11-2014

Organic Pollutants and Ocean Fronts Across the Atlantic Ocean: A Review

Rainer Lohmann

University of Rhode Island, rlohmann@uri.edu

Igor M. Belkin

University of Rhode Island, igormbelkin@gmail.com

Follow this and additional works at: <https://digitalcommons.uri.edu/gsofacpubs>

The University of Rhode Island Faculty have made this article openly available.
Please let us know how Open Access to this research benefits you.

This is a pre-publication author manuscript of the final, published article.

Terms of Use

This article is made available under the terms and conditions applicable towards Open Access Policy Articles, as set forth in our [Terms of Use](#).

Citation/Publisher Attribution

Lohmann, Rainer; Belkin, Igor M. (2014). "Organic pollutants and ocean fronts across the Atlantic Ocean: A review." *Progress in Oceanography*. 128: 172-184.

Available at: <https://doi.org/10.1016/j.pocean.2014.08.013>

This Article is brought to you for free and open access by the Graduate School of Oceanography at DigitalCommons@URI. It has been accepted for inclusion in Graduate School of Oceanography Faculty Publications by an authorized administrator of DigitalCommons@URI. For more information, please contact digitalcommons-group@uri.edu.

Organic Pollutants and Ocean Fronts

Across the Atlantic Ocean: A Review

Rainer Lohmann* and Igor Belkin

Graduate School of Oceanography, University of Rhode Island,

215 South Ferry Road, Narragansett, 02882 Rhode Island, USA

* Corresponding author: Tel: 001-401-874-6612, Fax: 001-401-874-6811,

E-mail: lohmann@gso.uri.edu

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

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

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

Regional Index terms: North Atlantic Ocean; Gulf Stream; Azores Current; Canary Current; Rhode Island Sound; South Atlantic Ocean; Rio de la Plata; Amazon River.

FOOTNOTE:

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

1. Introduction: Fronts and organic pollutants

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

2. Data Sources

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

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

3. Data Quality

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

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

4. Spatial Distribution of Pollutants in Relation to Ocean Fronts

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

Our analysis is based on an intuitively obvious notion that atmospherically-dominated surface distributions of pollutants are, at least initially, spatially smooth. The 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

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

4. a) Canary Current Front

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

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

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

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

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

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

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

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

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

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

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

4. b) Gulf Stream Front

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

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

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

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

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

4. c) River Plumes

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

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

plume that we sampled several hundred km offshore contributed an additional tens-to-hundreds pg L^{-1} of the various PFCs towards the Atlantic Ocean (**Figure 7**). The average 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 al., 2011). Consequently, ca. 1.4 t of PFCs are flushed annually into the open Atlantic Ocean (**Table 4**).

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

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

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

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

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

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

5. Conclusions

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

520

521 **Acknowledgements**

522 R.L. acknowledges support from NSF's Office of Polar Programs (ARC 1203486) to
523 study the transport pathways of organic pollutants into the Arctic Ocean. I.B.'s interest in
524 POPs and fronts has been stimulated by participation in the SETAC Asia Pacific 2010
525 Conference in Guangzhou; the travel support of the South China Sea Institute of
526 Oceanology, Chinese Academy of Sciences, is greatly appreciated.