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1 **Coastal ocean and shelf-sea biogeochemical cycling of trace elements and**
2 **isotopes: lessons learned from GEOTRACES**

3
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Abstract

Continental shelves and shelf seas play a central role in the global carbon cycle. However, their importance with respect to trace element and isotope (TEI) inputs to ocean basins is less well understood. Here, we present major findings on shelf TEI biogeochemistry from the GEOTRACES program as well as a proof-of-concept for a new method to estimate shelf TEI fluxes. The case studies focus on advances in our understanding of TEI cycling in the Arctic, transformations within a major river estuary (Amazon), shelf sediment micronutrient fluxes, and basin-scale estimates of submarine groundwater discharge. The proposed shelf flux tracer is ²²⁸radium ($T_{1/2}=5.75$ y), which is continuously supplied to the shelf from coastal aquifers, sediment porewater exchange, and rivers. Model-derived shelf ²²⁸Ra fluxes are combined with TEI/ ²²⁸Ra ratios to quantify ocean TEI fluxes from the western North Atlantic margin. The results from this new approach agree well with previous estimates for shelf Co, Fe, Mn, and Zn inputs and exceed published estimates of atmospheric deposition by factors of ~3-23. Lastly, recommendations are made for additional GEOTRACES process studies and coastal margin-focused section cruises

86 that will help refine the model and provide better insight on the mechanisms driving
87 shelf-derived TEI fluxes to the ocean.

88

89 **1. Introduction**

90 Continental shelves and shelf seas play an important role in modulating the transfer
91 of materials between the land and ocean. As such, quantifying processes occurring
92 within this key interface is essential to our understanding of the biogeochemistry of
93 trace elements and their isotopes (TEIs) in the ocean, a major goal of the
94 GEOTRACES program (www.geotraces.org). Moreover, the supply and removal of
95 elements in coastal oceans have direct influence on the structure of ocean
96 ecosystems and their productivity. Although coastal oceans comprise only around
97 7% of the total ocean area, they support 15-20% of total primary productivity and
98 provide 90% of the world's fish yield [1]. As a critical Earth system interface, a large
99 proportion of CO₂ exchange between the ocean and atmosphere occurs over the
100 shelf, which is thought to be a net sink for both atmospheric and terrestrial carbon
101 [2-4].

102

103 In the nearshore environment, estuaries are known to be important zones of TEI
104 processing [5]. One classic example is the removal of dissolved iron during estuarine
105 mixing, which has been shown in many cases to vastly diminish the riverine flux of
106 this element to the ocean [6-8]. Similarly, uranium has an active biogeochemistry in
107 estuaries and salt marshes, which generally, yet not exclusively, act as sinks for
108 dissolved U [9-11]. Dissolved organic matter (DOM) and several other trace
109 elements may also be removed, at different rates, along the salinity gradient of
110 estuaries and shelves [8, 12-15], while some TEIs like barium and radium are
111 known to be added due to desorption from riverine particles [16-20]. In addition to
112 rivers [21], submarine groundwater discharge (SGD) may represent a large source
113 of TEIs to the coastal ocean [22, 23]. Comprising a mixture of meteoric groundwater
114 and seawater circulated through coastal aquifers, SGD has been estimated to exceed
115 river discharge both regionally [24, 25] and by a factor of 3-4 on a global basis [26].
116 Furthermore, SGD has been shown to be an important source of micronutrients (e.g.

117 Fe [27]), contaminants (e.g. Hg [28] and Pb, [29]), and TEIs commonly used as
118 paleo-tracers (e.g. U and Ba [30]).
119
120 For some elements, boundary exchange processes involving sedimentary deposits
121 on the continental margins may have substantial or even greater fluxes to the ocean
122 than rivers. Diffusive benthic fluxes can be a major source of dissolved rare earth
123 elements (REE) to the ocean at levels that could explain the missing source
124 observed in recent isotopic modeling studies [31-33], where the REE flux from shelf
125 sediments is larger than other REE sources to the ocean [34]. The sedimentary
126 remobilization of Nd along continental margins, specifically due to sediment
127 dissolution, also illustrates the importance of shelf porewater exchange processes as
128 a source of TEIs to the ocean [31]. Studies at “mid-ocean” shelves, such as the
129 Kerguelen and Crozet Plateaus, showed a substantial role of sedimentary iron
130 release in alleviating Fe limitation and enhancing carbon sequestration in the
131 Southern Ocean [35-37].
132
133 The GEOTRACES program has carried out basin scale sections to quantify and
134 identify the processes that supply TEIs at ocean boundaries (atmosphere-ocean,
135 sediment-water, ocean crust-overlying water, continent-ocean [38-41]). However,
136 the coastal or shelf ocean is an interface that requires additional process studies to
137 investigate the key processes impacting on the biogeochemical cycles of TEIs. The
138 identification and quantification of TEI distributions and fluxes along ocean margins
139 are important for a number of reasons, including their sensitivity to changing
140 precipitation and wind patterns, and potential impacts on aquaculture and fisheries.
141 Particularly striking is the extent and rate at which humans have modified the
142 coastal zone worldwide [42], a narrow strip of land within 100 km of the ocean
143 where half of the world’s population lives and where three-quarters of all large
144 cities are located [43, 44]. The impacts are numerous and include large-scale bottom
145 water anoxia, eutrophication, acidification, overfishing and anthropogenic
146 contaminant inputs. For instance, global budgets of TEIs such as Pb and Hg have
147 already been significantly altered in the ocean as a result of human induced

148 activities such as acid mine drainage [45, 46]. The role of changing sea-ice cover
149 may affect shelf TEI transport rates, and TEI discharges associated with the
150 accelerated melting of large ice sheets have the potential to increase in magnitude
151 over the coming decades to centuries. For present-day Greenland, the Fe flux may
152 already be on par with the total amount of Fe delivered to the North Atlantic Ocean
153 via dust [47], but the scale of this impact depends on the quantification of fluxes
154 between the coast and open ocean [48].

155

156 An understanding of the mechanisms governing the linkages between the
157 terrestrial→shelf→open ocean continuum is crucial [49]. Although some
158 GEOTRACES process studies have focused more in near shelf regions, GEOTRACES
159 sections to date have, by design, focused primarily on open ocean transects. Here we
160 highlight several examples of where GEOTRACES studies have yielded significant
161 insight on shelf TEI processes, defined as those occurring along ocean margins at
162 water depths <200 m. We further propose a new approach for quantifying the shelf
163 flux of TEIs using a radium isotope tracer (^{228}Ra) and inverse modeling techniques.
164 Finally, we recommend a series of efforts that are necessary to constrain the
165 exchange processes at coastal/shelf ocean interfaces and to aid in the prediction of
166 fluxes of TEIs from this boundary to the ocean.

167

168 **2. Significant GEOTRACES contributions to our understanding of shelf impacts** 169 **on TEI budgets for the open ocean**

170 2.1 The Arctic

171 The Arctic Ocean is unique among the major ocean basins in having as much as one
172 half of its area taken up by shelves [50]. Further, the basin receives a
173 disproportionate percentage of the world's river discharge (10% [51]). Arctic
174 waters are also highly stratified, with a distinct low salinity surface mixed layer, a
175 strong halocline, and clear shelf and river inputs. Because of these features, the
176 impact of shelf-basin interactions on TEI distributions is particularly prominent
177 throughout the Arctic Ocean. However, TEI data have been limited due to the
178 logistical difficulties of reaching remote and ice-covered regions. The International

179 Polar Year 2007-2008 provided a launching pad for the GEOTRACES program, with
180 five cruises in the Arctic region between 2006-2009, which led to new insights
181 about important Arctic coastal processes acting on TEI distributions. More recently,
182 in summer 2015 three nations mounted full GEOTRACES Arctic cruises; the results
183 of that coordinated effort are forthcoming.

184

185 High concentrations of shelf-derived trace metals in surface waters of the central
186 Arctic were reported by Moore [52]. This included Cd, which has been found to
187 exhibit only minor isotope shifts compared to other ocean basins where greater
188 variations are generated through biological removal [53]. Data from the Swedish-
189 Russian GEOTRACES (GIPY13) cruise to the Siberian shelves found that Cd was not
190 removed in the Lena estuary, and there were further Cd additions to shelf waters
191 from the shelf sediments [54]. Another example of shelf influence on the deep basin
192 is the distribution of Ba, which is strongly enriched in estuarine waters due to
193 desorption from river sediments. In theory, Ba distributions can delineate shelf TEI
194 sources; however, isolating the terrestrial Ba source may be complicated due to
195 biogenic Ba uptake and vertical redistribution [55]. As part of the Canadian IPY-
196 GEOTRACES, a dissolved Ba cross-section through the Canadian Archipelago
197 revealed high surface water Ba concentrations near the Horton River and a
198 pronounced Ba maximum in the upper halocline waters (Fig. 1; [56]). The latter was
199 thought to be due in part to Ba released to subsurface waters in the wake of organic
200 matter remineralization, a finding similar to Roeske et al. [55] who reported that
201 remineralization from the Siberian shelf led to a similar Ba enrichment below the
202 surface mixed layer. This may represent a dynamic process that is not at steady-
203 state: such 'metabolic Ba' concentrations in the subsurface layer increase with the
204 arrival of organic matter sometime after the spring bloom, approaching maximum
205 values toward the end of winter [56].

206

207 A strong Mn enrichment was also found in the surface layer of the central basin due
208 to riverine inputs of Mn (Fig. 2; [57]), though the inferred river component indicated
209 that river waters were significantly depleted by estuarine processes. Mid-depth

210 enrichments of Mn on the shelf also suggested that there were benthic
211 contributions, though this sediment source did not extend a significant distance off-
212 shelf. The first measurements of Ga in Arctic waters found that its distribution
213 reflected mixing between Atlantic and Pacific waters, with evidence of both riverine
214 input and scavenging removal in shelf waters of the Beaufort Sea [58]. Further
215 studies of the shelf cycling of Ga and related elements (especially Al, which is
216 chemically similar to Ga though more readily scavenged) could provide insights into
217 how shelf scavenging removal affects the off-shelf transport of reactive TEIs.

218

219 Isotope variations in Nd have been widely used to understand shelf-water
220 interactions and riverine inputs. Within the Arctic Ocean, gradients between surface
221 and halocline waters reflected inputs from the Pacific [59] as well as a source that
222 isotopically matched the major rivers, indicating that the concentrations of the river
223 components reaching the central basin did not reflect the considerable estuarine Nd
224 losses commonly seen elsewhere [60]. These datasets were extended with samples
225 from the BERINGIA 2005 and GIPY13 GEOTRACES cruises, which clearly
226 demonstrated how Nd isotopes and concentrations in the Pacific layer were
227 modified while crossing the Bering Sea through sediment-water exchange processes
228 as was inferred for other shelf areas (Fig. 3; [61]). Furthermore, Lena River waters
229 did not suffer strong modification through estuarine losses like in the Amazon [62].

230

231 Data from GEOTRACES cruises have also documented the behavior of carbon on the
232 Arctic shelves. Alling et al. [63] demonstrated for the first time that substantial
233 degradation of DOC occurs in the Lena River estuary, with greater degradation in
234 the broad East Siberian Seas where shelf water residence times are several years;
235 along with degassing of CO₂, this process was clearly shown in DIC $\delta^{13}\text{C}$ signatures
236 [64]. Rising Arctic Ocean temperatures are leading to the thawing of permafrost and
237 release of its stored methane [65, 66]. Indeed, preliminary results from the recent
238 2015 U.S. GEOTRACES Arctic section (GN01) show shelf enrichments of tracers such
239 as CH₄ [67], though the impact of this process on other TEIs remains to be seen.

240 Essential to addressing these and other questions, are radioactive TEIs, which allow
241 for quantification of the time scales associated with these shelf-basin exchange
242 processes, as has been demonstrated by Rutgers van der Loeff et al. [68] for ^{228}Ra
243 and more recently by Rutgers van der Loeff et al. [69], who used the $^{228}\text{Th}/^{228}\text{Ra}$
244 daughter/parent ratio, which is depleted on the shelves but climbs in the particle-
245 depleted central basin, to estimate an age of 3 years for waters at the Gakkal Ridge.

246

247 2.2 The influence of major rivers

248 River-dominated shelves have the potential to be important point sources for TEI
249 delivery to marginal seas and their adjacent ocean basins. For example, Nd isotopic
250 compositions have been measured together with dissolved and colloidal REE
251 concentrations and radium isotope activities in the Amazon estuary salinity gradient
252 as part of the [GEOTRACES process study AMANDES](#) (Fig. 4; [13]). The sharp drop in
253 REE concentrations in the low-salinity region was driven by the coagulation of
254 colloidal material. At mid salinities, dissolved REE concentrations increased, a result
255 of REE release from lithogenic material, a conclusion supported by the Nd isotopic
256 signature within the estuary. Concurrent measurements of the short-lived Ra
257 isotopes (^{223}Ra , $t_{1/2}=11.4$ d and ^{224}Ra , $t_{1/2}=3.7$ d) revealed that this dissolution
258 process is rapid, on the time scale of 3 weeks. These findings have significant
259 implications for the global marine Nd budget and other TEIs that undergo similar
260 sediment-water exchange processes. This study reinforces one of the original
261 concepts of the GEOTRACES program: the power of synoptic and multiple TEI
262 sampling approaches to understanding ocean biogeochemical cycling.

263

264 2.3 Evidence for eddy-mediated cross-shelf transport of iron

265 Although dust deposition is considered the dominant source of iron to the open
266 ocean, it has now been well established that long-range transport of shelf Fe in high
267 nutrient low chlorophyll (HNLC) regions are a factor in the development of blooms
268 100's to 1000's of kilometers offshore (e.g. [37, 70-72]) and can dominate iron
269 supply on the global scale [73]. While radium isotopes have been used to quantify
270 this source [74-76], isolating the shelf source on basin-scales is not easily

271 accomplished in regions beyond the Southern Ocean where other inputs (e.g. dust,
272 hydrothermal vents) may be co-occurring. A 2008 GEOTRACES process study,
273 'FeCycle', focused on biogeochemical cycling within an eddy off the eastern seaboard
274 of the north island of New Zealand, which is seasonally oligotrophic and has spring
275 diatom blooms [77]. The study revealed that the iron supply for these blooms comes
276 from cross shelf transport of metals that are likely 'picked up' on the shelf and
277 moved offshore in an eddy. This conclusion was reached based on high dissolved
278 and particulate Mn within the eddy and from trajectory analysis using a satellite
279 altimetry model (Fig. 5).

280

281 2.4 Apportioning sources of iron using iron isotopes

282 In addition to transport models, isotopes of iron have recently been used as tracers
283 of oceanic Fe sources [78-81]. Novel high throughput methods [82] have enabled
284 high-resolution sampling on ocean section cruises like GEOTRACES. Recently,
285 Conway and John [83] used this approach to apportion iron sources to the North
286 Atlantic according to dust input, hydrothermal venting, and two types of sediment
287 fluxes: reductive and non-reductive sedimentary release. While they estimated that
288 dust was the dominant Fe source, they reported that non-reductive release from
289 sediments on the North American margin was a major local source that contributed
290 between 10-19% of the iron basin-wide (Fig. 6). In addition, Fitzsimmons et al. [84]
291 reported that ~60-80% of the dissolved Fe in this region was in the colloidal phase,
292 which has implications for the bioavailability and long-range transport of this
293 important micronutrient. At the African margin, reductive dissolution in sediments
294 accounted for 1-4% of the iron basin-wide [83]. Further south, Homoky et al. [85]
295 attributed a high-proportion of dissolved Fe present in margin sediments to non-
296 reductive release, and earlier studies of pore waters that were rich in colloidal iron
297 had similar isotope compositions [86, 87], which supports the view that colloids
298 may influence the stability and transport of iron from non-reductive sediment
299 sources in ocean basins [88].

300

301 2.5 Time variations in basin-scale submarine groundwater discharge

302 Submarine groundwater discharge has received increased attention over the past
303 two decades as a source of TEIs to the ocean. The majority of the early studies
304 focused on the local scale, though Moore et al. [24] was able to estimate SGD to the
305 Atlantic Ocean using ^{228}Ra ($T_{1/2}=5.75$ y) inventories from the Transient Tracers in
306 the Ocean (TTO) program, and determined that the SGD flux was $2\text{--}4\times 10^{13}$ m³/y,
307 equivalent to 80-160% of the freshwater discharge from rivers. Since the TTO data
308 had been collected in the 1980s, the Atlantic Ocean ^{228}Ra inventory had largely
309 decayed and been replaced by the time of the 2010-11 U.S. GEOTRACES North
310 Atlantic program. This afforded Charette et al. [89] the opportunity to evaluate
311 whether or not this ocean basin was in steady-state with respect to SGD inputs.
312 Using ^{228}Ra data collected along transects between North America and West Africa,
313 and Western Europe and West Africa, they observed essentially no change in the
314 upper ocean inventory of this tracer, suggesting that SGD had not changed despite
315 significant changes in groundwater withdrawals during the intervening period.

316

317 Kwon et al. [26] took this a step further and used inverse modeling techniques
318 applied to a global ^{228}Ra dataset to calculate total SGD to the ocean. This approach
319 yields the total ^{228}Ra flux from the shelf, which in addition to the SGD input includes
320 the riverine discharge and shelf sediment diffusive sources. Sediments of
321 continental shelves and aquifers are important areas for in situ production of Ra
322 isotopes through continuous decay of their parent thorium isotopes (e.g. Moore et
323 al. [90], while rivers supply dissolved Ra isotopes as well as Ra sourced from
324 desorption from suspended sediments in the estuarine mixing zone [91]. For a
325 number of TEIs, estimates for riverine inputs are generally well constrained,
326 however, due to estuarine processing and direct TEI inputs to the shelf we lack a
327 method or approach for quantifying the net flux of TEIs across the interface between
328 coastal and open ocean waters.

329

330 2.6 ^{228}Ra as a shelf TEI flux gauge

331 To this end we are proposing an approach for quantifying shelf TEI fluxes that
332 utilizes ^{228}Ra as a shelf flux gauge. This method takes advantage of the global inverse

333 model of Kwon et al. [26], which focused on isolating the flux ^{228}Ra via SGD to the
334 ocean, but at its root is designed to estimate the total ^{228}Ra flux from all shelf
335 sources required to balance the upper ocean ^{228}Ra inventory and decay. Because of
336 its strong shelf source and relatively short half life (on the time scale of mixing), the
337 majority of the upper 1000 m ^{228}Ra inventory in the basin can be traced back to the
338 shelf. This inverse approach to estimating shelf ^{228}Ra flux has the advantage of
339 integrating the shelf source of ^{228}Ra over annual to decadal timescales, which
340 averages out seasonal variability that hampers the use of nearshore ^{228}Ra gradients
341 to estimate shelf ^{228}Ra fluxes directly [92]. As a first order estimate, we propose to
342 use the ratio of nearshore gradients of dissolved TEI and ^{228}Ra measured over the
343 shelf and nearby stations during specific GEOTRACES cruises to link the model-
344 derived shelf-ocean ^{228}Ra flux to shelf-ocean TEI fluxes.

345

346 The full details of the global ^{228}Ra model can be found in Kwon et al. [26]. Briefly, the
347 model employs a $2^\circ \times 2^\circ$ global circulation model where the domain is restricted to
348 between 60°S and 70°N due to insufficient ^{228}Ra coverage in the polar oceans. The
349 vertical resolution is fine near the surface (~ 40 m) and coarse near the ocean
350 bottom (~ 600 m). The coastal ^{228}Ra source is defined as that originating from the
351 ocean grid boxes adjacent to land boxes with a depth of less than ~ 200 m. The
352 coastal source is optimized through a minimization scheme whereby the reported
353 fluxes are those that result in the best fit between the model and observed ^{228}Ra
354 activities in the basin. The total ^{228}Ra fluxes for each $2^\circ \times 2^\circ$ margin grid cell are
355 shown in Figure 7a. The highest total margin inputs are to the North Pacific and
356 Indian Ocean basins. For both the Atlantic and Pacific Oceans, the western margin
357 ^{228}Ra fluxes exceed those from the east, likely due to a combination of major river
358 inputs, SGD, and the presence of broad continental margins and/or extensive shelf
359 seas. The relatively narrow shelf along the North American active margin in the
360 Pacific appears to have the lowest inputs on average.

361

362 Assuming shelf-ocean exchange is primarily driven by eddy diffusion, the net cross-
363 shelf TEI flux can be linearly scaled with the net cross-shelf ^{228}Ra flux as follows:

364
$$TEI\ flux = {}^{228}Ra\ flux \times \left(\frac{\Delta TEI}{\Delta {}^{228}Ra} \right) = {}^{228}Ra\ flux \times \left(\frac{TEI_{shelf} - TEI_{ocean}}{{}^{228}Ra_{shelf} - {}^{228}Ra_{ocean}} \right) \quad (1)$$

365 where TEI_{shelf} and ${}^{228}Ra_{shelf}$ are the average concentrations of the TEI of interest and
366 ${}^{228}Ra$ over the shelf water column (<200 m). The TEI_{ocean} and ${}^{228}Ra_{ocean}$ are the
367 average dissolved TEI and ${}^{228}Ra$ in the open ocean (<200 m) (see supplementary
368 material). For highly reactive elements with very low open ocean concentrations,
369 this ratio may be close to $(TEI_{shelf} / {}^{228}Ra_{shelf})$. However, for this approach to be
370 applicable to TEIs with a wide range of particle reactivities, including those with
371 non-negligible open ocean concentrations relative to shelf concentrations,
372 $\Delta TEI / \Delta {}^{228}Ra$ should be employed. For shelves where the net cross-shelf advective
373 flux is substantial, the TEI flux would not scale linearly with ${}^{228}Ra$ flux as illustrated
374 in the supplementary materials.

375

376 It is important to recognize that fluxes derived from this approach are the net
377 dissolved TEI input rate to the ocean at the shelf break (200 m). Hence, the flux at
378 this boundary is not necessarily what might be expected to reach the ocean interior
379 due to the varying degrees of TEI particle reactivity and biological cycling. Further,
380 the method in theory should account for any TEI removal over the shelf; therefore,
381 fluxes may not equal the sum of the inputs along the boundary (e.g. rivers, SGD,
382 sediment diffusion). Finally, we note that many of the TEI shelf input and removal
383 processes vary seasonally, not necessarily in concert with seasonal variability in
384 ${}^{228}Ra$ sources, and that not all shelf sources are expected to have uniform
385 $\Delta TEI / \Delta {}^{228}Ra$. For example, sporadic sources due to rivers and SGD may hinder a
386 proper averaging of $\Delta TEI / \Delta {}^{228}Ra$ over large shelf areas. While the spatial and
387 temporal variability in a particular $\Delta TEI / \Delta {}^{228}Ra$ must be fully assessed before this
388 method is to be widely employed, we hope that this exercise provides a first order
389 assessment of the importance of shelf TEI fluxes to the ocean in comparison to other
390 external sources.

391

392 For the purpose of this exercise, we chose to focus on the North Atlantic Ocean basin
393 due to the availability of synoptic TEI and ${}^{228}Ra$ data from the U.S. GEOTRACES GA03

394 cruises, though the scope could be expanded as more GEOTRACES datasets become
395 available. These cruises crossed or approached three main shelf areas: the
396 Northwest Atlantic shelf south of Woods Hole, MA (USA), the Iberian margin, and
397 the Mauritanian upwelling zone off of Western Africa. For perspective, the combined
398 North Atlantic shelf ^{228}Ra flux ($23.9 \pm 4.6 \times 10^{22}$ atoms/y) accounts for
399 approximately 25% of the global shelf flux ($96 \pm 5 \times 10^{22}$ atoms/y; Fig. 7a; [26]). Of
400 the three GA03 cruise shelf crossings, however, only the Northwest Atlantic has
401 multiple stations in close proximity to the shelf break and a shelf where elemental
402 transport is dominated by eddy diffusion [93]. As a result, the western North
403 Atlantic shelves (0° - 70°N), which are responsible for about 60% of the shelf ^{228}Ra
404 input to this ocean basin ($14.3 \pm 1.9 \times 10^{22}$ atoms/y), will be the focus of our shelf
405 TEI flux calculations.

406

407 Though there is a long list of TEIs fluxes that could be determined using this
408 method, we chose to focus on four (dissolved Fe, Mn, Co, Zn) that span a range of
409 particle reactivity and play a role in upper ocean biogeochemical cycling. The
410 $\Delta\text{TEI}/\Delta^{228}\text{Ra}$ ratios were calculated using equation (1) from averaged concentration
411 data for the two Northwest Atlantic nearshore stations (GA03, KN204-1 stations
412 1,2) and open ocean station 16 (GA03, KN204-1; Fig. 7b).

413

414 By combining the model ^{228}Ra fluxes and $\Delta\text{TEI}/\Delta^{228}\text{Ra}$, we can estimate the annual
415 shelf TEI inputs to the western North Atlantic Ocean (Table 1). The western N.
416 Atlantic shelf Co flux ($1.4 \pm 0.4 \times 10^8$ mol/y) is consistent with literature estimates
417 from a variety of independent approaches. Saito et al. [94] estimated that the shelf
418 dissolved Co flux for the Peru upwelling region was 2.0×10^7 mol/y, which compares
419 well with our estimate considering that we integrated over a ~ 7 times larger area.
420 Lateral shelf area normalized Co fluxes of 6.2 - $10 \mu\text{mol m}^{-2} \text{y}^{-1}$ were reported by
421 Bown et al. [95] for the S. Atlantic near Cape Town. These are a factor of ~ 5 - 10
422 lower than the shelf-normalized fluxes for the western N. Atlantic margin (Table 1;

423 56 $\mu\text{mol m}^{-2} \text{y}^{-1}$), though their estimate was based on transport across a boundary
424 several hundred km from the shelf-break.

425

426 The $\Delta\text{TEI}/\Delta^{228}\text{Ra}$ approach yielded a shelf Fe flux of $3.9\pm 1.4\times 10^8$ mol/y for the
427 western N. Atlantic. When normalized to shelf-area, this flux is $160 \mu\text{mol m}^{-2} \text{y}^{-1}$.
428 Sedimentary Fe inputs [88], which are expectedly higher as they do not account for
429 any removal over the shelf, range from $900 \mu\text{mol m}^{-2} \text{y}^{-1}$ [73] to $1570 \mu\text{mol m}^{-2} \text{y}^{-1}$
430 [71] to $2700 \mu\text{mol m}^{-2} \text{y}^{-1}$ [96]. On a global scale, the shelf-sedimentary Fe inputs as
431 reported by Tagliabue et al. [73], Elrod et al. [71], and Dale et al. [96] are 2.7×10^{10}
432 mol/y, 8.9×10^{10} mol/y, and 7.2×10^{10} mol/y, respectively. The western N. Atlantic
433 Ocean total shelf input as determined by our method would therefore represent
434 only 0.4-1.4% of the global sediment flux. If we assume that our $\Delta\text{Fe}/\Delta^{228}\text{Ra}$ is
435 comparable to the global shelf average, our approach would predict a global shelf-
436 ocean Fe flux of 2.3×10^9 mol/y. If the western N. Atlantic shelf is representative of
437 shelf systems globally, our model suggests that only a small fraction of the shelf
438 sedimentary Fe input is exported to the open ocean and therefore available for
439 biological uptake where Fe may be limiting.

440

441 The western N. Atlantic Mn shelf flux is $5.4\pm 1.0\times 10^8$ mol/y or $220 \mu\text{mol m}^{-2} \text{y}^{-1}$.
442 Literature values for shelf Mn fluxes are largely focused on the shelf sediment
443 source. For example, Landing and Bruland [97] reported sedimentary Mn flux of up
444 to $140 \mu\text{mol m}^{-2} \text{y}^{-1}$ for the Monterey Shelf, while McManus et al. [98] observed much
445 higher values for the Oregon/California shelf ($2900\pm 900 \mu\text{mol m}^{-2} \text{y}^{-1}$). The former
446 agrees quite well with our estimate based on equation (1) while the latter is likely
447 higher due to the high productivity associated with the strong upwelling in that
448 region. Lastly, the total Zn shelf flux is $1.6\pm 0.6\times 10^9$ mol/y or $630 \mu\text{mol m}^{-2} \text{y}^{-1}$. To the
449 best of our knowledge, the shelf Zn flux estimates reported herein are the first of
450 their kind.

451

452 In terms of other major sources to the surface ocean, shelf inputs can be on par with
453 or even dominant for certain TEIs. The dissolved cobalt flux for the western N.
454 Atlantic shelf alone is over an order of magnitude higher than the atmospheric
455 deposition of soluble Co to the entire ocean basin as reported by two independent
456 studies ($\sim 11 \times 10^6$ mol/y; [99, 100]). Soluble Fe (wet+dry) atmospheric deposition to
457 the tropical N. Atlantic ranges from 2.9-43 $\mu\text{mol m}^{-2} \text{y}^{-1}$ [101]; scaled to the basin the
458 atmospheric Fe flux becomes 1.2-18 $\times 10^8$ mol/y or 31-460% of the western North
459 Atlantic dissolved shelf flux using the TEI/ ^{228}Ra approach. Powell et al. [101] also
460 reported soluble (wet+dry) atmospheric Mn fluxes, which we scaled to the N.
461 Atlantic ($0.75\text{-}15 \times 10^8$ mol/y), equivalent to 14-280% of the shelf inputs reported
462 herein. Assuming 15% solubility, Little et al. [102] estimated the atmospheric Zn
463 input to the surface ocean to be 6.9×10^7 mol/y; our estimates for the western North
464 Atlantic shelf alone exceed that flux by a factor of ~ 23 . Higher concentrations of Zn
465 along with lighter isotopes were observed at both eastern and western Atlantic
466 margins indicating sediments were a source of Zn to this region [83]. Our net shelf-
467 ocean flux of Zn is almost a factor of three higher than the Little et al. [102] *global*
468 estimate for riverine input (5.9×10^8 mol/y); this is in contrast with their suggestion
469 that scavenging removal of Zn and burial in continental margin sediments might
470 represent the “missing sink” for Zn in the global ocean mass balance for this
471 element.

472

473 **3. Recommendations for the future**

474 We have presented a possible path forward in quantifying TEI shelf-open ocean
475 exchange rates using ^{228}Ra and demonstrated the potential of the method by
476 focusing on the western North Atlantic Ocean. This exercise was made possible by
477 publication of a recent global model for shelf radium inputs and synoptic TEI and
478 ^{228}Ra measurements on a series of U.S. GEOTRACES cruises in 2010-11. Since Ra
479 isotope measurements are not a requirement for GEOTRACES compliance, we
480 suggest that future section cruises and shelf process studies include at least ^{228}Ra so
481 that we can better understand how to relate this tracer to other TEIs. Ra isotope
482 data are especially needed for the Indian and Pacific Oceans where historical data

483 coverage is sparse. Shelf process studies would be needed for a range of shelf
484 settings, i.e. how do $\Delta\text{TEI}/\Delta^{228}\text{Ra}$ ratios vary seasonally and as a function of
485 hydrological state, shelf width, and coastline lithology (e.g. karst vs. volcanic)?
486 Lastly, for shelf environments where advection plays an important role in TEI
487 transport, a second conservative tracer in addition to ^{228}Ra would be needed to
488 constrain the shelf-ocean TEI flux (Supplementary Material).

489

490 While we have used an inverse approach, which was based on a coarse resolution
491 model, in order to calculate shelf fluxes at a near basin-wide scale, a finer resolution
492 model needs to be combined with coastal ^{228}Ra and TEI data in order to constrain
493 various shelf TEI sources more precisely. Where ^{228}Ra measurements are not
494 possible on future GEOTRACES cruises, we advocate for concurrent physical
495 measurements that may also be used to quantify the shelf flux of TEIs. For example,
496 Tanaka et al. [103] combined DFe distributions with turbulence measurements
497 using a vertical microstructure profiler (VMP) in the Bering Sea; they found that
498 productivity in this region was driven in part by injections of iron-rich subsurface
499 layer at the southeastern shelf break.

500

501 Our discussion above highlights the potential importance of shelf processes on open
502 ocean TEI distributions. Results to date are somewhat limited because of the
503 programmatic emphasis placed on open ocean full depth profiles. For example, lack
504 of data over the shelf for GA03 precluded the inclusion of the eastern boundary
505 shelves in our analysis of TEI fluxes to the North Atlantic Ocean. To better
506 understand the role of shelf input to the open ocean (and vice versa) in global TEI
507 budgets, future GEOTRACES sections may need to be reconfigured with an increased
508 emphasis on shelf stations. Given the shallow depths involved, this change would
509 not impact ship-time requirements to any significant extent. Also, sections in
510 regions with wide shelves and high ratios of shelf area to open water will be
511 particularly useful. The recent 2015 Canadian, U.S., and German sections in the
512 Arctic Ocean are examples of this approach. Fortunately, Ra isotopes were measured
513 on all three cruises.

514

515 There are a number of margin-centric GEOTRACES sections that have been
516 identified in the program planning documents but have yet to be realized due to a
517 variety of factors. These include two of the three proposed for the coastal China
518 seas, Brazil margin, and the Gulf of Mexico. Regarding the latter, the 2007
519 GEOTRACES Atlantic Workshop Report identified a section through the Caribbean
520 and Gulf of Mexico that contains significant opportunities to examine shelf impacts.
521 Roughly a third of the area of the Gulf of Mexico is comprised of shelf waters less
522 than 200 m deep. Portions of the coastline are river dominated (Mississippi) while
523 others are groundwater runoff dominated carbonate platforms (Yucatan peninsula,
524 southern Florida). Furthermore, the Loop Current, a major oceanic current, runs
525 through the Gulf, variably interacting with the shelf. Thus, the Gulf of Mexico is a
526 unique basin for the study of margin/open ocean interactions. Surprisingly, though,
527 despite the significant interest in Louisiana Shelf hypoxia in the northern Gulf as
528 well as recent studies engendered by the Deepwater Horizon blowout, few studies
529 have addressed the issue of the shelf's influence on open Gulf waters and then
530 generally only in a tangential way. For instance, early studies by Brooks et al. [104],
531 Reid [105], and Todd et al. [106] all pointed to the likelihood of off-shelf transport of
532 methane and radium in the Gulf. Likewise, Trefry and Presley [107] suggested that
533 Mn fluxes from shelf sediments provided a source for 'excess' Mn in deep Gulf of
534 Mexico sediments. Nonetheless, these studies have not been followed up by more
535 detailed surveys or process studies. Surprisingly, TEI distributions in open waters of
536 the Gulf are generally unknown.

537

538 In this report, we have summarized evidence supporting the importance of
539 continental shelves and shelf seas in the oceanic mass balance of TEIs. Furthermore,
540 we have outlined a methodology utilizing ^{228}Ra to more consistently estimate the
541 flux of TEIs from the margins to the open ocean. To improve these estimates, we
542 recommend that GEOTRACES sections place more emphasis on sampling along the
543 margins and that increased consideration be given to completing margin-focused
544 sections, such as that previously proposed for the Gulf of Mexico.

545 **Data accessibility**

546 <http://data.bco-dmo.org/jg/dir/BCO/GEOTRACES/NorthAtlanticTransect/>

547

548 **Authors' contributions**

549 All authors contributed to the discussion that formed the basis of this manuscript
550 during the Royal Society workshop on “Quantifying fluxes and processes in trace-
551 metal cycling at ocean boundaries” (Chicheley Hall, UK, December 9-10, 2015).
552 M.A.C. wrote the manuscript with significant written contributions or editorial
553 comments from all authors. M.A.C., P.J.L., M.C.L, and E.Y.K. developed the concept for
554 ²²⁸Ra as a TEI shelf flux gauge. V.H. and G.A.C. wrote the introduction. A.M. organized
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557 All authors gave final approval for publication.

558

559 **Competing interests**

560 The authors' declare no competing interests.

561

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576

577 **Literature Cited**

- 578 1. Simpson JH, Sharples J. Introduction to the Physical and Biological
579 Oceanography of Shelf Seas: Cambridge University Press; 2012.
- 580 2. Bourgeois T, Orr JC, Resplandy L, Ethé C, Gehlen M, Bopp L. Coastal-ocean
581 uptake of anthropogenic carbon. *Biogeosci Disc.* 2016;2016:1-34.
- 582 3. Chen C-TA, Borges AV. Reconciling opposing views on carbon cycling in the
583 coastal ocean: Continental shelves as sinks and near-shore ecosystems as
584 sources of atmospheric CO₂. *Deep Sea Res (Part II: Top Stud Oceanogr).*
585 2009;56(8-10):578-90.
- 586 4. Regnier P, Friedlingstein P, Ciais P, Mackenzie FT, Gruber N, Janssens IA, et al.
587 Anthropogenic perturbation of the carbon fluxes from land to ocean. *Nature*
588 *Geo.* 2013;6(8):597-607.
- 589 5. Olausson E, Cato I, (Eds). *Chemistry and biochemistry of estuaries.*
590 Chichester: John Wiley & Sons Ltd; 1980. 452 p.
- 591 6. Boyle EA, Edmond JM, Sholkovitz ER. Mechanism of iron removal in
592 estuaries. *Geochim Cosmochim Acta.* 1977;41(9):1313-24.
- 593 7. Eckert JM, Sholkovitz ER. Flocculation of iron, aluminum and humates from
594 river water by electrolytes. *Geochim Cosmochim Acta.* 1976;40(7):847-8.
- 595 8. Sholkovitz ER, Copland D. The coagulation, solubility and adsorption
596 properties of Fe, Mn, Cu, Ni, Cd, Co and humic acids in a river water. *Geochim*
597 *Cosmochim Acta.* 1981;45(2):181-9.
- 598 9. Barnes CE, Cochran JK. Uranium geochemistry in estuarine sediments -
599 controls on removal and release processes. *Geochim Cosmochim Acta.*
600 1993;57(3):555-69.
- 601 10. Church TM, Sarin MM, Fleisher MQ, Ferdelman TG. Salt marshes: An
602 important coastal sink for dissolved uranium. *Geochim Cosmochim Acta.*
603 1996;60(20):3879-87.
- 604 11. Andersen MB, Stirling CH, Porcelli D, Halliday AN, Andersson PS, Baskaran M.
605 The tracing of riverine U in Arctic seawater with very precise U-234/U-238
606 measurements. *Earth Planet Sci Lett.* 2007;259(1-2):171-85.
- 607 12. Elderfield H, Upstillgoddard R, Sholkovitz ER. The rare-earth elements in
608 rivers, estuaries, and coastal seas and their significance to the composition of
609 ocean waters. *Geochim Cosmochim Acta.* 1990;54(4):971-91.
- 610 13. Rousseau TCC, Sonke JE, Chmeleff J, van Beek P, Souhaut M, Boaventura G, et
611 al. Rapid neodymium release to marine waters from lithogenic sediments in
612 the Amazon estuary. *Nature Comm.* 2015;6.
- 613 14. Sholkovitz E, Szymczak R. The estuarine chemistry of rare earth elements:
614 comparison of the Amazon, Fly, Sepik and the Gulf of Papua systems. *Earth*
615 *Planet Sci Lett.* 2000;179(2):299-309.
- 616 15. Sholkovitz ER, Cochran JK, Carey AE. Laboratory studies of the diagenesis
617 and mobility of Pu-239, Pu-240 and Cs-137 in nearshore sediments. *Geochim*
618 *Cosmochim Acta.* 1983;47(8):1369-79.

- 619 16. Carroll J, Falkner KK, Brown ET, Moore WS. The role of the Ganges-
620 Brahmaputra mixing zone in supplying barium and Ra-226 to the Bay of
621 Bengal. *Geochim Cosmochim Acta*. 1993;57(13):2981-90.
- 622 17. Coffey M, Dehairs F, Collette O, Luther G, Church T, Jickells T. The behaviour
623 of dissolved barium in estuaries. *Estuar Coast Shelf Sci*. 1997;45(1):113-21.
- 624 18. Edmond JM, Boyle ED, Drummond D, Grant B, Mislick T. Desorption of
625 barium in the plume of the Zaire (Congo) River. *Netherlands J of Sea Res*.
626 1978;12(3-4):324-8.
- 627 19. Hanor JS, Chan LH. Non-conservative behaviour of barium during mixing of
628 Mississippi River and Gulf of Mexico waters. *Earth Planet Sci Lett*.
629 1977;37(2):242-50.
- 630 20. Li YH, Chan LH. Desorption of Ba and Ra-226 from river-borne sediments in
631 the Hudson estuary. *Earth Planet Sci Lett*. 1979;43(3):343-50.
- 632 21. Martin JM, Meybeck M. Elemental mass-balance of material carried by major
633 world rivers. *Mar Chem*. 1979;7(3):173-206.
- 634 22. Burnett WC, Dulaiova H, Stringer C, Peterson R. Submarine groundwater
635 discharge: Its measurement and influence on the coastal zone. *J Coast Res*.
636 2006:35-8.
- 637 23. Moore WS. Large groundwater inputs to coastal waters revealed by Ra-226
638 enrichments. *Nature*. 1996;380(6575):612-4.
- 639 24. Moore WS, Sarmiento JL, Key RM. Submarine groundwater discharge
640 revealed by Ra-228 distribution in the upper Atlantic Ocean. *Nature Geo*.
641 2008;1(5):309-11.
- 642 25. Rodellas V, Garcia-Orellana J, Masque P, Feldman M, Weinstein Y. Submarine
643 groundwater discharge as a major source of nutrients to the Mediterranean
644 Sea. *Proc Natl Acad Sci USA*. 2015;112(13):3926-30.
- 645 26. Kwon EY, Kim G, Primeau F, Moore WS, Cho H-M, DeVries T, et al. Global
646 estimate of submarine groundwater discharge based on an observationally
647 constrained radium isotope model. *Geophys Res Lett*. 2014;41(23):8438-44.
- 648 27. Windom HL, Moore WS, Niencheski LFH, Jahrike RA. Submarine groundwater
649 discharge: A large, previously unrecognized source of dissolved iron to the
650 South Atlantic Ocean. *Mar Chem*. 2006;102(3-4):252-66.
- 651 28. Bone SE, Charette MA, Lamborg CH, Gonnee ME. Has submarine
652 groundwater discharge been overlooked as a source of mercury to coastal
653 waters? *Environ Sci Technol*. 2007;41(9):3090-5.
- 654 29. Trezzi G, Garcia-Orellana J, Santos-Echeandia J, Rodellas V, Garcia-Solsona E,
655 Garcia-Fernandez G, et al. The influence of a metal-enriched mining waste
656 deposit on submarine groundwater discharge to the coastal sea. *Mar Chem*.
657 2016;178:35-45.
- 658 30. Gonnee ME, Charette MA, Liu Q, Herrera-Silveira JA, Morales-Ojeda SM.
659 Trace element geochemistry of groundwater in a karst subterranean estuary
660 (Yucatan Peninsula, Mexico). *Geochim Cosmochim Acta*. 2014;132:31-49.
- 661 31. Arsouze T, Dutay JC, Lacan F, Jeandel C. Reconstructing the Nd oceanic cycle
662 using a coupled dynamical - biogeochemical model. *Biogeosciences*.
663 2009;6(12):2829-46.

- 664 32. Jeandel C, Oelkers EH. The influence of terrigenous particulate material
665 dissolution on ocean chemistry and global element cycles. *Chem Geol.*
666 2015;395:50-66.
- 667 33. Tachikawa K, Athias V, Jeandel C. Neodymium budget in the modern ocean
668 and paleo-oceanographic implications. *J Geophys Res:Oceans.* 2003;108(C8).
- 669 34. Abbott AN, Haley BA, McManus J, Reimers CE. The sedimentary flux of
670 dissolved rare earth elements to the ocean. *Geochim Cosmochim Acta.*
671 2015;154:186-200.
- 672 35. Blain S, Queguiner B, Armand L, Belviso S, Bombled B, Bopp L, et al. Effect of
673 natural iron fertilization on carbon sequestration in the Southern Ocean.
674 *Nature.* 2007;446(7139):1070-U1.
- 675 36. Bowie AR, van der Merwe P, Queroue F, Trull T, Fourquez M, Planchon F, et
676 al. Iron budgets for three distinct biogeochemical sites around the Kerguelen
677 Archipelago (Southern Ocean) during the natural fertilisation study, KEOPS-
678 2. *Biogeosciences.* 2015;12(14):4421-45.
- 679 37. Pollard RT, Salter I, Sanders RJ, Lucas MI, Moore CM, Mills RA, et al. Southern
680 Ocean deep-water carbon export enhanced by natural iron fertilization.
681 *Nature.* 2009;457(7229):577-U81.
- 682 38. Anderson RF, Mawji E, Cutter GA, Measures CI, Jeandel C. GEOTRACES
683 Changing the Way We Explore Ocean Chemistry. *Oceanography.*
684 2014;27(1):50-61.
- 685 39. Anderson RF, Henderson GM. Program update: GEOTRACES—A Global study
686 of the marine biogeochemical cycles of trace elements and their isotopes.
687 *Oceanography.* 2005;18(3):76-9.
- 688 40. Plan GS. GEOTRACES: An international study of the marine biogeochemical
689 cycles of traces elements and their isotopes: Scientific Committee in Ocean
690 Research; 2006.
- 691 41. Mawji E, Schlitzer R, Dodas EM, Abadie C, Abouchami W, Anderson RF, et al.
692 The GEOTRACES Intermediate Data Product 2014. *Mar Chem.* 2015;177:1-8.
- 693 42. Glavovic BC, Limburg K, Liu KK, Emeis KC, Thomas H, Kremer H, et al. Living
694 on the Margin in the Anthropocene: engagement arenas for sustainability
695 research and action at the ocean-land interface. *Curr Opin Env Sustain.*
696 2015;14:232-8.
- 697 43. McGranahan G, Balk D, Anderson B. The rising tide: assessing the risks of
698 climate change and human settlements in low elevation coastal zones.
699 *Environ Urban.* 2007;19(1):17-37.
- 700 44. Small C, Nicholls RJ. A global analysis of human settlement in coastal zones. *J*
701 *Coast Res.* 2003;19(3):584-99.
- 702 45. Boyle EA, Lee J-M, Echegoyen Y, Noble A, Moos S, Carrasco G, et al.
703 Anthropogenic Lead Emission in the Ocean The Evolving Global Experiment.
704 *Oceanography.* 2014;27(1):69-75.
- 705 46. Lamborg CH, Hammerschmidt CR, Bowman KL, Swarr GJ, Munson KM,
706 Ohnemus DC, et al. A global ocean inventory of anthropogenic mercury based
707 on water column measurements. *Nature.* 2014;512(7512):65-+.

- 708 47. Bhatia MP, Kujawinski EB, Das SB, Breier CF, Henderson PB, Charette MA.
709 Greenland meltwater as a significant and potentially bioavailable source of
710 iron to the ocean. *Nature Geo.* 2013;6(4):274-8.
- 711 48. Hopwood MJ, Bacon S, Arendt K, Connelly DP, Statham PJ. Glacial meltwater
712 from Greenland is not likely to be an important source of Fe to the North
713 Atlantic. *Biogeochemistry.* 2015;124(1-3):1-11.
- 714 49. Jeandel C. Solid river inputs and ocean margins as critical sources of elements
715 to the oceans. *Philos Trans R Soc London, Ser A.* 2016;In Press (this issue).
- 716 50. Jakobsson M. Hypsometry and volume of the Arctic Ocean and its constituent
717 seas. *Geochim Geophys Geosystems.* 2002;3.
- 718 51. Aagaard K, Carmack EC. The role of sea ice and other freshwater in the arctic
719 circulation. *J Geophys Res:Oceans.* 1989;94(C10):14485-98.
- 720 52. Moore RM. Oceanographic distributions of zinc, cadmium, copper and
721 aluminum in waters of the central Arctic. *Geochim Cosmochim Acta.*
722 1981;45(12):2475-82.
- 723 53. Ripperger S, Rehkaemper M, Porcelli D, Halliday AN. Cadmium isotope
724 fractionation in seawater - A signature of biological activity. *Earth Planet Sci*
725 *Lett.* 2007;261(3-4):670-84.
- 726 54. Lambelet M, Rehkaemper M, de Fliedrt Tv, Xue Z, Kreissig K, Coles B, et al.
727 Isotopic analysis of Cd in the mixing zone of Siberian rivers with the Arctic
728 Ocean-New constraints on marine Cd cycling and the isotope composition of
729 riverine Cd. *Earth Planet Sci Lett.* 2013;361:64-73.
- 730 55. Roeske T, Bauch D, Van Der Loeff MR, Rabe B. Utility of dissolved barium in
731 distinguishing North American from Eurasian runoff in the Arctic Ocean. *Mar*
732 *Chem.* 2012;132:1-14.
- 733 56. Thomas H, Shadwick E, Dehairs F, Lansard B, Mucci A, Navez J, et al. Barium
734 and carbon fluxes in the Canadian Arctic Archipelago. *J Geophys Res:Oceans.*
735 2011;116.
- 736 57. Middag R, de Baar HJW, Laan P, Klunder MB. Fluvial and hydrothermal input
737 of manganese into the Arctic Ocean. *Geochim Cosmochim Acta.*
738 2011;75(9):2393-408.
- 739 58. McAlister JA, Orians KJ. Dissolved gallium in the Beaufort Sea of the Western
740 Arctic Ocean: A GEOTRACES cruise in the International Polar Year. *Mar*
741 *Chem.* 2015;177:101-9.
- 742 59. Andersson PS, Porcelli D, Frank M, Bjork G, Dahlqvist R, Gustafsson O.
743 Neodymium isotopes in seawater from the Barents Sea and Fram Strait
744 Arctic-Atlantic gateways. *Geochim Cosmochim Acta.* 2008;72(12):2854-67.
- 745 60. Porcelli D, Andersson PS, Baskaran M, Frank M, Bjork G, Semiletov I. The
746 distribution of neodymium isotopes in Arctic Ocean basins. *Geochim*
747 *Cosmochim Acta.* 2009;73(9):2645-59.
- 748 61. Dahlqvist RM, Andersson PS, Porcelli D. REE seawater concentrations in the
749 Bering Strait and the Chukchi Sea. *Ocean Sciences 2008 Meeting Poster*
750 *session #0722008.*
- 751 62. Persson P, Andersson PS, Porcelli D, Semiletov I. The influence of Lena River
752 water inflow and shelf sediment-sea water exchange for the Nd isotopic

753 composition in the Laptev Sea and Arctic Ocean. European Geosciences
754 Union 2011 Meeting Abstract 1012032011.

755 63. Alling V, Sanchez-Garcia L, Porcelli D, Pugach S, Vonk JE, van Dongen B, et al.
756 Nonconservative behavior of dissolved organic carbon across the Laptev and
757 East Siberian seas. *Global Biogeochem Cycles*. 2010;24.

758 64. Alling V, Porcelli D, Morth CM, Anderson LG, Sanchez-Garcia L, Gustafsson O,
759 et al. Degradation of terrestrial organic carbon, primary production and out-
760 gassing of CO₂ in the Laptev and East Siberian Seas as inferred from delta C-
761 13 values of DIC. *Geochim Cosmochim Acta*. 2012;95:143-59.

762 65. Portnov A, Smith AJ, Mienert J, Cherkashov G, Rekant P, Semenov P, et al.
763 Offshore permafrost decay and massive seabed methane escape in water
764 depths > 20m at the South Kara Sea shelf. *Geophys Res Lett*.
765 2013;40(15):3962-7.

766 66. Shakhova N, Semiletov I, Salyuk A, Yusupov V, Kosmach D, Gustafsson O.
767 Extensive Methane Venting to the Atmosphere from Sediments of the East
768 Siberian Arctic Shelf. *Science*. 2010;327(5970):1246-50.

769 67. Whitmore L, Shiller AM. Dissolved methane in the US GEOTRACES Arctic
770 section. *Ocean Sciences 2016 Meeting Poster A44A-26832016*.

771 68. Rutgers van der Loeff M, Key RM, Scholten J, Bauch D, Michel A. Ra-228 as a
772 tracer for shelf water in the Arctic Ocean. *Deep Sea Res (Part II: Top Stud*
773 *Oceanogr)*. 1995;42(6):1533-53.

774 69. Rutgers van der Loeff M, Cai P, Stimac I, Bauch D, Hanfland C, Roeske T, et al.
775 Shelf-basin exchange times of Arctic surface waters estimated from Th-
776 228/Ra-228 disequilibrium. *J Geophys Res:Oceans*. 2012;117.

777 70. Aguilar-Islas AM, Hurst MP, Buck KN, Sohst B, Smith GJ, Lohan MC, et al.
778 Micro- and macronutrients in the southeastern Bering Sea: Insight into iron-
779 replete and iron-depleted regimes. *Prog Oceanogr*. 2007;73(2):99-126.

780 71. Elrod VA, Berelson WM, Coale KH, Johnson KS. The flux of iron from
781 continental shelf sediments: A missing source for global budgets. *Geophys*
782 *Res Lett*. 2004;31(12):art. no.-L12307.

783 72. Tyrrell T, Merico A, Waniek JJ, Wong CS, Metzl N, Whitney F. Effect of seafloor
784 depth on phytoplankton blooms in high-nitrate, low-chlorophyll (HNLC)
785 regions. *J Geophys Res: Biogeosci*. 2005;110(G2).

786 73. Tagliabue A, Aumont O, Bopp L. The impact of different external sources of
787 iron on the global carbon cycle. *Geophys Res Lett*. 2014;41(3):920-6.

788 74. Charette MA, Gonneea ME, Morris PJ, Statham P, Fones G, Planquette H, et al.
789 Radium isotopes as tracers of iron sources fueling a Southern Ocean
790 phytoplankton bloom. *Deep Sea Res (Part II: Top Stud Oceanogr)*.
791 2007;54(18-20):1989-98.

792 75. Dulaiova H, Ardelan MV, Henderson PB, Charette MA. Shelf-derived iron
793 inputs drive biological productivity in the southern Drake Passage. *Global*
794 *Biogeochem Cycles*. 2009;23.

795 76. van Beek P, Bourquin M, Reyss JL, Souhaut M, Charette MA, Jeandel C. Radium
796 isotopes to investigate the water mass pathways on the Kerguelen Plateau
797 (Southern Ocean). *Deep Sea Res (Part II: Top Stud Oceanogr)*. 2008;55(5-
798 7):622-37.

- 799 77. Boyd PW, Strzepek R, Chiswell S, Chang H, DeBruyn JM, Ellwood M, et al.
800 Microbial control of diatom bloom dynamics in the open ocean. *Geophys Res*
801 *Lett.* 2012;39.
- 802 78. John SG, Adkins J. The vertical distribution of iron stable isotopes in the
803 North Atlantic near Bermuda. *Global Biogeochem Cycles.* 2012;26.
- 804 79. Labatut M, Lacan F, Pradoux C, Chmeleff J, Radic A, Murray JW, et al. Iron
805 sources and dissolved-particulate interactions in the seawater of the
806 Western Equatorial Pacific, iron isotope perspectives. *Global Biogeochem*
807 *Cycles.* 2014;28(10):1044-65.
- 808 80. Lacan F, Radic A, Jeandel C, Poitrasson F, Sarthou G, Pradoux C, et al.
809 Measurement of the isotopic composition of dissolved iron in the open ocean.
810 *Geophys Res Lett.* 2008;35(24):5.
- 811 81. Radic A, Lacan F, Murray JW. Iron isotopes in the seawater of the equatorial
812 Pacific Ocean: New constraints for the oceanic iron cycle. *Earth Planet Sci*
813 *Lett.* 2011;306(1-2):1-10.
- 814 82. Conway TM, Rosenberg AD, Adkins JF, John SG. A new method for precise
815 determination of iron, zinc and cadmium stable isotope ratios in seawater by
816 double-spike mass spectrometry. *Anal Chim Acta.* 2013;793:44-52.
- 817 83. Conway TM, John SG. Quantification of dissolved iron sources to the North
818 Atlantic Ocean. *Nature.* 2014;511(7508):212-+.
- 819 84. Fitzsimmons JN, Carrasco GG, Wu J, Roshan S, Hatta M, Measures CI, et al.
820 Partitioning of dissolved iron and iron isotopes into soluble and colloidal
821 phases along the GA03 GEOTRACES North Atlantic Transect. *Deep Sea Res*
822 *(Part II: Top Stud Oceanogr).* 2015;116:130-51.
- 823 85. Homoky WB, John SG, Conway TM, Mills RA. Distinct iron isotopic signatures
824 and supply from marine sediment dissolution. *Nature Comm.* 2013;4:10.
- 825 86. Homoky WB, Severmann S, Mills RA, Statham PJ, Fones GR. Pore-fluid Fe
826 isotopes reflect the extent of benthic Fe redox recycling: Evidence from
827 continental shelf and deep-sea sediments. *Geology.* 2009;37(8):751-4.
- 828 87. Homoky WB, Hembury DJ, Hepburn LE, Mills RA, Statham PJ, Fones GR, et al.
829 Iron and manganese diagenesis in deep sea volcanogenic sediments and the
830 origins of pore water colloids. *Geochim Cosmochim Acta.* 2011;75(17):5032-
831 48.
- 832 88. Homoky WB, Weber T, Berelson WM, Conway TM, Henderson GM, van Hulst
833 M, et al. An assessment of oceanic trace element and isotope exchange at the
834 sediment-water boundary. *Philos Trans R Soc London, Ser A.* 2016;In Press
835 (this issue).
- 836 89. Charette MA, Morris PJ, Henderson PB, Moore WS. Radium isotope
837 distributions during the US GEOTRACES North Atlantic cruises. *Mar Chem.*
838 2015;177:184-95.
- 839 90. Moore WS, Astwood H, Lindstrom C. Radium isotopes in coastal waters on
840 the Amazon shelf. *Geochim Cosmochim Acta.* 1995;59(20):4285-98.
- 841 91. Krest JM, Moore WS, Rama. Ra-226 and Ra-228 in the mixing zones of the
842 Mississippi and Atchafalaya Rivers: indicators of groundwater input. *Mar*
843 *Chem.* 1999;64(3):129-52.

- 844 92. Moore WS. Inappropriate attempts to use distributions of Ra-228 and Ra-226
845 in coastal waters to model mixing and advection rates. *Cont Shelf Res.*
846 2015;105:95-100.
- 847 93. Moore WS. Determining coastal mixing rates using radium isotopes. *Cont*
848 *Shelf Res.* 2000;20(15):1993-2007.
- 849 94. Saito MA, Moffett JW, DiTullio GR. Cobalt and nickel in the Peru upwelling
850 region: A major flux of labile cobalt utilized as a micronutrient. *Global*
851 *Biogeochem Cycles.* 2004;18(4).
- 852 95. Bown J, Boye M, Baker A, Duvieilbourg E, Lacan F, Le Moigne F, et al. The
853 biogeochemical cycle of dissolved cobalt in the Atlantic and the Southern
854 Ocean south off the coast of South Africa. *Mar Chem.* 2011;126(1-4):193-206.
- 855 96. Dale AW, Nickelsen L, Scholz F, Hensen C, Oschlies A, Wallmann K. A revised
856 global estimate of dissolved iron fluxes from marine sediments. *Global*
857 *Biogeochem Cycles.* 2015;29(5):691-707.
- 858 97. Landing WM, Bruland KW. The Contrasting Biogeochemistry of Iron and
859 Manganese in the Pacific-Ocean. *Geochim Cosmochim Acta.* 1987;51(1):29-
860 43.
- 861 98. McManus J, Berelson WM, Severmann S, Johnson KS, Hammond DE, Roy M, et
862 al. Benthic manganese fluxes along the Oregon-California continental shelf
863 and slope. *Cont Shelf Res.* 2012;43:71-85.
- 864 99. Saito MA, Moffett JW. Temporal and spatial variability of cobalt in the Atlantic
865 Ocean. *Geochim Cosmochim Acta.* 2002;66(11):1943-53.
- 866 100. Dulaquais G, Boye M, Rijkenberg MJA, Carton X. Physical and
867 remineralization processes govern the cobalt distribution in the deep
868 western Atlantic Ocean. *Biogeosciences.* 2014;11(6):1561-80.
- 869 101. Powell CF, Baker AR, Jickells TD, Bange HW, Chance RJ, Yodle C. Estimation of
870 the Atmospheric Flux of Nutrients and Trace Metals to the Eastern Tropical
871 North Atlantic Ocean. *J Atmos Sci.* 2015;72(10):4029-45.
- 872 102. Little SH, Vance D, Walker-Brown C, Landing WM. The oceanic mass balance
873 of copper and zinc isotopes, investigated by analysis of their inputs, and
874 outputs to ferromanganese oxide sediments. *Geochim Cosmochim Acta.*
875 2014;125:673-93.
- 876 103. Tanaka T, Yasuda I, Kuma K, Nishioka J. Vertical turbulent iron flux sustains
877 the Green Belt along the shelf break in the southeastern Bering Sea. *Geophys*
878 *Res Lett.* 2012;39.
- 879 104. Brooks JM, Reid DF, Bernard BB. Methane in the upper water column of the
880 northwestern Gulf of Mexico. *J Geophys Res:Oceans.* 1981;86(NC11):1029-
881 40.
- 882 105. Reid DF. Radium variability produced by shelf-water transport and mixing in
883 the western Gulf of Mexico. *Deep Sea Res (Part I: Oceanogr Res Papers).*
884 1984;31(12):1501-10.
- 885 106. Todd JF, Wong GTF, Reid DF. The geochemistries of Po-210 and Pb-210 in
886 waters overlying and within the Orca Basin, Gulf of Mexico. *Deep Sea Res*
887 *(Part I: Oceanogr Res Papers).* 1986;33(10):1293-306.
- 888 107. Trefry JH, Presley BJ. Manganese fluxes from Mississippi Delta sediments.
889 *Geochim Cosmochim Acta.* 1982;46(10):1715-26.

890 108. Sholkovitz ER. The geochemistry of rare-earth elements in the Amazon River
891 estuary. *Geochim Cosmochim Acta*. 1993;57(10):2181-90.
892

893 **Tables**

894

895 Table 1. Western North Atlantic Ocean margin TEI flux estimates derived from shelf
 896 ^{228}Ra inputs ($14.3 \pm 1.9 \times 10^{22}$ atoms/y; 0-70°N) and $\Delta\text{TEI}/\Delta^{228}\text{Ra}$ ratios. The
 897 integrated shelf area used to normalize the basin-scale fluxes was 2.5×10^{12} m².

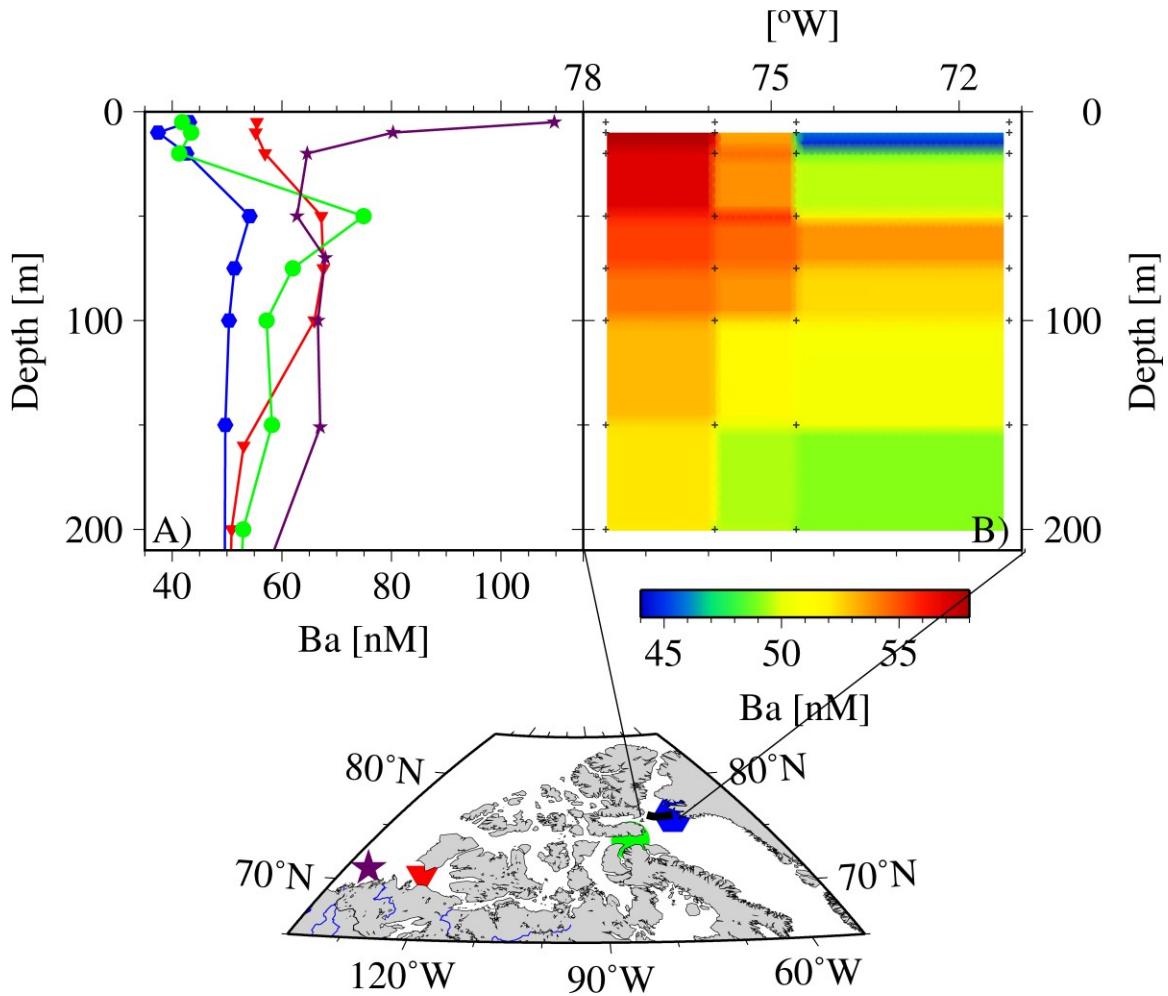
	dCo	dFe	dMn	dZn
TEI/ ^{228}Ra ($\times 10^{-6}$ nmol/atom)	1.0	2.7	3.8	11
TEI Flux ($\times 10^8$ mol/y)	1.4	3.9	5.4	16
TEI Flux ($\mu\text{mol}/\text{m}^2/\text{y}$)	56	160	220	630

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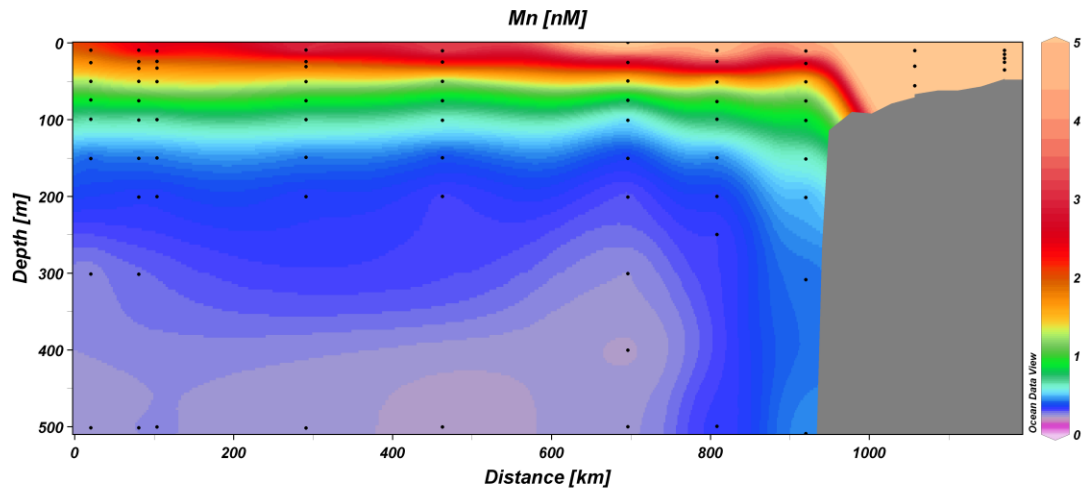
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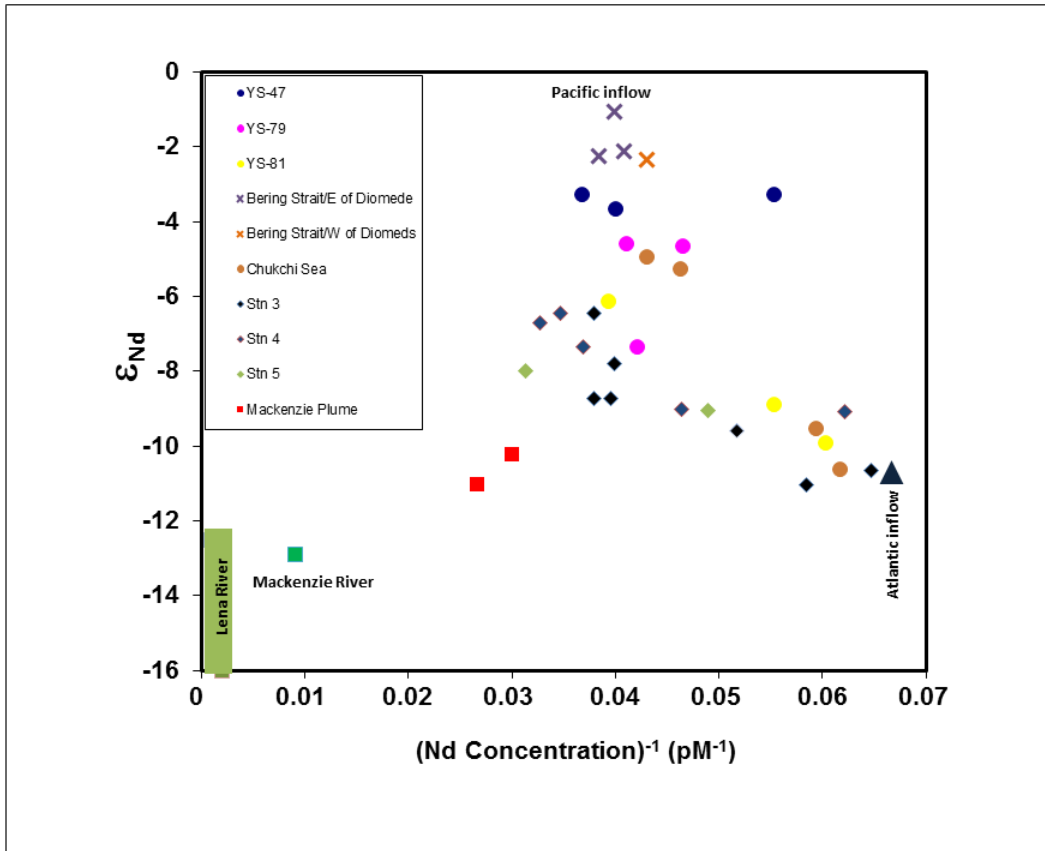
901 **Figures**



902
 903 Figure 1. Dissolved Ba concentrations observed in the Canadian Arctic Archipelago
 904 during the Canadian CFL-IPY-GEOTRACES program in 2007-2008. A) Profiles of four
 905 selected stations across the Archipelago. The easternmost station (blue symbols) is
 906 under the influence of northward flowing North Atlantic waters, which reveal
 907 substantially lower Ba concentrations than waters sampled at stations within the
 908 Archipelago. The westernmost station (purple stars) near the Horton River estuary
 909 depicts the riverine surface source of Ba. In Archipelagic waters (green circles), Ba
 910 displays a subsurface maximum, which in turn can be used to trace the eastward
 911 transport of waters through the Archipelago (redrawn after Thomas et al. [56]). B)
 912 Ba contour section across the head of Baffin Bay, approximately along 76° N, as
 913 indicated by the black line in the inserted map in A). The easternmost station is
 914 identical with the one shown in A) (blue symbols).



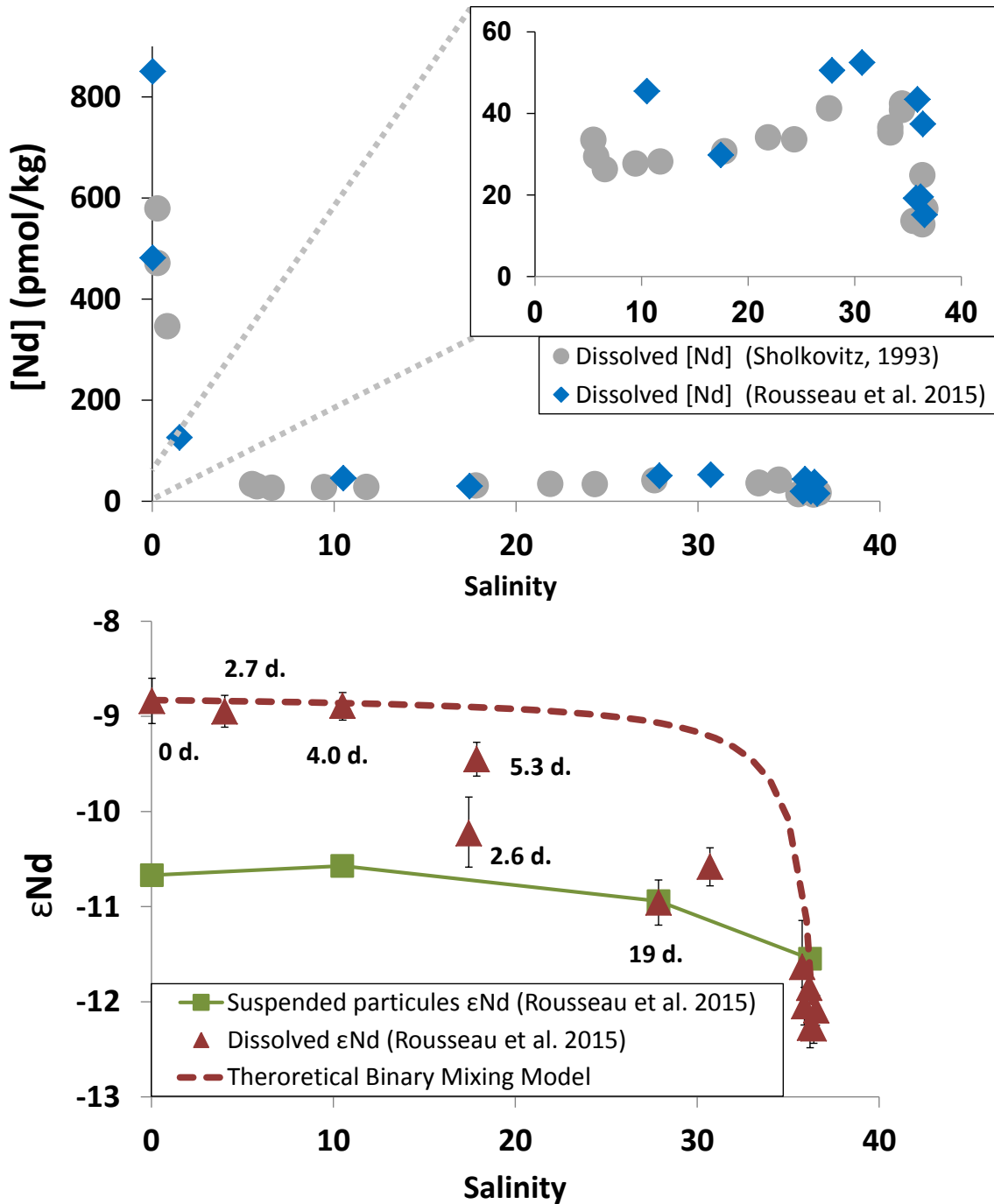
915
916 Figure 2. Dissolved Mn (nM) concentrations in the upper 500 m of the Laptev Sea
917 illustrating the strong Mn source over the shelf and its subsequent transport toward
918 the central Arctic basin (Middag et al. [57]).



920

921 Figure 3. Nd concentration and isotope data for Arctic Ocean waters. The isotope
 922 ratios of waters flowing from the Pacific decrease during passage through the
 923 Bering Sea before entering the Chukchi Sea in the Arctic due to interaction with
 924 shelf sediments (Dahlqvist et al. [61]).

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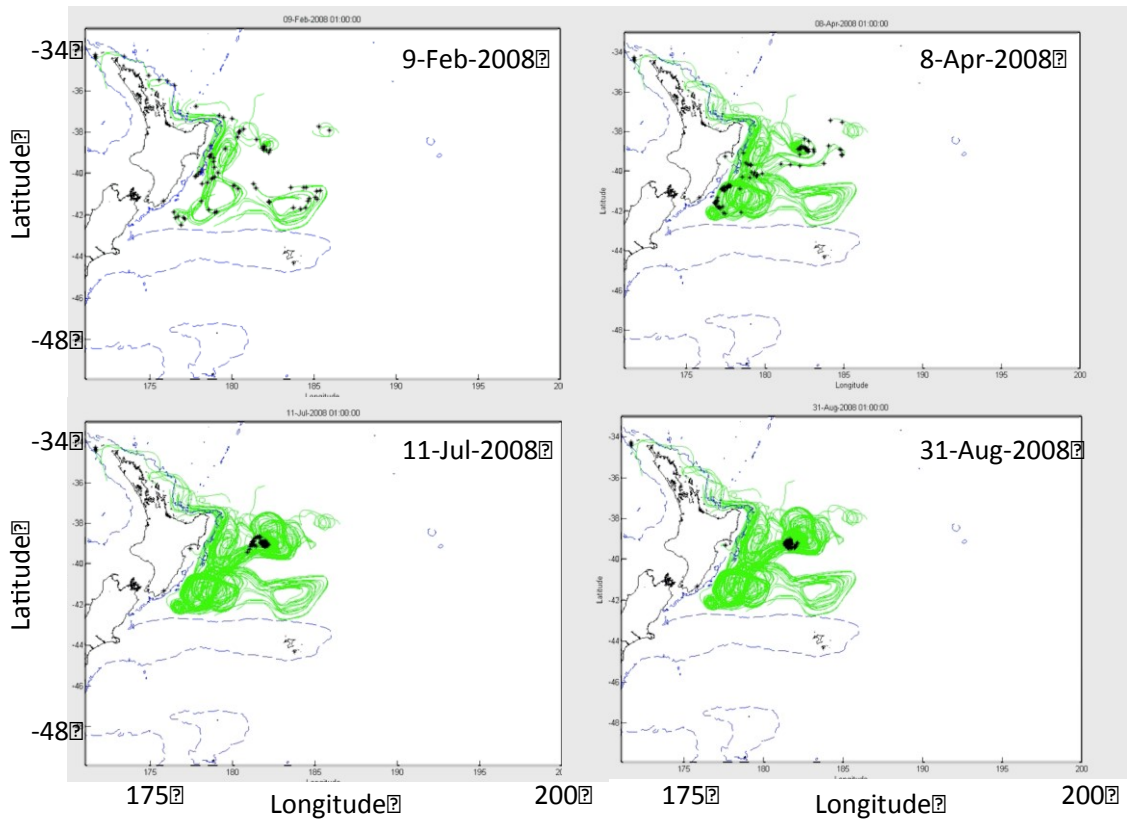
928 Figure 4. *Upper panel:* Amazon estuary [Nd] from Sholkovitz [108] (grey circles) and

929 Rousseau et al. [13] (blue diamonds) are reported against the salinity gradient.

930 *Lower panel:* Amazon estuary dissolved (red triangles), particulate (green squares)

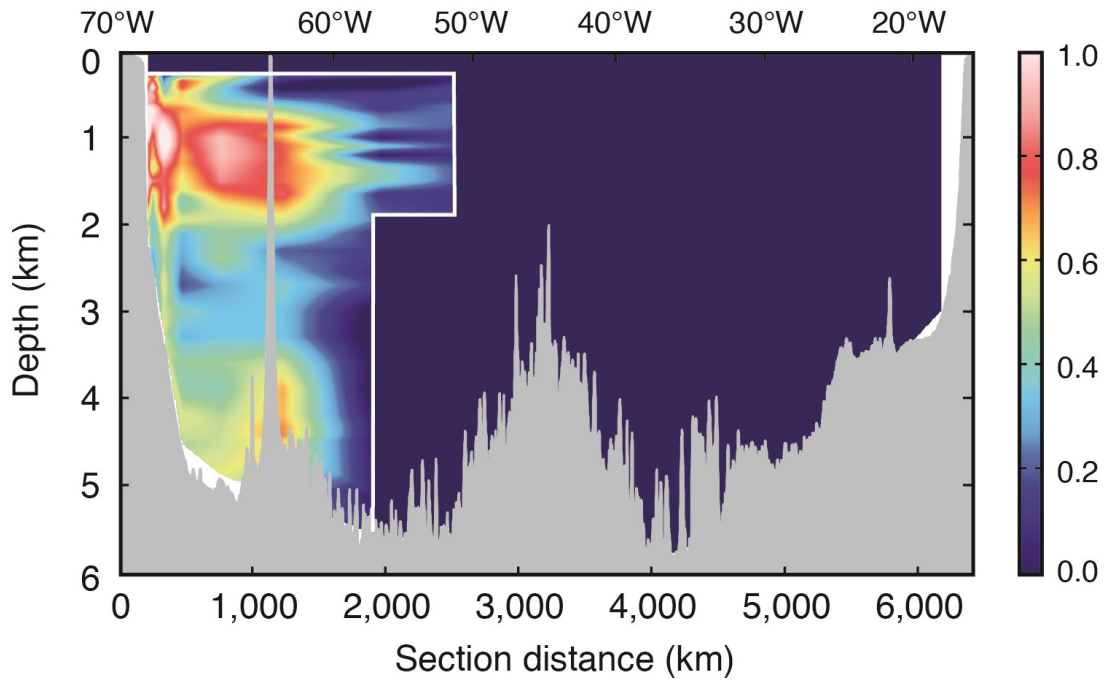
931 εNd and radium-derived water mass ages (in days) are reported against the salinity

932 gradient.



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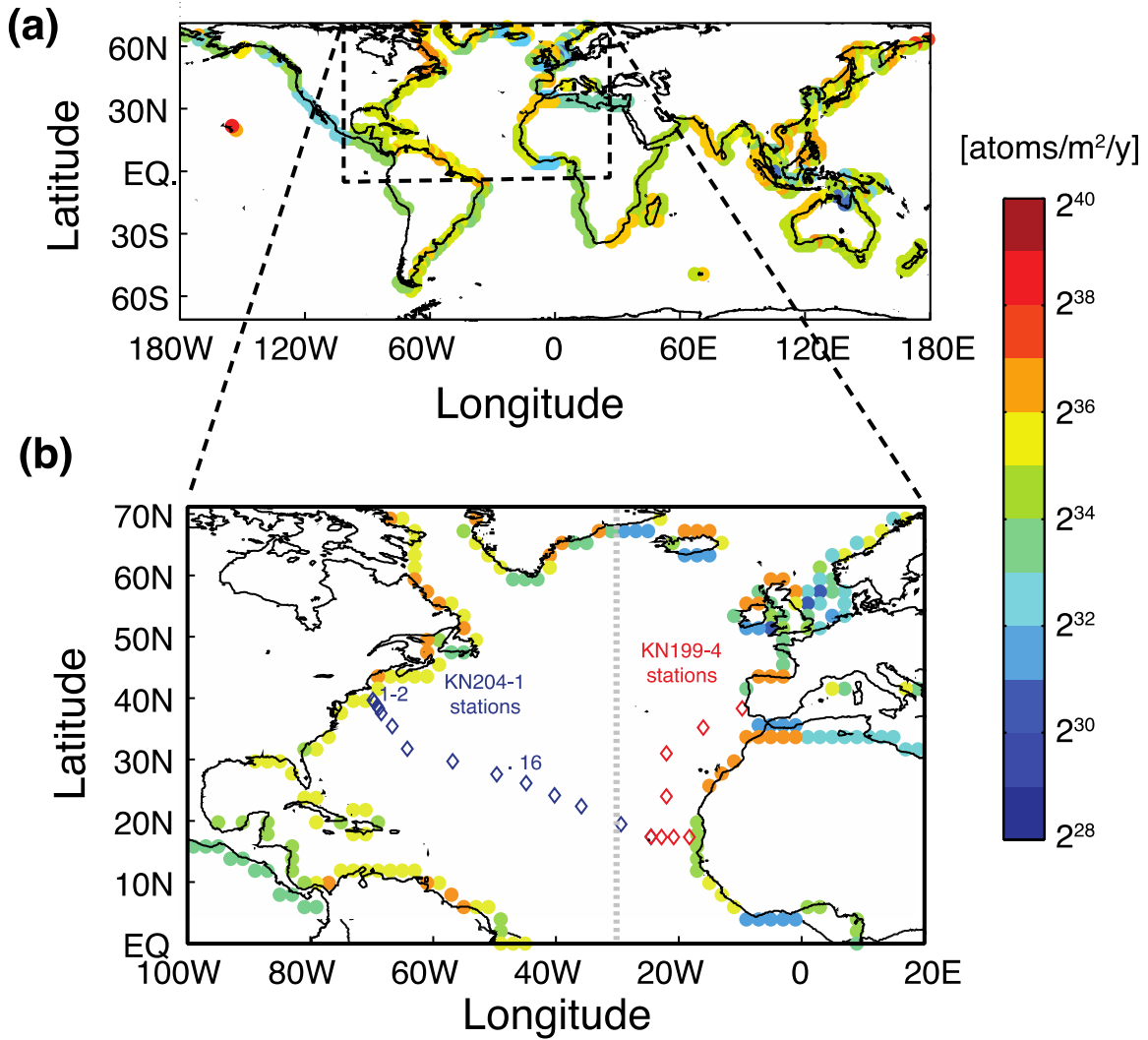
935 Figure 5. Particle trajectories (green lines) from an altimetry model designed to
 936 investigate the origin of water masses within a counterclockwise eddy studied as
 937 part of the GEOTRACES FeCycle process study (Boyd et al. [77]). Model snapshots
 938 are from (clockwise starting at top left) 9 Feb, 8 April, 11 July and 31 Aug 2008. The
 939 particles (black) traverse the waters on and across the 200 m deep shelf break (blue
 940 contours) adjacent to the eastern seaboard of the northern island of New Zealand.



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943 Figure 6. Fraction of water column Fe associated with input from oxygenated
944 sediments along the North Atlantic margin (from Conway and John [83]).

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947 Figure 7. Model derived shelf ^{228}Ra flux (units are log base (2) atoms m⁻² y⁻¹) from

948 the model of Kwon et al. [26]. Also shown in (b) are the U.S. GEOTRACES GA03

949 cruise stations (diamonds). The dashed line in (b) is the boundary between the

950 eastern and western Atlantic margins. The innermost coastal and central Atlantic

951 stations were used to derive the $\Delta\text{TEI}/\Delta^{228}\text{Ra}$ averages.

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