

1 **Towards Constraining Sources of Lithogenic Metals in the Northern Gulf of Mexico**

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6 **Key Points:**

- 7 • An upper bound on the contribution of North African dust toward dissolved thorium
8 supply in the northern Gulf of Mexico may be around 30%
- 9 • Thorium and other tracers suggest significant additional sources from the Gulf of Mexico
10 shelf
- 11 • Thorium-based lithogenic supply of iron suggests dissolved iron residence time in the
12 northern Gulf of Mexico is less than 6 months

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14

15 **Plain Language Summary**

16 The ocean's nutrients generally come from land. The specific route a nutrient takes depends on
17 the nutrient. For the nutrient iron, the rain of airborne dust blown from deserts is thought to be a
18 significant source, especially in the remote ocean. This is because iron is very insoluble and
19 cannot travel far in the water. The Gulf of Mexico is a semi-enclosed sea with significant contact
20 with ocean margin sediments and rivers. It is uncertain how this margin source might compare to
21 airborne dust in the Gulf of Mexico. In this study we used another element, thorium, to trace
22 these two sources and found that dust is likely a significant but not dominant source.

23

24 **Abstract**

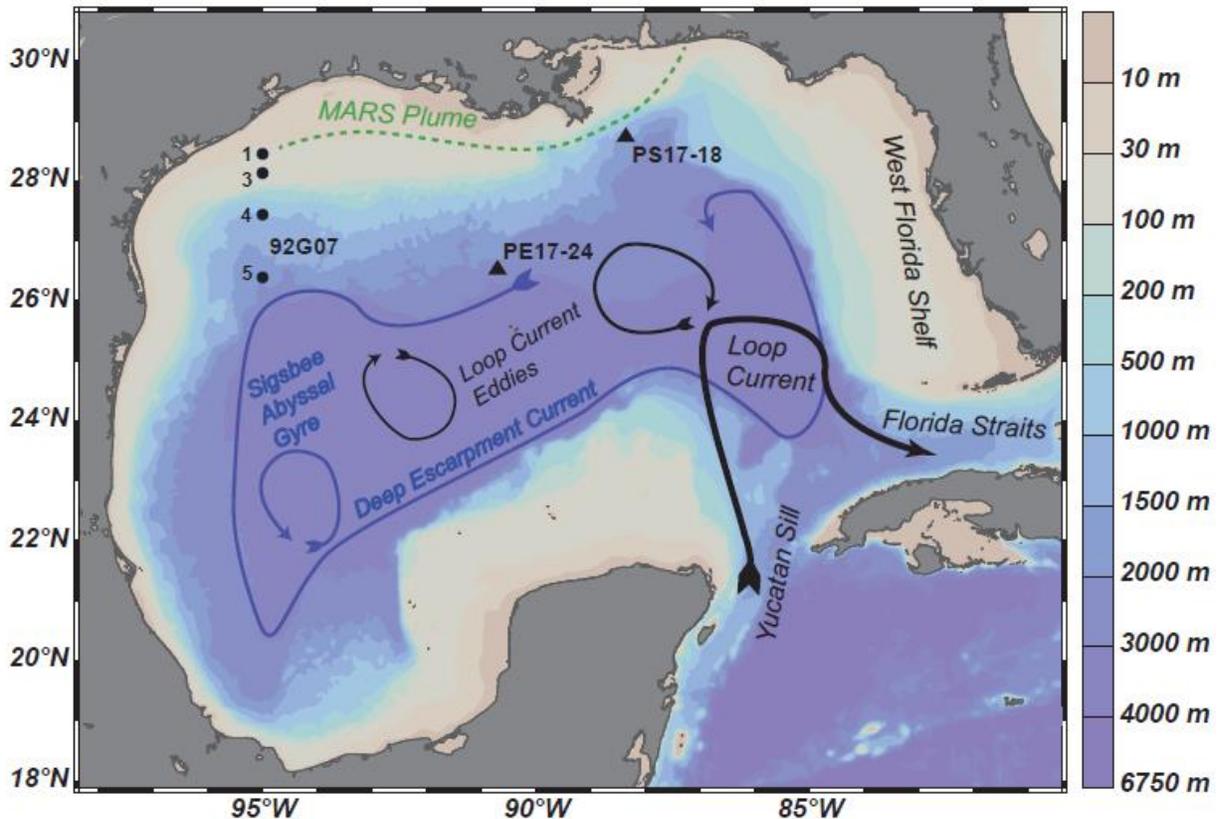
25 North African dust is known to be deposited in the Gulf of Mexico, but its deposition rate and
26 associated supply of lithogenic dissolved metals, such as the abiotic metal thorium or the
27 micronutrient metal iron, have not been well-quantified. ^{232}Th is an isotope with similar sources
28 as iron and its input can be quantified using radiogenic ^{230}Th . By comparing dissolved ^{232}Th
29 fluxes at three sites in the northern Gulf of Mexico with upwind sites in the North Atlantic, we
30 place an upper bound on North African dust contributions to ^{232}Th and Fe in the Gulf of Mexico,
31 which is about 30% of the total input. Precision on this bound is hindered by uncertainty in the
32 relative rates of dust deposition in the North Atlantic and the northern Gulf of Mexico. Based on
33 available radium data, shelf sources, including rivers, submarine groundwater discharge and
34 benthic sedimentary releases are likely as important if not more important than dust in the budget
35 of lithogenic metals in the Gulf of Mexico. In other words, it is likely there is no one dominant
36 source of Th and Fe in the Gulf of Mexico. Finally, our estimated Fe input in the northern Gulf
37 of Mexico implies an Fe residence time of less than 6 months, similar to that in the North
38 Atlantic despite significantly higher supply rates in the Gulf of Mexico.

39 **1 Introduction**

40 The transfer of material from land to sea is one of the primary drivers of the chemical
41 composition of the ocean. There are five main pathways through which this transfer occurs: river
42 discharge, atmospheric deposition, release from sediments, submarine groundwater discharge,
43 and hydrothermal activity (Jeandel, 2016). Any given chemical element in the ocean was
44 delivered from some mixture of these sources and any constraint on the absolute or relative
45 magnitude of each source improves our ability to predict its behavior. The Gulf of Mexico is in
46 some regards a model ocean to study with respect to chemical sources, with supplies from all the
47 major pathways. The Gulf of Mexico receives material input from: one of the world's largest
48 rivers in terms of sediment discharge, the Mississippi River (Milliman & Meade, 1983);
49 atmospheric deposition of North African dust (Prospero, 1999; Prospero et al., 2010) and North
50 American aerosol (Bozlaker et al., 2019; Kok et al., 2021a); a sediment-laden continental shelf
51 that occupies one third of its seafloor; and submarine groundwater discharge in both the northern
52 (McCoy & Corbett, 2009; Sanial et al., 2021) and southern (Gonneea et al., 2014) margins.
53 Hydrothermal activity is not known within the Gulf of Mexico, although it potentially receives
54 material of hydrothermal origin from upstream vent sites on the Mid-Cayman Rise (Kinsey &
55 German, 2013; McDermott et al., 2018) in the Caribbean Sea.

56 We are motivated to constrain lithogenic sources in the Gulf of Mexico, as sources of
57 trace metals in particular, because of their impact on marine ecosystems. Biological productivity

58 in much of the Gulf is likely limited by supply of the major nutrient nitrogen (Yingling et al.,
 59 2021; Zhao & Quigg, 2014). However, there is some evidence that availability of the
 60 micronutrient, iron, which is heavily impacted by lithogenic sources (Tagliabue et al., 2017),
 61 may alter phytoplankton communities on the West Florida Shelf (see map in Fig. 1) through the
 62 high-iron requirement of nitrogen-fixing cyanobacteria (Lenes et al., 2001; Walsh et al., 2006). It
 63 has been shown that dissolved Fe concentrations on the West Florida Shelf can become elevated
 64 during a season of higher North African dust deposition (Mellett & Buck, 2020). However, Gulf
 65 of Mexico coastal waters in general are known to be enriched in trace metals compared to
 66 interior waters (Boyle et al., 1984; Joung & Shiller, 2016; Lenes et al., 2001; Mellett & Buck,
 67 2020; Tang et al., 2002; Wen et al., 2011). Thus it can be difficult to ascribe sources from trace
 68 metal data alone.



69
 70 **Figure 1.** Gulf of Mexico study sites presented here for dissolved ^{232}Th and ^{230}Th (black
 71 triangles). The black dots have historical Th isotope data from cruise 92G07, with station number
 72 indicated (Guo et al., 1995). Overlain are schematic representations of surface (black arrows) and
 73 deep (blue arrows) circulation patterns from Hamilton et al., (2018) and the climatological extent
 74 of the Mississippi-Atchafalya River System (MARS) plume (green dotted line), defined as 50%
 75 frequency of salinity less than 31 (da Silva & Castelao, 2018).

76

77 The trace metal thorium is supplied to the ocean predominantly from lithogenic sources.
 78 In this study we ask the question, can the thorium cycle provide useful information on the
 79 balance of sources for lithogenic metals in the Gulf of Mexico? Unfortunately, all continental

80 sources are known to supply dissolved ^{232}Th to seawater (Hayes et al., 2013, 2017; Huh &
81 Bacon, 1985). In the remote ocean, one can usually assume the dominant source is atmospheric
82 dust input because Th has a short residence time (years) with respect to its removal by adsorption
83 onto sinking particles, limiting its lateral transport from other coastal sources (Anderson et al.,
84 2016; Hsieh et al., 2011). Furthermore, atmospheric dust deposition is significant for biological
85 iron requirements since it can be directly supplied to the euphotic zone. Dissolved ^{232}Th in the
86 Gulf of Mexico, however, is likely to be sourced from a mixture of several continental sources.
87 Our strategy in this study is to compare observed dissolved Th distributions in the northern Gulf
88 of Mexico with that observed in the remote western North Atlantic, which likely receives only a
89 North African dust source. As a preliminary investigation, this comparison can approximate an
90 upper bound on the importance of North African dust as a lithogenic source of ^{232}Th and Fe in
91 the northern Gulf of Mexico. Our goal is to determine whether or not dust or any other source
92 appears dominant the cycling of these metals based on available data. Future studies will be
93 necessary to better quantify metal fluxes associated with North African dust deposition, as well
94 riverine discharge, submarine groundwater discharge, and diffusion from sediments in the Gulf
95 of Mexico, all of which are likely significant. We further estimate the residence time of dissolved
96 Fe in the Gulf of Mexico based on a ^{232}Th -based supply to demonstrate the sensitivity of iron
97 supplies to potential changes in lithogenic supply.

98 **2 Materials and Methods**

99 **2.1 Th isotope sampling and analysis in the Gulf of Mexico**

100 Water samples for Th isotopes were collected on two expeditions in the Gulf of Mexico
101 in 2017: cruise PS17-18 (R/V *Point Sur*; April 1, sea surface salinity 36.4) to the site of the
102 former Deepwater Horizon rig (28.72°N, 88.33°W) and cruise PE17-24 (R/V *Pelican*; June 26,
103 sea surface salinity 36.5) to the north-central Gulf of Mexico (26.53°N, 90.83°W) near the Shell
104 Alcyone Buoy (National Data Buoy Center station 42395). At the time of sampling, these sites
105 were outside the direct influence of the Mississippi-Atchafalaya River System (MARS) plume
106 (Fig. 1), using a definition of salinity >31 (da Silva & Castelao, 2018). The MARS plume is also
107 usually characterized by elevated chlorophyll *a* concentrations and satellite images confirm that
108 the sampling sites were outside the plume (Figs. S1 and S2). The interior Gulf of Mexico can be
109 influenced by a northwestward extension of the Loop Current, anticyclonic Loop Current eddies
110 shed from the Loop Current, or cyclonic eddies that can interact with Loop Current eddies and
111 coastal waters. At the time of sampling, site PS17-18 was not influenced by a coherent eddy
112 based on maps of sea-surface height (Supplemental Figs. S3 and S4), and site PE17-24 was near
113 the center of a Loop Current eddy. Thus both sites likely represent the oligotrophic waters of the
114 northern Gulf of Mexico.

115 Water samples were filtered from a conventional Niskin bottle rosette with 0.45 μm
116 Acropak 500 cartridges into 4 L acid-washed cubitainers, following GEOTRACES protocols
117 (Cutter et al., 2017). Filtered water samples were acidified to 0.024 M HCl with Optima HCl
118 (Fisher) once they were returned to the laboratory and left to sit acidified for at least 2 months
119 before being analyzed to recover any adsorptive loss of Th. Using methods described in Hayes et
120 al. (2017), Th in water samples was pre-concentrated using iron oxyhydroxide coprecipitation
121 after addition of yield tracer ^{229}Th , centrifugation, acid digestion (HNO_3 , HCl, HF and H_2O_2) of
122 the precipitate, and column chromatography using anion-exchange resin AG1-X8. Th isotope
123 concentrations were determined by isotope dilution inductively-coupled plasma mass

124 spectrometry on a Thermo-Fisher Element XR. These data are publicly available (Hayes, 2020a,
 125 2020b). Precision on these analyses averaged 1.2% for ^{232}Th and 10.4% for ^{230}Th , with blank
 126 corrections representing < 5% of the sample size for ^{232}Th and < 9% for ^{230}Th . Accuracy was
 127 assessed using analysis of the GEOTRACES standard solution SWS2010-1 (Anderson et al.,
 128 2012). Our results for SWS2010-1 ($n = 4$) during these analysis were 1005 ± 15 pg/g ^{232}Th and
 129 245 ± 22 fg/g ^{230}Th , within error of the reported intercalibration values. Measured concentrations
 130 for ^{230}Th were corrected to the time of sampling, accounting for ingrowth from ^{234}U decay during
 131 sample storage.

132 We present our new data along with published dissolved ^{232}Th and ^{230}Th data from July
 133 1992 (cruise 92G07) in the northwest Gulf of Mexico (Guo et al., 1995), including 1 deep profile
 134 at station 5 (92G07-05) and 3 surface stations between there and the Texas coast (Fig. 1).
 135 Satellite information was not available for the 1992 time period to determine the eddy field. The
 136 deep site, 92G07-05, and station 4 had a surface salinity of ~ 36 and station 3 was 32.5, indicating
 137 the absence of a river plume influence using the $S < 31$ threshold. Only station 92G07-01 had
 138 surface salinity below 31 (at 30.6). This station is also near the edge of the 50% occurrence line
 139 of MARS plume (da Silva & Castelao, 2018; Fig. 1) and thus may have had some riverine
 140 influence.

141 2.2 Deriving dissolved ^{232}Th flux

142 The residence time of dissolved Th with respect to scavenging removal from an
 143 integrated water column (τ_{dTh}) can be derived from the budget of dissolved ^{230}Th assuming
 144 sources from ^{234}U decay, advection and diffusion:

$$145 \tau_{\text{dTh}} = \frac{\int d^{230}\text{Th}_{\text{xs}} dz}{P + AD} \quad (1)$$

146 Here, $\int d^{230}\text{Th}_{\text{xs}} dz$ is the integrated inventory of dissolved ^{230}Th corrected for lithogenic
 147 sources (denoted with “xs”). This correction is based on measured dissolved ^{232}Th , assuming a 4
 148 ppm ratio of $^{230}\text{Th}/^{232}\text{Th}$ in lithogenic material (Roy-Barman et al., 2002). P is the integrated
 149 production rate of ^{230}Th by ^{234}U decay, and AD represents any integrated sources or sinks due to
 150 advection or diffusion. In the case of the Gulf of Mexico, we have ignored advective or diffusive
 151 sources of ^{230}Th , as there appear to be relatively weak lateral gradients in dissolved ^{230}Th in the
 152 deep Gulf (Sec. 3.1). The deep Gulf contains persistent deep gyre circulation (Hamilton et al.,
 153 2018) as well as a high degree of isopycnal and diapycnal diffusivity compared to the open ocean
 154 (Ledwell et al., 2016), leading to relatively efficient mixing of deep Gulf waters. Once τ_{dTh} is
 155 calculated, we can then calculate the integrated input flux of dissolved ^{232}Th ($F_{\text{d}232}$; Eq. 2).

$$157 F_{\text{d}232} = \frac{\int d^{232}\text{Th} dz}{\tau_{\text{dTh}}} \quad (2),$$

158 where $\int d^{232}\text{Th} dz$ is the inventory of dissolved ^{232}Th integrated over the same depth range as in
 159 calculating τ_{dTh} . The integration is done from the surface to a depth of interest, assuming a
 160 steady-state balance of Th isotopes within that depth range. The depth of interest is chosen based
 161 on the process to be quantified. For instance, studies focusing on atmospheric dust input have
 162 chosen depth horizons such as 500 m or 250 m, above which dissolved ^{232}Th input is assumed to
 163 be due solely to dissolution of atmospheric dust (Hayes et al., 2013, 2017; Hsieh et al., 2011;
 164 Lopez et al., 2015). This is likely a good assumption in the remote ocean; however, benthic and

165 other margin sources of ^{232}Th are documented in some areas (e.g., Pérez-Tribouillier et al., 2020)
 166 which would add to the derived flux. In other words, although we have neglected lateral inputs of
 167 ^{230}Th at depth to derive τ_{dTh} , it is possible there are lateral inputs of ^{232}Th at depth since the
 168 sources of ^{232}Th and ^{230}Th are distinct. The application of τ_{dTh} to derive a dissolved ^{232}Th flux
 169 only requires the assumption that Th scavenging is equal to Th inputs in the integrated water
 170 column.

171 **2.3 Distinguishing lithogenic and dust sources in the Gulf of Mexico**

172 In the case of the Gulf of Mexico, the measured flux of dissolved ^{232}Th itself does not
 173 indicate its component sources. We can, however, look to remote western North Atlantic sites
 174 that are upwind of the North African dust source as an upper bound on the North African dust
 175 source that our northern Gulf of Mexico sites are receiving. Any dissolved ^{232}Th flux measured
 176 in the Gulf of Mexico in excess of the remote North Atlantic estimate would therefore be
 177 attributable to sources from North America and its margins. For North Atlantic sites, we use Th
 178 isotope data from GEOTRACES section GA03, stations KN204-1-10 (coincident with the
 179 Bermuda Atlantic Time-series Station, or BATS) and KN204-1-12 (Hayes et al., 2018), both
 180 found in the oligotrophic waters of the Sargasso Sea, collected in November 2011. These stations
 181 are denoted GA03-10 and GA03-12, for short (see Fig. 2 for map). In this section we provide
 182 further justification for our assumption of the North Atlantic sites as an upper bound for Saharan
 183 dust in our Gulf of Mexico sites from (1) available dust deposition observations and (2) the dust
 184 deposition ranges predicted in global models. This assumption is of course only a working
 185 assumption for this initial investigation into the lithogenic sources in the Gulf of Mexico. The
 186 balance of lithogenic sources if the Gulf deserves further scrutiny as more observations in the
 187 region become available.

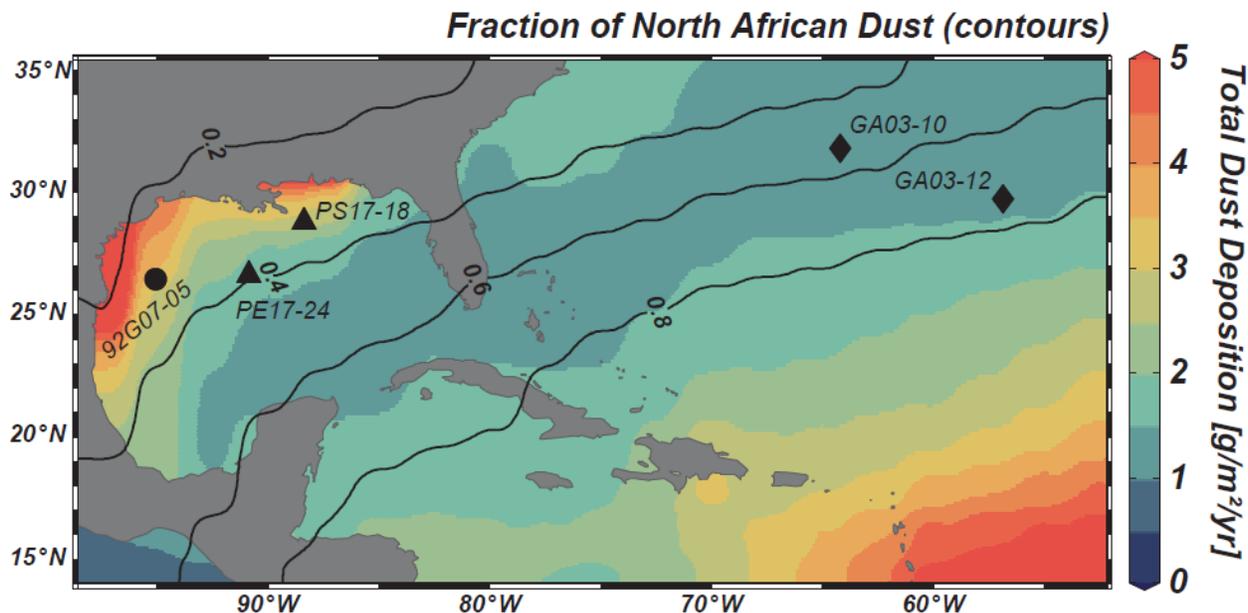
188 Our first expectation based simply on proximity to North Africa is that the GA03 stations
 189 likely receive a similar or larger amount of North African dust deposition compared to our
 190 northern Gulf of Mexico sites. The only available direct observations of bulk dust deposition
 191 (wet and dry deposition) in the region are in Miami (Prospero et al., 1987) of $1.26 \text{ g/m}^2/\text{yr}$
 192 (average over 1982-1983), near Bermuda (Jickells et al., 1998) of $1.9 \text{ g/m}^2/\text{yr}$ (averaged over
 193 1981-1991, ranging from 1.3 to $3.4 \text{ g/m}^2/\text{yr}$ interannually) and from a suite of 10 sites throughout
 194 the state of Florida (Prospero et al., 2010) that averaged $2.0 \text{ g/m}^2/\text{yr}$ (1994-1996). Based on these
 195 observations alone, it appears that the regions spanning the eastern Gulf of Mexico to Bermuda
 196 receive similar amounts of North African dust deposition, within an uncertainty of about a factor
 197 of 2.

198 For more detail on the expected relative rates of dust deposition between the western
 199 North Atlantic and the northern Gulf of Mexico, we make use of an improved representation of
 200 global dust deposition (Kok et al., 2021b) that is constrained by surface dust concentration and
 201 deposition measurements as well as satellite-derived dust-aerosol optical depth. This product
 202 provides 1 sigma uncertainties for each gridded estimation as well as an estimate of the fractional
 203 contribution of the deposition from the world's different dust sources (Kok et al., 2021a). We
 204 show the estimates from this product in Figure 2, using the annual total (wet+dry) deposition of
 205 PM₂₀ (particulate matter greater than $20 \mu\text{m}$ in geometric diameter), along with the locations of
 206 our study sites. Overall, in the region between Bermuda and South Florida, this product agrees
 207 well with the available deposition constraints of $1\text{-}2 \text{ g/m}^2/\text{yr}$. However, the dust product also
 208 suggests significant deposition of North American dust (coming from the southwestern US and

209 northeastern Mexico), particularly in the northwestern quadrant of the Gulf of Mexico. We
210 point out that this result is based largely on the observations of satellite optical dust in the area,
211 as the closest deposition measurement constraints for this source are from the southwestern US
212 (Reheis, 2006). There is other evidence that suggests because of the dynamics of the
213 southwestern monsoon, relatively little of the North American dust is deposited in the Gulf of
214 Mexico (Zhao et al., 2012). In August 2014, it was observed that 19-48% of PM_{2.5} at Houston
215 and Galveston was African dust during a 9-day episode (Bozlaker et al., 2019). The remainder of
216 aerosol sources were mainly anthropogenic aerosols such as road dust and vehicle emissions,
217 with little indication of Southwest US dust. Further regional measurements of aerosols along the
218 Gulf Coast would be helpful for constraining the importance of North American aerosol sources.
219 Nonetheless, of our study sites, we suspect that the northwestern Gulf site 92G07-05 would be
220 most likely to receive significant amounts of North American dust deposition, and the other two
221 sites less so.

222 Looking in more detail at the Kok et al. (2021a,b) dust estimates at our sites illustrates the
223 uncertainty in predicting deposition rates, yet they are still broadly consistent with the assumption
224 of the North Atlantic sites as an upper bound on North African supply to the Gulf. At the model
225 grid nodes nearest the GA03 sites, the range of dust deposition predicted, including 1 sigma
226 uncertainty, is 0.5 to 2.1 g/m²/yr, of which 50-70% is North African (i.e., 0.3 to 1.3 g/m²/yr
227 North African dust). For our two north-central Gulf sites, the Kok et al. product gives a range of
228 0.5 to 6.4 g/m²/yr dust deposition, of which 30-40% is North African in origin (equal to 0.2 and
229 2.2 g/m²/yr North African dust). It is also worth noting that uncertainty in local dust deposition
230 can be even larger in other available global deposition models (Albani et al., 2014). Given the
231 large uncertainties in the model predictions, it is difficult to precisely quantify the relative rates
232 of North African dust deposition at our study sites. Nonetheless, we use the more modest
233 assumption of the North Atlantic sites as an upper bound on North African dust contribution to
234 the northern Gulf sites to perform an initial investigation into the balance of lithogenic sources
235 implied by the ²³²Th flux observations.

236 Finally, with regard to seasonal cycling, neither the GA03 sites (November) or PS17-18
237 (early April) were sampled in the June-July-August timeframe when Saharan dust makes its most
238 northwestward extension, causing, for example a predictable increase in surface dust
239 concentrations in Miami (Zuidema et al., 2019). PE17-24 was sampled in this summer time
240 frame (late June). However, because the residence time of dissolved Th is typically a year or
241 longer in the mixed layer of the open ocean and longer at depth (Hayes et al., 2018; Hayes,
242 Fitzsimmons et al., 2015), we expect seasonal patterns to be largely averaged out in dissolved
243 ²³²Th concentrations and fluxes. Interannual differences between 2011 and 2017 (6 years) could,
244 however, be expected. There is evidence from the Miami time-series that there was a higher
245 Saharan dust load in the region in 2011 compared to 2017 (Zuidema et al., 2019). This evidence
246 reinforces the concept that the GA03 sampling represents an upper bound on the magnitude of
247 North African dust deposited on the Gulf.



248
 249 **Figure 2.** Thorium isotope study sites as plotted in Figure 1 for the Gulf of Mexico (black circle
 250 is 92G07-05 from Guo et al., 1995 and black triangles are PS17-18 and PE17-24 from this study)
 251 as well as the western North Atlantic sites from GEOTRACES GA03 transect (black diamonds,
 252 Hayes et al., 2018). The colormap shows the total (wet plus dry) PM₂₀ deposition from Kok et
 253 al. (2021b) and the contours are the fraction of that deposition sourced from North Africa
 254 (combining source area numbers 1 thru 3 from Kok et al., 2021a). The balance of depositional
 255 fraction is largely made up from North American dust in this dust product.

256 **2.4 Extrapolating to the iron cycle from dissolved ²³²Th flux**

257 In addition to assessing overall lithogenic sources, the measured flux of dissolved ²³²Th
 258 can be converted into the flux of other specific elements, defined in the present case for
 259 dissolved Fe (Eq. 3). This approach assumes an Fe/Th ratio of the source material (Fe/Th_{source})
 260 and the relative fractional solubility of the two elements (S_{Fe}/S_{Th}). Here we use an Fe/Th ratio of
 261 $15,700 \pm 200$ mol/mol and $S_{Fe}/S_{Th} = 1 \pm 0.4$, consistent with observations of North Atlantic
 262 aerosol and aerosol leaches, respectively (Hayes et al., 2018; Shelley et al., 2018). There are few
 263 available measurements of S_{Fe}/S_{Th} and some recent measurements suggest S_{Fe}/S_{Th} could be as
 264 low as 0.2-0.3 (Baker et al., 2020; Roy-Barman et al., 2021). It may be that these operationally
 265 defined fractional solubilities are significantly method-dependent. Thus, we acknowledge our
 266 assumed 40% uncertainty in this parameter may be an underestimate. As Eq. 3 is a linear
 267 conversion, our approach assumes that the balance of different dissolved ²³²Th sources applies to
 268 dissolved Fe as well. North American margin sources (including North American dust) could
 269 have different Fe/Th composition and solubility ratios; we do not have constraints on this at
 270 present and this is a goal for future work. In particular, because Th is not redox sensitive in
 271 seawater while Fe is, dissolution of Fe from anoxic/suboxic settings is likely not represented by
 272 dissolved Th fluxes. In addition, Fe emissions from combustion aerosols (e.g., Matsui et al.,
 273 2018) likely are not co-occurring with Th emissions. In this sense the dissolved Fe fluxes derived
 274 from Eq. 3 likely represent oxic dissolution of lithogenic material and only a fraction of the total
 275 sources of dissolved Fe.

$$F_{dFe} = F_{d232} \times \left(\frac{Fe}{Th}\right)_{source} \times \left(\frac{S_{Fe}}{S_{Th}}\right) \quad (3)$$

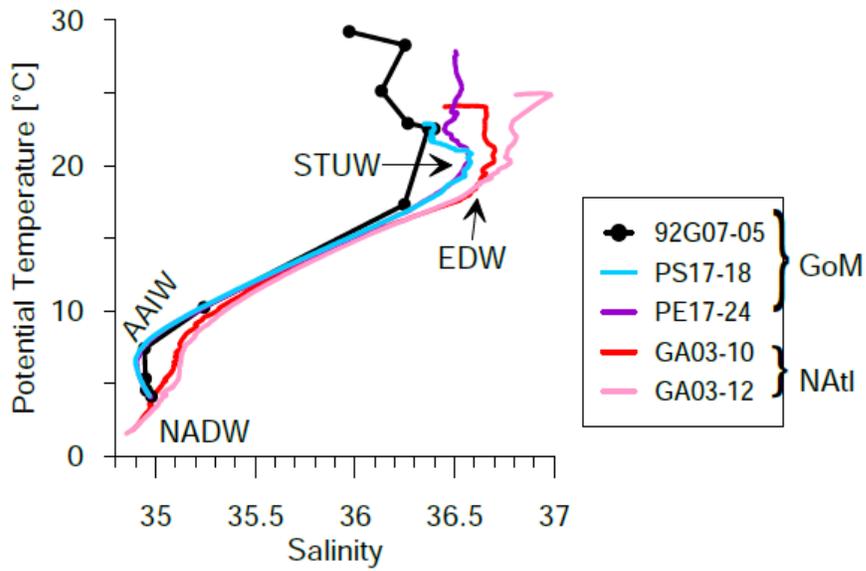
277 Finally, to assess the residence time of dissolved iron (τ_{dFe}), we compare the inventory of
 278 dissolved iron $\int dFe dz$ measured in the Gulf of Mexico with our estimated dissolved iron flux
 279 (Eq. 4). This also produces an estimate as a function of integrated depth; e.g., a flux integrated to
 280 500 m would be used to estimate τ_{dFe} in the upper 500 m of the water column. For iron data in the
 281 deep northern Gulf of Mexico, we use the deep water survey of the former site of the Deepwater
 282 Horizon oil rig (Joung & Shiller, 2013). These authors determined that the 2010 oil spill at this
 283 site did not significantly affect Fe distributions there, and at the time of this writing these are the
 284 only published observations of dissolved Fe in the Gulf of Mexico deeper than 500 m (see
 285 review by Hayes et al., 2019). For dissolved Fe in the GA03 North Atlantic stations, we use the
 286 data from Conway & John (2014).

$$\tau_{dFe} = \frac{\int dFe dz}{F_{dFe}} \quad (4)$$

288 3 Results and Discussion

289 3.1 Hydrography

290 The hydrography of the three Gulf of Mexico profiles presented here are relatively
 291 similar (Figure 3 and 4a). These subtropical surface waters ranged from 22°C to 29°C in potential
 292 temperature and 36.0 to 36.4 in practical salinity. Mixed layers were relatively shallow (< 30 m,
 293 defined by 0.125 kg/m³ increase in potential density from the surface value), giving way to some
 294 increases in salinity indicative of Subtropical Underwater within 100-200 m depth and then a
 295 permanent thermocline and halocline between 200 m and 800 m depth. Salinities as low as 34.8
 296 around 600 m depth are indicative of Antarctic Intermediate Water which has been advected
 297 northward throughout the Atlantic and into the Caribbean Sea-Gulf of Mexico system (Hofman
 298 & Worley, 1986). Deep waters (>1000 m) are relatively homogenous in temperature and salinity
 299 in the Gulf of Mexico, largely reflecting the character of North Atlantic Deep Water that has
 300 entered deep passages in the Caribbean Sea and flowed over the Yucatan sill into the Gulf after
 301 some mixing with Caribbean mid-waters (Morrison et al., 1983). The main distinguishing
 302 characteristic when comparing the Gulf of Mexico hydrography with that in the western North
 303 Atlantic sites shown is the more prominent presence of the 18-degree mode water (Worthington,
 304 1959) between 200 and 600 m depth in the North Atlantic sites (Fig. 4a).



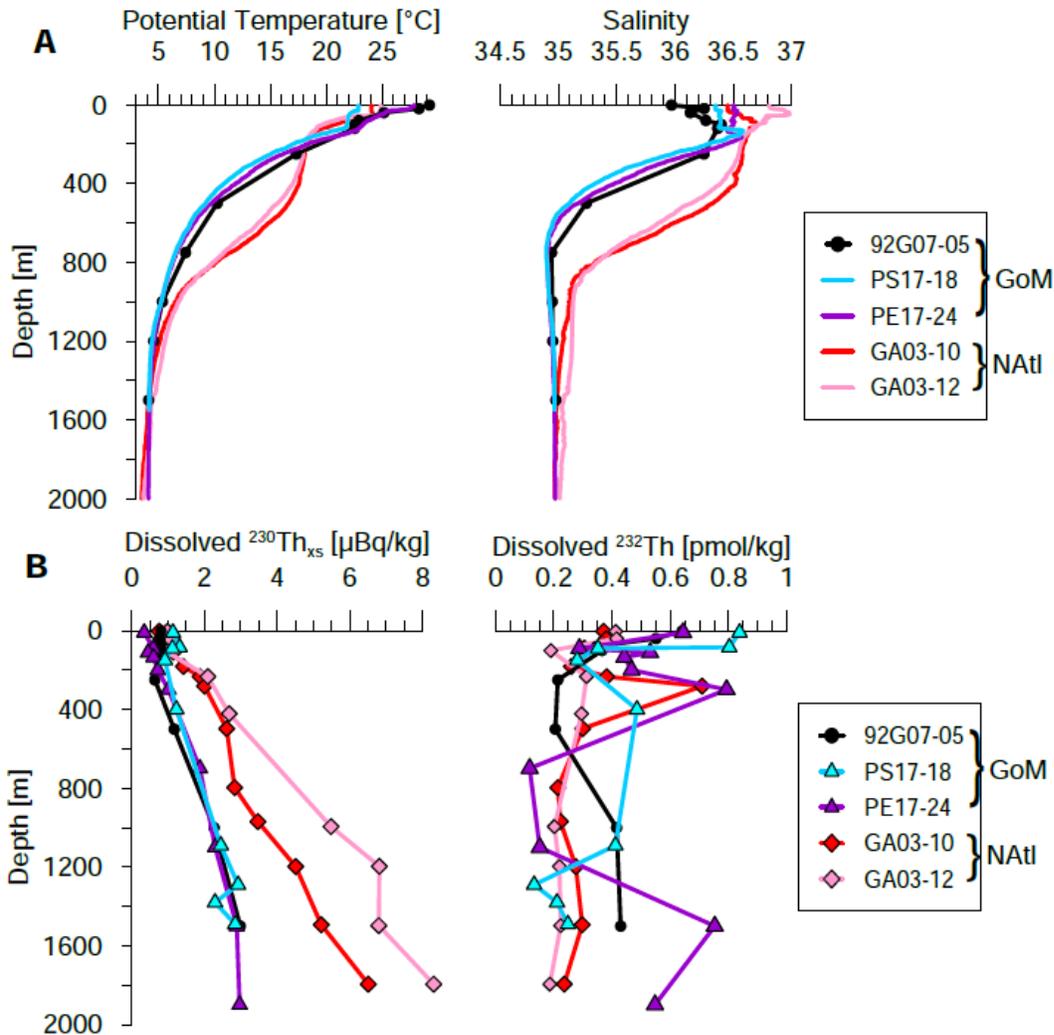
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306 **Figure 3.** Temperature-Salinity diagram of the 5 deep sites shown in Fig. 2 in the Gulf of
 307 Mexico (GoM) and North Atlantic (NATl). Only discrete bottle values were available for station
 308 92G07-05. All sites show evidence of warm, subtropical surface waters, Subtropical Underwater
 309 (STUW) just below the surface, and North Atlantic Deep Water (NADW) at depth. The Sargasso
 310 Sea sites (GA03-10 and -12) had more prominent 18°C water (EDW) in the thermocline and
 311 the Gulf sites had more clear evidence of the salinity minimum associated Antarctic Intermediate
 312 Water (AAIW) that has traveled northward through the Caribbean.

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316

317 **Figure 4.** (a) Potential temperature and practical salinity and (a) dissolved $^{230}\text{Th}_{\text{xs}}$ and dissolved
 318 ^{232}Th as a function of water depth at the Gulf of Mexico (GoM) and North Atlantic (NATl)
 319 sites indicated in Figure 2. Error bars on the thorium data are smaller than or equal to the symbol size.

320 3.2 ^{230}Th activity profiles

321 The depth profiles of $d^{230}\text{Th}_{\text{xs}}$ presented here (Fig. 4b) all demonstrate a roughly linear
 322 increase with depth, consistent with the model of reversible scavenging (Bacon & Anderson,
 323 1982) in which the uniformly produced ^{230}Th undergoes cycles of adsorption and desorption onto
 324 settling particles, allowing relatively little lateral transport. There is, however, variability in the
 325 upper water column (< 200 m depth), with mixed layer $d^{230}\text{Th}_{\text{xs}}$ ranging from 0.35 $\mu\text{Bq/kg}$ at
 326 PE17-24 to 1.14 $\mu\text{Bq/kg}$ at PS17-18. This range more than spans the range seen in the mixed
 327 layer of the western North Atlantic stations (0.3 to 0.4 $\mu\text{Bq/kg}$) and could potentially be related
 328 to surface circulation patterns, such as upwelling, downwelling, vertical mixing, or real
 329 differences in particle flux at the sites. The dissolved Th residence times implied by the mixed
 330 layer $d^{230}\text{Th}_{\text{xs}}$ at these sites is 0.8 to 2.6 years (Fig. 5). These timescales suggest that seasonal
 331 patterns in particle flux will largely be averaged out. It may also be that vertical mixing or

332 upwelling is supplying a variable magnitude of upward ^{230}Th flux (Luo et al., 1995; Pavia et al.,
 333 2020). This effect has important implications for the calculation of dissolved Th fluxes and is
 334 discussed more in section 3.4.

335 Despite variability in the upper 200 m, there are clearly distinct slopes in the $d^{230}\text{Th}_{\text{xs}}$
 336 profiles between the Gulf of Mexico and the western North Atlantic data. At about 1500 m, there
 337 is about 2 times as much $d^{230}\text{Th}_{\text{xs}}$ at the North Atlantic sites compared to the Gulf sites,
 338 indicating reduced scavenging removal by lower particulate fluxes in the remote Atlantic sites.
 339 The $d^{230}\text{Th}_{\text{xs}}$ concentrations at GA03-12 below 500 m are about 20% larger than at GA03-10 and
 340 this may be due to a combination of a younger ventilation age at the more northern site (GA03-
 341 10) or a slightly lower particle flux at GA03-12 (Hayes, Anderson et al., 2015).

342 The deep Gulf of Mexico in summer is just as oligotrophic as the Sargasso Sea (Howe et
 343 al., 2020; Muller-Karger et al., 1991; Stukel et al., 2021), though the northern Gulf can
 344 sometimes be impacted by Mississippi River outflow (Kil et al., 2014; da Silva & Castelao, 2018)
 345 potentially leading to a higher annual average biological particle flux in the northern Gulf.
 346 Furthermore, the proximity of the extensive continental shelf and slope to the Gulf of Mexico
 347 sites (Fig. 1) implies higher total lithogenic particles fluxes, including resuspended nepheloid
 348 layers (Diercks et al., 2018), in the Gulf compared to the Sargasso Sea. Thus, both increased
 349 biological and lithogenic particulate fluxes likely contribute to greater scavenging removal of
 350 $d^{230}\text{Th}_{\text{xs}}$ at the Gulf sites compared to the remote Atlantic sites. The dissolved Th residence time
 351 (Fig. 5) at all three Gulf sites is 1-2 years in surface water and increases linearly with integration
 352 depth to about 4 years at 1500 m depth. In comparison, at the Sargasso Sea sites the Th residence
 353 times increase to 8-11 years at 1500 m depth.

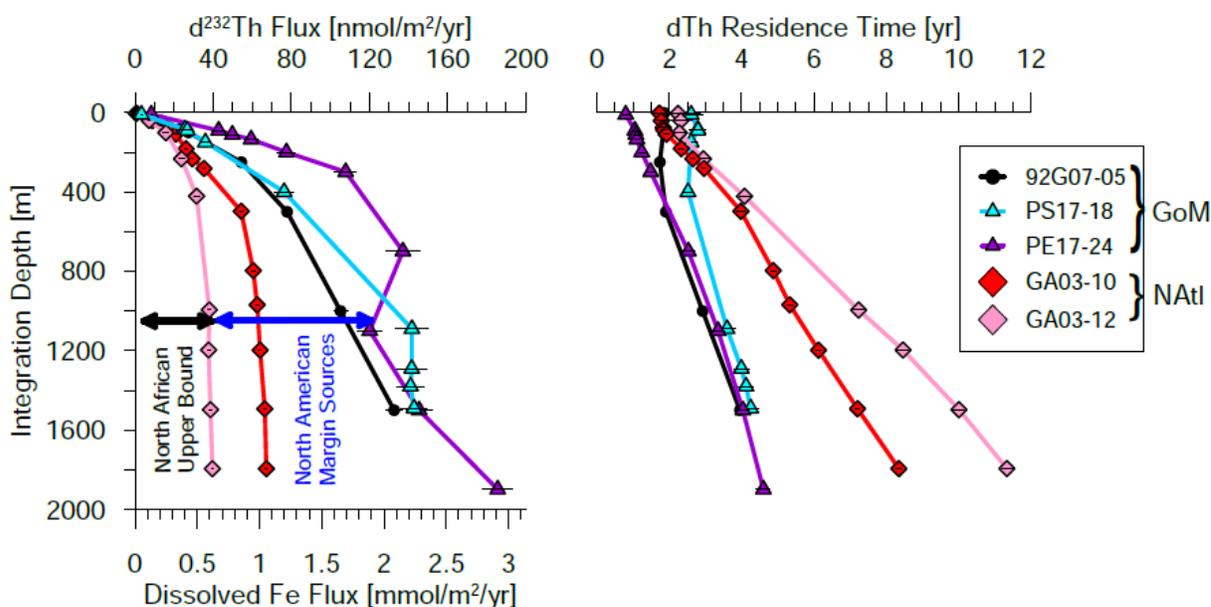
354 **3.3 ^{232}Th concentration profiles**

355 For a tracer supplied predominantly at the surface, say through atmospheric dust, the
 356 reversible scavenging model predicts a constant concentration with depth, as the adsorption-
 357 desorption balance on particles continues throughout the water column. The profiles of $d^{232}\text{Th}$
 358 presented here (Fig. 4b) are not constant with depth, indicating subsurface sources of ^{232}Th such
 359 as lateral advection of waters from areas of benthic sediment resuspension, and likely more so
 360 for the Gulf of Mexico sites compared with the North Atlantic sites. Beam transmission data
 361 would have been useful to support the inference of lateral transport but unfortunately it was not
 362 available from the Gulf of Mexico CTD casts. It is worth noting that in contrast to the relative
 363 homogeneity of ^{230}Th , the larger spatial gradients in ^{232}Th seen here do imply that advection and
 364 diffusion in the Gulf could physically transport ^{232}Th to regions other than where it was first
 365 introduced into seawater.

366 Significant increases in $d^{232}\text{Th}$ concentration near the surface in profiles from PS17-18
 367 and PE17-24 could reflect dust deposition but also could indicate lateral sources as well. Near
 368 surface $d^{232}\text{Th}$ concentrations are about 30% higher in PS17-18 than in PE17-24, possibly
 369 reflecting a coastal shelf source for PS17-18, which is by proximity closer to the northern Gulf
 370 Coast. Surface waters of PE17-24 were within a Loop Current eddy (Fig. S4) and thus this water
 371 had been relatively recently advected from the Caribbean Sea and may have inherited the effects
 372 of North African dust deposited in the Caribbean (Fig. 2) and/or other Caribbean margin sources
 373 such as the Amazon/Orinoco outflows (Hayes et al., 2017). In the northwestern Gulf, Guo et al.
 374 (1995) found that surface water $d^{232}\text{Th}$ increased from ~ 0.6 pmol/kg at 92G07 stations 5 and 4 to
 375 1.3 and 1.4 pmol/kg at stations 3 and 1, respectively, station 1 having evidence for MARS

376 influence (see Fig. 1). This is one indication of a riverine/shelf source of $d^{232}\text{Th}$ in this sector.
 377 Seasonality could possibly play a role in the observed variability within the Gulf of Mexico
 378 stations, as the Saharan dust plume reaches its most northwestward extent in summer (Prospero,
 379 1999; Prospero et al., 1987; 2010). However, with dissolved Th residence times around 1 year in
 380 the mixed layer and longer at depth (Fig. 5, sec. 3.2), it would be expected that seasonal effects
 381 would largely be averaged out. Therefore interannual (in the case of PS17-18/PE17-24 versus
 382 92G07) or spatial variations are more likely to be responsible for the dissolved ^{232}Th variations
 383 seen here.

384 The average $d^{232}\text{Th}$ concentration at all of the Gulf sites (~ 0.43 pmol/kg) is about 40%
 385 higher than the average of the North Atlantic sites (~ 0.30 pmol/kg in the upper 1800 m of the
 386 water column). Furthermore the increased scavenging intensity in the Gulf evidenced by the
 387 ^{230}Th data means that there must be a much higher flux of $d^{232}\text{Th}$ into the Gulf than the North
 388 Atlantic sites to support the dissolved concentrations observed.



389
 390 **Figure 5.** (left) Dissolved ^{232}Th flux as a function of integration depth from the surface for the
 391 sites in Fig. 2. Assuming the observed flux in the Gulf of Mexico (GoM) sites is a combination
 392 of North African dust and North American margin sources, the western North Atlantic (NAtl)
 393 sites, which receive only North African dust, can be used as an approximate upper limit of the
 394 North African dust source in the GoM. Note the upper and lower x-axes are linearly related by
 395 Eq. 3. Error bars are shown for dissolved ^{232}Th fluxes which are about 5%, while error bars for
 396 dissolved Fe fluxes (not shown) are significantly larger, about 40%, mainly due to uncertainty in
 397 the relative Fe/Th solubility. (right) Dissolved Th residence time with respect to scavenging
 398 based on integrated $d^{230}\text{Th}_{\text{xs}}$ inventories compared to production by ^{234}U decay.

399 3.4 Dissolved ^{232}Th fluxes and the balance of lithogenic sources

400 When converted to flux, the Gulf of Mexico sites indeed have 2-3 times higher dissolved
 401 ^{232}Th flux than the North Atlantic sites (Fig. 5). The apparent increasing ^{232}Th fluxes with
 402 integration depth in the upper 500 m has been observed in most other sites around the global
 403 ocean and may relate to a flaw in our assumptions in defining the residence time of Th. Prior
 404 work suggested that ^{230}Th could be scavenged by a different mechanism than ^{232}Th in the

405 euphotic zone where particle flux is greatest (Hayes et al., 2017). However, as mentioned in Sec.
406 3.2 it seems a more likely explanation is that vertical mixing or advection in the upper water
407 column causes an upward flux of dissolved ^{230}Th into the mixed layer (Luo et al., 1995; Pavia et
408 al., 2020). This causes the apparent ^{230}Th -based residence time to be too high in the upper water
409 column, driving the flux estimate low. Adding to this effect, the vertical concentration gradient
410 of $d^{232}\text{Th}$ is often reversed (lower concentrations at depth), resulting in downward mixing of
411 some of the ^{232}Th deposited at the surface.

412 The net effect is that our estimates of dissolved ^{232}Th (and extrapolated Fe flux) in Fig. 5
413 are likely too low, especially in the upper 500 m of the water column. Furthermore, unfortunately
414 we cannot resolve in detail how the profile shape of fluxes might look in this upper water
415 column. As more inventory is integrated with depth, the upper water column effects are
416 accounted for since all of the vertically transported Th is integrated together, and dissolved ^{232}Th
417 flux profiles in the remote ocean tend to be relatively constant with increasing integration depth
418 below about 500-1000 m (Hayes et al., 2018; Pavia et al., 2020; Fig. 5). When this is the case, it
419 is fair to assume that the flux achieved around 500-1000 m integration depth is likely similar to
420 the actual flux being received in surface waters. An exception to this, however, occurs when
421 fluxes continue to increase with integration depth toward the seafloor, as in the case of the Gulf
422 of Mexico profiles (Fig. 5). This situation means there must be dissolved ^{232}Th sources at depth
423 (Hayes et al., 2013), indicating some combination of benthic sources. Additionally, it is difficult
424 to extrapolate what flux might have been received only in surface waters since there is not clear
425 break between surface and benthic sources.

426 Using the integrations to about 1000 m as a deep water reference since this is where
427 $d^{232}\text{Th}$ flux in the GA03 stations finally plateaus with integration, the dissolved ^{232}Th flux from
428 the Gulf of Mexico sites ranges from 100 to 140 $\text{nmol}/\text{m}^2/\text{yr}$. The flux at the North Atlantic sites
429 ranges from 40 to 60 $\text{nmol}/\text{m}^2/\text{yr}$. While the relative magnitude of North African dust deposition
430 occurring between the western North Atlantic and the northern Gulf is still uncertain, using the
431 smaller of the two North Atlantic fluxes (40 $\text{nmol}/\text{m}^2/\text{yr}$) and the larger of the two Gulf fluxes
432 (140 $\text{nmol}/\text{m}^2/\text{yr}$), we estimate an upper bound of 30% of lithogenic sources in the northern Gulf
433 of Mexico being due to North African dust. The same bound would apply to dissolved Fe under
434 our assumptions in Sec. 2. This result translates to the Gulf receiving a dissolved Fe flux from
435 total oxic, lithogenic sources of 1.7-2.2 $\text{mmol}/\text{m}^2/\text{yr}$, and a likely upper bound of about 0.6
436 $\text{mmol}/\text{m}^2/\text{yr}$ specifically from North African dust.

437 **3.5 What can we learn about the possible margin sources of Th and Fe in the Gulf?**

438 Our analysis up to this point has focused on determining what proportion of the Th and
439 Fe flux in the Gulf of Mexico is due to North African dust deposition. The flux in excess of the
440 North African dust source must be due to North American margin sources (including possibly
441 North American aerosols), but can we glean any further information here about what sources
442 those might be? Setting aside North American aerosols for the moment, the three remaining
443 candidates are rivers, submarine groundwater discharge (SGD) and diffusion from sediments.
444 Because Fe and Th are very insoluble and particle-reactive, it has often been thought that any
445 riverine sources would be attenuated close to the coast as the river deltas usually provide a high
446 particle flux environment to trap the metals near the shelf (Boyle et al., 1977). While this largely
447 appears to be the case for Fe in the Mississippi-Atchafalaya system (Ho et al., 2019; Joung &
448 Shiller, 2016), we cannot fully rule out the importance of riverine sources. More detailed

449 transects of trace metals from the Gulf of Mexico river plumes to the interior Gulf will be
450 required to fully assess this.

451 To estimate the flux of trace elements and isotopes (TEI flux) to the ocean due to
452 combined shelf sources (including rivers, SGD, continental and shelf slope sediments), Charette
453 et al. (2016) developed a method based on inverse-model-derived flux of ^{228}Ra from the shelf
454 (Kwon et al., 2014). In this method the ratio of the relative enrichment between shelf waters and
455 the adjacent open ocean for ^{228}Ra and the TEI of interest (Eq. 5) is multiplied by the shelf ^{228}Ra
456 flux to estimate a shelf TEI flux. While ^{228}Ra can sometimes be used as a specific tracer for
457 SGD, this method cannot distinguish between the multiple shelf sources listed above. In this
458 sense, estimates from this approach could be viewed as a maximum value for SGD input. It is
459 also important to note that this method views shelf flux as being the interfacial flux to the ocean
460 at the shelf break (or across the 200 m isobath). This method cannot account for further
461 scavenging of a shelf-sourced TEI that might occur between the shelf break and the ocean interior
462 region in question.

$$463 \quad \text{TEI flux} = {}^{228}\text{Ra flux} \times \left(\frac{\text{TEI}_{\text{shelf}} - \text{TEI}_{\text{ocean}}}{{}^{228}\text{Ra}_{\text{shelf}} - {}^{228}\text{Ra}_{\text{ocean}}} \right) \quad (5)$$

464 The shelf ^{228}Ra flux estimate for the Gulf of Mexico is $11,800 \pm 3,900$ dpm/m²/yr
465 (Charette et al., 2016). In this case, the flux is normalized by shelf area, which for the shelf of the
466 Gulf of Mexico (water depths <200 m) is 330,000 km² (Davis, 2017). Thus, for the whole Gulf
467 of Mexico, the shelf ^{228}Ra flux into the upper 200 m of the open Gulf is $3.9 \pm 1.3 \times 10^{15}$ dpm/yr.
468 For coastal and interior Gulf of Mexico concentrations of dissolved ^{232}Th we use the 92G07
469 transect (Fig. 1) of 1.4 pmol/kg (shelf) and 0.6 pmol/kg (ocean) (Guo et al., 1995). For ^{228}Ra , we
470 use observations from a similar transect measured in July 1975 of 23.6 dpm/100kg (shelf) and
471 6.4 dpm/100kg (ocean) (Reid, 1984). Assuming a modest 20% uncertainty in each of these
472 concentrations (which admittedly may be an underestimate of the true uncertainty since the
473 measurements are sparse), this results in a shelf-to-ocean ^{232}Th to ^{228}Ra ratio (as in Eq. 5) of 4.6
474 ± 2.2 pmol/dpm and a Gulf-wide shelf flux of $1.8 \pm 0.9 \times 10^4$ mol ^{232}Th /yr. We recognize that
475 that this calculated is based on $d^{232}\text{Th}$ data from only the northern Gulf shelf, but the ^{228}Ra data
476 does cover both northern and southern margins (Reid, 1984) and we consider this a preliminary
477 estimate until more ^{232}Th data are available.

478 For comparison to the shelf flux, we need to scale up our estimated total $d^{232}\text{Th}$ flux from
479 the deep Gulf sites for the entire open ocean Gulf (water depths >200 m). The surface area of the
480 deep Gulf is 1,170,000 km² (Davis, 2017), and again the estimated total $d^{232}\text{Th}$ flux at the deep
481 sites is 100-140 nmol/m²/yr (Fig. 5), giving an integrated flux of $14 \pm 2.3 \times 10^4$ mol ^{232}Th /yr (cf.
482 shelf flux of $1.8 \pm 0.9 \times 10^4$ mol ^{232}Th /yr calculated above). This analysis suggests that the shelf
483 $d^{232}\text{Th}$ flux is a significant, though not dominant, percentage ($13 \pm 7\%$) of the Gulf-wide sources
484 and may be on par with the atmospheric deposition source (upper-limit of 30%, Sec. 3.4). It
485 appears that we have yet to find a single source that dominates $d^{232}\text{Th}$ flux in the Gulf of Mexico,
486 or put another way, it is likely that multiple sources contribute a significant levels.

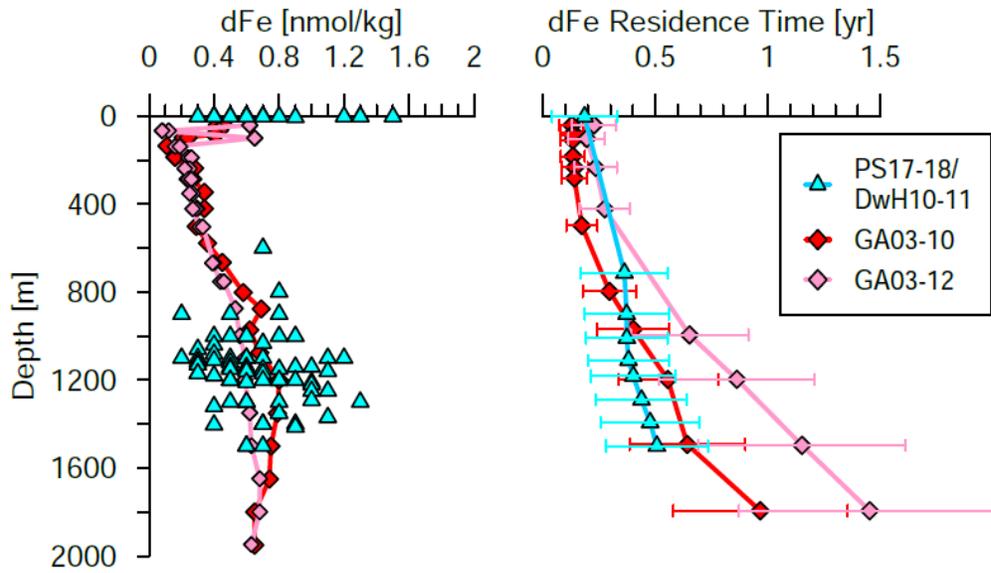
487 Estimates of dissolved Fe on the Louisiana Shelf range from 20-50 nmol/kg (Joung &
488 Shiller, 2016) and in surface waters of the interior Gulf the range is 0.3 to 1.5 nmol/kg (Joung &
489 Shiller, 2013). Using the same Ra-based method, we estimate a maximum dissolved Fe flux from
490 shelf sources of $4.1 \pm 1.1 \times 10^8$ mol Fe/yr in the Gulf of Mexico. Our estimate of total dissolved
491 Fe flux from the deep sites is 1.7-2.2 mmol/m²/yr (Fig. 5), and when scaled for the interior Gulf

492 surface area this is $23 \pm 3 \times 10^8$ mol Fe/yr. As with ^{232}Th , this analysis implies a significant shelf
493 source ($18 \pm 5\%$) of dissolved Fe to the upper water column of the Gulf of Mexico. One large
494 uncertainty in this analysis stems from the difficulty in characterizing an overall “shelf” and
495 “interior” concentration of the tracers which could themselves vary significantly in different
496 regions of the two domains. Additionally, as was the case for ^{232}Th , the ^{228}Ra method in its
497 current form cannot distinguish between riverine, submarine groundwater or shelf sediment
498 sources. Better characterization of spatial concentration gradients of radium, thorium and iron in
499 the Gulf of Mexico and relevant groundwater and riverine sources will reduce this uncertainty in
500 the future.

501 Diffusion from benthic sediments below 200 m depth is likely also a significant source in
502 the Gulf of Mexico, though the magnitude is currently highly uncertain. There is evidence for
503 benthic Fe fluxes from both oxic and suboxic/anoxic sediments (Conway & John, 2014; Homoky
504 et al., 2016, 2021). Joung & Shiller (2016) found that the hypoxic Louisiana Shelf sediments
505 could be an Fe source seasonally, though this source could be related to SGD as well. A recent
506 empirically-informed diagenetic model estimated that Gulf of Mexico sediments range from
507 being a sink of dissolved Fe to being a source as high as about $0.5 \text{ mmol/m}^2/\text{yr}$ (Dale et al.,
508 2015). Benthic chamber experiments in diverse sedimentary environments will narrow this range
509 in the future. In sum, the Gulf of Mexico potentially has significant lithogenic Fe sources from
510 four pathways (aerosols, SGD, rivers and sediments). We note that our measured dissolved ^{232}Th
511 flux likely includes oxic dissolution, but since ^{232}Th is not redox sensitive, this likely neglects
512 any suboxic sedimentary Fe release. Furthermore, ^{232}Th likely has no sources from biomass or
513 fossil fuel burning as iron does (Hamilton et al., 2020).

514 **3.6 Dissolved Fe residence time in the Gulf of Mexico**

515 With the estimated dissolved Fe fluxes and observations of dissolved Fe in these waters,
516 we can calculate the dissolved Fe residence time (or replacement time) with respect to the input.
517 Dissolved Fe was measured directly at sites GA03-10 and -12 (Conway & John, 2014) in
518 November 2011 and at the Deepwater Horizon site (Joung & Shiller, 2013) in May 2010,
519 October 2010 and October 2011 (Fig. 6). The Deepwater Horizon site Fe data was not measured
520 as a vertical profile, but rather deepwater was surveyed at several locations around the rig site.
521 Additionally Joung & Shiller (2013) found that Fe concentrations tended to increase near the
522 seafloor which occurred at a different depth at each particular site. For the residence time
523 calculation, we use a depth-binned average dissolved Fe concentration profile to compare with
524 the flux profile (the depth bins were 1-5 m at the surface, and roughly every 100 m between 600
525 and 1500 m depth). Within uncertainties, the residence time of dissolved Fe at the Deepwater
526 Horizon site is nearly indistinguishable between that in the western North Atlantic (Fig. 6),
527 ranging from 0.2 ± 0.1 years (or 70 ± 35 days) in the surface to 6 months at depth. The similarity
528 of this residence time to that in the North Atlantic occurs despite a much larger source term in
529 the Gulf of Mexico (Fig. 5). In other words, the higher input rate of dissolved Fe into the Gulf of
530 Mexico must be balanced by increased removal processes, likely scavenging by the greater
531 particle flux in the Gulf. This idea could be tested by assessing the adsorbed component of Fe in
532 particulate material (water column or sediment) and we would predict a greater adsorbed
533 component in the Gulf versus the North Atlantic.



534

535 **Figure 6.** Dissolved iron concentration profiles (left) from the western North Atlantic sites
 536 (Conway & John, 2014) and the site of the former Deepwater Horizon in 2010 and 2011
 537 (DwH10-11; Joung & Shiller, 2013) which is roughly coincident with the location of PS17-18
 538 from this study. The DwH study surveyed several sites around the former oil rig, focusing on
 539 water depths where the deep oil spill occurred. Dissolved iron residence times (right) were
 540 computed using dissolved Fe inventories from the data on the left and the dissolved iron fluxes
 541 shown in Fig. 5, with propagated uncertainties shown in the colored error bars.

542 Constraining the residence time of iron in the upper ocean has been a major focus in
 543 oceanography since it was realized that iron availability limits the overall productivity in many
 544 ecosystems (Landing & Bruland, 1987; Martin & Gordon, 1988). A recent compilation of
 545 dissolved Fe residence time estimates suggests that τ_{dFe} in the upper 250 m of the water column
 546 is on the order of sub-annual, consistent with our findings, but there are large variations between
 547 studies (Black et al., 2020). A caveat here (as mentioned in Sec. 3.4) is that due to the mixed
 548 layer effect on ^{230}Th distributions, our calculated fluxes are likely too low in the upper 500 m.
 549 Higher fluxes would reduce the apparent Fe residence time. Furthermore, by defining the
 550 residence time with respect to a ^{232}Th -based source, we are also overestimating the residence
 551 time since we are neglecting dissolved Fe sources from suboxic sediments and combustion-
 552 related aerosols. Additionally, when dFe concentrations increase with depth in the upper ocean,
 553 seasonal vertical mixing may provide an additional source of dFe to the mixed layer not
 554 accounted for by the Th-based flux.

555 Thus, particularly in surface waters, we estimate that the dissolved Fe residence time in
 556 the Gulf of Mexico is likely considerably less than 2 months. Given that a non-negligible fraction
 557 of this iron is sourced from atmospheric dust, seasonal or shorter term dust events are likely to
 558 impact Fe availability and could easily impact phytoplankton community structure, as has been
 559 hypothesized on the West Florida Shelf (Lenes et al., 2001; Walsh et al., 2006; Walsh &
 560 Steidinger, 2001). That said, temporal changes in submarine groundwater discharge, river
 561 discharge or sedimentary diffusion would be equally valid candidates for changing iron supplies,
 562 given their likely substantial contributions to the iron budget in the Gulf. Future work

563 determining the impact of iron availability in the Gulf will need to independently assess at least
 564 these three major iron sources. The possibility for Fe input from North American lithogenic and
 565 anthropogenic aerosols should also be investigated further.

566 **4 Conclusions**

567 In this study, we have mapped the distribution of dissolved ^{232}Th , ^{230}Th and dissolved
 568 ^{232}Th flux at three deep sites in the northern Gulf of Mexico. This distribution demonstrates a
 569 higher particle scavenging intensity in the Gulf, compared to sites in the adjacent Sargasso Sea,
 570 as well as clearly elevated margin sources of ^{232}Th in the Gulf. This total flux likely includes
 571 contributions from atmospheric dust, and shelf sources, including submarine groundwater
 572 discharge, riverine discharge and benthic sedimentary release, based on available radium data.
 573 Using upwind sites in the Sargasso Sea, we suggest an upper bound of 30% for the North African
 574 dust contribution to Gulf of Mexico ^{232}Th and Fe supplies. Our thorium-based method neglects
 575 some sources of iron including suboxic sediment release and combustion aerosol sources and
 576 uncertainties remain in distinguishing the relative role of the remaining North American margin
 577 sources. Implied maximum residence times of dissolved iron of about 2 months in the upper 250
 578 m and 6 months in the entire Gulf, clearly indicate the ability of iron supply changes to result in
 579 dynamic ecosystem responses. Future work to more accurately determine the spatial
 580 concentration gradients of radium and other trace metals of interest between coastal and interior
 581 Gulf water and in relevant groundwater and riverine end-members will significantly improve
 582 estimates of submarine groundwater discharge sources as well as better constraining the overall
 583 budget of lithogenic sources.

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 591 [dmo.org/dataset/819622](https://www.bco-dmo.org/dataset/819674); <https://www.bco-dmo.org/dataset/819674>) and derived parameters are
 592 available at Zenodo (<https://zenodo.org/record/6014268>).

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Figure 1.

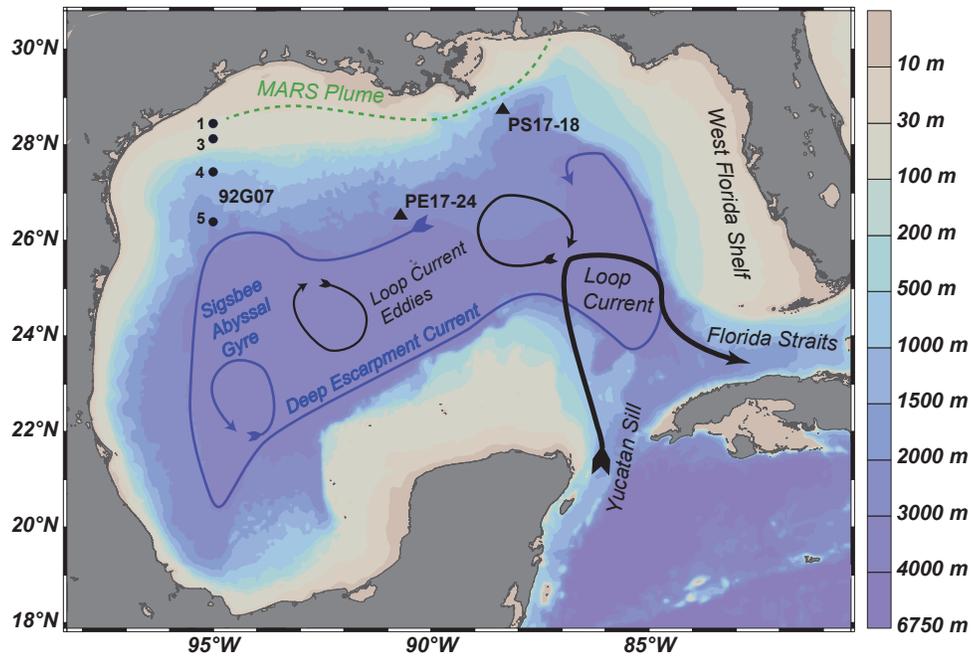


Figure 2.

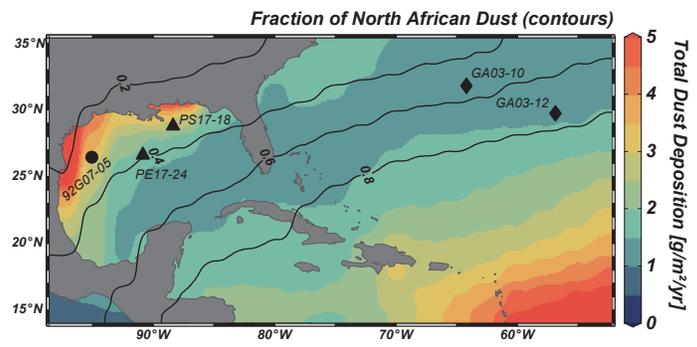


Figure 3.

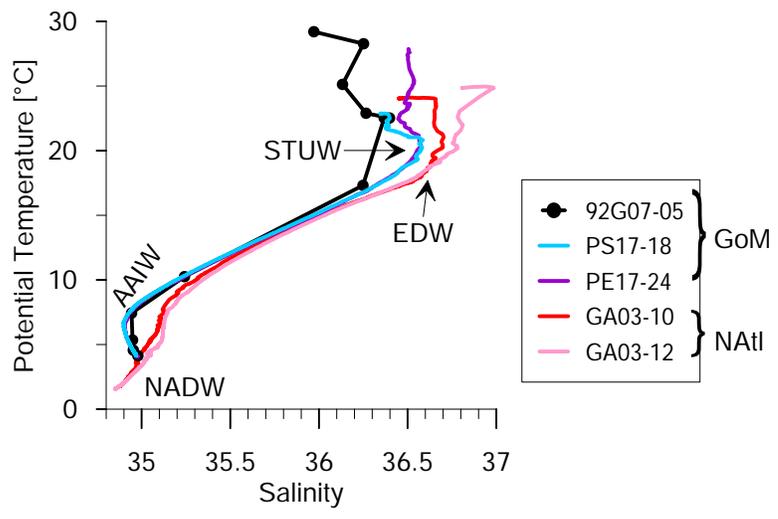


Figure 4.

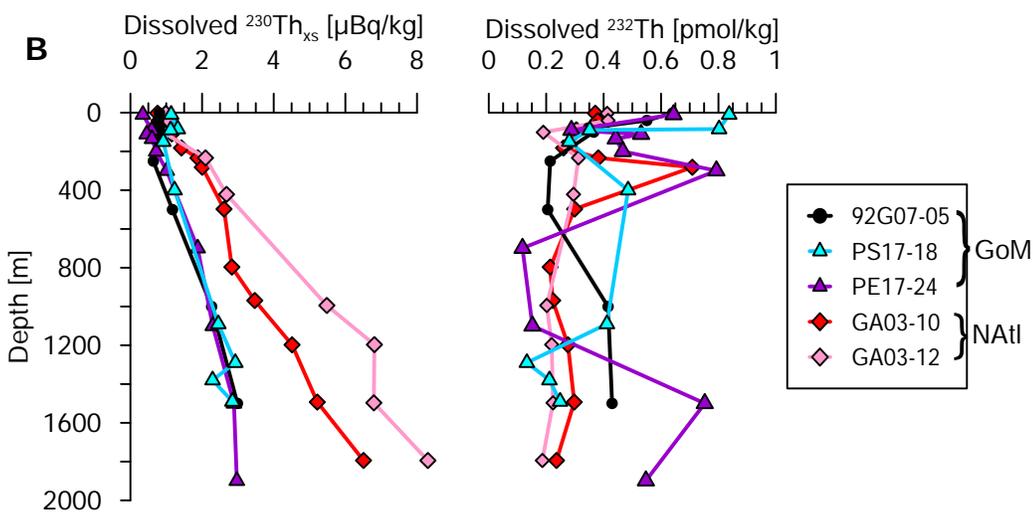
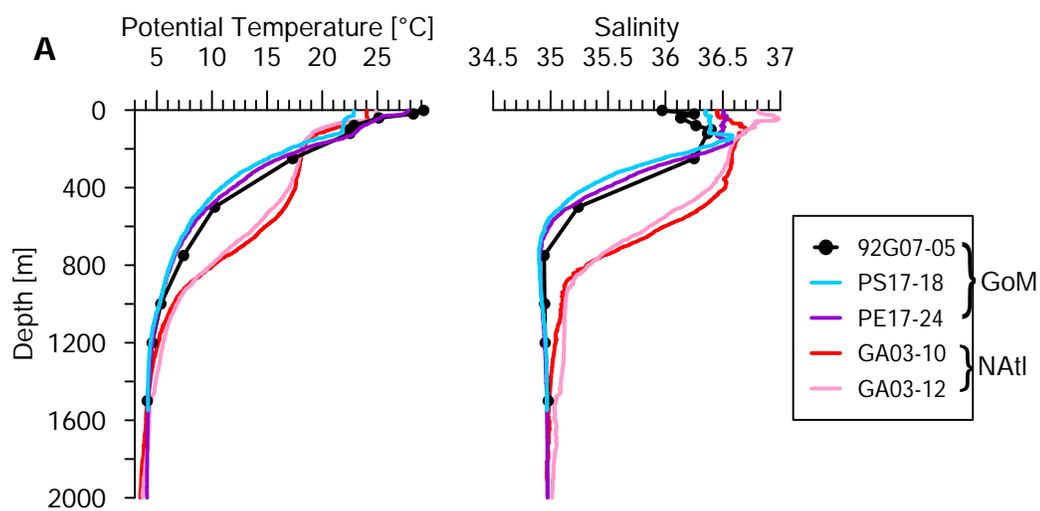


Figure 5.

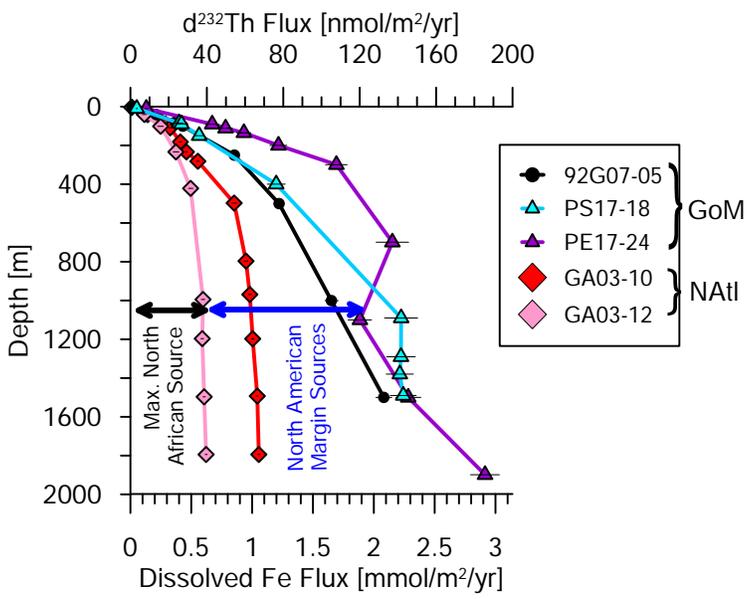


Figure 6.

