Dissolved cobalt and labile cobalt speciation in the Ross Sea from RVIB Nathaniel B. Palmer NBP0601, NBP0608 cruises in the Ross Sea Southern Ocean (CORSACS project)

Website: https://www.bco-dmo.org/dataset/3367
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Project
» Controls of Ross Sea Algal Community Structure (CORSACS)

Program
» Ocean Carbon and Biogeochemistry (OCB)

Contributors	Affiliation	Role
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Dataset Description

Dissolved cobalt and labile cobalt speciation in the Ross Sea, Antarctica from the CORSACS 2005/2006 expedition.

Methods & Sampling

Sampling and Analytical Methodology:

From Saito et al. (2010)
Mak A. Saito, Tyler J. Goepfert, Abigail E. Noble, Erin M. Bertrand, Peter N. Sedwick, Giacomo R. DiTullio. (in press) A Seasonal Study of Dissolved Cobalt in the Ross Sea, Antarctica: Micronutrient Behavior, Absence of Scavenging, and Relationships with Zn, Cd, and P. Bigeosciences, 7, 4059-4082, 2010. Open Access: http://www.biogeosciences.net/7/4059/2010/bg-7-4059-2010.html doi:10.5194/bg-7-4059-2010

Sampling Methodologies
Seawater samples for trace metals analysis were collected using either 5 L Teflon-coated external spring Niskin-X samplers (General Oceanics Inc., described as NX samples) or 2.5 L and 10 L Go-Flo samplers (General Oceanics Inc.). The Niskin-X and 10 L Go-Flo bottles were deployed on a non-metallic line (Spectra) and closed using solid PVC messengers, whereas the 2.5 L Go-Flo samplers were mounted on an 11-position rosette unit modified for trace metal sampling, which was deployed on the Spectra line. The rosette unit was programmed to close the samplers at pre-determined times on the upcast, with the precise depth of sampler closure determined using an integrated pressure sensor. The NX vertical profiles typically consisted of samples obtained from 9 Niskin-X samplers and two additional 10 L Go-Flo samplers; two vertical profiles (Station 54 and JR23) were obtained using only the Go-Flo samplers. Upon recovery, seawater samples were filtered

through either 0.2 micro-m Supor Acropak filter cartridges (Pall Corp., for NX samples) pre-rinsed with filtered surface seawater, or 0.4 micro-m 144mm polycarbonate membrane filters (GE, Osmonics, for Go-Flo samples) pre-cleaned with hydrochloric acid and Milli-Q deionized water. Cobalt was also measured in samples from three surface transects during CORSACS-1, collected using a trace-metal clean towed fish sampler deployed at ~3 m depth while underway at ~5 knots, with samples filtered using in-line 0.2 μm Supor Acropak filters (Bruland, 2005). All sample bottles were washed by soaking in 1% citranox overnight, rinsing thoroughly with Milli-Q, soaking in 10% Instra-analyzed HCl (Baker, Inc) for two weeks, followed by thorough Milli-Q rinsing and soaking with dilute (pH 2) Instra-analyzed HCl overnight. Bottles were rinsed with seawater prior to filling, and samples were refrigerated in darkness until analysis.

Total Dissolved Cobalt Analyses

Total dissolved cobalt (dCo), which is defined as total Co determined in filtered UV-irradiated seawater samples, was analyzed using a cathodic stripping voltammetry (CSV) protocol modified from our previous studies (Saito and Moffett, 2001; Saito et al., 2004; Saito et al., 2005; Saito and Moffett, 2002), with the addition of an automated titration system and a slight decrease in reagent usage. Briefly, seawater samples were digested in quartz tubes for 1 hour at ambient pH using a Metrohm UV digestor cooled with a Brinkmann water chiller. After this treatment, 9.25 mL of sample were pipetted into a Teflon sample cup that had been pre-rinsed with a small aliquot of sample; to this was added 50 microL of 0.5 M N-(2-hydroxyethy)piperazine-N-(3-propanesulfonic acid) buffer (EPPS, Sigma), 30 microL of 0.1 M dimethylglyoxime (DMG; Sigma-Aldrich), and 0.75 mL of 1.5 M sodium nitrite (Fluka). These three reagents were purified as previously described (Saito and Moffett, 2001; Saito et al., 2004; Saito et al., 2005). Instrumentation consisted of two Metrohm 663 hanging mercury drop stands, each interfaced to an Eco-Chemie mAutolab III, IME interface device, and portable Windows XP computer running GPES Electrochemical software (Eco-Chemie). Samples were purged for 3 minutes with filtered ultra high purity nitrogen gas, and voltammetric scans were performed at stirrer speed 5 using the large drop size. The CSV analysis involved deposition for 180 seconds at -0.6 V followed by a high speed scan from -0.6 V to -1.4 V at 10V s^-1. Total dissolved cobalt was quantified by standard additions with a Metrohm Dosimat, using a 5 x 10^-9 M CoCl2 standard solution prepared from a 1000 ppm Co atomic absorption standard (Fisher Scientific). A GPES script was programmed for three replicate scans of the sample prior to adding Co, followed by a scan after each of four automated 25 pM Co additions. Cobalt concentrations were calculated by dividing the mean of the triplicate sample scans by the standard addition slope determined by linear regression analysis, followed by reagent dilution and blank corrections for each set of reagents: 5.5 +/- 1.0 pM for the CORSACS-1 dCo profiles, 13.4 pM for the CORSACS-1 dCo surface transects and labile Co measurements, and 8.3 ± 1.3 pM for the CORSACS-2 dCo and labile Co measurements, as determined by running blank seawater as previously described (Saito and Moffett, 2001). Triplicate analysis of a surface sample from the Ross Sea using this automated method yielded 27.8 pM ± 0.7 pM (2.6% RSD). Linear regressions of the standard additions data typically yielded r2 values of 0.99 or greater, with samples being reanalyzed if r2 < 0.99. Analyses were primarily conducted at sea, although some refrigerated samples from CORSACS-2 were analyzed in our shore-based laboratory within two months after the cruise. This analytical method is identical to that used for our submitted analyses of the intercalibration samples and vertical profile from the US GEOTRACES intercalibration program (Bruland, 2010), with the exception that these CORSACS samples were run 'fresh' at ambient pH, while GEOTRACES samples were acidified, stored, and neutralized prior to analysis.

Cobalt Chemical Speciation: Labile Cobalt

The chemical speciation of dissolved cobalt was determined using a high-throughput labile Co method as previously described (Saito et al., 2004; Saito et al., 2005). Briefly this approach involves the analytical system described above for total dissolved cobalt, now with overnight equilibration of filtered seawater with 3x10-4 M DMG, which allows for quantification of ligand within the detection window for KCoL of 1013.7 to 1015.7, calculated using an estimated 50 pM natural organic cobalt ligand concentration and 10-fold range above and below a side reaction coefficient of aCoHDMG2 of 28460 (Saito et al., 2005). Conditional stability constants are not calculated in this high-throughput method. After equilibration, EPPS and nitrite are added and the sample is titrated with a Co standard as described for the dCo determinations above, but without the UV-irradiation treatment. The result is an estimation of what we refer to as labile cobalt, which is the dissolved cobalt that is not bound by the natural strong organic ligands following equilibration.

References:

Bertrand, Erin M.; Sa, Mak A.;Lee, Peter A.; Dunbar, Robert B.; Sedwick, Peter N.; DiTullio, Giacomo R. (2011) "Iron limitation of a springtime bacterial and phytoplankton community in the Ross Sea: implications for vitamin B12 nutrition" Frontiers in Microbiology. vol 2 no. 00160. ISSN=1664-302X. DOI: 10.3389/fmicb.2011.00160 http://journal.frontiersin.org/Journal/10.3389/fmicb.2011.00160/abstract

Bruland, K. W. 2010. GEOTRACES Co Intercalibration Results,

http://www.geotraces.org/documents/SAFeReferenceSample-Co.pdf

Saito, M. A., and 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, Mar. Chem., 75, 49-68.

Saito, M. A., and Moffett, J. W. 2002. Temporal and spatial variability of cobalt in the Atlantic Ocean, Geochim. Cosmochim. Acta, 66, 1943-1953.

Saito, M. A., Moffett, J. W., and DiTullio, G. 2004. Cobalt and Nickel in the Peru Upwelling Region: a Major Flux of Cobalt Utilized as a Micronutrient, Global Biogeochem. Cycles, 18.

Saito, M. A., Rocap, G., and Moffett, J. W. 2005. Production of cobalt binding ligands in a Synechococcus feature at the Costa Rica Upwelling Dome, Limnol. Oceanogr., 10 50, 279-290.

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Data Files

File
dissolved_cobalt.csv(Comma Separated Values (.csv), 22.53 KB) MD5:12ee816dd4de4bfe65dabd8512cedb82 Primary data file for dataset ID 3367

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Parameters

Parameter	Description	Units
cruise_ID	Cruise identifier	dimensionless
sta_name	station name	dimensionless
date	date of sampling (GMT)	YYYYMMDD
lon_360	longitude 0-360 degrees	decimal degrees
lat	latitude (South is negative)	decimal degrees
seafloor	bottom depth at sampling location	meters
depth	depth sample bottle was fired	meters
sample_num	sample number	integer
lineOut	winch reading prior to correction for deck height off water	meters
PO4	dissolved inorganic phosphate concentration	micromoles per liter
NO2	dissolved nitrite concentration	micromoles per liter
NO3_NO2	dissolved nitrate plus nitrite concentration	micromoles per liter
NH4	dissolved ammonium concentration	micromoles per liter
SiO2	dissolved silicic acid concentration	micromoles per liter
Co_diss	dissolved cobalt	picomoles per liter
Co_labile	labile cobalt	picomoles per liter
lon	longitude; converted from longitude 360 (West is negative)	decimal degrees

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Instruments

Dataset-specific Instrument Name	GO-FLO Teflon Trace Metal
Generic Instrument Name	GO-FLO Teflon Trace Metal Bottle
Dataset-specific Description	2.5 L and 10 L Go-Flo samplers (General Oceanics Inc.)
Generic Instrument Description	GO-FLO Teflon-lined Trace Metal free sampling bottles are used for collecting water samples for trace metal, nutrient and pigment analysis. The GO-FLO sampling bottle is designed specifically to avoid sample contamination at the surface, internal spring contamination, loss of sample on deck (internal seals), and exchange of water from different depths.

Dataset-specific Instrument Name	Niskin-1010X
Generic Instrument Name	Niskin-1010X
Dataset-specific Description	5 L Teflon-coated external spring Niskin-X samplers (General Oceanics Inc., described as NX samples)
Generic Instrument Description	The Model 1010X NISKIN-X External Spring Niskin Water Sampler is a Niskin water sample bottle with the stainless steel closure springs mounted externally. The external closure mechanism is designed to support applications such as trace metal analysis where the inside of the sampler must be totally free of contaminants. The 1010X Niskin bottle, manufactured by General Oceanics Inc., is available in a variety of sizes (sample volume). It can be activated by the GO Devil Messenger (1000-MG) if individually or serially attached to a hydrocable or can be deployed as part of a Rosette multibottle array. The bottles can be teflon-lined and are available as GO-FLO bottles to further avoid sample contamination. (more from General Oceanics)

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Deployments

NBP0601

Website	https://www.bco-dmo.org/deployment/57985
Platform	RVIB Nathaniel B. Palmer
Report	http://data.bco-dmo.org/CORSACS/cruises/Dunbar_Hydrography_report_NBP0601.pdf
Start Date	2005-12-17
End Date	2006-01-30
Description	This was the first of two Controls of Ross Sea Algal Community Structure (CORSACS) project cruises and was funded by the NSF Office of Polar Programs. The NBP0601 cruise was conducted in the Ross Sea in December 2005 and January 2006, Ross Sea, ca. 65.21°S-78.65°S, 164.98°E-164.70°W, and supported by NSF research grant, OPP-0338097. The 'Science Pan and Project Description' document includes details of the cruise sampling strategy. Related Files: Science Plan and Project Descriptions (PDF file)Cruise track map (PDF file)Photo of Ice Breaker Nathaniel B. Palmer on station near Beaufort Island (JPG image) Related Sites: MGDS catalog: http://www.marine-geo.org/tools/search/entry.php?id=NBP0601

NBP0608

Website	https://www.bco-dmo.org/deployment/57986
Platform	RVIB Nathaniel B. Palmer
Report	http://data.bco-dmo.org/CORSACS/cruises/Dunbar_Hydrography_report_NBP0608.pdf
Start Date	2006-11-01
End Date	2006-12-15
Description	This was the second of two Controls of Ross Sea Algal Community Structure (CORSACS) project cruises and was funded by the NSF Office of Polar Programs. The NBP0608 cruise was conducted in the Ross Sea in November and December 2006, ca. 65.21°S-78.65°S, 164.98°E-164.70°W. Related files: Cruise track map (PDF file) Related Sites: MGDS catalog: http://www.marine-geo.org/tools/search/entry.php?id=NBP0608

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Project Information

Controls of Ross Sea Algal Community Structure (CORSACS)

Website: http://www.whoi.edu/sites/corsacs

Coverage: Ross Sea Southern Ocean

Project summary

The Controls of Ross Sea Algal Community Structure (CORSACS) project was funded by the NSF Office of Polar Programs as "Collaborative Research: Interactive Effects of Iron, Light and Carbon Dioxide on Phytoplankton Community Dynamics in the Ross Sea". Two cruises were completed in 2006 to investigate the interactions between the primary productivity of the Ross Sea and pCO2, iron and other trace elements. Data sets of carbon, nutrient, metal, and biological measurements will be reported.

The main objective in the proposed research was to investigate the relative importance and potential interactive effects of iron, light and CO2 levels in structuring algal assemblages and growth rates in the Ross Sea. The investigators hypothesized that the interaction of these three variables largely determines the bottom-up control on these two dominant Southern Ocean phytoplankton taxa. While grazing and other loss processes are important variables in determining the relative dominance of these two taxa, the CORSACS research project was designed to focus on the bottom-up control mechanisms. It is important to understand such environmentally-driven taxonomic shifts in primary production, since they are expected to impact the fixation and export of carbon and nutrients, and the production of DMS, thus potentially providing both positive and negative feedbacks on climate.

The CORSACS investigators considered a range of ambient iron, light and pCO2 levels that span those typically observed in the Ross Sea during the growing season. That is, dissolved iron ranging from ~0.1 nM (low iron) to greater than 1 nM (high iron) (Fitzwater et al. 2000; Sedwick et al. 2000); mean irradiance (resulting from vertical mixing/self shading) ranging from less than 10% Io (low light) to greater than 40% (high light) (Arrigo et al., 1998, 1999), possibly adjusted based on field observations during the CORSACS cruises; and pCO2 ranging (Sweeney et al. 2001) from ~150 ppm (low CO2) to the probable higher levels of pCO2 - 750 ppm as a conservative estimate - that are likely to be attained later this century due to anthropogenic perturbation of the global carbon cycle (IPCC, 2001).

From the information previously available from both field observations and experiments, the investigators formulated the following specific hypotheses regarding the interactive role of iron, light and CO2 in regulating algal composition in the Ross Sea: diatoms bloom in the southern Ross Sea only under optimum conditions of high iron, light and pCO2; colonial Phaeocystis dominate under conditions of high iron with either (or both) low

light or low pCO2; and solitary Phaeocystis are predominant under conditions of low iron with either (or both) low light or low pCO2.

References:

Fitzwater, S.E., K.S. Johnson, R.M. Gordon, K.H. Coale, and W.O. Smith, Jr. (2000). Trace metal concentrations in the Ross Sea and their relationship with nutrients and growth. Deep-Sea Research II, 47: 3159-3179.

Martin JH, Gordon RM, Fitzwater SE. Iron in Antarctic waters. Nature 1990 ;345(6271):156-158. Martin JH. 1990. Glacial-interglacial CO2 change: The iron hypothesis. Paleoceanography 5(1):1-13

P. N. Sedwick, G. R. DiTullio, and D. J. Mackey, Iron and manganese in the Ross Sea, Antarctica: Seasonal iron limitation in Antarctic shelf waters, Journal of Geophysical Research, 105 (C5), 11,321-11,336, 2000.

Sweeney, C. K. Arrigo, and G. van Gijken (2001). Prediction of seasonal changes in surface pCO2 in the Ross Sea, Antarctica using ocean color satellite data. 2001 Annual AGU meeting, San Fransisco, CA Dec. 10-15.

IPCC, 2001: Climate Change 2001: Synthesis Report. A Contribution of Working Groups I, II, and III to the Third Assessment Report of theIntegovernmental Panel on Climate Change [Watson, R.T. and the Core Writing Team (eds.)]. Cambridge University Press, Cambridge,United Kingdom, and New York, NY, USA, 398 pp.

Publications

Saito, M. A., Goepfert, T. J., Noble, A. E., Bertrand, E. M., Sedwick, P. N., and DiTullio, G. R.: A seasonal study of dissolved cobalt in the Ross Sea, Antarctica: micronutrient behavior, absence of scavenging, and relationships with Zn, Cd, and P, Biogeosciences, 7, 4059-4082, doi:10.5194/bg-7-4059-2010, 2010 (http://www.biogeosciences.net/7/4059/2010/bg-7-4059-2010.html)

Bertrand EM, Saito MA, Lee PA, Dunbar RB, Sedwick PN and DiTullio GR (2011) Iron limitation of a springtime bacterial and phytoplankton community in the Ross Sea: implications for vitamin B12 nutrition. Front. Microbio. 2:160. doi: 10.3389/fmicb.2011.00160 (http://www.frontiersin.org/Aquatic_Microbiology/10.3389/fmicb.2011.00160/abstract)

Program Information

Ocean Carbon and Biogeochemistry (OCB)

Website: http://us-ocb.org/

Coverage: Global

The Ocean Carbon and Biogeochemistry (OCB) program focuses on the ocean's role as a component of the global Earth system, bringing together research in geochemistry, ocean physics, and ecology that inform on and advance our understanding of ocean biogeochemistry. The overall program goals are to promote, plan, and coordinate collaborative, multidisciplinary research opportunities within the U.S. research community and with international partners. Important OCB-related activities currently include: the Ocean Carbon and Climate Change (OCCC) and the North American Carbon Program (NACP); U.S. contributions to IMBER, SOLAS, CARBOOCEAN; and numerous U.S. single-investigator and medium-size research projects funded by U.S. federal agencies including NASA, NOAA, and NSF.

The scientific mission of OCB is to study the evolving role of the ocean in the global carbon cycle, in the face of environmental variability and change through studies of marine biogeochemical cycles and associated ecosystems.

The overarching OCB science themes include improved understanding and prediction of: 1) oceanic uptake and release of atmospheric CO2 and other greenhouse gases and 2) environmental sensitivities of biogeochemical cycles, marine ecosystems, and interactions between the two.

The OCB Research Priorities (updated January 2012) include: ocean acidification; terrestrial/coastal carbon fluxes and exchanges; climate sensitivities of and change in ecosystem structure and associated impacts on biogeochemical cycles; mesopelagic ecological and biogeochemical interactions; benthic-pelagic feedbacks on biogeochemical cycles; ocean carbon uptake and storage; and expanding low-oxygen conditions in the coastal and open oceans.

Funding

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NSF Antarctic Sciences (NSF ANT)	ANT-0732665
NSF Office of Polar Programs (formerly NSF PLR) (NSF OPP)	OPP-0338097
NSF Antarctic Sciences (NSF ANT)	ANT-0440840