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1 **Organic Pollutants and Ocean Fronts**

2 **Across the Atlantic Ocean: A Review**

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8
9 **Abstract.** Little is known about the effect of ocean fronts on pollutants dynamics,
10 particularly organic pollutants. Since fronts are associated with convergent currents and
11 productive fishing grounds, any possible convergence of pollutants at fronts would raise
12 concerns. The focus here is on relatively persistent organic pollutants, POPs, as non-
13 persistent organic pollutants are rarely found in the open ocean. Results from recent
14 cruises in the Atlantic Ocean are examined for POPs distribution across ocean fronts in
15 (i) the Canary Current; (ii) the Gulf Stream; and (iii) the Amazon and Rio de la Plata
16 Plumes. Few studies achieved a spatial resolution of 10 to 20 km, while most had 100 to
17 300 km between adjacent stations. The majority of the well-resolved studies measured
18 perfluorinated compounds (PFCs), which seem particularly well suited for frontal
19 resolution. In the NE Atlantic, concentrations of PFCs sharply decreased between SW
20 Europe and NW Africa upon crossing the Canary Current Front at 24°-27°N. In the
21 Western Atlantic, the PFC concentrations sharply increased upon entering the Amazon
22 River Plume and Rio de la Plata Plume. In the NW Atlantic, concentrations of several
23 pollutants such as polycyclic aromatic hydrocarbons are very high in Rhode Island Sound,
24 decreasing to below detection limit in the open ocean. The more persistent and already

25 phased-out polychlorinated biphenyls (PCBs) displayed elevated concentrations in the
26 Gulf Stream and Rhode Island Sound, thereby highlighting the importance of ocean
27 fronts, along-front currents, and cross-frontal transport for the dispersal of PCBs.

28 **Keywords:** fronts, organic pollutants, PFC, PCB, river plumes

29 **Regional Index terms:** North Atlantic Ocean; Gulf Stream; Azores Current; Canary

30 Current; Rhode Island Sound; South Atlantic Ocean; Rio de la Plata; Amazon River.

31

32 **FOOTNOTE:**

33 POPs: persistent organic pollutants; PCBs: polychlorinated biphenyls; PFCs: perfluorinated compounds; PAHs:
34 polycyclic aromatic hydrocarbons; PFOA: perfluorooctanoic acid; PFOS: perfluorooctane sulfonate; HCHs:
35 hexachlorocyclohexanes; HCB: hexachlorobenzene; PBDEs: polybrominated diphenylethers

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39 **1. Introduction: Fronts and organic pollutants**

40 Front is a narrow band of enhanced gradients of physical, chemical and biological
41 properties (temperature, salinity, nutrients etc.) that separates distinctly different water
42 bodies (Belkin, 2002). Cross-frontal ranges (steps) of temperature and salinity of up to
43 10°C and 3 psu respectively are routinely observed, though generally these steps are
44 much smaller, typically 2-to-3°C and 0.5-1.0 psu. Fronts are typically associated with
45 enhanced productivity at all trophic levels, including fishery grounds; yet a low-
46 productivity front was observed (Caldeira et al., 2001). Fronts are formed by numerous
47 processes, including tides and tidal mixing, winds, solar heating, current convergence,
48 upwelling/downwelling, advection, convection, precipitation/evaporation, sea ice
49 formation etc. (Belkin, 2002).

50 Fronts and frontal processes play important roles in spatial distribution and temporal
51 variability of pollutants (**Figure 1**). The five key oceanic processes associated with fronts
52 (yellow arrows in **Figure 1**) are (1) particle sinking, (2) downwelling, (3) turbulent
53 mixing, (4) convection, and (5) upwelling. Many fronts are convergent (Belkin et al.,
54 2009), hence associated with downwelling, which enhances particle sinking. Some fronts
55 feature downwelling on one side and upwelling on the opposite side, thus exerting
56 opposite effects on particle sinking. Turbulent mixing at fronts can be enhanced by up to
57 two orders of magnitude vs. ambient ocean (D'Asaro et al., 2011). Downwelling and
58 upwelling are two components of ocean convection, hence water mass formation and
59 conversion. Cascading along continental slope (dark blue arrow in **Figure 1**) is often
60 associated with shelf-slope fronts located over the shelf break. The three key
61 atmospheric processes associated with fronts (light blue arrows in **Figure 1**) are (1) dry

62 deposition, (2) wet deposition, and (3) volatilization. Major fronts associated with the
63 western boundary currents – Gulf Stream, Kuroshio etc. - and with the Antarctic
64 Circumpolar Current can impact the entire lower troposphere up to 1 km above sea
65 surface (Small et al., 2008), thereby directly affecting dry deposition and wet deposition
66 rates. Such fronts also modulate near-surface wind stress (Small et al., 2008), hence
67 volatilization rates. In shallow seas, fronts extend vertically throughout the entire water
68 column and interact with bottom currents (dark blue arrow in **Figure 1**). Even in the deep
69 ocean, fronts associated with western boundary currents can generate strong bottom
70 currents (“benthic storms”) with a speed of >30 cm/s, leaving ripple marks at depths over
71 4,000 m (Hollister and McCave, 1984).

72 Fronts separate water masses with different concentrations of pollutants. Most major
73 fronts are associated with along-front geostrophic currents that transport pollutants across
74 a wide variety of scales. Conservative pollutants can be carried by along-front currents
75 across oceans and around the globe. Rate of turbulent energy dissipation in major frontal
76 zones (Kuroshio, Gulf Stream, Antarctic Circumpolar Current etc.) is “enhanced by one
77 to two orders of magnitude, suggesting that the front, rather than the atmospheric forcing,
78 supplied the energy for the turbulence” (D’Asaro et al., 2011), thereby greatly enhancing
79 dissipation of pollutants in these frontal zones. Surface convergence and downwelling at
80 fronts may result in reduction of surface concentrations of pollutants; this effect was
81 dubbed “self-cleaning” (of fronts) by Sherstyankin (1999). When upwelling develops
82 along one side of a front, it brings relatively pristine deep waters to the surface. Deep
83 convection associated with some fronts (e.g., formation of the Subantarctic Mode Water
84 north of the Subantarctic Front) tends to pump surface contaminants to intermediate and

85 deep layers. Frontal eddies and intra-thermocline lenses effectuate cross-frontal transfer
86 of pollutants between water masses separated by fronts, acting on the synoptic, meso- and
87 small scales, while frontal interleaving, double diffusion, and turbulent mixing effectuate
88 cross-frontal flux of pollutants on the fine scale. Some physical processes are endemic to
89 fronts, e.g., interleaving (especially active across density-compensated fronts) and
90 cabbeling (densification and sinking of a mixture of two water parcels of the same
91 density but different temperature and salinity). Some chemical processes – even if not
92 truly endemic to fronts - may intensify in frontal zones owing to either high gradients of
93 properties or vigorous ocean-atmosphere-ice interaction or elevated biological activity or
94 all of the above – and more. For example, estuarine fronts act as “marginal filters”
95 (Lisitsyn, 1995) by trapping fine river sediments that carry contaminants (Macdonald et
96 al., 2005); the main processes acting at these marginal filters are “flocculation and
97 coagulation of dissolved (colloidal) and suspended matter” (Lisitsyn, 1995).

98 Little is known about the effect of ocean fronts on organic pollutants, but any
99 possible convergence of pollutants in productive fishing grounds associated with fronts
100 would be a cause for concern, especially given the effect of biomagnification since many
101 frontal species are top predators, e.g., tuna and billfish. The pioneering work by Tanabe
102 et al. (1991) in the Seto Inland Sea (Japan) has demonstrated that organic pollutants,
103 particularly those bound to particles, can be enriched in fronts. Since organic pollutants
104 are not routinely investigated across ocean fronts, it is appropriate to first outline the
105 possible effects of fronts on organic pollutant dynamics. As most fronts are associated
106 with surface convergence toward the front, we expect a truly dissolved compound to have
107 a frontal concentration that changes monotonously across the front (**Figure 2, top**) in the

108 same fashion as temperature and salinity. Yet at the same convergence, floating particles
109 or flotsam, e.g., phytoplankton or floating plastic debris, would have a maximum
110 concentration at the surface, within the front, while the water masses separated by the
111 front would sink owing to downwelling circulation along the frontal interface (**Figure 2,**
112 **bottom**). The same logic applies to pollutants concentrated in the sea surface microlayer
113 (Wurl and Obbard, 2004). The importance of plastic particles as vectors of organic
114 pollutants is currently under debate (Teuten et al., 2007; Gouin et al., 2011), while there
115 is agreement that many organic pollutants strongly sorb to man-made polymers present in
116 the ocean. Thus, dissolved versus particle-bound pollutants are expected to have different
117 cross-frontal distribution patterns at convergent fronts.

118 Not all fronts are convergent. Some fronts feature downwelling on one side and
119 upwelling on another. Typically, the upwelled deep water is less polluted than surface
120 water, thereby creating a strong contrast in dissolved organic pollutant concentrations
121 across surface manifestations of upwelling fronts. Fronts with a complex multi-layer
122 vertical structure have been reported. For example, Houghton (2002) performed a dye
123 experiment in the shelf-break front (SBF) on Georges Bank. At the front, surface
124 convergence caused downwelling while bottom convergence caused upwelling. The
125 surface-intensified downwelling and bottom-intensified upwelling converged at mid-
126 depth, resulting in mid-depth divergence or a returning mid-depth flow on both sides of
127 the front (Houghton, 2002).

128 Beyond these purely physical mixing processes, there is also evidence for the
129 enhancement of phytoplankton at fronts (Belkin and O'Reilly, 2009). For example, Ryan
130 et al. (1999a, 1999b) observed a strong seasonal chlorophyll enhancement at the shelf

131 break of the Mid-Atlantic Bight in the spring that lasted into late June. Such massive
132 chlorophyll blooms along physical fronts must have profound effects on distribution of
133 organic pollutants. Major fronts are associated with elevated primary production and
134 enhanced vertical flux of carbon-rich particles that lead to the increased vertical export of
135 organic contaminants on sinking particles from the surface layer to intermediate and deep
136 waters (Dachs et al., 2002; Macdonald et al., 2005).

137 In terms of organic pollutants, we are focusing on relatively persistent organic
138 pollutants, POPs, as non-persistent organic pollutants are rarely found in the open oceans.
139 We can divide these persistent pollutants in two categories: (1) those that are
140 predominantly dissolved, with little tendency to bioaccumulate or sorb significantly; and
141 (2) organic pollutants that bioaccumulate and sorb to either organic matter such as
142 phytoplankton or floating particles such as plastic debris (Rios et al., 2007) (**Table 1**).
143 Whether a contaminant is predominantly dissolved or bound to organic matter (particles,
144 but also to colloidal material and dissolved organic matter, DOM) depends primarily on
145 the compound's physico-chemical properties (Schwarzenbach et al., 2003). The dissolved
146 vs. sorbed dichotomy is also affected by temperature, salinity, the abundance of organic
147 matter and particles in the water. Lastly, the chemical make-up of the particles also
148 affects the pollutant's propensity to sorb. This holds true both for natural particles and
149 floating synthetic polymers. The disposition of compounds to sorb to organic matter is
150 often estimated by relying on a proxy, such as the compound's partitioning constant
151 between octanol and water, K_{ow} , (Schwarzenbach et al., 2003). Compounds with low K_{ow}
152 values prefer to stay dissolved, while those with high K_{ow} values ($> 10^4$) tend to bind to
153 organic particles. The sorption of organic compounds to DOC is more complex, but most

154 studies have focused on DOC isolated from freshwater and sediments (Burkhard, 2000).
155 In a study with coastal DOC, Friedman et al. (2011) suggested that it might sorb PCBs
156 much more strongly than freshwater DOC.

157 Examples of predominantly dissolved POPs include the perfluorinated acids and
158 sulfonates, such as perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS) and
159 its salts, but also low molecular weight pesticides (hexachlorocyclohexanes, HCHs),
160 chlorinated biphenyls with few chlorines and hexachlorobenzene (HCB). In contrast, the
161 higher molecular weight polychlorinated biphenyls (PCBs) with four or more chlorines,
162 but also polybrominated diphenylethers (PBDEs), strongly bind to organic matter in the
163 water column. A compound that is completely persistent, fully dissolved, and does
164 neither interact with particles nor volatilizes constitutes a perfect tracer for water masses.
165 Recently, Yamashita et al. (2005, 2008) proposed to make use of PFOS and PFOA as
166 water tracers, as they are persistent, dissolved and display little tendency to bind to
167 organic matter. The compounds mentioned above have all been targeted by the
168 Stockholm Convention on Persistent Organic Pollutants, which means they have shown
169 to be persistent, bioaccumulate (i.e., enrich up the food chain), prone to long-range
170 transport, and elicit adverse effects. The earliest group of POPs was also known as the
171 'dirty dozen', consisting of PCBs, DDT, dioxins and furans, HCB and other
172 organochlorine pesticides [http://www.chem.unep.ch/gpa_trial/01what.htm].

173 Ocean currents were thought to contribute to the long-range transport of POPs, as
174 evidenced by the 'global fractionation' theory developed by Wania and Mackay (1993,
175 1996). Yet the observational programs focused on the global fate of POPs were biased
176 towards atmospheric vs. oceanic transport (Bidleman et al., 1995; Jantunen and Bidleman,

177 1996), mostly due to logistical and technical constraints of measuring POPs in the water.
178 Ship-based measurements are further complicated by the problem of sampling sufficient
179 volumes of water to overcome detection limits and alleviate contamination concerns on-
180 board ship (Lohmann et al., 2004).

181 In the Arctic Ocean, the importance of currents as pollutant pathways has been
182 recognized, particularly for POP transport. A good example is the fate of two contrasting
183 isomers of hexachlorocyclohexanes (HCHs). While α -HCH is mostly transported via the
184 atmosphere, the more water-soluble and less volatile β -HCH (i.e., with a smaller Henry's
185 Law Constant) is thought to be mostly transported via the ocean (Li et al., 2002; Sahuvar
186 et al., 2003; Pucko et al., 2013). Mass-balance model results for α -HCH in the Arctic
187 Ocean imply that ocean transport has become the dominant clearance mechanism for α -
188 HCH in the Arctic Ocean (Li et al., 2004), although microbial degradation dominated α -
189 HCH decrease in the Western Arctic Ocean (Pucko et al., 2013).

190 Similarly, the more recent concerns about the presence of perfluorinated compounds
191 PFOS and PFOA in the Arctic Ocean have pitched their atmospheric transport and
192 oxidation of precursors against their transport with ocean currents (Armitage et al., 2006;
193 Armitage et al., 2009a, 2009b). Overall, the importance of ocean currents as a transport
194 vector for certain POPs has been recognized, but the explicit role of individual fronts in
195 organic pollutant dynamics and distribution has not been investigated in detail.

196

197 **2. Data Sources**

198 We surveyed the literature for case studies measuring organic pollutants in the
199 Oceans. While plenty of studies have reported organic pollutants in coastal areas and the

200 Baltic, Mediterranean and other marginal seas, this article focuses on measurements in
201 the open ocean. Relatively few such studies are available for the open ocean for legacy
202 compounds, such as PCBs, PCDD/Fs and OCPs (**Table 2**). For classical POPs that are
203 present at around 1 pg/L, such as PCBs (Gioia et al., 2008b), polychlorinated dioxins and
204 furans (Nizzetto et al., 2010), polybrominated diphenylethers or PBDEs (Xie et al.,
205 2011a) and many legacy pesticides (e.g., DDTs) (Lohmann et al., 2009), sampling
206 volumes of around 1,000 L need to be collected to routinely overcome detection limits.
207 This equates to sampling times of around 24 hours, making front resolution in the ocean
208 difficult. As an approximation of frontal resolution, we included an estimation of the
209 typical distance between two consecutive sampling points (**Table 2**). Only few studies
210 achieved a spatial resolution of 10 - 20 km, while most had 100 to 300 km between
211 adjacent stations. Studies with such coarse resolution make the detection of fronts
212 difficult. The high cost of trace-level analysis also prevented continuous water sampling
213 on ocean transects for many years. In the Arctic Ocean, the much higher concentrations
214 of HCHs and HCB enabled their detection in just tens of liters (Jantunen and Bidleman,
215 1996). The recent focus on emerging polar POPs, such as perfluorinated compounds,
216 PFCs (Giesy and Kannan, 2002), went hand-in-hand with the technological advances in
217 life sciences and liquid chromatography-based detection systems, enabling the detection
218 of various PFCs in just one liter of seawater (Yamashita et al. 2005, 2008). For the
219 following discussion, we chose several recent studies that achieved high spatial resolution
220 of POPs concentrations across the Atlantic Ocean.

221

222 **3. Data Quality**

223 Data quality is of paramount importance when using organic tracer trends across the
224 Oceans. There are numerous challenges to trace-level analysis of organic pollutants in the
225 ocean, which fall into the categories of accuracy and precision of results. Accuracy
226 ('trueness') describes how correct the stated concentration is relative to the 'true' value
227 (if it was known). Laboratories demonstrate the validity of their methods by including
228 standard reference materials (which come with certified concentration ranges) in their
229 analytical runs. Participation in round-robin studies is another way of demonstrating
230 accuracy of results. A major concern regarding shipboard measurements is the
231 contamination of samples during sampling or processing of samples on-board, which
232 would lead to deviations from accurate results. The inclusion of laboratory and field
233 blanks is a necessary, but not sufficient, quality control step in achieving accurate results.
234 Precision deals with the ability of a laboratory to demonstrate reproducible results. For
235 the scope of this paper, samples need not be accurate, but need to be precise in their
236 results to detect the influence of fronts on the distribution of tracers. Precision can be
237 demonstrated through repeat analysis of the same sample, having multiple samples taken
238 at the same time or, at the very least, through repeat injections of the same extract.
239 Typical results of repeat analysis are in the tens of percent, which means that a change in
240 POP concentration of a factor of 2 safely identifies variability outside of analytical
241 uncertainty. As an example, coefficients of variation for triplicate analyses by the same
242 laboratory ('precision') were 14% to 20% for PFOA and PFOS in seawater (Benskin et
243 al., 2012). Interlaboratory agreement (closer to 'accuracy') for PFCs in seawater were
244 generally within a factor of 2 (Benskin et al., 2012). Sampling of the more hydrophobic
245 POPs is more challenging (Muir and Lohmann, 2013), but similar precision can be

246 achieved. For the purpose of this paper, we did not perform a statistical analysis of data,
247 as would be appropriate, e.g., for algorithmic detection of fronts from satellite data, etc.
248 Yet as evident from the Discussion and Figures, in most instances cross-frontal
249 concentration changes were steep enough that no statistical test was needed to identify
250 the location of the front.

251

252 **4. Spatial Distribution of Pollutants in Relation to Ocean Fronts**

253 Global distribution of pollutants is believed to be determined largely by two factors:
254 (1) atmospheric transport and (2) oceanic transport. Most studies to date focused on
255 atmospheric transport, whereas few focused on oceanic transport. The problem of
256 pollutant transport partitioning between atmosphere and ocean can be looked at from
257 different angles, e.g., from theoretical considerations or numerical simulations with
258 global coupled ocean-atmosphere circulation models. Yet one of the most promising
259 approaches is an exploratory analysis of long oceanic transects that might hold clues. In
260 this section we review published data obtained along such transects, looking for front
261 signals and linking them to physical fronts. Biological fronts (e.g., fronts in chlorophyll
262 field) must play an important role, which sometimes might rival the role played by
263 physical fronts. Yet the science of biological fronts is still in its infancy (e.g., Belkin and
264 O'Reilly, 2009), therefore here we focus on physical fronts in temperature, salinity and
265 density fields.

266 Our analysis is based on an intuitively obvious notion that atmospherically-
267 dominated surface distributions of pollutants are, at least initially, spatially smooth. The
268 inherent smoothness of atmospheric fields (compared with oceanic fields) stems mostly

269 from the former's relatively large temporal variability. While bearing certain similarities
270 with oceanic fronts, the atmospheric fronts (Berry et al., 2011) lack stability: Their
271 spatio-temporal scales of variability and corresponding magnitudes are drastically
272 different from those of oceanic fronts. Therefore, the atmospheric fronts are much less
273 likely to leave a lasting imprint on the ocean. Most atmospheric fronts are relatively
274 short-lived (a few days or weeks), although some of them, e.g. the famous Mei-yu Front
275 in East Asia, may persist for up to a few months, and only a couple of fronts in the
276 Northern Hemisphere are semi-permanent, namely the Polar Front and Arctic Front,
277 while the Polar Front in the Southern Hemisphere is probably the only truly permanent
278 atmospheric front. Nonetheless, pollutants can be transported by various mechanisms,
279 including those linked to atmospheric fronts, e.g. cyclones traveling along these fronts.
280 Sometimes pollutants are transported across oceans as long filaments reminiscent of
281 fronts or as isolated blobs of air (Wilkening et al., 2000) similar to oceanic rings spawned
282 by fronts. The atmospheric fronts also play an important role in wet deposition of
283 pollutants. Indeed, up to 90% of rainfall in major storm-track bands is associated with
284 atmospheric fronts (Catto et al., 2012). The bulk of long-distance moisture transport is
285 carried by front-like atmospheric rivers (Newell et al., 1992; Rutz et al., 2014) linked to
286 heavy rainfalls (Lavers et al., 2011). Therefore, atmospheric rivers must be crucial to wet
287 deposition of pollutants. Each of the above features can leave a distinct event-like
288 signature in the surface layer of the ocean. Yet the inherently high variability of these
289 atmospheric features precludes their long-term impact on the ocean. It also means that
290 time-averaged atmospheric deposition of any substance onto the sea surface is bound to
291 be spatially smooth. Hence stepwise discontinuities in spatial distributions of pollutants

292 along oceanic transects are likely linked to oceanic discontinuities, i.e. fronts. To prevent
293 contamination of our analysis by step-like features at the sea surface caused by transient
294 atmospheric phenomena, we emphasize the importance of *repeat* oceanographic transects
295 that allow the researcher to distinguish quasi-stationary features from transients. To date,
296 by far the most complete archive of pollutant measurements along repeat transects has
297 been assembled – and is appended annually – thanks to regular Antarctic voyages by RV
298 *Polarstern*. Even though there is no central repository of pollutant data, *Polarstern* data
299 are promptly reported in peer-reviewed journal papers accompanied by supplementary
300 materials that include data tables. The below analysis is mostly based on these data,
301 particularly those for perfluorinated alkyl acids and sulfonates. Owing to our reliance on
302 data reported from cruises by RV *Polarstern*, the emphasis is on fronts in the Eastern
303 Atlantic Ocean.

304

305 **4. a) Canary Current Front**

306 The Antarctic voyages of RV *Polarstern* follow the same pattern, departing from
307 Bremerhaven and having first stations occupied in the North Sea, English Channel or Bay
308 of Biscay. Here we focus on the northern segments of these tracks as the ship proceeds
309 from European coastal waters southward into much less polluted waters off NW Africa
310 and farther south into even less polluted waters of the Equatorial Atlantic (albeit elevated
311 concentrations of some banned POPs have been observed off West Africa (Gioia et al.,
312 2008b, 2011), possibly due to a combination of illegal waste dumping coupled to
313 atmospheric emissions). As we are about to see below, transitions between these waters
314 are not gradual. Instead, concentrations of individual pollutants decrease southward in a

315 stepwise fashion as the ship crosses over sharp fronts associated with major oceanic
316 currents. These fronts act as water mass boundaries. While thermohaline signatures of
317 these fronts have been studied for decades, this is the first time that these fronts are
318 identified in distributions of pollutants.

319 During the 2007 voyage, RV *Polarstern* has crossed a sharp front between 38°N and
320 36°N, which manifests in north-south distributions of individual PFC concentrations
321 (**Figure 3**). For example, PFNxA and PFNA exhibit little variability from Sta.1 up to
322 Sta.10, where PFNxA drops 6-fold to St.11, while PFNA drops two-fold. These drastic
323 changes are collocated with the Azores Current (Front), which is known to extend zonally
324 along 34°-35°N (Gould, 1985). Coincident with these sharp drops is the PFNpA
325 emergence at Sta.11, after which PFNpA remains fairly constant up to Sta. 20. This
326 location marks the point where the Canary Current veers offshore from the African coast
327 westward.

328 The sharp drops in PFC concentrations seem to contrast with the rather gradual
329 southward increase of SST along the ship track until 20°N (Ahrens et al., 2009), which
330 can be explained by the divergent nature of the NW African upwelling area, one of the
331 largest and most persistent eastern boundary upwelling regions in the World Ocean. This
332 phenomenon illustrates the profound difference between the largely divergent nature of
333 eastern boundaries and largely convergent nature of western boundaries. Indeed, the
334 western boundary regions feature convergences of cold and warm currents that create the
335 largest SST gradients in the World Ocean (e.g., Labrador Current and Gulf Stream;
336 Falkland/Malvinas Current and Brazil Current; Oyashio and Kuroshio). A study in
337 contrast, the mostly divergence-dominated environments along eastern boundaries of the

338 Atlantic, Indian, and Pacific oceans are not conducive to forming exceptionally strong
339 SST fronts. Thus, the rather gradual north-south increase in SST along the *Polarstern*
340 track is not at all surprising.

341 Data from the 2008 voyage of RV *Polarstern* (**Figure 4**) reveal a different picture,
342 devoid of sharp fronts. It is hard to rationalize the drastic change of pattern. The most
343 obvious interpretation of this striking metamorphosis is temporal variability of either the
344 front itself, varying concentrations of PFCs upstream of the cruise track and/or trends
345 masked by varying sampling stations. Either way, this is a topic of a separate
346 investigation, which is well beyond the scope of this study.

347 There was no sampling of PFCs during the 2009 voyage. The PFC sampling resumed
348 during the 2010 voyage, when, again, sharp fronts, albeit at different locations (compared
349 with 2009), were observed (**Figure 5**). Two fronts stand out, the Canary Current Front
350 between Stas. 12-13 (20°-25°N) and South Equatorial Current Front between Stas. 19-20
351 (3°-7°S). The best indicator of the Canary Current Front is PFOA: Its concentration drops
352 precipitously below MDL across this front. Concentrations of PFHxA and PFHpA also
353 drop across this front, albeit less abruptly. The best indicator of the South Equatorial
354 Front is PFHxA, whose concentration drops below MDL across this front.

355 Data collected by RV *Polarstern* in 2010 across the Canary Current Front are
356 consistent with observations in the 2007 cruise of RV *Oden* (**Figure 6**). All four PFCs
357 dropped precipitously across this front between Stas. 6-7 (23.6°-27.3°N), immediately
358 SW of the Canary Islands. In both cruises (*Oden*-2007 and *Polarstern*-2010) the front
359 was detected at approximately the same location south or southwest of the Canary Islands.
360 However, the PFOS signatures of this front observed in 2007 and 2010 were quite

361 different: Whereas in 2007 the PFOS (alongside with PFOA) was an excellent tracer of
362 the front, in 2010 the PFOS concentrations have not changed across this front – unlike the
363 PFOA concentrations that fell below MDL across the front. Another prominent feature
364 along this section sampled by RV *Oden* in 2007 is the Rio de La Plata Plume in the SW
365 Atlantic revealed by maximum concentrations of all PFCs (especially PFOS and PFOA)
366 except for PFHpA.

367 Measurements of HCH from RV *Polarstern* in November 2008 (Xie et al., 2011b,
368 Fig. 1b therein) revealed the same sharp transition from polluted European waters to
369 relatively pristine waters off West Africa. In 2008, this sharp transition occurred in two
370 steps (38°N-31°N and 25°N-16°N) (Xie et al., 2011b, Fig. 1b and Table 3 therein), which
371 is consistent with the location of the same transition based on our measurements from RV
372 *Oden* in 2007 (27°N-24°N) (**Figure 6**). Measurements of polycyclic aromatic
373 hydrocarbons (PAHs) in October 2005 along a similar north-south transect in the NE
374 Atlantic (Nizzetto et al., 2008, Fig. 1b therein) revealed a stepwise decline in dissolved
375 PAHs concentrations south of the Canary Islands, between 22°N and 17°N, slightly south
376 of the front location in 2007 and 2008. Lakaschus et al. (2002) compiled measurements
377 of HCHs made from RV *Polarstern* between the North Sea and Antarctica in 1987, 1989,
378 1991, 1993, 1995, 1997, and 1999. These data consistently show a sharp decline in α -
379 HCH from the Portugal Current to the Canary Current (*ibid.*, supporting info). The best
380 spatial resolution along this track was achieved in 1999, revealing a steep α -HCH drop
381 (front) between 25°N and 20°N (*ibid.*, Fig.3a). Taking together, these data show that
382 notwithstanding the manifold decrease in α -HCH over the last decades, the contaminant's
383 spatial pattern remains fairly robust, featuring a sharp transition from European waters to

384 the subtropical gyre. The temperature step of a few degrees across the Canary Front
385 cannot cause a noticeable change in HCH concentrations. Strong atmospheric deposition
386 of POPs can leave an oceanic imprint such as elevated aqueous PCB concentrations off
387 West Africa, likely from atmospheric emissions (including those from illegal waste
388 dumping of banned POPs) rather than ocean currents (Gioia et al., 2008b, 2011).

389

390 **4. b) Gulf Stream Front**

391 One of the strongest fronts of the World Ocean – the Gulf Stream Front – was sampled
392 during the 2009 cruise 464 of RV *Endeavor*, EN 464 (**Figures 7-9**). The cross-Gulf
393 Stream pattern revealed by *Endeavor* was quite peculiar. The warm (southern) front of
394 the Gulf Stream was not detected in SST, apparently because the SST signature of the
395 Gulf Stream is extremely weak in late July when summer heating all but obliterates
396 surface fronts. The salinity signature of the Gulf Stream was still noticeable (Benskin et
397 al., 2012b, supporting information, Table S9) although salinity data were rudimentary.
398 All four PFCs peaked as *Endeavor* left the Gulf Stream by crossing over the cold
399 (northern) front bounding the Gulf Stream between Sta. 29-30 (37.3°-38.2°N).
400 Concentrations of all four PFCs remained very high at Stas. 30-31 (38.2°-39.0°N),
401 decreased as *Endeavor* proceeded northward, and peaked over the New England Shelf, in
402 the proximity of Rhode Island Sound and Narragansett Bay.

403 Along the same RV *Endeavor* transect in 2009, samples were also taken for
404 hydrophobic organic compounds, including various organochlorine pesticides, PCBs,
405 PAHs and PBDEs. Results show that several pollutants are still predominantly land-
406 derived, i.e. those where on-going emissions from urban/industrial areas (manifested in

407 enhanced concentrations in coastal regions) exceed concentrations in the open ocean.
408 Examples of these pollutants are PAHs, PBDEs, α -HCH and lindane with higher
409 concentrations in Rhode Island Sound, decreasing to concentrations below detection limit
410 in the open ocean (**Table 3**). As noted above, there is only a small (with respect to
411 physico-chemical properties) temperature gradient (around 7 K) between the Sargasso
412 Sea and Rhode Island Sound, so the sharp decrease in concentration of most pollutants is
413 due to removal (by particle settling, photolysis and biodegradation) and dilution, rather
414 than redistribution. For example, the dissolved concentration of α -HCH decreased
415 roughly 4-fold between the Gulf Stream and Rhode Island Sound, while the temperature
416 difference affects air-water partitioning by less than a factor of 2 (**Table 3**).

417 In contrast, the more persistent and already phased-out PCBs and HCB displayed
418 concentration distributions that suggest ocean fronts' importance in maintaining
419 concentration gradients (**Figure 8**): PCB 28 and HCB had higher concentrations in the
420 Gulf Stream (probably originating from the Gulf of Mexico) than in Rhode Island Sound.
421 The higher molecular weight PCBs 52, 101 and 118 displayed a distribution that shows a
422 decrease in concentrations between the Gulf Stream and Rhode Island Sound, possibly
423 due to sorption to particles in-between these two regions. For PCBs 28 and 52, the Gulf
424 Stream carried higher concentrations than the Sargasso Sea, while the opposite was true
425 for PCBs 101 and 118. Elevated concentrations of HCB and PCBs 28 and 52 could
426 originate from the Gulf of Mexico/Mississippi River. Taken together, the transect off the
427 U.S. Northeast showed the importance of the Gulf Stream with its associated fronts
428 coupled with the pollutant characteristics (dominated by primary or secondary emissions).

429 The sampling was not detailed enough to find evidence of other fronts closer to shore
430 (mid-shelf front, shelf-slope front).

431

432 **4. c) River Plumes**

433 River plumes are notable features crossed by research vessels traversing the Atlantic
434 Ocean (Benskin et al., 2012b). Two outstanding river plumes in the western Atlantic
435 Ocean were crossed by RV *Endeavor* in 2009, namely the Amazon River and Rio de la
436 Plata plumes. We estimated the influence of the Amazon River and Rio de la Plata
437 plumes based on salinity differences for PFCs (**Table 4**). We applied a two-endmember
438 approach to estimate the source strength of the river plumes, assuming that any increase
439 of PFCs in the plume was solely due to the river outflow. The background (fully marine)
440 PFC concentration was subtracted, and the remaining difference normalized to the
441 freshwater fraction of the sample (**Table 4**) to obtain the concentration delivered by the
442 river's plume.

443 In the case of the *Amazon River plume*, dissolved concentrations increased by up to
444 10 pg L^{-1} relative to the concentrations in fully marine waters, while salinity was at 27
445 psu (a dilution of seawater (36.4 psu in this region) by 26%). As evident from **Table 4**,
446 the four consecutive samples taken in the Amazon River plume revealed substantial
447 differences in concentrations (Benskin et al., 2012b). This most likely reflected the
448 heterogeneity of the plume. This subject is poorly studied, largely because it requires
449 high-resolution observations across a river plume and such data sets are extremely rare.
450 Another reason is the plume scale. Small plumes naturally tend to be more uniform than
451 large plumes created by such rivers as the Amazon River. The Amazon (freshwater)

452 plume that we sampled several hundred km offshore contributed an additional tens-to-
453 hundreds pg L^{-1} of the various PFCs towards the Atlantic Ocean (**Figure 7**). The average
454 discharge of the Amazon River is ca. $1.6 \times 10^5 \text{ m}^3 \text{ sec}^{-1}$ or $5 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$ (Salisbury et
455 al., 2011). Consequently, ca. 1.4 t of PFCs are flushed annually into the open Atlantic
456 Ocean (**Table 4**).

457 Waters affected by the *Rio de la Plata plume* were sampled during the RV *Oden*
458 cruise in 2007 at two stations (Benskin et al., 2012b), as evidenced by decreases in
459 salinity in samples 24 and 25 (by 2 psu), coupled to a marked increase in PFCs (**Figure**
460 **6**). Concentrations of sum PFCs increased from $\sim 100 \text{ pg/L}$ outside the plume to 350 –
461 540 pg/L in the plume. The dominant PFCs were PFOS, which increased 4-fold to 140 –
462 170 pg/L in the plume, and PFOA, which increased at least 10-fold to 100 pg/L in the
463 plume. Other notable PFCs were PFUnA, which reached 90 pg/L in the plume, and
464 PFHxA, which increased three- to tenfold in the plume (**Table 4**).

465 The average discharge of the Rio de la Plata is ca. $2.2 \times 10^4 \text{ m}^3 \text{ sec}^{-1}$ or $7 \times 10^{11} \text{ m}^3$
466 yr^{-1} (Framiñan and Brown, 1996). Combining the increase attributed to the freshwater
467 with the river's annual discharge results in an annual delivery of 3.5 t of PFCs from the
468 Rio de la Plata into the South Atlantic Ocean (**Table 4**). The striking differences between
469 the Amazon River vs. Rio de la Plata discharges of PFCs likely reflect profound
470 differences in demographics and economic geography of their respective watersheds.
471 Indeed, the Amazon River Basin is populated by just about 5 million people spread over
472 7 million km^2 . A study in contrast, the Rio de la Plata drains the Buenos-Aires
473 megalopolis, with 14 million people and most of Argentina's industrial capacity

474 (Colombo et al., 2011), and the Montevideo agglomeration (Uruguay) with 2 million
475 people.

476 To put the total mass of PFCs delivered to the Atlantic into perspective, we
477 calculated the outflow of PFCs from Narragansett Bay, where concentrations of PFCs is
478 very high (5.8 ng/L, after Benskin et al., 2012b). Yet long-term average annual
479 freshwater discharge of the Bay is only 107.5 m³/s (or 3.4 x 10⁹ m³/yr) (Ries, 1990),
480 resulting in an average annual delivery of total PFCs of ca. 77 kg/yr. This amount pales in
481 comparison with the amounts of PFCs discharged by the Amazon River and Rio de la
482 Plata.

483 The same RV *Endeavor* transect in 2009, which reported PFC concentrations across
484 the Amazon River plume, has also reported PCBs, pesticides, PAHs and PBDEs
485 (Lohmann et al., 2012, 2013a, 2013b). In most cases, no significant change in
486 concentrations was found. Concentrations of PCBs increased slightly across the Amazon
487 plume (**Figure 9**), but the scatter in PCB concentrations is clearly elevated relative to that
488 in PFCs, making it difficult to draw firm conclusions.

489 On a more general note, river plumes have the potential to be important pathways
490 into the oceans for water-soluble and persistent compounds (Li and Daler, 2004) beyond
491 PFCs, such as herbicides (Alegria and Shaw, 1999), pharmaceuticals (Zhang et al., 2012)
492 and personal care products (Qi et al., 2014). For example, the more recalcitrant artificial
493 sweetener sucralose has been detected in part of the Gulf Stream already (Mead et al.,
494 2009).

495

496

497 **5. Conclusions**

498 Examining recent cruise results of organic pollutant concentrations across the
499 Atlantic Ocean revealed the importance of major fronts for their dispersal, coupled with
500 pollutant-specific characteristics linked to their sources, partitioning and persistence.
501 Strong increases in concentrations of the sum of perfluorinated compounds (Σ PFCS) were
502 observed in two river plumes: from 100 pg/L outside the plumes to 540 pg/L in the Rio
503 de la Plata plume and to 170 pg/L in the Amazon River plume. A sharp transition (front)
504 from polluted European waters to the relatively pristine trade winds zone could be
505 observed on a transect from the Bay of Biscay to southern Argentina. North of the front
506 (which is linked to the Canary Current), concentrations of PFOA, PFOS and PFBS were
507 >100 pg/L, decreasing to <50 pg/L (and below detection limit for PFBS) south of the
508 front. The same transition across the Canary Current was observed for hydrophobic
509 organic pollutants, such as hexachlorocyclohexanes and even polycyclic aromatic
510 hydrocarbons. More complex pollutant patterns were observed between the Gulf Stream
511 and Rhode Island Sound. The more persistent polychlorinated biphenyls and
512 hexachlorobenzene actually displayed higher concentrations in the Gulf Stream than in
513 the Sargasso Sea or Rhode Island Sound. In contrast, the emerging perfluorinated
514 compounds displayed a strong increase from the Gulf Stream towards Rhode Island
515 Sound. The sampling campaigns we re-evaluated were not detailed enough to assess the
516 effect of mid-shelf and shelf-break fronts on pollutant dynamics, though the possibility of
517 detecting perfluorinated compounds in one liter samples opens the door to a much more
518 detailed understanding of the interplay between fronts and organic pollutant dynamics in
519 the oceans.

520

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