowing, M. M., & Davoll, P. J., (1986), The association of photosynthetic picoplankton and ultraplankton with pelagic detritus through the water column (0-2000 m), *Canadian Bulletin of Fisheries and Aquatic Sciences*, 214, 311-341

- Shelley, R. U., Zachhuber, B., Sedwick, P. N., Worsfold, P. J., & Lohan, M. C. (2010), Determination of total dissolved cobalt in UV-irradiated seawater using flow injection with chemiluminescence detection. *Limnology & Oceanography*, 8, 352–362, doi:10.1029/2009JC005880.
- Shelley, R. U., Sedwick, P. N., Bibby, T. S., Cabedo-Sanz, P., Church, T. M., Johnson, R. J., Macey, A. I., Marsay, C. M., Sholkovitz, E. R., Ussher, S. J., Worsfold, P. J., & Lohan, M. C. (2012), Controls on dissolved cobalt in surface waters of the Sargasso Sea: Comparisons with iron and aluminum. *Global Biogeochemical Cycles*, 26 (2) GB2020.
- Sherrell R. M. & Boyle E. A. (1992), The trace metal composition of suspended particles in the oceanic water column near Bermuda. *Earth & Planetary Sciences Letters*, 111, 155–174.
- Smoak, J. M., Krest, J. M., & Swarzenski, P. W. (2006), Geochemistry of the Amazon estuary. *Estuaries* (pp. 71-90). Springer Berlin Heidelberg.
- Stramma, L., & England, M. (1999). On the water masses and mean circulation of the South Atlantic Ocean. *Journal of Geophysical Research: Oceans (1978–2012)*, 104(C9), 20863-20883.
- Strickland, J.D.H. & Parsons, T.R. (1968), A practical handbook of seawater analysis. First Edition, Fisheries Research Board of Canada, Bulletin. No 167, p.65.
- Subramaniam, A., Yager, P. L., Carpenter, E. J., Mahaffey, C., Björkman, K., Cooley, S., Kustka, A. B., Montoya, J. P., Sañudo-Wilhelmy, S. A., Shipe, R., & Capone, D. G. (2008), Amazon River enhances diazotrophy and carbon sequestration in the tropical North Atlantic Ocean. *Proceedings of the National Academy of Sciences*, 105(30), 10460-10465.
- Sunda, W.G., & S.A. Huntsman (1995), Cobalt and zinc inter-replacement in marine phytoplankton: biological and geochemical implications, *Limnology & Oceanography*, 40, 1404-1417.
- Swanner, E. D., Planavsky, N. J., Lalonde, S. V., Robbins, L. J., Bekker, A., Rouxel, O. J., Saito, M. A., Kappler, A., Mojzsis, S.J. & Konhauser, K. O. (2014). Cobalt and marine redox evolution. *Earth and Planetary Science Letters*, 390, 253-263.
- Takahashi, M., & Bienfang, P. K., (1983), Size-structure of phytoplankton biomass and photosynthesis in subtropical Hawaiian waters, *Marine Biology*, 76, 203-211.
- Tang, D., & Morel, F. F. M. (2006). Distinguishing between cellular and Fe-oxide-associated trace elements in phytoplankton. *Marine chemistry*, 98(1), 18-30.
- Tegen, I., Werner, M., Harrison, S.P. & Kohfeld, K.E., (2004), Relative importance of climate and land use in determining present and future global soil dust emission. *Geophysical Research Letters* 31 (5), L05105. doi:10.1029/2003GL019216.
- Thomalla, S., Turnewitsch, R., Lucas, M. & Poulton, A., (2006), Particulate organic carbon export from the North and South Atlantic gyres: The $^{234}\text{Th}/^{238}\text{U}$ disequilibrium approach. *Deep-Sea Research part II* 53 (14-16), 1629-1648
- Tomczak, M. & Godfrey, J.S. (2003), *Regional Oceanography: an Introduction*. 2nd edition. Pergamon, Oxford, 422 pp.
- Tovar-Sanchez, A., Sañudo-Wilhelmy, S. A., Kustka, A. B., Agusti, S., Dachs, J., Hutchins, D. A., Capone, D. G. & Duarte, C. M. (2006), Effects of dust deposition and river discharges on trace metal composition of *Trichodesmium spp.* in the tropical and subtropical North Atlantic Ocean. *Limnology & Oceanography*, 51(4), 1755–1761.
- Tovar-Sanchez, A., Duarte, C. M., Alonso, J. C., Lacorte, S., Tauler, R., & Galban-Malagon, C. (2010), Impacts of metals and nutrients released from melting multiyear Arctic sea ice, *Journal of Geophysical Research: Oceans*, 115, C07003, doi:10.1029/2009JC005685.

- Tovar-Sanchez, A. & Sañudo-Wilhelmy, S. A. (2011): Influence of the Amazon River on dissolved and intra-cellular metal concentrations in *Trichodesmium* colonies along the western boundary of the sub-tropical North Atlantic Ocean. *Biogeosciences*, 8, 217–225, doi:10.5194/bg-8-217-2011.
- Trapp, J. M., F. J. Millero, & J. M. Prospero (2010), Temporal variability of the elemental composition of African dust measured in trade wind aerosols at Barbados and Miami, *Marine Chemistry*, 120(1–4), 71–82, doi:10.1016/j.marchem.2008.10.004
- Twining, B. S., Baines, S. B., Bozard, J. B., Vogt, S., Walker, E. A., & Nelson, D. M. (2011). Metal quotas of plankton in the equatorial Pacific Ocean. *Deep Sea Research Part II: Topical Studies in Oceanography*, 58(3), 325-341.
- Twining, B. S., & Baines, S. B. (2013), The trace metal composition of marine phytoplankton. *Annual review of marine science*, 5, 191-215.
- van Hulst, M. M. P., Sterl, A., Tagliabue, A., Dutay, J. C., Gehlen, M., De Baar, H. J., & Middag, R. (2013). Aluminium in an ocean general circulation model compared with the West Atlantic Geotraces cruises. *Journal of Marine Systems*, 126, 3-23.
- van Ooijen, J. (2010). Nutrient measurements. *Cruise report 64PE319*, 17-19.
- Vink, S. & Measures, C.I., (2001), The role of dust deposition in determining surface water distributions of Al and Fe in the South West Atlantic. *Deep-Sea Research part II* 48 (13), 2787–2809.
- Weinstein, S. E., & Moran, S. B. (2004). Distribution of size-fractionated particulate trace metals collected by bottles and in-situ pumps in the Gulf of Maine–Scotian Shelf and Labrador Sea. *Marine chemistry*, 87(3), 121-135.
- Xia, L., & Gao, Y. (2010), Chemical composition and size distributions of coastal aerosols observed on the US East Coast. *Marine Chemistry*, 119(1), 77-90.

Table 1. Comparison of dissolved cobalt analyses obtained in the UV-oxidized samples by the FIA-Chemiluminescence method used in the present study with consensus values reported by the Sampling and Analysis of iron (SAFe) and GEOTRACES programs.

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

Table 2. Summary of dissolved cobalt (FDCo) and phosphorus (FP) fluxes integrated for the upper 100 meters at the BATS station in the Sargasso Sea. Relative errors are indicated in brackets.

	Atmospheric deposition ^a	River input	Lateral Advection ^b	Vertical diffusion ^b	Scavenging ^c	Uptake	Regeneration
FDCo (nmol m ⁻² d ⁻¹)	+ 0.7 ± 0.1	Negl.	+ 0.08 ± 0.01	+ 0.05 ± 0.01	Negl.	- 45 ± 15	+ 37 ± 15
FP (μmol m ⁻² d ⁻¹)	+ 0.14 ± 0.03	Negl.	+ 0.02 ± 0.01	+ 0.72 ± 0.1)	Negl.	- 175 ± 53	+ 61 ± 18

^a See 4.2.2 for the calculation

^b from and following the method of *Dulaquais et al.*, [2014] with:

$$FDCo_{diffusion} = - (K_z + D_T) * (\partial DCo / \partial z)$$

$$FDCo_{adv} = GradDCo_{(x,y)} * velocity_a * z$$

^c Scavenging could not be discerned from biological uptake

Table 3. Cobalt to organic carbon ratio in particles at 100 m derived from measurements ($PCo_{>0.2\mu m}/POC_{>1\mu m}$), and the integrated export fluxes of Co on large particles ($>53 \mu m$) at 100 m (FCo_{export}).

	Domain					
	SAG	NASG	N-EA	S-EA	SASG	SAW
$PCo_{>0.2\mu m}/POC_{>1\mu m}$ ($\mu M M^{-1}$)	2.1 ± 0.6	6.9 ± 1.4	1.5 ± 0.4	1.5 ± 0.4	2.16*	0.4*
FCo_{export} ($nmol m^{-2} d^{-1}$)	4.2 ± 3.4	12.9 ± 32.4	3.6 ± 2.0	5.5 ± 1.5	4.9 ± 1.2	2.3 ± 0.5

Table 4 Stock and residence time of dissolved (DCo) and particulate (PCo) cobalt in the upper 100 meters for the different biogeochemical domains.^a

	SAG	NASG	N-EA	S-EA	SASG	SAW
PCo stock ($\mu\text{mol}\cdot\text{m}^{-2}$)	0.93 ± 0.47	0.60 ± 0.34	0.52 ± 0.34	0.27 ± 0.17	0.11 ± 0.03	0.31 ± 0.19
τPCo (year)	0.6 ± 0.5	$< 0.1 \pm 0.1$	0.4 ± 0.2	0.1 ± 0.1	$< 0.1 \pm 0.1$	0.3 ± 0.2
DCo stock ($\mu\text{mol}\cdot\text{m}^{-2}$)	5.9 ± 1	3.3 ± 0.8	3 ± 1	3.4 ± 1.0	2.4 ± 0.5	3.8 ± 0.8
$\tau\text{DCo}_{\text{biogeo.}}$ (year)	12.1 ± 6.1	1.4 ± 1.2	∞	3.4 ± 0.5	1.7 ± 0.5	∞
$\tau\text{DCo}_{\text{phy.}}$ (year)	0.7 ± 0.2	9.0 ± 2.2	1.0 ± 0.3	0.9 ± 0.3	6.6 ± 1.4	0.7 ± 0.2
$\tau\text{DCo}_{\text{bio.}}$ (year) [*]	0.2	0.1	0.3	0.3	0.1	0.5

^a The residence times of DCo are given considering biogeochemical processes ($\tau\text{DCo}_{\text{biogeo.}}$) and physical processes ($\tau\text{DCo}_{\text{phy.}}$) (see text for the explanation and calculation). The biological transfer time of the DCo stock ($\tau\text{DCo}_{\text{bio.}}$) is also indicated.

^{*} Estimated by $\tau\text{DCo}_{\text{bio.}} = \text{DCo stock} / \text{DCo uptake}$ (using DCo uptake from Table 5)

Table 5. Summary of the dissolved (DCo) and particulate (PCo) cobalt fluxes for the upper 100 meters (averaging all stations of each biogeochemical domain) along the GEOTRACES-A02 section.

	Domain	SAG	NASG	N-EA	S-EA	SASG	SAW
	Period of sampling	spring	dry season			dry season	summer
Fluxes (nmol m⁻² d⁻¹)							
PCo (-) or DCo (+)	(1) Scavenging ^a	Negl.	Negl.	Negl.	Negl.	Negl.	Negl.
	(2) Uptake ^b	(-) 106 [20-220]	(-) 64 [18- 197]	(-) 27 [21 - 30]	(-) 31 [15-47]	(-) 33 [14-51]	(-) 22 [7-30]
	(3) Regeneration ^b	10 [2-50]	51 [14-130]	21 [16-23]	11 [5-20]	28 [10-40]	7 [2-10]
	(4) Dust dissolution	0.5 [0.4-0.6]	1.0 [0.3-1.3]	0.5 [0.2-0.7]	Negl [0.1-0.3]	Negl [0-0.2]	0.5 [0.3-0.7]
PCo	(5) Dust	(+) 3 [3-4]	(+) 7 [5-8]	(+) 8 [6-10]	(+) 4 [1-7]	(+) 1.5 [0.8-2]	(+) 9 [5-16]
	(6) Export	(-) 4 [3 - 5]	(-) 13 [0 - 30]	(-) 4 [2 - 6]	(-) 6 [5 - 8]	(-) 5 [3 - 7]	(-) 2 [1-3]
	ΣFPCo	(+) 94.5	(+) 6.5	(+) 9.5	(+) 18	(+) 1.5	(+) 21.5
DCo	(7) Amazon ^c	Negl.	Negl.	(+) 1 [0 - 4]	Negl.	Negl.	Negl.
	(8) Vertical diffusion ^d	(+) 7 [(-) 2-10]	(+) 1 [0 - 2]	(+) 7 [2 - 10]	(+) 7 [3 - 10]	(+) 1 [0 - 2]	(+) 9 [4-15]
	(9) Lateral advection ^e	(+) 15	Negl.	(+) 2	(+) 4	Negl.	(+) 7
	ΣFDCo	(-) 73.5	(-) 11.5	(+) 4.5	(-) 9	(-) 4	(+) 2
Basin fluxes (tons/year)							
PCo + DCo	Sum^f	(+) 380	(-) 970	(+) 330	(+) 190	(-) 160	(+) 280

^a Scavenging is assumed negligible

^b Using Equations (1) and (3) with Co:C of $2.1 \pm 0.6 \mu\text{M M}^{-1}$ in the SAG (this study); $2.16 \pm 0.7 \mu\text{M M}^{-1}$ in the NASG and the SASG (after Tovar-Sanchez et al., 2006; Bertilsson et al., 2003); $1.48 \pm 0.4 \mu\text{M M}^{-1}$ in the NEA and SEA (this study); $0.4 \mu\text{M M}^{-1}$ in the SAW (Bown et al., 2011).

^c The Amazon flux of DCo is determined using $\text{FDCo}_{\text{Amazon}} = (\text{DCo}_{\text{Amazon}} * z/100) / \tau\text{DCo}$

^dThe diffusion fluxes are estimated as described in *Dulaquais et al.* [2014] and Table 3.^{ee} The lateral advection of DCo is estimated in the SAG from ΔDCo concentrations between St.#2 and St.#13, an area of $8.4 * 10^5 \text{ km}^2$ and a mean water flow of 5 Sv in the upper 100 meters [Reid et al., 1994; Flatau et al., 2003]. In the SAW it is estimated from ΔDCo concentrations between St.#1b and St.#6b, an area of $5.5 * 10^5 \text{ km}^2$ and a mean water flow of 2.5 - 3 Sv in the

upper 100 meters [Peterson et al., 1996]. In the NEA, it is estimated from ΔDCo concentrations between St. #41 and St. #35, an area of $1 \cdot 10^6 \text{ km}^2$ and a mean water flow of 5 Sv in the upper 100 meters [Tomczak, 2003]. In the SEA, it is estimated from ΔDCo concentrations between St.#15b and St.#41 an area of $1.1 \cdot 10^6 \text{ km}^2$ and a mean water flow of 5 Sv in the upper 100 meters [Tomczak, 2003].

^f The sum is calculated using $(\text{Sum DCo} + \text{Sum PCo}) * S$, where S is the surface of the different domain ($0.84 \cdot 10^{12} \text{ m}^2$ for SAG; $9 \cdot 10^{12} \text{ m}^2$ for NASG; $1.1 \cdot 10^{12} \text{ m}^2$ for NEA; $1 \cdot 10^{12} \text{ m}^2$ for SEA; $3 \cdot 10^{12} \text{ m}^2$ for SASG; $0.55 \cdot 10^{12} \text{ m}^2$ for SAW).

Accepted Article

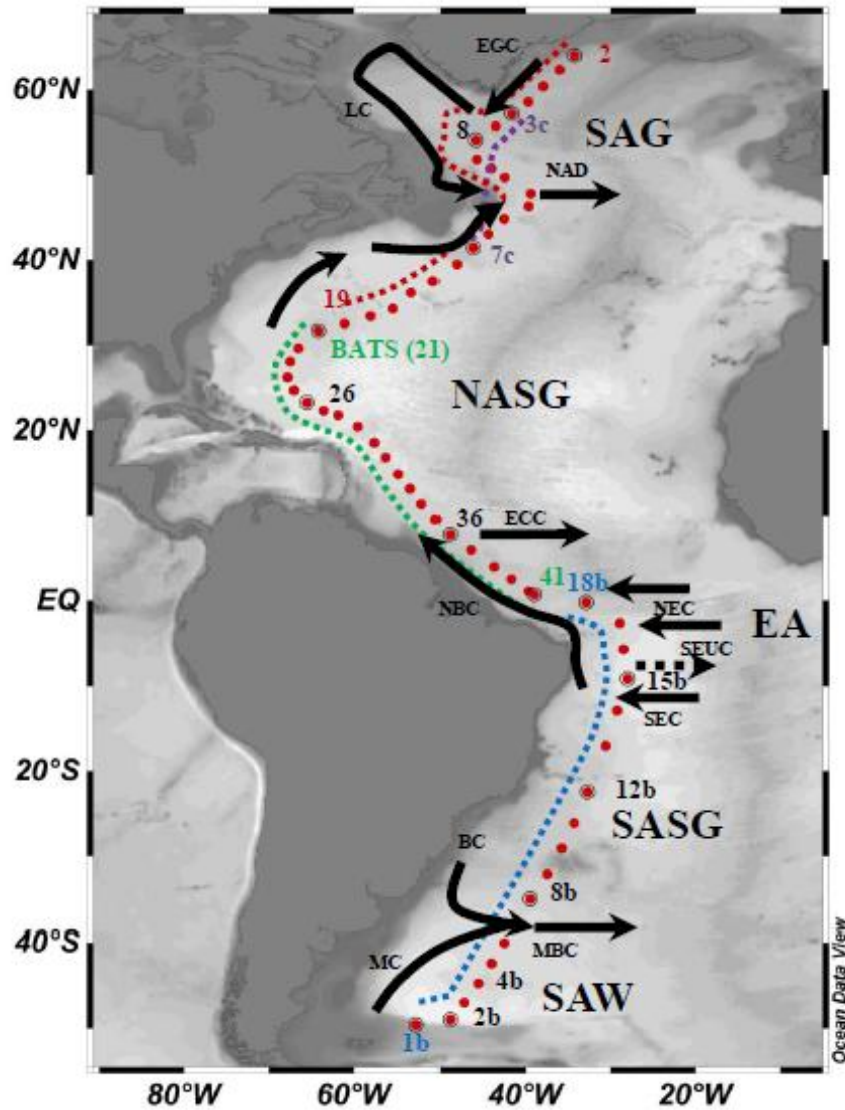


Figure 1. (a) Surface physical features and cruise track along the GEOTRACES-A02 section (b) Sampling location of the different four Legs are shown (Leg 1 in red dashed line from station 2 to station 19, Leg 2 in green dashed line from station 21 to station 41, Leg 3 in blue dashed line from station 1b to 18b and Leg 4 in purple dashed line from station 3c to 7c).

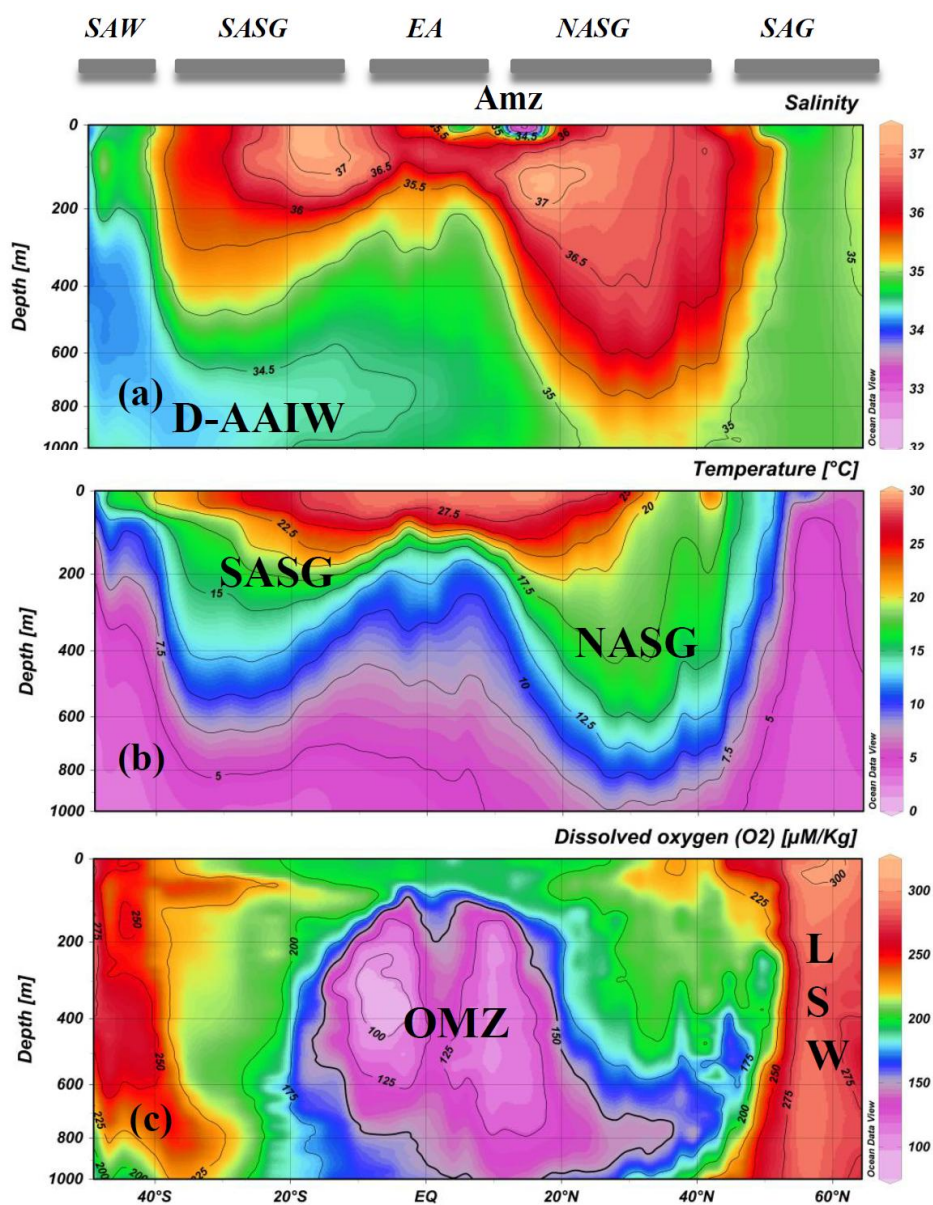


Figure 2. Interpolated vertical sections in the upper 1000 m of (a) Temperature (TMP), (b) Salinity (S) and (c) dissolved oxygen along the GA02 section, based on CTD data. Drake Antarctic Intermediate Waters (D-AAIW), Amazon River influence (Amz), South Atlantic Subtropical Gyre (SASG), North Atlantic Subtropical Gyre (NASG), Labrador Sea Waters (LSW) and Oxygen Minimum Zone (OMZ) are indicated.

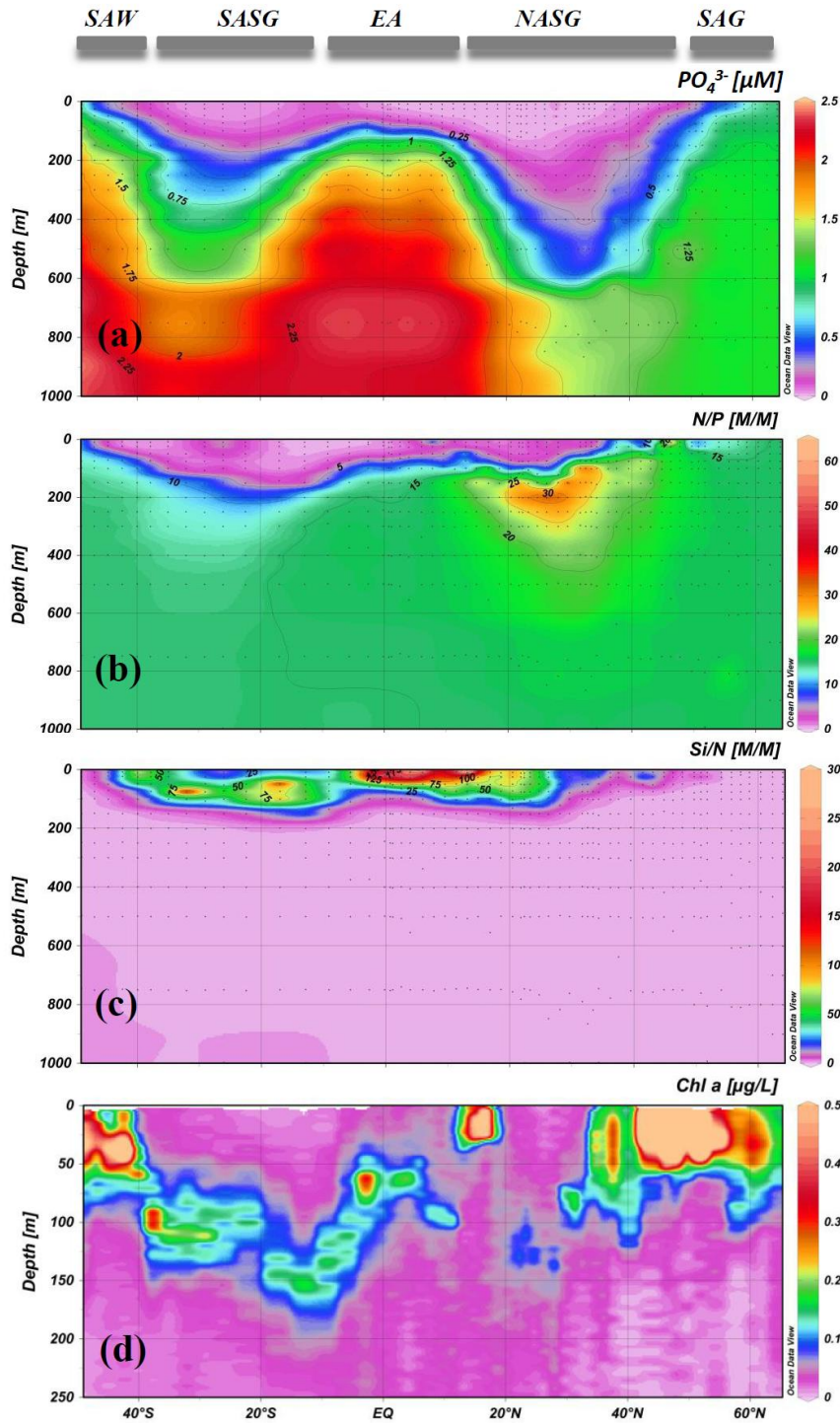


Figure 3. Interpolated vertical sections in the upper 1000 m of (a) phosphate, (b) N:P ratio (c) Si/N ratio, based on 735 analyses of water-column samples collected along the GA02 section, and (d) Chl a distribution in the upper 250 meters derived from CTD data.

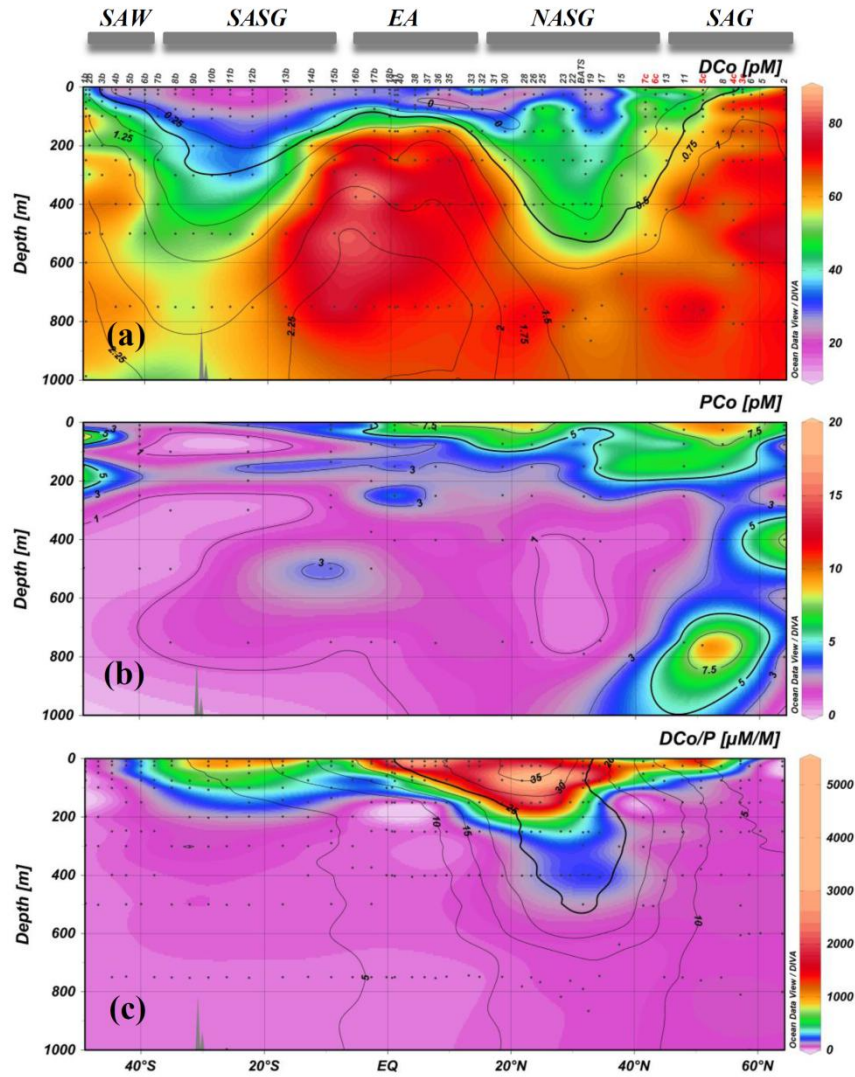


Figure 4. Interpolated vertical section in the upper 1000 m of (a) dissolved cobalt concentration (DCo) with phosphate contours overlaid on the profile; (b) particulate cobalt concentrations (PCo); (c) DCo/P ratio with dissolved aluminium concentration (DAI) contours overlaid on the profile (*Middag et al.*, unpublished data).

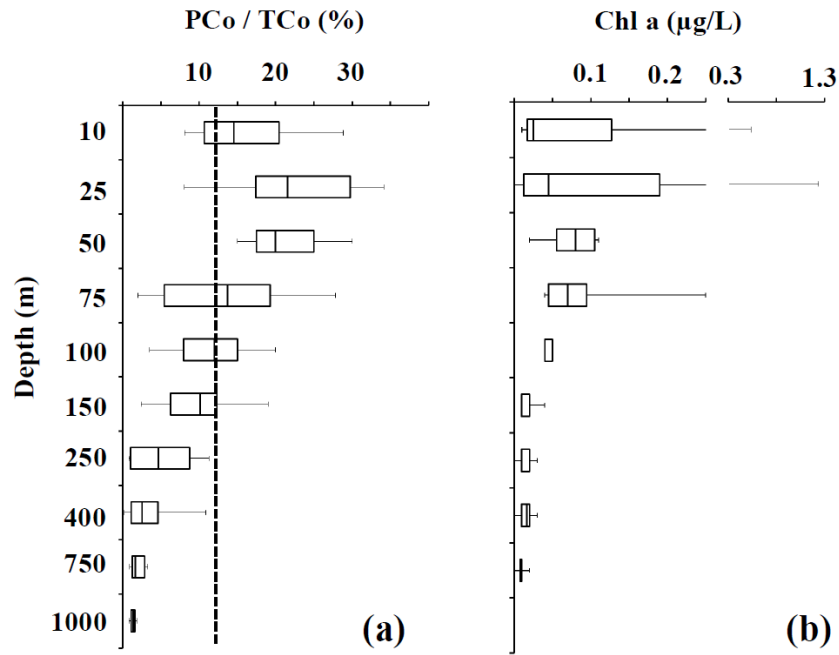


Figure 5. a) Box plot representing the relative proportion of particulate cobalt (PCo) to total cobalt (TCo). Using all data for a given depth along the section. Dashed line represents the average (mean = $12 \pm 12\%$; $n = 76$). b) Box plot representing estimated Chl a (derived from CTD data) using all data, where PCo is available, for a given depth along the section.

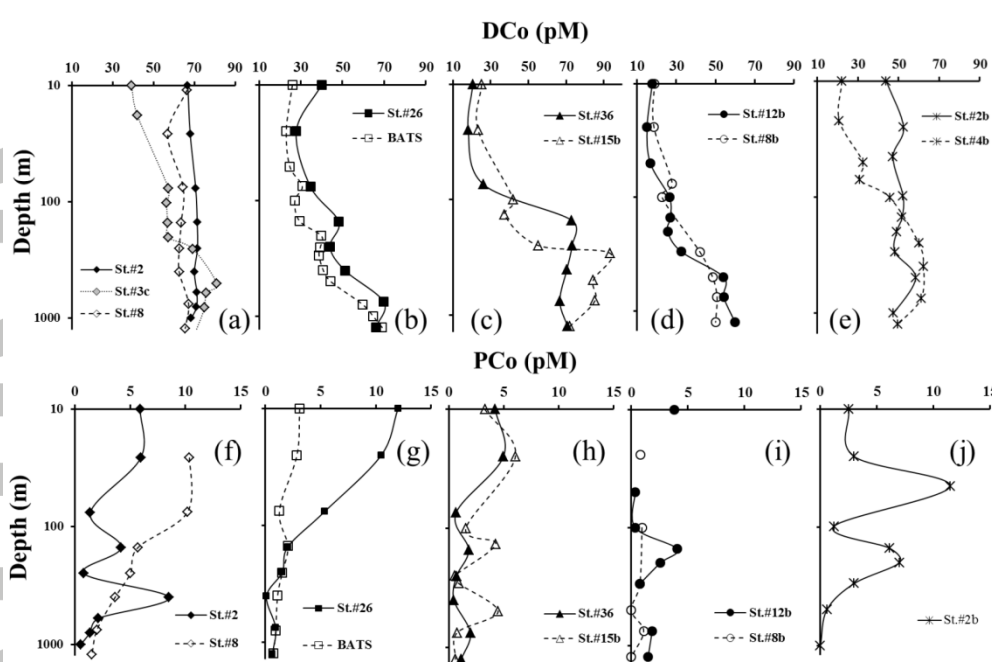


Figure 6. Typical vertical distribution of dissolved (DCo) and particulate (PCo) cobalt against depth in the different biogeochemical domains. In the SAG, DCo (a) and PCo (f) are shown for Station 2 (Leg-1; 64°N 34.25°W), St. 8 (Leg-1; 54°N 45.84°W) and St. 3c (Leg-4; 57°N 44°W). In the northern subtropical domain, DCo (b) and PCo (g) are shown at St. 26 (Leg-2; 23°N 65.55°W) and at the BATS station (Leg-2; 31.7°N 64.2°W). In the Equatorial area, DCo (c) and PCo (h) are presented at St. 36 (Leg-2; 7.8°N 48.9°W) and St.15b (Leg-3; 9°S 28°W);). In the southern subtropical domain, DCo (d) and PCo (i) are shown for St.12b (Leg-3; 22.47°S 32.7°W) and St. 8b (Leg-3; 35°S 39.4°W). In the subantarctic area DCo (e) and PCo (j) are shown at St.12b (Leg-3; 49°S 48.9°W) and St. 4b (Leg-3; 44.7°S 45.6°W).

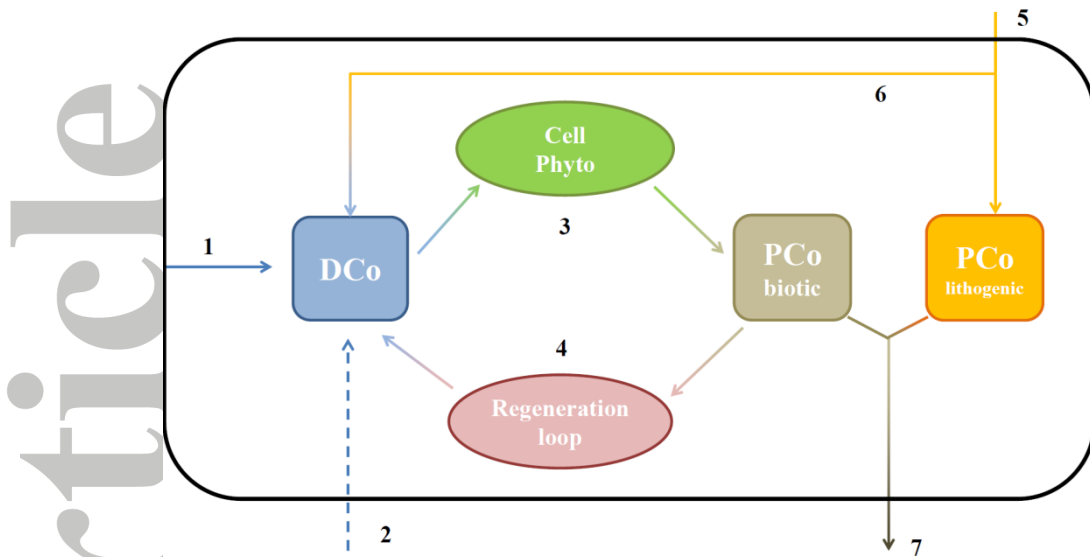


Figure 7. Simplistic conceptual schema of the cobalt cycling in the upper 100 meters. Arrows represent the fluxes as: 1: lateral advection; 2: vertical diffusion; 3: uptake; 4: regeneration; 5: Co deposition; 6: dust dissolution; 7: export. Here scavenging could not be discerned from biological uptake and is considered negligible.

Accepted Article

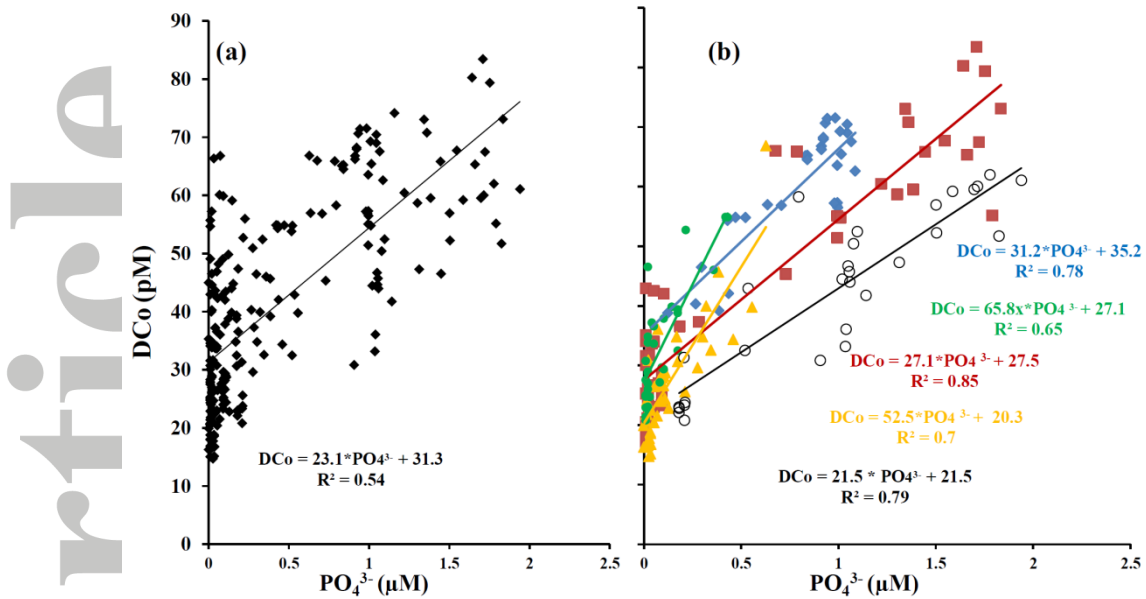


Figure 8. Scatter plots of the DCo data versus phosphate in the upper 250 meters, showing (a) the global DCo-P relationship ($n = 228$) along the section, and (b) the regional DCo-P relationships obtained in the SAG ($n = 28$; blue diamonds), the NASG ($n = 32$; green dots), the Equatorial area ($n = 53$; red squares), the SASG ($n = 51$; yellow triangles) and the SAW ($n = 22$; white dots).

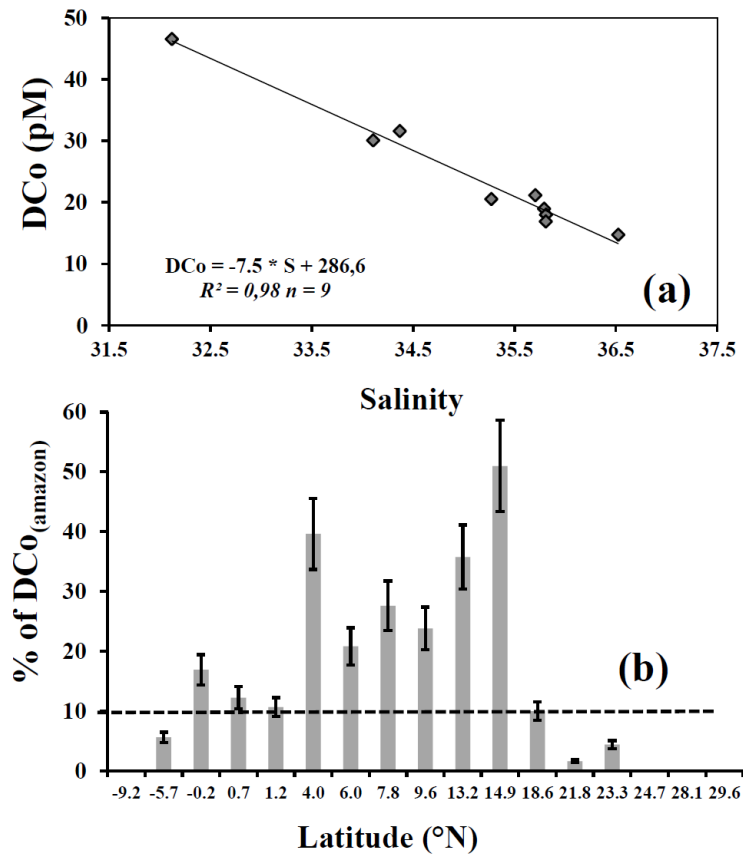


Figure 9. (a) Inverse linear correlation ($R^2 > 0.97$) between dissolved cobalt (DCo) and the salinity in the waters influenced by the discharge of the Amazon (dark stars). (b) Percentage of the DCo stock in the mixed layer attributed to the input by the Amazon. The dashed line indicates 10% contribution of the Amazon to the DCo stock.

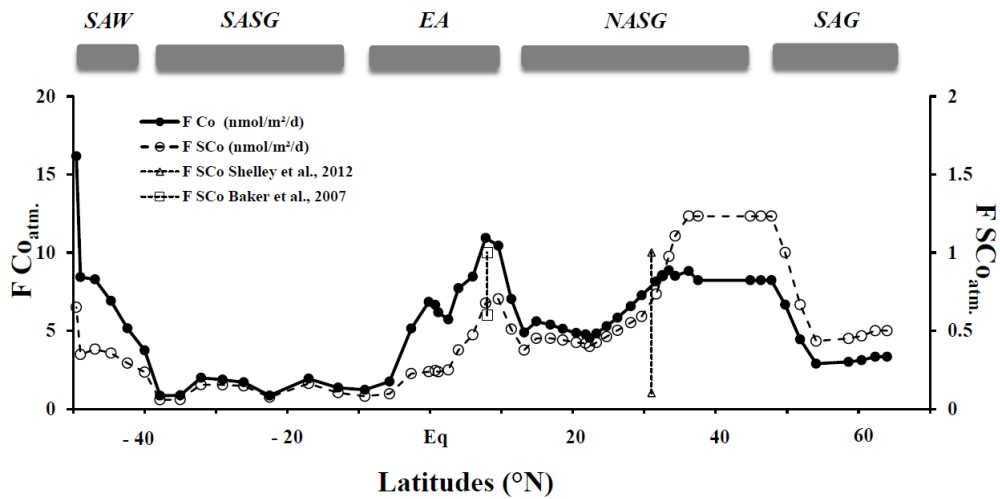


Figure 10. Estimation of the sea-surface atmospheric deposition of dry (dark circles, solid line) and soluble (open circles, dashed line) cobalt, along the section. The soluble Co deposition estimated by *Shelley et al.* [2012] and *Baker et al.* [2007] are shown for comparison.

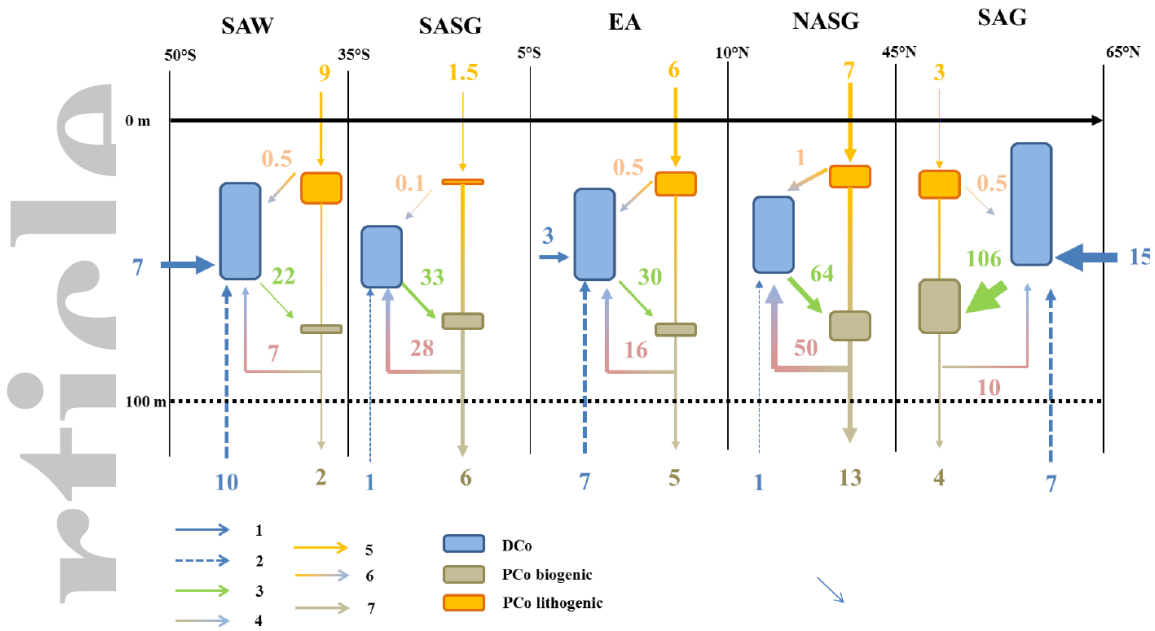


Figure 11. Conceptual schema of cobalt cycling in the different biogeochemical domains along the section. Wideness of the boxes represents the relative proportion of Co stock (at time of observation). Intensities of the fluxes are indicated and the numeration is described in Figure 7.