# Elevated sources of cobalt in the Arctic Ocean

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1 **Abstract**
2 Cobalt (Co) is an important bioactive trace metal that is the metal co-factor in cobalamin
3 (vitamin B$_{12}$) which can limit or co-limit phytoplankton growth in many regions of the ocean.
4 Total dissolved and labile Co measurements in the Canadian sector of the Arctic Ocean during
5 U.S. GEOTRACES Arctic expedition (GN01) and the Canadian International Polar Year-
6 GEOTRACES expedition (GIPY14) revealed a dynamic biogeochemical cycle for Co in this
7 basin. The major sources of Co in the Arctic were from shelf regions and rivers, with only
8 minimal contributions from other freshwater sources (sea ice, snow) and aeolian deposition. The
9 most striking feature was the extremely high concentrations of dissolved Co in the upper 100 m,
10 with concentrations routinely exceeding 800 pmol L$^{-1}$ over the shelf regions. This plume of high
11 Co persisted throughout the Arctic basin and extended to the North Pole, where sources of Co
12 shifted from primarily shelf-derived to riverine, as freshwater from Arctic rivers was entrained in
13 the Transpolar Drift. Dissolved Co was also strongly organically-complexed in the Arctic,
14 ranging from 70-100% complexed in the surface and deep ocean, respectively. Deep water
15 concentrations of dissolved Co were remarkably consistent throughout the basin (~55 pmol L$^{-1}$),
16 with concentrations reflecting those of deep Atlantic water and deep ocean scavenging of
17 dissolved Co. A biogeochemical model of Co cycling was used to support the hypothesis that the
18 majority of the high surface Co in the Arctic was emanating from the shelf. The model showed
19 that the high concentrations of Co observed were due to the large shelf area of the Arctic, as well
20 as dampened scavenging of Co by manganese (Mn)-oxidizing bacteria due to the lower
21 temperatures. The majority of this scavenging appears to have occurred in the upper 200 m, with
22 minimal additional scavenging below this depth. These limited temporal results are consistent
23 with other tracers showing increased continental fluxes to the Arctic ocean, and imply both dCo
24 and LCo increasing over time on the Arctic shelf. These elevated surface concentrations of Co
25 likely lead to a net flux of Co out of the Arctic, with implications for downstream biological
26 uptake of Co in the North Atlantic and elevated Co in North Atlantic Deep Water. Understanding
27 the current distributions of Co in the Arctic will be important for constraining changes to Co
28 inputs resulting from regional intensification of freshwater fluxes from ice and permafrost melt
29 in response to ongoing climate change.
30

## 1. Introduction

Cobalt (Co) is an essential micronutrient in the ocean. It is utilized by eukaryotic phytoplankton as a substitute for zinc (Zn) in the metalloenzyme carbonic anhydrase (Lane and Morel, 2000; Sunda and Huntsman, 1995; Yee and Morel, 1996), and cyanobacteria have an absolute requirement for Co (Hawco and Saito, 2018; Saito et al., 2002; Sunda and Huntsman, 1995). Co is also the metal center in the micronutrient cobalamin, or vitamin $B_{12}$. In most ocean basins, dissolved Co (dCo; < 0.2 μm) is extremely scarce in surface waters (< 10 pmol $L^{-1}$), and is strongly complexed by a pool of thus far uncharacterized organic Co-binding ligands (Saito et al., 2005; Saito and Moffett, 2001). Due to its low concentrations, strong organic complexation, and its presence in cobalamin, dCo or cobalamin have been found to be limiting or co-limiting nutrients for phytoplankton growth in several regions (Bertrand et al., 2007, 2015; Browning et al., 2017; Hawco et al., 2020; Martin et al., 1989; Moore et al., 2013; Panzeca et al., 2008; Saito et al., 2005). Growth limitation can be due to either a lack of dCo, or cobalamin (Bertrand et al., 2012; Bertrand et al., 2007; Browning et al., 2017), as cobalamin is only synthesized by cyanobacteria and some archaea (Doxey et al., 2015). However, many phytoplankton utilize cobalamin for the synthesis of methionine (Yee and Morel, 1996; Zhang et al., 2009), and therefore must obtain it from the natural environment (Heal et al., 2017).

Co is taken up as a micronutrient by phytoplankton in surface waters and is regenerated from sinking organic matter at depth, but it is also prone to intense scavenging throughout the mesopelagic ocean (Dulaquais et al., 2014b; Hawco et al., 2018; Saito et al., 2017). The strongest removal mechanism for dissolved Co (dCo) is through co-precipitation of dCo with manganese (Mn) by Mn-oxidizing bacteria, due to their similar redox properties and ionic radii (Cowen and Bruland, 1985; Moffett and Ho, 1996; Sunda and Huntsman, 1988). Several sources of Co to the ocean have been identified, including riverine (Tovar-Sánchez et al., 2004; Zhang et al., 1990), coastal sediments (Dulaquais et al., 2014a, 2017; Hawco et al., 2016; Noble et al., 2012, 2016), and to a lesser extent hydrothermal and aeolian inputs (Shelley et al., 2012; Thuróczy et al., 2010). The largest reservoirs of dCo thus far have been seen in oxygen deficient zones, likely due to a combination of low oxygen concentrations at the sediment-water interface and advection from reducing sediments, as well as enhanced regeneration in low oxygen waters (Dulaquais et al., 2014b; Hawco et al., 2016; Noble et al., 2012, 2016). These oxygen minimum zone sources of dCo exert an important control on the inventory of dCo, which is likely sensitive to small perturbations in bottom water oxygen concentrations (Hawco et al., 2018; Tagliabue et al., 2018).

It is important to understand the sources and sinks and internal cycling of dCo due to its key role as a micronutrient. However, Co has one of the most complex biogeochemical cycles of all of the trace metals. Thousands of measurements of both total dCo and weakly complexed and/or inorganic or "labile" Co (LCo) and particulate Co (pCo) now exist in the ocean, greatly improving our understanding of Co cycling and have facilitated the representation of the biogeochemical model of Co to be included in global ocean models (Tagliabue et al., 2018). Several observational zonal transects have been generated by large-scale programs including the international GEOTRACES program, among others. Large datasets now exist in the North Atlantic (Baars and Croot, 2015; Dulaquais et al., 2014a; Dulaquais et al., 2014b; Noble et al.,

76   2017), South Atlantic (Noble et al., 2012), South Pacific (Hawco et al., 2016), Southern Ocean
77   (Bown et al., 2011; Saito et al., 2010), and Mediterranean Sea (Dulaquais et al., 2017).
78
79   Although the global coverage of Co measurements has greatly improved over the last decade, no
80   published measurements to our knowledge have been made in the Arctic Ocean. The Arctic
81   Ocean is arguably the most dynamic of the ocean basins, and is changing rapidly due to warmer
82   temperatures affecting the maximal sea ice extent (Screen and Simmonds, 2010; Stroeve et al.,
83   2012), the melting of permafrost (Jorgenson et al., 2006), and additional inputs of meltwater and
84   river water (Johannessen et al., 2004; Serreze and Barry, 2011). The Arctic Ocean is also likely
85   distinct in terms of Co cycling compared to other ocean basins due to its large shelf area,
86   restricted circulation, and potentially distinct Co sources including sea ice, snow, and highly
87   seasonal riverine inputs. The Arctic Ocean is known to have high concentrations of dissolved
88   organic matter (DOM), which could influence the organic complexation of Co in this ocean
89   basin. This study examined dCo, LCo, and pCo in two different transects in the Canadian sector
90   of the Arctic Ocean. We then used a Co biogeochemical model (Tagliabue et al., 2018) in order
91   to evaluate hypotheses about the role of external sources and internal cycling to the observed Co
92   distributions, the potential of the Arctic to be a net source of Co to the North Atlantic, and to
93   identify Co sources and sinks that may be sensitive to future changes in this rapidly changing
94   ocean basin.
95
96   **2. Methods**
97
98   *2.1 Sample collection and handling*
99
100  *2.1.1. Water column samples*
101  Samples were collected on two expeditions in the Canadian section of the Arctic Ocean (Fig. 1).
102  The first set of samples ($n = 107$) were collected on board the CCGS *Amundsen* from August 27,
103  2009 to September 12, 2009 in the Beaufort Sea as part of the Canadian IPY-GEOTRACES
104  program (ArcticNet 0903; GIPY14). The second set of samples ($n = 361$) were collected on
105  board the USCGC *Healy* (HLY1502) on the U.S. GEOTRACES Arctic expedition (GN01) from
106  August 9, 2015-October 12, 2015. The Canadian GEOTRACES expedition sampled along the
107  shelf and slope in the Beaufort Sea. The U.S. GEOTRACES expedition sailed in and out of
108  Dutch Harbor, Alaska, and traversed across the Bering Shelf and Makarov Basin before reaching
109  the North Pole on September 5, 2015 and returning south across the Canada Basin. Samples from
110  the Canadian GEOTRACES expedition were collected using a trace metal rosette system fitted
111  with 12 x 12 L GO-FLO bottles (General Oceanics), and only the dCo and LCo samples
112  collected in the water column from this study are discussed here. All other metadata from this
113  expedition can be found at http://www.bodc.ac.uk/geotraces/data/. Samples from the U.S.
114  GEOTRACES expedition were collected using the U.S. GEOTRACES trace metal clean rosette
115  outfitted with twenty-four 12 L GO-FLO bottles and a Vectran conducting hydrowire (Cutter and
116  Bruland, 2012). Two GO-FLO bottles were triggered at each depth during the trace metal
117  hydrocasts. One bottle was used for particulate trace metal sampling, and the other was used for
118  all dissolved metal and macronutrient analyses. Upon recovery of the sampling system, the GO-
119  FLO bottles were immediately brought inside a twenty-foot ISO container van. Sampling for
120  bulk particulate trace metal samples has been described in detail elsewhere (Twining et al.,
121  2015). The filters for particulate analyses were stored in trace metal clean centrifuge tubes and

122  frozen at -20°C until analysis (Twining et al., 2015). Dissolved trace metal and nutrient samples
123  were filtered with a 0.2 µm capsule filter (Acropak-200, VWR International) under pressurized
124  filtered air (Cutter and Bruland, 2012). Samples for dCo and LCo from the Canadian
125  GEOTRACES expedition were collected similarly, but were unfiltered. Samples for dCo were
126  placed in two separate 60 mL Citranox-soaked (1%) and acid-cleaned low-density polyethylene
127  (LDPE) bottles and were filled until there was no head space (Noble et al., 2012; Noble et al.,
128  2017). One sample was used for LCo analyses and the other was used for total dCo analyses.
129  Nutrient samples were analyzed immediately on-board by the Ocean Data Facility at Scripps
130  Institution of Oceanography.
131
132  *2.1.2 Ice hole samples*
133
134  Ice hole samples were only analyzed from the U.S. GEOTRACES cruise (GN01). Seawater from
135  ice holes for Co analyses was collected using Teflon coated Tygon tubing and a rotary pump
136  with plastic wetted parts (IWAKI magnetic drive pump, model WMD-30LFY-115) from a hole
137  at the station's sea ice floe. The hole was made with an ice corer (Kovacs 9 cm diameter Mak II
138  corer), and allowed to sit undisturbed for ~ 1 hour under a canvas tent prior to sampling. Samples
139  were collected from 1, 5 or 20 m at several sites. Seawater was filtered in-line with a 0.2 µm
140  filter (Acropak-200 capsule filter) and dispensed into a carboy, where it was homogenized and
141  brought back to the clean lab on board the ship. Sub-samples were taken for dCo from this
142  carboy, and stored as described below for other water column dissolved samples. Additional
143  details on ice hole samples can be found elsewhere (Marsay et al., 2018).
144
145  *2.2 Sample storage*
146
147  Total dCo and LCo samples were stored in two distinct ways. Oxygen concentrations have been
148  found to have a significant effect on storage of dCo samples (Noble et al., 2017). Although the
149  mechanism has not been fully explained, loss of some dCo species has been observed in the
150  presence of oxygen on both acidified and non-acidified samples across regions with active
151  biological gradients (Hawco et al., 2016; Noble et al., 2012; Noble et al., 2017, 2008). Since dCo
152  and LCo analyses were not able to be performed at sea on either expedition, groups of six dCo
153  samples from the U.S. expedition from a single cast were double-bagged and stored in a gas-
154  impermeable plastic bag (Ampac) along with 3-4 gas-absorbing satchels (Mitsubishi Gas
155  Chemical- model RP-3K). This outer bag was heat-sealed and samples were kept refrigerated
156  (4°C) and un-acidified until analysis (Hawco et al., 2016, 2018; Noble et al., 2016). LCo samples
157  were double-bagged and stored at 4°C and un-acidified until analysis. Samples were hand-
158  carried at the termination of the GN01 expedition to Woods Hole Oceanographic Institution, and
159  all samples were analyzed within three months. Samples from the Canadian GEOTRACES
160  expedition (GIPY14) were initially collected as unfiltered samples prior to filtration and analysis
161  and were not stored in gas-impermeable bags prior to analysis, as the effects of oxygen on dCo
162  loss were not known at the time of the expedition. It is possible there could have been some loss
163  of dCo during the time between sample collection and analyses (approximately one year), and
164  thus these concentrations could be underestimated. Additional discussion on how storage may
165  have impacted these results is discussed in section *3.2.2* and *4.3*.
166
167  *2.3 Reagent preparation*

168

169 All reagents were prepared in acid-clean plastic bottles and in large batches in order to have
170 consistent reagent batches for all sample analyses. For dCo and LCo analyses, a 0.5 mol $L^{-1}$
171 EPPS (N-(2-hydroxyethyl)piperazine-N-(3-propanesulfonic acid)) buffer and a 1.5 M $NaNO_2$
172 solution were prepared in Milli-Q (18 MΩ) and chelexed (Chelex-100, Biorad) to remove trace
173 metal contaminants. Dimethylglyoxime (DMG) was prepared by first making a $10^{-3}$ mol $L^{-1}$
174 EDTA solution in Milli-Q and adding 1.2 g of DMG. This solution was warmed by carefully
175 microwaving at 50% power to prevent boiling, until the DMG was fully dissolved. The solution
176 was placed on ice and left at 4°C to recrystallize overnight. The supernatant was decanted, and
177 the remaining crystals were poured into an acid-cleaned plastic weigh boat and the remaining
178 liquid was left to evaporate overnight in a Class-100 clean hood. Once dry, the remaining DMG
179 was added to an Optima methanol solution for a final concentration of 0.1 mol $L^{-1}$ DMG. A 1.5
180 mol $L^{-1}$ solution of sodium nitrite was prepared by placing sodium nitrite in Milli-Q and
181 chelexing the solution before use to remove trace metal contaminants. A Co standard solution
182 was prepared weekly by adding 29.5 μl of a 1 mg $L^{-1}$ Co AA standard (SPEX CertiPrep) to 100
183 mL of Milli-Q in a volumetric flask. For each new Co standard that was prepared during sample
184 runs, an approximately 1 mL aliquot was saved for later analyses to ensure no variation was seen
185 between batches. More information on reagent preparations can be found at
186 https://www.protocols.io/researchers/randie-bundy/publications.

187

188 *2.4 Dissolved and labile cobalt determinations*

189

190 The dCo and LCo measurements were determined using a modified cathodic stripping
191 voltammetry method (Saito and Moffett, 2001) for the GIPY14 samples, and a fully automated
192 method based on Hawco et al. (2016) for the GN01 samples (Hawco et al., 2016). Measurements
193 for both sample sets were performed using a Metrohm 663 VA stand connected to an Eco-
194 Chemie μAutolabIII system. Peak determinations for samples collected on GIPY14 were
195 completed as described in Noble et al. (2012). Sample automation and data acquisition for
196 samples from GN01 was completed using NOVA 1.8 software (Metrohm Autolab), and peak
197 determination was completed using a custom MATLAB code (see section 2.6).

198

199 The dCo samples were UV-irradiated for one hour in a temperature-controlled UV system prior
200 to analysis to remove any strong organic ligands that may prevent DMG from effectively binding
201 the entire dCo pool. For the GIPY14 samples, a modified temperature controlled UV system
202 (Metrohm 705 Digestor) was used (Hawco et al., 2016), while for GN01 samples an integrated
203 temperature-controlled (18°C) digestor was used (Metrohm 909 Digestor). In both cases samples
204 were placed in acid-cleaned and Milli-Q conditioned 15 mL quartz tubes. After irradiation, 11
205 mL of each sample was placed into acid-cleaned and sample-rinsed 15 mL polypropylene tubes.
206 For GIPY14 samples a final concentration of 353 μmol $L^{-1}$ DMG and 3 mmol $L^{-1}$ EPPS was
207 added to each sample before analysis (Noble et al., 2016), and for GN01 samples a final
208 concentration of 400 μmol $L^{-1}$ DMG and 7.6 mmol $L^{-1}$ EPPS was added to each sample before
209 analysis. Samples were then inverted several times before either being analyzed individually or
210 being placed on the autosampler (Metrohm 858 Sample Processor). For autosampler analyses,
211 the system was flushed with Milli-Q and 2 mL of sample were used to condition the tubing and
212 the Teflon analysis cup. Then 8.5 mL of sample was dosed into the cup automatically by a
213 Dosino 800 burette (Metrohm), along with 1.5 mL addition of 1.5 M $NaNO_2$ for a final analysis

214 volume of 10 mL. Samples were purged for 180 s with $N_2$ (high purity, > 99.99%) and
215 conditioned at -0.6 V for 90 s. The inorganic Co in the sample that was complexed by DMG
216 ($\log K^{cond}$ = 11.5$\pm$0.3) forms a bis-complex with $Co^{2+}$ that absorbs to the hanging mercury drop
217 electrode (Saito and Moffett, 2001). The $Co^{2+}$ and the DMG are both reduced at the electrode
218 surface using a fast-linear sweep (from -0.6 V to -1.4 V at 10 V s$^{-1}$) and the height of the
219 Co(DMG)$_2$ reduction peak that appears at -1.15 V is proportional to the dCo concentration in the
220 sample. The dCo was quantified by triplicate scans of the sample, followed by four standard
221 additions of either 25 or 50 pmol L$^{-1}$ per addition that were dosed directly into the Teflon
222 analysis cup. The slope of the linear regression of these additions and triplicate "zero" scans
223 were used to calculate the individual sample-specific sensitivity (nA pmol$^{-1}$ L$^{-1}$). The average of
224 the three "zero addition" scans was then divided by the sensitivity and then corrected for the
225 volume of the reagent, and the blank (see section 2.5). In between sample batches, or before
226 analyzing LCo samples, the entire auto-sampling system was rinsed with 10% HCl and then
227 Milli-Q.
228
229 LCo measurements were made similarly to the dCo measurements, with the following
230 amendments. LCo samples were not UV-irradiated, and 400 $\mu$mol L$^{-1}$ DMG was added to 11 mL
231 of sample and was equilibrated for at least 8 hours (overnight) in conditioned 15 mL
232 polypropylene tubes. Immediately prior to placement of the sample on the autosampler, EPPS
233 was added and the samples were analyzed as described above for dCo analyses. LCo
234 measurements are thus operationally defined as the fraction of dCo that is labile to 400 $\mu$mol L$^{-1}$
235 DMG over the equilibration period (Hawco et al., 2016; Noble et al., 2012).
236
237 *2.5 Blanks and standards*
238
239 The blank for GN01 samples was prepared by UV-irradiating low dCo seawater for one hour.
240 After UV-irradiation, the seawater was passed slowly through a Chelex-100 column to remove
241 any metals. The clean seawater was then UV-irradiated a second time before being analyzed. The
242 blank used for GIPY14 samples was analyzed at the beginning and the end of the sample
243 analyses to ensure the blank was consistent between runs. GEOTRACES consensus reference
244 materials were also analyzed along with GIPY14 samples, the results of which are reported
245 elsewhere (Noble et al., 2016).
246
247 For the GN01 samples, enough seawater was prepared in order to use the same blank seawater
248 for all of the subsequent sample analyses and the blank was analyzed regularly with each batch
249 of samples (every 10-20 samples). A combination of consensus reference materials and an in-
250 house seawater consistency standard were used throughout the sample analyses (Table 1). SAFe
251 and GEOTRACES standards were analyzed to ensure the accuracy of the sample measurements,
252 and were slowly neutralized drop wise with 1 N ammonium hydroxide (Optima, Fisher
253 Scientific) until reaching a pH of approximately 8. Aliquots of the SAFe and GEOTRACES
254 samples were then placed in conditioned quartz tubes and UV-irradiated for one hour, before
255 being analyzed as described above for dCo measurements. The consistency standard was
256 prepared by UV-irradiating 2 L of Southern Ocean trace metal clean seawater as described above
257 and was analyzed with each batch of samples to ensure consistency between sample runs.
258
259 *2.6 Dissolved and labile cobalt data processing*

260
261 Peak heights for the dCo and LCo samples for the GIPY14 dataset were determined in NOVA
262 1.8 software (Noble et al., 2016). All dCo and LCo peaks from the GN01 dataset were calculated
263 using custom MATLAB code available on GitHub (https://github.com/rmbundy/voltammetry).
264 Text files of the data output from NOVA 1.8 software were saved automatically from each scan,
265 and processed in MATALB to determine the dCo and LCo peak heights. The signal was
266 smoothed using the Savitzky-Golay smoothing function (span 5, degree 3), and the first
267 derivative of the voltammetric signal between -1.4 and -1.1 V was calculated in order to find the
268 start and end of the $Co(DMG)_2$ peak. The baseline was drawn and linearly interpolated between
269 the start and the end of the peak. The final peak height was determined by finding the maximum
270 of the signal and subtracting it from the baseline. Peak heights from the "zero addition" scans
271 were plotted along with the standard additions, and a linear regression was computed from all
272 seven scans. Data was flagged if the $r^2$ of the slope was < 0.97, and samples were re-analyzed.
273
274 *2.7 Dissolved and particulate manganese measurements*
275
276 The 0.2 µm-filtered seawater samples for dissolved manganese (dMn) were acidified to pH 2
277 using sub-boiling distilled HCl. The filtered subsamples were drawn into acid pre-washed 125
278 mL polymethylpentene bottles after three sample rinses, and the sample bottles were stored in
279 polyethylene bags in the dark at room temperature before analyses, which was usually within 24
280 h of collection. Prior to analysis, samples for manganese (dMn) were acidified by adding 125 µL
281 sub-boiling distilled 6 N HCl. Since the samples were used to determine dissolved iron (dFe) as
282 well, the obtained samples were then microwaved in groups of 4 for 3 min in a 900 W
283 microwave oven to achieve a temperature of $60\pm10°C$ in an effort to release dFe from
284 complexation in the samples. Samples were allowed to cool for at least 1 h prior to flow injection
285 analysis. The dMn measurements were determined in the filtered, acidified, microwave-treated
286 subsamples using a shipboard flow injection analysis (FIA) method (Resing and Mottl, 1992).
287 Samples were analyzed in groups of 8, and the samples collected at each station were generally
288 analyzed together during the same day. A 3-minute pre-concentration of sample (~9 ml) onto an
289 8-hydroxyquinoline (8-HQ) resin column yielded a detection limit of 0.55 nmol $L^{-1}$ and a
290 precision of 1.16% at 2.7 nmol $L^{-1}$.
291
292 Particulate trace element concentrations were determined through a total digestion procedure as
293 described in Ohnemus et al. (2014) and Twining et al. (2015). Briefly, approximately 7 L of
294 contamination-free seawater were filtered directly from Teflon-coated GO-Flo sampling bottles
295 over acid-washed 47-mm (shelf stations) or 25-mm (open basin stations) PES Supor filters.
296 Filters were divided in half, and one half was digested for 3 hours at 100-120°C in sealed Teflon
297 vials containing 4 M HCl, 4 M $HNO_3$, and 4 M HF (Fisher Optima), which digests the marine
298 suspended particulate matter (SPM) but leaves the PES filter mostly intact. The PES filters were
299 rinsed with ultrahigh purity water (18.2 MΩ $cm^{-1}$) and removed from the digestion vials, and 60
300 µL of sulfuric acid (Optima) and 20 µL of hydrogen peroxide (Fisher Optima) were added to the
301 vials to digest any filter fragments. The digest solution was taken to dryness at ~210°C (8-24
302 hours). The digest residue was re-dissolved in 4 mL of 0.32 M $HNO_3$ before measuring the total
303 particulate Co, Mn and phosphorous (pCo, pMn, pP) concentrations by inductively coupled
304 plasma mass spectrometry (ICP-MS; Thermo Element 2, National High Magnetic Field
305 Laboratory, Tallahassee, Florida). Major and trace element concentrations were calibrated using

306 an external multi-element standard curve and corrected for instrument drift using a 10 ppb
307 indium internal standard (Twining et al., 2019).
308
309 *2.8 Biogeochemical modeling of Co in the Arctic*
310
311 Modeling runs in the Arctic Ocean were completed using a previously published biogeochemical
312 model for Co (Tagliabue et al., 2018). Briefly, the Co model is part of the PISCES-v2 model and
313 has an additional six tracers for Co, including dCo, scavenged Co (associated with Mn oxides),
314 Co within in diatoms, Co in nanoplankton, small particulate organic Co, and large particulate
315 organic Co (Tagliabue et al., 2018). Phytoplankton uptake of Co in the model allows for variable
316 Co/C ratios and are based on a maximum cellular quota. The PISCES model is an excellent
317 platform for these studies as it has a detailed representation of ocean biogeochemical cycling and
318 has been used for a range of different studies. Measured pCo is equal to the sum of all of the
319 particulate Co tracers in the model (including living and non-living pools). Excretion of Co is
320 also simulated in a similar manner as Fe in PISCES-v2, with a fixed Co/C ratio in both mico-
321 and meso-zooplankton that sets the excretion of dCo as a function of the Co content of their food
322 (Tagliabue et al., 2018). The background biogeochemical model presented in Tagliabue et al.
323 (2018) was modified slightly for this work, most notably an improved particle flux scheme
324 (Aumont et al., 2017), with the Co-specific parameterizations left unchanged. We used the model
325 to assess the role of different processes by conducting sensitivity tests whereby the sedimentary
326 Co source was eliminated, the riverine Co source was eliminated, the slowdown of Co
327 scavenging at lower oxygen was removed (meaning oxygen did not affect Co scavenging) and
328 the change in Co scavenging due to variations in bacterial biomass was instead set to a constant
329 value. By comparing the results of these four sensitivity experiments to the control model, we
330 were able to quantify the relative contributions of different external sources and internal cycling
331 processes.
332
333 **3. Results**
334
335 *3.1 Oceanographic context*
336
337 The Arctic Ocean is a unique ocean basin. The surface circulation in the Arctic is characterized
338 by a clockwise current that entrains shelf water from the Chukchi and Eurasian shelfs, before
339 being swept across the North Pole by the Transpolar Drift (TPD; Fig. 1). This current is
340 distinguished by its low salinity and elevated concentrations of dissolved organic carbon (DOC)
341 (Klunder et al., 2012; Wheeler et al., 1997). The Arctic Ocean is a highly stratified system, with
342 little mixing between the main water masses (Steele et al., 2004). The major water masses that
343 enter the Arctic through the Bering Strait are the upper modified Pacific water (mPW) and the
344 Pacific halocline water (PHW). The mPW includes inputs from the Bering shelf, as well as
345 freshwater inputs from rivers, sea ice melt, and glacially modified waters. PHW includes some
346 influences from Bering Sea water (BSW; including both summer and winter water (Steele et al.,
347 2004)). Atlantic water (AW) comprises the bulk of the intermediate and deep waters of the
348 Arctic basin. These major water masses (mPW, PHW, AW) can be distinguished from the high-
349 resolution nutrient, oxygen and salinity data from the conventional CTD rosette stations in the
350 sampling region (Fig. 2). The mPW is characteristic of low salinity ($31 < S < 32$) and nutrients
351 (Fig. 2), and contains contributions from Alaskan Coastal Water (Steele et al., 2004), as well as

9

other modified water masses from the shelf. The PHW can be clearly identified from the elevated macronutrient concentrations (Fig. 2D), and temperature maximum within the salinity range of 31-33 (Steele et al., 2004; Steele and Boyd, 1998) (Fig. 2A, C). The AW comprises a relatively uniform deep layer throughout the entire Arctic basin. AW enters the Arctic through the Fram Strait and Barents Sea and cycles in a cyclonic direction around the Eurasian Basin and Canadian Basin (Aagaard and Carmack, 1989; Carmack et al., 1995) and is characterized by higher salinities (> 33), its temperature (~ -1.0°C) and lower nutrient concentrations (silicate < 5 μmol $L^{-1}$).

*3.2 Dissolved cobalt distributions*

*3.2.1 Elevated dissolved cobalt in surface waters*

Blank and consensus values for the GIPY14 dataset are reported elsewhere (Noble et al., 2016) and the dCo blanks and standards for the GN01 analyses are reported in Table 1. The dCo profiles in the Arctic resembled a "scavenged-like" profile throughout the majority of the transect and were distinct from recent U.S. GEOTRACES efforts in the North Atlantic (Noble et al., 2016) and Eastern Tropical South Pacific (Hawco et al., 2016; Fig. 3). When median dCo concentrations from this study are binned by depth, the upper 50 m in the Arctic contains a median dCo concentration approximately 10 times higher than that of surface waters in the North Atlantic or South Pacific (Dulaquais et al., 2014; Hawco et al., 2016; Noble et al., 2017, 2012). Profiles in the Arctic also show no perceptible mid-depth maximum analogous to either the Atlantic or Pacific (Fig. 3), and instead dCo concentrations rapidly decline until reaching values of approximately 50-60 pmol $L^{-1}$. These concentrations in deep waters are slightly lower than the deep Atlantic and closer to background Pacific levels (~30-40 pmol $L^{-1}$).

The dCo concentrations were highly elevated in surface waters (< 100 m) in the shelf regions (Fig. 4A-C, P-R) and these high concentrations persisted into the basin in the vicinity of the North Pole (Fig. 4F-H). In the Bering Sea, dCo in surface waters ranged from 131-156 pmol $L^{-1}$ in the upper 40 m, with an apparent surface or sub-surface minimum associated with biological drawdown (Fig. 4A). Concentrations notably increased in stations near the Bering Strait (stations 2-6; Fig. 4B), where dCo reached up to 457 pmol $L^{-1}$ in surface waters (Fig. 4B; Fig. 5), and was even higher in bottom waters, sometimes exceeding 1.5 nmol $L^{-1}$ (Fig. 4B; Fig. 5). Surface enrichment of dCo was even more pronounced on the Chukchi shelf, where concentrations consistently exceeded 800 pmol $L^{-1}$ (Fig. 4Q; Fig. 5). The dCo and LCo concentrations from the Canadian GEOTRACES expedition in 2009 also had near surface maxima in dCo and LCo, with up to 300 pmol $L^{-1}$ dCo (Fig. 4R). These concentrations were lower than nearby samples collected in 2015 (Fig. 4P, Q), which contained up to three times more dCo in the upper 100 m.

The elevated dCo concentrations on both shelves traversed by the U.S. expedition persisted throughout the marginal ice zone (MIZ; stations 12-17, 51-54) and into the Canada basin (stations 12-26), following similar patterns in dFe and dMn (L. Jensen and M. Hatta pers. comm.). Water mass fractions and sea ice melt in in the MIZ in this study were determined based on δ^{18}O data (Newton et al., 2013). Some high concentrations of dCo were observed in the region of the MIZ and in samples with pronounced influence from meltwater (> 1.5% sea ice melt; Table 2) in the upper 30 m, with median dCo concentrations equal to 358 pmol $L^{-1}$ in the

398    MIZ, though with large variability (range 26-546 pmol L$^{-1}$) likely due to surface drawdown and
399    additional dCo sources. Surface concentrations in this region ranged from approximately 100-
400    500 pmol L$^{-1}$ (Fig. 4D-F, M-N). The dCo in surface waters decreased slightly in the Makarov
401    Basin and reached some of the lowest observed concentrations at the North Pole (210 pmol L$^{-1}$;
402    Fig. 4H; Fig. 5), though concentrations were still slightly higher than at Station 1, the only
403    Pacific station (Fig. 4A). Although some elements such as dFe showed noticeable elevated
404    concentrations in the vicinity of North Pole in surface waters compared to surrounding waters (L.
405    Jensen, pers. comm.), dCo remained lower than on the shelf and in the MIZ (Fig. 5). Surface dCo
406    at the North Pole was approximately 250 pmol L$^{-1}$, nearly half the concentrations observed in the
407    Canada Basin (Fig. 4H).

409    *3.2.2 Dissolved cobalt in Pacific halocline and deep waters*

411    While silicate (SiO$_3$) and phosphate (PO$_4^{3-}$) concentrations were indicative of the advection of
412    PHW (Fig. 2E, F), dCo did not show a prominent enhancement within this feature (Fig. 5A),
413    likely due to the lower relative concentrations of dCo in Pacific waters compared to shelf waters
414    (station 1; Fig. 4A). Median concentrations of dCo in waters dominated by Pacific water (> 95%)
415    were 270 pmol L$^{-1}$ (range 64-687 pmol L$^{-1}$) while on the shelf they were 526 pmol L$^{-1}$ (Table 2).
416    Any elevated dCo concentrations observed within the PHW density layer ($\sigma_\theta$= 26.2-27.2; Steele
417    et al., 2004) was likely added along the flow path of Pacific water across the Bering Shelf (Fig.
418    4B). Thus, stronger relationships were observed with other elements which are also elevated on
419    the shelf (e.g. dFe and dMn; M. Hatta pers. comm.) than with SiO$_3$ or other macronutrients (e.g.
420    PO$_4^{3-}$).

422    The dCo was remarkably constant within the deep Arctic, reflective of both AW and deep Arctic
423    bottom water (Fig. 5A; Swift et al., 1983). Concentrations in AW (> 95% AW, and all depths >
424    500 m) had a median value of 62 pmol L$^{-1}$ (Table 2), in between the average deep water dCo
425    concentrations found in the Pacific and Atlantic (Fig. 3). The near-bottom sample from some
426    profiles also showed slightly lower dCo (< 5 pmol L$^{-1}$) than the sample immediately above it
427    (Fig. 4C, D, F), perhaps indicating some influence of the weak nepheloid layers on bottom-water
428    scavenging of dCo in the Arctic (Noble et al., 2016).

430    *3.3 Labile cobalt distributions*

432    *3.3.1 Labile cobalt in surface waters*

434    LCo is the fraction of total dCo that is either not organically complexed or weakly bound by
435    organic ligands, and represents the "labile" fraction of the total dCo pool either in terms of
436    biological uptake or scavenging (Saito et al., 2004; Saito and Moffett, 2001). LCo distributions
437    looked remarkably similar to dCo in the upper water column (Fig. 4, 5). Concentrations were
438    lower than dCo, ranging from 0 (not detectable) to 600 pmol L$^{-1}$ on the Canadian side of the
439    Chukchi Shelf (station 61, 66). LCo comprised 20-35% of the total dCo pool in the upper water
440    column (Fig. 6), with the highest percentage of LCo found over the Chukchi shelf and
441    approximately 20% LCo in Pacific waters (station 1; Fig. 6). LCo decreased more rapidly with
442    respect to distance from the shelf than dCo in the Canada Basin and towards the North Pole, with
443    the North Pole region containing significantly lower median concentrations of LCo (10 pmol L$^{-1}$,

444    $p < 0.05$) than surrounding waters (148 and 117 pmol L$^{-1}$ on the shelf and MIZ, respectively;
445    Table 2). The majority of the LCo appeared to either be removed via scavenging or biological
446    uptake in the upper water column in the Canada Basin and along the Lomonosov Ridge. Some of
447    the highest median LCo concentrations were observed in the upper 30 m in the MIZ and in
448    waters containing significant sea ice melt (> 1.5%, Table 2), with median concentrations rivaling
449    those on the shelf (Table 2). The LCo in these samples had a large range in many cases (49-233
450    pmol L$^{-1}$ in samples with > 1.5% sea ice melt), suggesting that sea ice may be a source of LCo,
451    and that it is taken up quickly in surface waters after input from meltwater.

453    *3.3.2 Labile cobalt in Pacific halocline waters and deep waters*

455    LCo was extremely low, and often undetectable, in the deep waters of the Arctic (Fig. 4). Any
456    detectable LCo at these depths represented less than 10% of total dCo (Fig. 6), and the majority
457    of the dCo in the deep Arctic was strongly organically complexed. Similar to dCo, there was no
458    observable enhancement of LCo in PHW, with LCo distributions closely following that of dCo
459    and other shelf-enhanced trace metals such as dFe and dMn (L. Jensen, pers. comm.; Jensen et
460    al., 2019; Tonnard et al., 2020). LCo decreased below the upper 250 m, and the median
461    concentration of LCo in the Atlantic layer was 2 pmol L$^{-1}$ (Table 2) virtually equal to the
462    detection limit of the method, suggesting scavenging or uptake of LCo in the upper water column
463    and little to no detectable LCo in deep waters of the Arctic.

465    *3.4 Dissolved and particulate manganese and particulate cobalt distributions*

467    DCo and dMn had very similar distributions across the transect. The pCo and pMn
468    concentrations were slightly decoupled from the dissolved concentrations, with a subsurface
469    peak in both (Fig. 7), as opposed to the surface peak observed in dCo and dMn. The maximum in
470    pCo and pMn occurred at depths of approximately 200-300 m, corresponding to a region of
471    significantly elevated concentrations of particulate Mn-oxides (P. Lam pers. comm.). Overall,
472    pCo and pMn concentrations were the highest on the shelf, with visible increases at the base of
473    the profiles near the sediment water interface (Fig. 7B, C). Concentrations of pCo and pMn
474    declined by almost an order of magnitude from the shelves into the Arctic basin, with
475    concentrations ranging from 20-40 pmol L$^{-1}$ and 1-10 nmol L$^{-1}$ for pCo and pMn, respectively.
476    Deep water (> 1000 m) particulate concentrations for both metals were extremely consistent,
477    with concentrations varying slightly over the entire Arctic basin (Fig. 7D, H). These deep water
478    pMn and pCo concentrations are notably higher than in other regions, such as deep Pacific
479    waters (Lee et al., 2018).

481    *3.5 Modeling sensitivity experiments*

483    The control model run agreed well with the data over a number of different depth strata (Fig. 8).
484    In the surface layer (0-50m), the model output was most consistent with the observations (Fig.
485    8A), although in general, the model tends to produce maximum levels of dCo that underestimate
486    the highest dCo concentrations observed. Part of this is likely due to the fact that the model is
487    comparing an annual mean output against the synoptic scale of the in-situ observations.
488    However, the model may underestimate sources of dCo in the Arctic. Below 50 m, there is also
489    good agreement with observations (Fig. 8B), with the model capturing the much lower dCo

490 characteristic of these waters and in particular the contrast between our data in the Arctic and
491 other data from the North Atlantic (Dulaquais et al., 2014). In the deepest layers (Fig. 8C and D),
492 the model again is able to reproduce the decline in dCo to ~60 pmol L$^{-1}$ and the consistency
493 between the deep Arctic and North Atlantic.

495 In order to explore the major processes contributing to the modeled dCo sources and sinks, the
496 proportion of the dCo signal in two distinct depth horizons was further investigated using a set of
497 sensitivity experiments. In the 0-50 m depth range (Fig. 9), rivers in the model were shown to
498 have no large-scale impact on the Arctic-wide dCo signal (Fig. 9A), while removing sediment
499 margin sources reduced dCo by over 80% (Fig. 9B). Enhanced sediment Co supply under low
500 oxygen also had no impact in this region. Similarly, modulating the effect of oxygen on Co
501 scavenging had little impact in the Arctic (Fig. 9C). It was notable that in sensitivity experiments
502 where bacteria scavenging due to Mn-oxide formation was kept constant (e.g. by eliminating the
503 effect of bacterial biomass on scavenging) the dCo concentrations were reduced by over 60% in
504 surface waters in some regions, indicating that lower rates of scavenging were also contributing
505 to the high concentrations of dCo in the surface ocean (Fig. 9D). Thus, our model experiments
506 suggest that the high levels of dCo in the Arctic surface waters are due to high supply from
507 sediments, combined with reduced scavenging rates due to lower metabolic activity of Mn-
508 oxidizing bacteria due to the colder temperatures. In the 700-800 m depth horizon, we similarly
509 found that changing sediment supply was more important than rivers (Fig. 10A and B), but that
510 the effect of sediments was reduced at these depths compared to the surface. Equally, retardation
511 of Co scavenging under low oxygen had a minor role in the ocean interior (Fig. 10C), with
512 bacterial biomass again having a significant effect on the dCo signal (Fig. 10D). Thus, in contrast
513 with the surface, we find that in the 700-800 m stratum there is a roughly equal role played by
514 sediment Co supply and low rates of Co removal by Mn-oxidizing bacteria in maintaining the
515 dCo concentrations.

517 **4. Discussion**

519 *4.1 Quantifying external sources of cobalt to the Arctic Ocean*

521 The coherence of the dCo and LCo distributions with that of dMn, along with evidence from the
522 model output, suggest that shelf sediments are one of the primary sources of Co in the Canadian
523 sector of the Arctic Ocean (Fig. 5, 9). Mn is known to be an excellent tracer of sediment input
524 due to the high solubility of reduced Mn from anoxic sediments (Johnson et al., 1992; März et
525 al., 2011; McManus et al., 2012; Noble et al., 2012). By using the dMn concentrations as a tracer
526 for shelf input, we can quantify the proportion of the variance in the dCo and LCo observations
527 that are explained by this shelf proxy. Linear regressions between dCo or LCo distributions and
528 dMn in the upper 200 m across all of the stations explained 73% and 79% of the variance in the
529 dCo and LCo concentrations, respectively (Fig. 11A; $p < 0.05$). This trend is driven primarily by
530 the data in the upper 50 m. The variance explained decreases however, if only the shelf stations
531 (stations 2-10, 57-66) are included in the analysis (data not shown), suggesting that some process
532 other than shelf inputs couples the dMn and Co distributions within the basin. The amount of the
533 variance in the Co distributions that is explained by shelf inputs as indicated by dMn is slightly
534 less than that observed in the model (Fig. 9B), though both agree that shelf inputs are the
535 dominant source.

536
537    The modeling results suggest that nearly all of the dCo in the upper 50 m can be accounted for
538    by a combination of a sediment source and diminished scavenging in the Arctic relative to other
539    ocean basins (Fig. 9B and D, (Tagliabue et al., 2018)). However, the observations suggest that
540    20-30% of the variance cannot be explained by a shelf source alone. If the dCo and LCo is
541    examined against salinity for all stations from GN01 in the upper 200 m, then salinity can
542    explain 24% and 28% of the variance for dCo and LCo, respectively (data not shown). This
543    relationship is improved if only the stations in the central Arctic basin are included (stations 30-
544    43), and then salinity explains 47% of the dCo and 57% of the LCo distributions (Fig. 11B). The
545    coherence of dCo and LCo with salinity across the dataset, and particularly in this region,
546    appears to be due to a contribution of low salinity water from rivers, rather than from sea ice
547    melt (Fig. 12C), as no relationship was observed with the fraction of sea ice melt determined
548    from $\delta^{18}O$ isotopic measurements of seawater (Bauch et al., 2005; Cooper et al., 1997, 2005;
549    Newton et al., 2013). Instead, the relationship with salinity is driven by freshwater inputs from
550    rivers, as a strong relationship is observed with the fraction of meteoric water (Fig. 12D). These
551    stations correspond to a region of anomalously high dFe and DOC concentrations (Charette et
552    al., 2020), interpreted to be indicative of river inputs carried across the basin in the Transpolar
553    Drift (TPD) (Gascard et al., 2008; Klunder et al., 2012; Middag et al., 2011; Wheeler et al.,
554    1997). This is supported by measurements of $^{228}Ra$, which has been used as a tracer of shelf
555    inputs throughout the Arctic (Kipp et al., 2018; van der Loeff et al., 2018). A similar relationship
556    was also observed with salinity in the North Atlantic, supporting the role of rivers as a source of
557    dCo (Dulaquais et al., 2014a; Noble et al., 2016; Saito and Moffett, 2001). In our model
558    sensitivity experiments, we found a small effect of rivers on dCo (Fig. 9A, 10A), and the Co/N
559    river endmember in the model was similar to that measured by the Arctic Great Rivers
560    Observatory (Holmes et al., 2018). It appears that the data suggest a larger role for rivers than
561    what is captured by the model, which could imply that gross riverine fluxes are underestimated
562    by our model. However it is difficult to disentangle riverine processes from other processes
563    happening on the shelf like groundwater inputs (Charette et al., 2020). It is possible that there is
564    some mixing of river and sediment dCo occurring in the coastal zone or that our global scale
565    model is not able to properly account for the physical transport of fluvial signals into the open
566    basin.
567
568    The presence of such high concentrations of trace elements and isotopes at the North Pole was
569    surprising, yet several tracers indicate that this is an area significantly influenced by river and
570    shelf input from the surrounding continents (Charette et al., 2020; Colombo et al., 2020; Kipp et
571    al., 2018; van der Loeff et al., 2018). The elevated concentrations of dCo at great distances from
572    the continental shelf is also likely partially due to the enhanced organic complexation of dCo in
573    TPD waters. Averaged over the entire dataset, dCo is 79±13% organically complexed (21±13%
574    labile) in the upper 200 m of the water column. However, at TPD influenced stations (stations
575    29-34; Charette et al., 2020), dCo is 92±6% organically complexed, significantly higher than in
576    the rest of the transect (*paired sample t*-test, $p < 0.05$). This suggests that elevated concentrations
577    of DOC from Arctic rivers entrained in the TPD or ligands produced in-situ may play a role in
578    stabilizing a portion of the dCo pool during transport towards the North Pole, as has been
579    observed for other metals such as dFe (Slagter et al., 2017, 2019) and dissolved copper (Nixon et
580    al., 2019). Although the exact character of the organic dCo-binding ligands in seawater are
581    unknown, in the Arctic it is likely that humic-like substances contribute some portion of the

582 organic complexation observed, due to the presence of elevated colored DOM (CDOM) in the
583 TPD (Wheeler et al., 1997), consistent with the presence of humic substances (Del Vecchio and
584 Blough, 2004). Despite the presence of humic substances, it seems somewhat unlikely that
585 humics account for all of the ligands complexing dCo in this region. Our analytical method
586 distinguishes organically-bound Co as the fraction of total dCo that is more strongly complexed
587 than our competing ligand (DMG). The complexation of humic and fulvic-like substances with
588 Co has been shown to be much weaker than the $Co(DMG)_2$ complex ($\log K_{Co(HS)}^{cond}$ ~ 8 versus
589 $\log K_{Co(DMG)_2}^{cond}$= 11.5±0.3; Yang and Van Den Berg, 2009). Ligands similar to those suspected to
590 complex Co in open ocean waters of the Atlantic or Pacific could be responsible for Co
591 stabilization in the TPD waters (Saito and Moffett, 2001). These ligands are presumed to have
592 functional groups similar to cobalamin (vitamin $B_{12}$), with a Co atom tightly bound inside a
593 corrin ring. Cyanobacteria and some archaea are known cobalamin producers (Bertrand et al.,
594 2007; Doxey et al., 2015; Heal, 2018; Heal et al., 2017; Lionheart, 2017) and both are found in
595 the Arctic (archaea; Cottrell and Kirchman, 2009; cyanobacteria; Waleron et al., 2007; Zakhia et
596 al., 2008), although in very low abundance. The nature of the organic molecules binding dCo in
597 this region will be interesting to explore further in future studies.
598
599 Overall, both the modeling results and observations agree that the dominant source of Co in the
600 Arctic is from the extensive shelf sediments surrounding the Arctic Ocean, with additional
601 contributions from Arctic rivers. The observations however, show that sources vary in
602 importance in space, with sediment sources clearly dominating in stations close to the shelf, and
603 river sources dominating in the central Arctic basin through the influence of the TPD. The
604 interaction between rivers and shelves requires further inquiry, as the shelf sediments might
605 behave as "capacitor" for dCo, accumulating Co from rivers and sinking organic matter and then
606 releasing Co to the overlying water during reductive dissolution in the sediments (Bruland et al.,
607 2001; Chase et al., 2007). Although the mechanism is uncertain, it is clear that the riverine
608 source dominates the distribution observed near the North Pole where dCo and LCo
609 concentrations remain high despite the distance from land, and that organic complexation likely
610 plays a role in the distal transport of this dCo (Charette et al., 2020).
611
612 *4.2 Cobalt scavenging and internal cycling*
613
614 A striking feature of the dCo and LCo dataset is the vertical transition in the water column from
615 very high to low Co concentrations throughout the deep Arctic (Fig. 5). The question remains
616 whether or not 1) this elevated dCo is scavenged at a shallow depth horizon, or 2) if the high dCo
617 concentrations in the surface layer (< 200 m) are simply physically isolated from deeper water
618 masses, or a combination of the two. This would suggest that the Atlantic water characteristic of
619 the deep Arctic doesn't mix with the modified surface Arctic water containing high
620 concentrations of Co. We examined both hypotheses within a modeling framework and
621 compared this to the observations. In the model, the dCo is scavenged primarily in the upper 50
622 m with almost no scavenging below 200 m (data not shown). The dCo scavenging in the model
623 is primarily controlled by Mn-oxidizing bacteria, which have a strong temperature dependence in
624 the model (Tebo et al., 2004). The cold temperatures in the majority of the Arctic prevent
625 enhanced scavenging of dCo by this mechanism compared to other basins (Hawco et al., 2018;
626 Saito et al., 2017; Tagliabue et al., 2018). However, relatively warmer temperatures on the
627 shallow shelves suggest that scavenging is enhanced in this region (Fig. 4), and the coherence of

628    the pCo and pMn peaks in the upper 200-250 m (Fig. 7) support this mechanism of upper ocean
629    scavenging. Evidence from [234]Th data shows very little particulate organic carbon (POC) flux in
630    the upper water column along this transect, however strong lateral transport from the shelves to
631    the basin was observed (Black et al. 2018). This lateral transport was observed both in the upper
632    water column and at depth, suggesting fast-moving currents through the deep canyons may be
633    significant in transporting material from the shelf into the basin (Black et al. 2018). It is possible
634    that additional scavenging of Co may occur along this flow path. Some of the profiles observed
635    in the deep basin also show evidence for bottom water scavenging in the Atlantic water (e.g. Fig.
636    4E, H, P).

638    Additional insights on Co scavenging in this basin can be observed by exploring the dCo:
639    phosphate (P) ratios (pmol L$^{-1}$:µmol L$^{-1}$) along the transect (Fig. 13). The relationship between
640    dCo and P in the Arctic water column yields insights into biological uptake and regeneration
641    processes acting on the dCo inventory, as well as scavenging. An analysis completed by Saito et
642    al. (2017) showed that positive slopes in the dCo:P relationship were indicative of regeneration,
643    while negative slopes were indicative of biological uptake or scavenging (Saito et al., 2017). The
644    high dCo in the Arctic yields a unique dCo:P relationship compared to the North Atlantic (Fig.
645    13A; Saito et al., 2017). When dCo:P slopes ($r^2 > 0.6$) are binned according whether they are
646    positive (Fig. 13B) or negative (Fig. 13C) and then plotted versus depth (Fig. 13D), a few
647    patterns are apparent. Positive dCo:P slopes are observed largely within a confined depth layer in
648    the PHW (Fig. 13D). This is not surprising, given that deep Pacific waters carry a strong
649    regeneration signal. However, at most other depths the dCo:P slopes are negative, showing that
650    scavenging is occurring to some extent throughout the water column (Fig. 13D). With one
651    exception, the magnitude of the negative dCo:P slopes are greater in the upper water column,
652    supporting the model results and our interpretations of the pCo profiles that most of the
653    scavenging occurs in the upper water column, but also continues to occur throughout the deep
654    Arctic.

656    This evidence, combined with the coinciding maxima observed in pCo and pMn, suggest that
657    scavenging occurs in the upper water column, but that additional scavenging continues to occur
658    in deeper waters. The elevated pCo concentrations in the deep Arctic compared to other regions
659    (Lee et al., 2018) suggest that scavenging over long timescales continues to add to the pCo pool.
660    The strong stratification in the Arctic likely prevents high concentrations of dCo from mixing
661    between the modified surface waters, the PHW, and the deep Atlantic water (Steele et al., 2004).
662    Thus, it is likely a combination of limited upper ocean scavenging, and strong stratification
663    between water masses, that keeps the elevated dCo and LCo confined to the surface waters in
664    Arctic, yielding the intense scavenged-like profile of Co in this region compared to other basins
665    (Fig. 3).

667    *4.3 Increases in Co inventories over time in the Canadian sector of the Arctic Ocean*

669    Samples collected on the shelf in the Beaufort Sea in 2009 in proximity to the U.S.
670    GEOTRACES transect in 2015 (Fig. 1) had significantly lower dCo (*paired t*-test, *p* < 0.05) than
671    shelf samples from 2015 (Fig. 14). Shelf samples for dCo from 2015 were approximately four
672    times higher than the dCo and approximately eight times higher in LCo than in 2009 (Fig. 14C).
673    The maximum dCo concentration measured in 2009 was 301 pmol L$^{-1}$, while in 2015 it was 1852

674  pmol L$^{-1}$. The dCo and LCo concentrations below 150 m agreed very well however, between the
675  two years (Fig. 14A, B). Several factors could account for the higher dCo and LCo observed in
676  2015 compared to 2009. The Co samples from 2009 were initially unfiltered, and were not stored
677  with gas-absorbing satchels like the samples from 2015. Recently, loss of dCo has been observed
678  in the presence of oxygen during storage, however this loss was most pronounced for samples in
679  low oxygen regions (Noble, 2012). The mechanism of the dCo loss is unknown and is difficult to
680  quantify from these samples, however the waters are well oxygenated in this region (Fig. 2B)
681  and thus the loss due to storage was likely minimal. However, we cannot say for certain how
682  much of the observed increase in dCo over time is due to a storage artifact. Previous work has
683  shown a maximum loss of dCo of 40% after 5 months of storage (Noble, 2012). If we consider
684  that 40% of the dCo could have been lost in the samples collected from 2009, the data from 2015
685  still show an increase in dCo of approximately 400%. Thus, although we cannot quantify with
686  certainty the percent increase in dCo over time in the Canadian sector of the Arctic, it is likely
687  that a large increase in dCo was observed.
688
689  The increase in dCo over time in the Arctic is interesting, and has been documented for other
690  tracers in the Arctic. Kipp et al. (2018) and van der Loeff et al. (2018) noted that $^{228}$Ra has
691  increased over time in the central Arctic. They suggest that increases in shelf and/or river inputs
692  from thawing permafrost are the source of this elevated $^{228}$Ra (Kipp et al., 2018; van der Loeff et
693  al., 2018). A similar mechanism is likely increasing metal inventories over time on Arctic
694  shelves. The majority of the variance (~70%) in dCo in the upper 100 m on the U.S.
695  GEOTRACES transect could be explained by a shelf source, and the remainder was likely
696  associated with river inputs (Fig. 11). If these sources are similar to the sources of dCo in 2009,
697  then an increase in either a shelf or river flux could be responsible for the dramatic increase in
698  dCo over time. While there is not enough data to state whether the river dCo flux has in fact
699  changed over time in the Arctic and the observed changes could be due to seasonal or interannual
700  variability, several other studies have documented an increase in river discharge due to increases
701  in permafrost melt over time (Doxaran et al., 2015; Drake et al., 2018; Kipp et al., 2018; van der
702  Loeff et al., 2018; Tank et al., 2016; Toohey et al., 2016). The increase in river discharge has the
703  potential to considerably increase trace metal inventories in the future Arctic Ocean, perhaps
704  particularly for those metals that are strongly organically complexed, thus protecting against
705  scavenging in the estuarine mixing zone (Bundy et al., 2015). We recognize these two Arctic
706  dCo datasets are limited in temporal coverage and have methodological differences; however, we
707  felt a responsibility to transparently present these observations of dCo increases in the Arctic
708  Ocean to raise community awareness of this potential environmental change. These increases in
709  metals over time may have implications for metal stoichiometries and phytoplankton growth in a
710  changing Arctic Ocean.
711
712  *4.4 Implications of the Arctic as a net source of Co to the North Atlantic Ocean*
713
714  The concentrations of dCo and LCo in this region of the Arctic are some of the highest that have
715  been observed thus far in the ocean. In some cases, the dCo was almost ten times higher than in
716  the low oxygen region of the Eastern Pacific (Hawco et al., 2016). Although the Arctic is
717  considered to be a macronutrient poor system, in contrast to other oligotrophic regions the Arctic
718  is quite enriched in micronutrients (Charette et al., 2020; Colombo et al., 2020; Jensen et al.,
719  2019; Marsay et al., 2018; Slagter et al., 2017). These distinct micronutrient ratios may have

implications for Arctic phytoplankton communities, as well as communities in the North Atlantic that are influenced by inputs from the Arctic.

Arctic waters are thought to primarily exit the basin and impact the North Atlantic via the Canadian archipelago and the Fram and Davis Straits (Talley, 2008). The organic complexation and stabilization as well as the high concentrations of dCo suggest that some of this dCo might exit the Arctic and impact nutrient distributions in the North Atlantic. Noble et al. (2016) noted a plume of elevated dCo in the western portion of the U.S. GEOTRACES North Atlantic (GA03) transect that did not correspond with a signature from reducing sediments as on the North Atlantic eastern boundary. Noble et al. (2016) postulated that high dCo in Labrador Seawater (LSW) was the source of this signal, due to the presence of a corresponding signature of low silica that is characteristic of this water mass. The authors noted this anomalously high dCo could be from elevated dCo in Arctic waters, or due to high dCo on the shelf that is picked up along the flow path of the LSW, or a combination of the two (Dulaquais et al., 2014a; Noble et al., 2016). This observation was also noted by Dulaquais et al. (2014) in the GEOTRACES GA02 section (Dulaquais et al., 2014a, 2014b). Our data suggests that likely a combination of the high dCo observed in this study and additional Co entrained on the shelf in the Labrador Sea contribute to that signal, and when observed in temperature and salinity space the data support this hypothesis (Fig. 15). The Arctic source waters that contribute to the formation of LSW have a low salinity signature, and are likely significantly modified as they exit the Canadian archipelago, Fram Strait and Davis Straits (Yashayaev and Lodor, 2017). From this data we cannot quantitatively connect the elevated dCo and LCo observed in the Arctic source waters to the LSW seen in the western Atlantic (Dulaquais et al., 2014a; Noble et al., 2016), given the complex history (e.g. transformation, mixing) of source waters in the Labrador Sea region (Le Bras et al., 2017). However, it is apparent that the low salinity Arctic waters contain high Co (Fig. 15), which given the advective pathways of these water masses from the Arctic, suggests that they may act as a source of Co to lower latitude waters. Interestingly, the high dCo in the Arctic has a distinct LCo/dCo signature compared to that observed in the western North Atlantic (Fig. 15A). Due to the significant impact that Arctic shelves and rivers have on the dCo signature observed in this study, it is likely that additional Co may be added to these waters as they pass through the Canadian archipelago. The fate of these waters and their Co as they exit via the Fram and Davis Straits is unknown. Constraining these Arctic endmembers and how they contribute to dCo distributions in the North Atlantic deserves further attention, as it has interesting implications for nutrient resource ratios for North Atlantic phytoplankton communities.

The possibility that elevated micronutrient concentrations from the Arctic are being exported to the North Atlantic could have implications for phytoplankton nutrient utilization and community composition. The dCo and dZn for example, which can be interchanged within carbonic anhydrase in some eukaryotes (Lane and Morel, 2000; Sunda and Huntsman, 1995; Yee and Morel, 1996), are elevated in the Arctic (Jensen et al., 2019) compared to the North Atlantic and South Pacific (Fig. 16A, B (Schlitzer et al., 2018)). The higher concentrations of both metals results in a dCo/dZn ratio that is quite similar to that observed in the North Atlantic, however the range in this ratio is large (Fig. 16C). Small changes in the sources of each of these metals could manifest as big impacts on the ratio of these micronutrients in surface waters, which laboratory studies have shown to have significant effects on growth (Hawco and Saito, 2018; Kellogg et al., 2020; Sunda and Huntsman, 1995). The cellular Co/Zn ratios are also slightly higher in the

Arctic compared to the North Atlantic but span a similar range (Twining et al. in prep, Figure 16D). However, if river inputs continue to increase with an increase in permafrost thawing in the warming Arctic (Jorgenson et al., 2006) and similar increases in dCo are observed over time as seen in this work, then the inventory of dCo in the Arctic may begin to influence the North Atlantic to a greater extent. These increases in metal sources may disproportionately affect Co compared to Zn, whose primary source was found to be from a regeneration signal on the shelf rather than from river input (Jensen et al., 2019), and whose total inventory is small compared to Zn. For example, diatoms that have enhanced growth rates when metabolically substituting Co for Zn may be favored in surface waters with higher dCo/dZn ratios (Kellogg et al., 2020), although there is no experimental data to our knowledge examining the influence of Zn and Co on Arctic phytoplankton. Understanding how future changes in metal sources in the Arctic may impact the North Atlantic or shifts in phytoplankton community structure will be important to constrain.

## 5. Conclusions

The unique dissolved and labile Co distributions observed in the Arctic compared to other open ocean basins have potential implications for future changes in micronutrients in the warming Arctic Ocean. Sediment and river inputs to the Arctic appear to be the dominant mechanisms for the input of dCo to the Arctic, and these elevated signals persist over a broad area of the western Arctic far from their source regions. In part, this appears to be due to relatively slow scavenging of Co in the Arctic, highlighting the impact of lower temperatures and slower kinetics of Mn-oxide formation in this basin. The dCo in the Arctic is also strongly organically-complexed, which may also prevent scavenging and lead to the persistently high concentrations observed in surface waters. Notably, Co was also shown to be increasing over time on the shelf in the Canadian Arctic, likely due to increases in river inputs from thawing permafrost, consistent with other Arctic tracers. The increase in the inventory of dCo over time in the Arctic may have downstream impacts on dCo/dZn ratios in North Atlantic waters, as the dCo inventory will be disproportionately magnified relative to dZn with additional future increases from Arctic rivers. Higher dCo/dZn ratios in the Arctic and North Atlantic may also favor organisms that have elevated growth rates if Co is metabolically substituted for Zn. These ecological impacts are likely to become increasingly important in the future, with increased warming and changes to Co sources in the Arctic basin.

## 6. Author contributions
RMB analyzed the samples and wrote the manuscript. MRC developed the data processing code and helped write the manuscript. MAS designed the study and helped write the manuscript. AT, NJH, PLM, BST, MH, AN, SGJ, and JTC contributed data and helped write the manuscript.

## 7. Data availability
The metadata for this manuscript are available through BCO-DMO for GN01 (https://www.bco-dmo.org/project/638812) and through BODC for GIPY14 (https://www.bodc.ac.uk/geotraces/data/inventories/0903/). The dissolved and labile cobalt data for GN01 specifically is available at https://www.bco-dmo.org/dataset/722472.

## 8. Acknowledgements

**Table 1:** Average dCo concentrations from blank, internal standard, and consensus standard runs.

|  | n | dCo (pmol L$^{-1}$) | std dev |
|---|---|---|---|
| blank | 29 | 2.5 | 0.7 |
| internal standard | 26 | 50.3 | 7.6 |
| SAFe D1 | 3 | 47.9 | 2.1 |
| SAFe D2 | 3 | 45.2 | 2.1 |
| GSP | 3 | 2.4 | 1.8 |
| GSC | 3 | 77.9 | 2.8 |

**Table 2:** Median, maximum and minimum concentrations of total dissolved (dCo) and labile cobalt (LCo) in samples with representative water masses and sources in the Arctic Ocean. Median concentrations were determined in each water mass type by using water masses that contained > 95% Atlantic water, > 95% Pacific water, > 10% meteoric water, and > 1.5% sea ice melt. Shelf stations were stations 2-10 and 60-66, MIZ stations 10-17 and 51-57 (< 30 m), and North Pole stations 27-36 (< 200 m). Ice hole samples were sampled from 1 and 5 m. The notation 'nd' means not determined.

| | dCo (pmol L$^{-1}$) | max | min | *n* | LCo (pmol L$^{-1}$) | max | min | *n* |
|---|---|---|---|---|---|---|---|---|
| Atlantic | 61.6 | 126.3 | 36.9 | 37 | 2.2 | 5.8 | 0.2 | 27 |
| Pacific | 269.6 | 687.3 | 64.1 | 41 | 45.8 | 133.8 | 2.5 | 35 |
| Meteoric | 266.1 | 497.2 | 64.1 | 27 | 77.5 | 139.8 | 11.6 | 25 |
| Shelf | 526.0 | 1852.1 | 25.9 | 30 | 148.0 | 578.7 | 6.1 | 30 |
| MIZ | 357.5 | 546.2 | 25.9 | 19 | 117.0 | 158.6 | 6.1 | 19 |
| North Pole | 139.8 | 280.2 | 64.2 | 14 | 10.3 | 22.0 | 1.5 | 14 |
| sea ice melt | 526.0 | 1021.5 | 207.3 | 3 | 151.1 | 233.0 | 48.8 | 3 |
| ice hole | 281.1 | 316.2 | 259.4 | 4 | nd | nd | nd | 4 |

**Figure Captions**

**Figure 1**: Standard CTD sampling stations (green) and trace metal rosette (TM) sampling stations (blue) from the GN-01 expedition in 2015, and trace metal sampling locations from the GIPY14 expedition in 2009 (red).

**Figure 2**: *In-situ* temperature (A), nitrate (B), salinity (C), phosphate (D), oxygen (E), and silicate (F) with neutral density anomaly contours from the northern and southern legs of the GN-01 transect as shown in Figure 1. Major water masses are labeled as modified Pacific Water (mPW), Pacific Halocline Water (PHW) and Atlantic Water (AW).

**Figure 3:** Median dCo concentrations at specific depth intervals from the Arctic Ocean (this study; red circles), Atlantic Ocean (blue triangles), and the Pacific Ocean (orange squares). Shaded regions indicate the upper and lower quartiles of the data in each dataset.

**Figure 4**: Dissolved cobalt (dCo; black circles) and labile cobalt (LCo; open circles) from all stations from the 2015 (A-Q) and 2009 (R) studies.

**Figure 5:** (A) dCo concentrations and (B) LCo concentrations in the Arctic Ocean.

**Figure 6**: The ratio of LCo (pmol $L^{-1}$) to total dCo (pmol $L^{-1}$) along the transect from south to north in the upper 1000 m.

**Figure 7:** Particulate manganese (pMn; open circles) and particulate cobalt (pCo; x) from several stations along the northern (A-D) and southern (E-H) legs of transect, with the same station designations as in Figure 4.

**Figure 8:** Model output (colors) compared to observations (dots) from 0-50 m (A), 50-150 m (B), 700-800 m (C) and 1500-2000 m (D).

**Figure 9:** (A) Model output of the proportion of the dCo signal from 0-50 m that is controlled by (A) rivers, (B) sediment input, (C) oxygen concentrations, and (D) removal by Mn-oxidation from Mn-oxidizing bacteria.

**Figure 10:** (A) Model output of the proportion of the dCo signal from 700-800 m that is controlled by (A) rivers, (B) sediment input, (C) oxygen concentrations, and (D) removal by Mn-oxidation from Mn-oxidizing bacteria.

**Figure 11:** dCo (closed circles) and LCo (open circles) in the upper 200 m plotted against (A) dMn in shelf stations only (stations 2-10, 57-66), as well as (B) salinity from only the stations influenced by the Transpolar Drift (stations 30-43).

**Figure 12:** dCo and LCo from select stations versus (A) the fraction of Atlantic water ($F_{atl}$; all stations < 500 m), (B) the fraction of Pacific water ($F_{pac}$; all stations < 500 m), (C) fraction of sea ice melt ($F_{ice}$; < 100 m and south of 84ºN) and (D) the fraction of meteoric water ($F_{met}$; < 500 m and north of 84ºN).

**Figure 13:** (A) The dCo (pmol $L^{-1}$) compared to phosphate (dP; μmol $L^{-1}$) from the GN01 dataset. (B) 5-point two-way linear regression of positive dCo:P slopes ($r^2 > 0.6$). (C) 5-point two-way linear regression of negative dCo:P slopes ($r^2 < -0.6$). (D) Depths where either a positive (blue) or negative (red) dCo:P slope was identified in the GN01 dataset. Additional details on the regression analysis can be found in Saito et al., (2017).
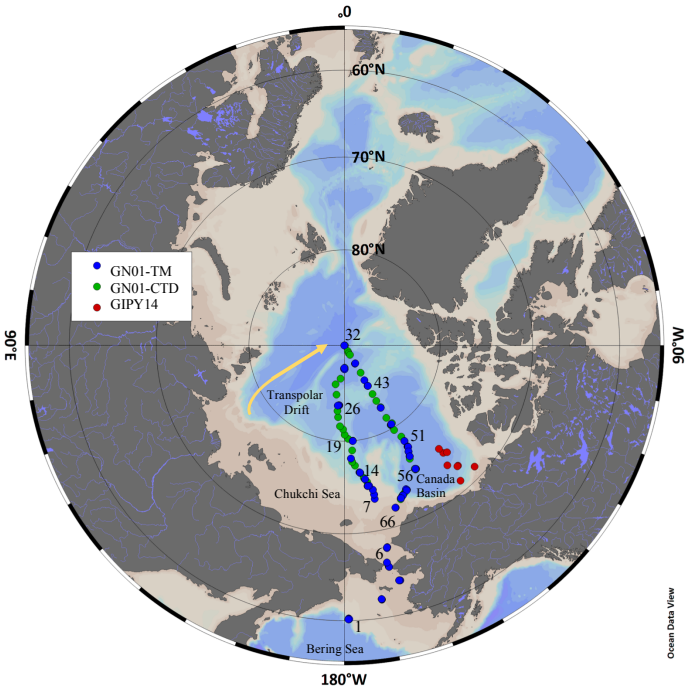
**Figure 14:** The dCo on the shelf measured in 2009 (GIPY14; black triangles) and 2015 (GN01; blue circles) in the upper 3500 m (A) and upper 500 m (B). Average and dCo and LCo in the upper 150 m from 2009 (grey) and 2015 (blue). Error bars represent the standard deviation and a (*) denotes a significant difference.

**Figure 15:** (A) The ratio of LCo to dCo (colors) from this study and the western portion of the GA03 North Atlantic transect (Noble et al., 2016) along with dCo concentrations (B) in temperature-salinity space, with Labrador Sea Water (LSW) source waters (solid black box) and
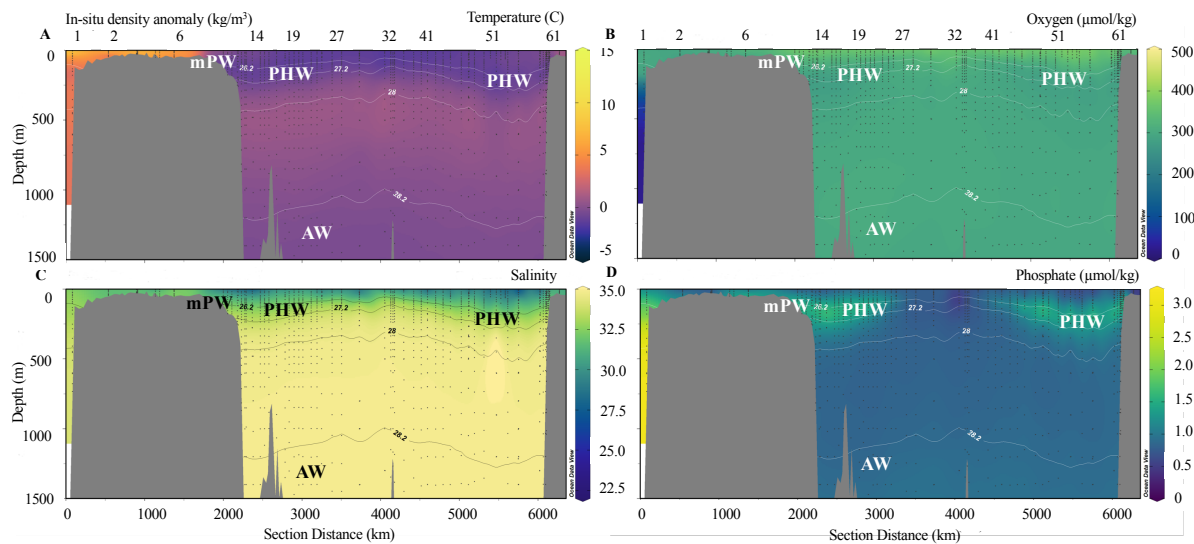
873    signature in the Atlantic (dashed box) are highlighted. (C) Sampling region in this study and the

874    stations used from Noble et al. (2016).

875    **Figure 16:** Median dCo concentrations (A), dissolved Zn concentrations (B) and dCo/dZn ratios

876    (C) in the upper 200 m in the Arctic (this study), North Atlantic (Noble et al., 2016), and in the

877    Southern Eastern Pacific (Hawco et al., 2016). (D) Co/Zn ratios in phytoplankton from the Arctic

878    and North Atlantic (Twining et al., in prep). Whiskers represent the lower (25%) and upper

879    (75%) quartiles.

880 **Figure 1.**

**Figure 2.**

882    **Figure 3.**

**Figure 4.**

**Figure 5.**

885    **Figure 6.**

886 **Figure 7.**

**Figure 8.**

A

0-50 m

B  50-150 m

C

700-800 m

D  1500-2000 m

**Figure 9.**

**A** Proportion controlled by rivers

**B** Proportion controlled by sediments

**C** Proportion controlled by oxygen

**D** Proportion controlled by bacteria

889    **Figure 10.**

**A** Proportion controlled by rivers

**B** Proportion controlled by sediments

**C** Proportion controlled by oxygen

**D** Proportion controlled by bacteria

890    **Figure 11.**

**Figure 12.**

892    **Figure 13.**
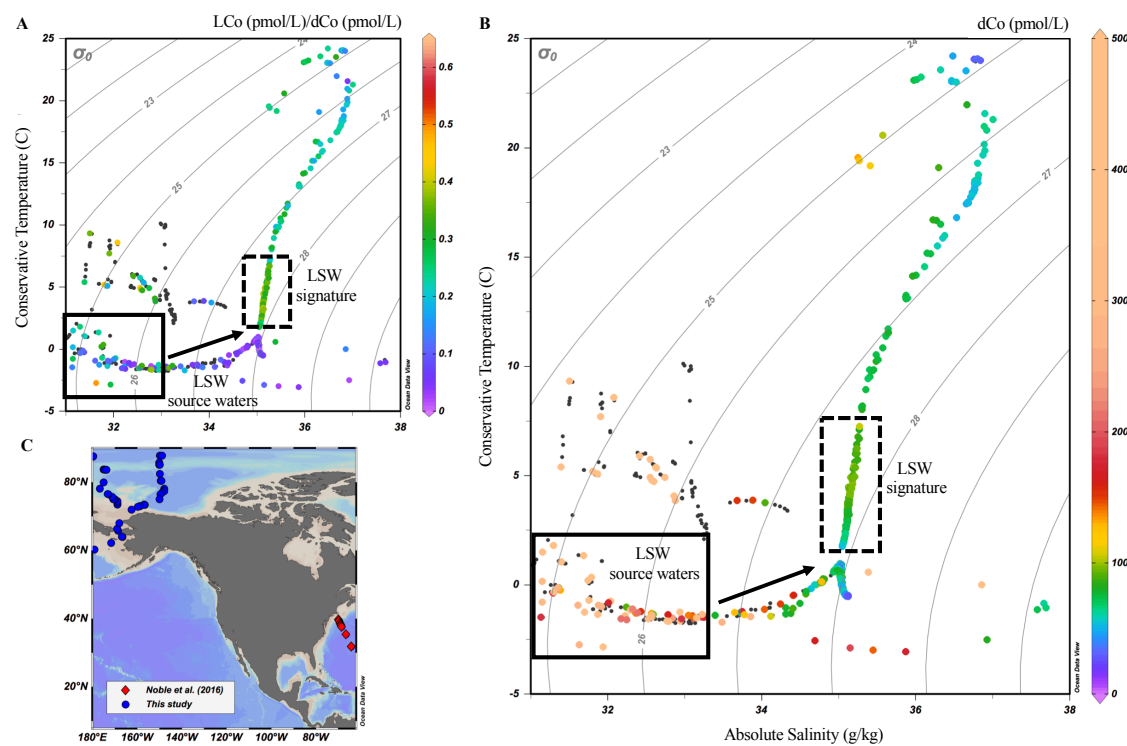
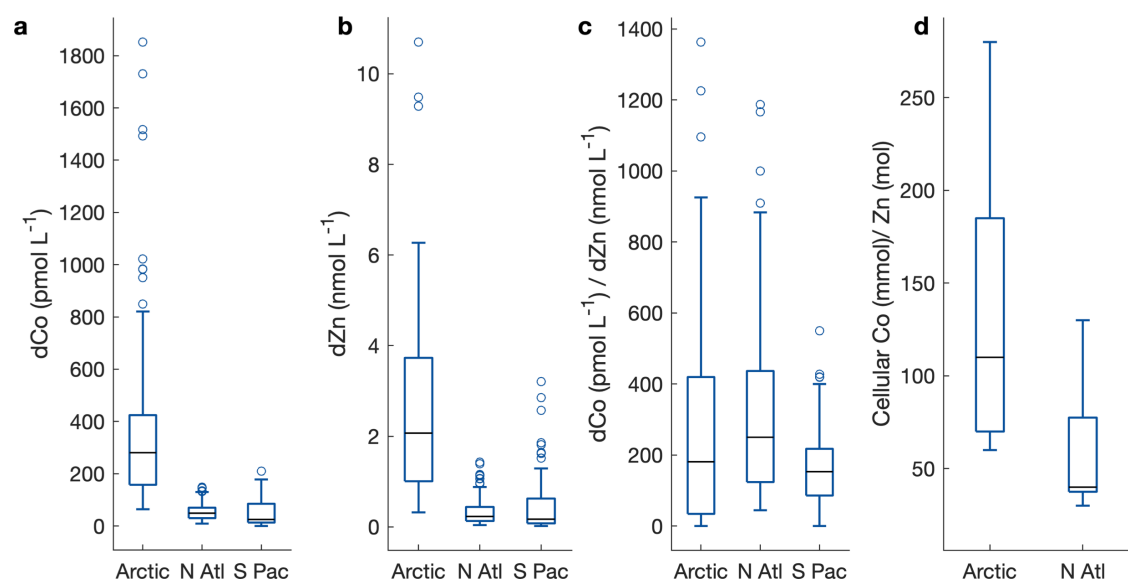893 **Figure 14.**

**Figure 15.**

895    **Figure 16.**

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