Environ. Sci. Technol. **2005**, *39,* 6555−6560

Trifluoroacetate Profiles in the Arctic, Atlantic, and Pacific Oceans

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A series of depth profiles was collected at 22 sites in the Arctic, North and South Atlantic, and Pacific Oceans to determine spatial patterns for trifluoroacetate (TFA) concentrations in the marine environment and to investigate possible natural sources of TFA. Profiles were also taken over underwater vents in the North and South Pacific and the Mediterranean Sea. At the profile sites, TFA values ranged from <10 ng/L in the Pacific Ocean to greater than 150 ng/L in the Atlantic Ocean. Samples from the Canada Basin of the Arctic Ocean exhibited variable TFA concentrations (60−160 ng/L) down to 700 m. Below this depth, in water having ^{14}C ages exceeding 1000 years, the TFA concentrations were constant (150 ng/L). Water returning to the Atlantic through the Canadian Arctic Archipelago had constant high TFA values. Profiles from the Northern Atlantic exhibited high values at all depths but were more consistent in the Western Atlantic. The northwestern Pacific Ocean surface profile sites exhibited low TFA concentrations in the top 100 m increasing to a maximum of 60 ng/L with depth. Samples from the South Pacific Ocean site had generally low values with a few depths (>800 m) having concentrations of 50 ng/L or more. To determine if underwater vents could contribute to the TFA concentrations in the oceans, profiles were taken over three vents in the Pacific and Mediterranean Oceans. The results suggest that some deep-sea vents may be natural sources of TFA.

Introduction

Trifluoroacetate (TFA), a mildly phytotoxic (*1*), strong acid, is almost ubiquitous throughout the aquatic environment. It has been detected in precipitation (*2*, *3*), snow (*4*), surface waters of rivers (*5*, *6*) and lakes (*7*, *8*), water columns of lakes (*9*), and in the marine environment (*10*, *11*). Only old groundwater samples have been consistently reported to contain nondetectable TFA levels (*11*, *12*).

There is no known pathway for the environmental breakdown of TFA (*13*). This implies that TFA will continue to accumulate in the environment and persist even if all anthropogenic sources are eliminated. TFA concentrations are elevated in terrestrial surface waters and in effluents near urbanized industrial areas (*6*, *9*), and since these waters eventually flow into the marine environment, the oceans are the global TFA sink. Known sources of TFA include the thermolysis of perfluorinated chemicals (*14*), the atmospheric oxidation of hydrochlorofluorocarbons and hydrofluorocarbons (*13*), and fluorotelomer alcohols (*15*). Based on two ocean profiles in the North and South Atlantic Oceans, Frank et al. (*11*) estimated the oceanic inventory of TFA. This inventory, which is based on few samples, exceeds the cumulative amount of TFA from anthropogenic sources entering the oceans via runoff and precipitation. Therefore a natural oceanic source is implied, a promising candidate being hydrothermal vents.

To examine the distribution of TFA concentrations in the marine environment and to infer possible sources, we collected a number of vertical seawater profiles from the oceans of the world. Included in these profiles were sites located over three vents which are possible natural sources of TFA.

Experimental Section

Sample Collection. The profile sampling sites are shown in Figure 1 with their coordinates and sampling dates listed in the Supporting Information. Profiles were collected from seven oceanographic vessels from four countries, generally using Niskin bottles and adhering to a protocol provided by the analytical laboratories. Prior to storing the samples, the collection bottles were rinsed twice with 30 mL of the sample water. The samples were collected in either 1 L wide mouth polyethylene bottles with double lids provided by the Burlington laboratories or glass bottles, provided by the Heidelberg laboratories, with no Teflon or PTFE product coming into contact with the sample. No other special treatment was given to the bottles. The samples were kept cool and in the dark until returned to the Burlington laboratories for analysis where they were stored at 4 °C in a dark coldroom. This protocol has been used previously for a number of other studies and yielded samples that exhibited no signs of TFA contamination (*7*, *9*). Environmental samples stored in both container types have been shown to yield similar results (*7*). In addition, samples have been collected on Lake Superior using Niskin bottles, van Dorn bottles, and PFTE-free pumps and tubing. The measured TFA concentrations did not vary with collection method. Degradation or loss is not anticipated, as TFA will not decompose under normal conditions (*13*) nor migrate to and adhere to the glass (*9*). All analyses were performed on whole water samples, except for the deep northeast Pacific Ocean profile. For this profile, each sample was filtered through a precombusted GF/F filter on board, and the filtrate was placed in the polyethylene storage bottles to be returned to the laboratory. In preliminary work, it was determined that such filters do

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10.1021/es047975u CCC: $30.25

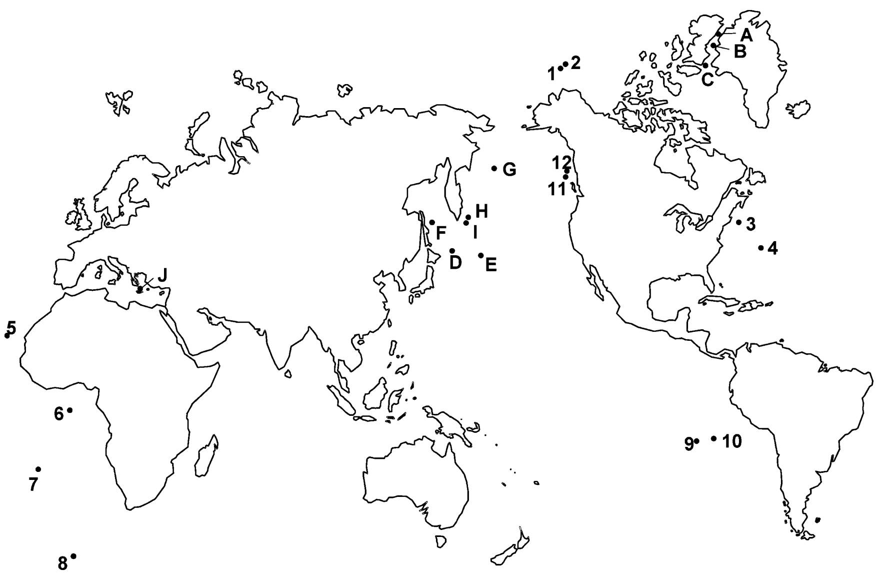

FIGURE 1. Sampling locations. Sites 1–12 denote profiles referred to in the text, and sites a–j denote profiles shown in the Supporting Information.

not interfere with the analysis and that TFA is not retained on particulate material from centrifuged water.

Analysis. The method used for the analysis of TFA involved derivatization of the acid with 2,4-difluoroanaline in the presence of dicyclohexylcarbodiimide and has been previously described (*16*, *9*). The resulting anilide was analyzed by GC-MSD using ions 225 and 156 amu. A laboratory blank was included in each daily sample set analyzed. The only modification to the method was related to the reduction of the sample volume. For freshwater samples, a 1-L volume is reduced to 50 mL using a rotary evaporator under reduced pressure. As the salt content of seawater samples is high, care was taken to remove these samples from the rotary evaporator just as a precipitate was forming in the sample. This usually occurred at 70 mL. Complete (95 ± 7%) recovery of C_{13} labeled TCA (Isotec Inc., Miamisburg, OH) indicated that none of the TFA was occluded in the precipitate and the precipitate did not interfere with the reaction. A 0.42 ng spike solution of the isotopically labeled trichloroacetic acid was added to many of the samples (~75%) just prior to introduction of reagents to ensure derivatization was complete. Recoveries of TCA were quantitative (80–105% with a relative standard deviation of 15%), hence the results were not recovery corrected. Field blanks, which were provided for several cruises, exhibited no significant contamination. The minimum detection limit was 0.5 ng/L based on 3× the standard deviation of blank values. Typical TFA chromatograms for the lab blank and an environmental sample are shown in the Supporting Information.

Results

Depth profiles were collected at 22 sites (Figure 1), at a total of 279 depths, of which 68% of the depths had duplicates. TFA values ranged from <10 ng/L to greater than 150 ng/L at the profile sites (Table 1). Samples from the Atlantic Ocean exhibited more consistent levels, generally >100 ng/L, while sites in the Pacific Ocean contained low levels of TFA, usually <10 ng/L. The reproducibility of concentrations between duplicates at most of the sites was better than 15% (Table 1), including sites with high (Nares Strait) and low (northwestern Pacific) TFA values.

TFA Depth Profiles. Depicted in Figure 2 are the concentrations of TFA for the two profiles (sites 1 and 2) collected in the Canada Basin of the Arctic Ocean. For the first several hundred meters there is considerable variation in the concentrations. Below 800 m down to the ocean floor is a region containing water of Atlantic Ocean origin that has ^{14}C age of over 1000 years (*17*). The higher concentrations occur from 800 to 3000 m with little variation (160 ng/L). At the surface there is a mixed layer (0–50 m) and then the Pacific halocline (down to ~200 m) that overlays Atlantic water (*18*).

A series of three profiles was collected in the North Water polynya in the Nares Strait where surface water flows out of the Arctic Ocean over a 200 m sill. Concentrations were constant throughout the water column of the two most northern sites at 150 ng/L (see Supporting Information, Figure Ia–c) with good agreement between duplicate samples (difference between duplicates <7%). Results at the other site indicate a high surface concentration but significantly lower values down to 250 m where the concentrations increase to values similar to those observed at the other two stations. Agreement between duplicates for the upper 60 m is poor (50%), but duplicates below this depth had reasonable agreement (<20%) for both low concentrations determined between 100 and 250 m and high concentrations at 360 m. The southern station is situated at the north end of Baffin Bay, close to Jones Sound. The surface water flow from Jones Sound is also strongly influenced by the Arctic Ocean outflow from the Canada Basin, whereas the deeper water in Baffin Bay is derived from the Atlantic.

Two profiles extending to depths of 1000 m were obtained in the northwestern Atlantic Ocean, one 150 km off the Virginia coast and the other in the Sargasso Sea. Both profiles exhibited some variation (20–160 ng/L) with the lowest concentrations occurring in the upper 50 m. Throughout the rest of the water column, the concentration of TFA was generally about 150 ng/L (Figure 2, sites 3 and 4). An additional North Atlantic profile was collected close to a site previously reported by Frank et al. (*11*). The concentrations of TFA we obtained (175 ng/L) agreed with values in that study (200 ng/L) (Figure 2, site 5). The three profiles collected in the South Atlantic Ocean exhibited consistent TFA concentrations throughout the water column at ~150 ng/L (Figure 2, sites 6–8). One of the profiles (site 8) is closest to the southern site where a profile had been taken previously (*11*), and, again, there is good agreement between these two sets of results. In general there is a consistent TFA concentration throughout the water column of the Atlantic Ocean of ≥150 ng/L.

TABLE 1. Site Locations, Sampling Dates, Research Vessels

site location	site designation in Figure 1	max depth monitored (m)	TFA concn range (ng/L)	difference between duplicates[a] (%)	no. of samples
Canada Basin (Western Arctic)	1	1500	34–181	7	20(X2)
Canada Basin (Western Arctic)	2	3000	61–172	8	15(X2)
Nares Strait (Eastern Arctic)	a	489	120–170	7	7(X2)
Nares Strait (Eastern Artic)	b	579	120–170	5	8(X2)
Nares Strait (Eastern Arctic)	c	365	8–125	20	6(X2)
North Atlantic	3	1000	28–190	27	6(X2)
North Atlantic	4	947	17–150	38	7(X2)
North Atlantic	5	3800	120–150	24	5(X2)
South Atlantic	6	3875	145–100	12	6(X2)
South Atlantic	7	5300	64–155	8	8(X2)
South Atlantic	8	5053	200–130	6	6(X2)
South Pacific	9	3830	1–150		16(X1)
South Pacific	10 (vent)	2500	1–90		16(X1)
North Pacific	d	175	1–25	12	13(X2)
North Pacific	e	200	1–30	8	11(X2)
North Pacific	f	300	1–68	8	10(X2)
North Pacific	g	300	1–80	3	9(X2)
North Pacific	h	300	1–20	8	8(X2)
North Pacific	i	300	2–50	10	11(X2)
North Pacific	11 (vent)	1000–2200	3–140		
North Pacific	12 (vent)	3968	2–230		23(X1)
Mediterranean Sea	j (vent)	200	0.5–50		20(X1)

[a] Average difference in concentration between duplicates collected at a site expressed as a percent.

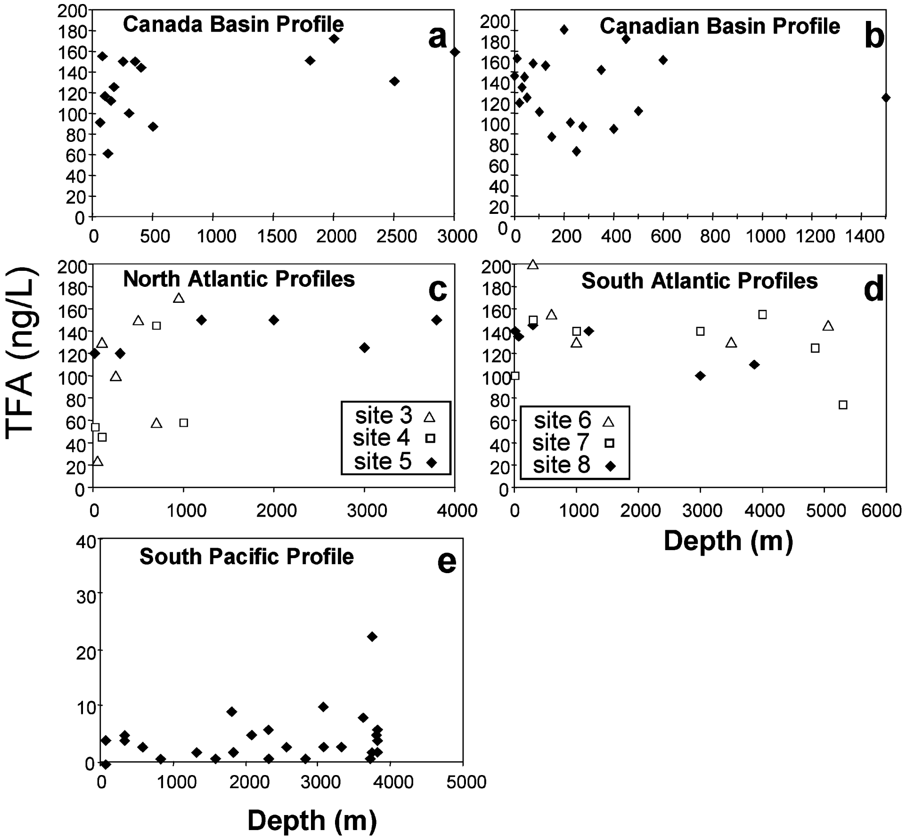

FIGURE 2. (a) TFA concentrations (ng/L) as a function of depth (m) for the Canada Basin (Arctic Ocean) at site 1, (b) TFA concentrations (ng/L) as a function of depth (m) for the Canada Basin at site 2, (c) TFA concentrations (ng/L) for sites 3–5 in the North Atlantic, (d) TFA concentrations as a function of depth for South Atlantic sites 6–8, and (e) TFA concentrations (ng/L) as a function of depth (m) for South Pacific site 9. See Figure 1 for sampling site locations.

One Pacific Ocean profile was taken at site near Easter Island in the South Pacific Ocean. Throughout the water column the TFA concentrations were generally below 20 ng/L (Figure 2, site 8). At maximum depths, higher concentrations

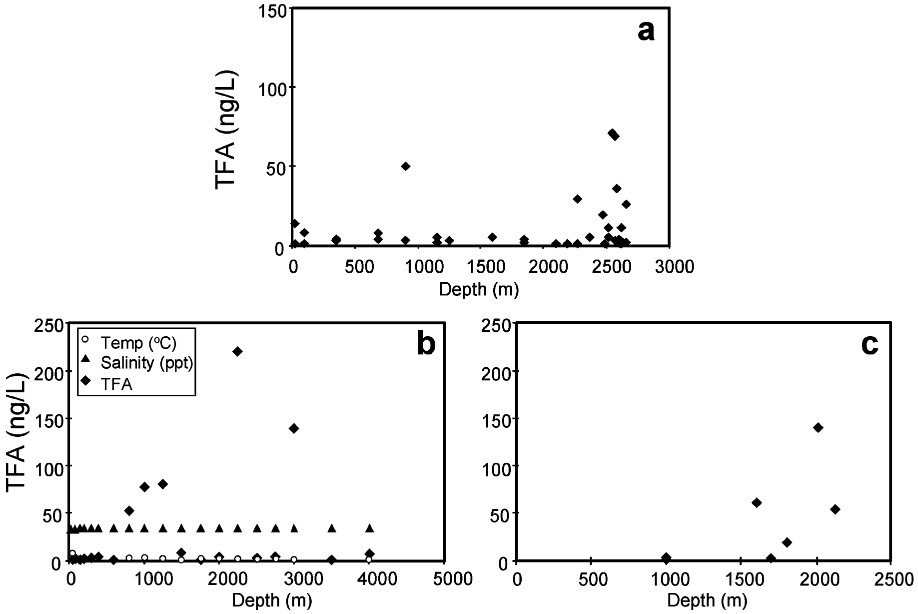

FIGURE 3. TFA concentrations (ng/L) as a function of depth (m) for sites over active vents: (a) site 10, (b) site 11, and (c) site 12. See Figure 1 for sampling site locations.

were measured but still were lower than measured in the Atlantic. Surface water profiles (0–300 m) were obtained at six sites in the North Pacific Ocean, off the coast of Japan. At all of these stations the concentrations of TFA were <10 ng/L in the upper 50 m, but then increased to 30–60 ng/L at middle depths (150–200 m), and subsequently decreased (<10 ng/L) below 300 m (Supporting Information, Figures IId–f,h,i, and IIIj). There appears be a layer of water (50–200 m) in that region of the Pacific Ocean distinguished by slightly higher TFA concentrations.

TFA Vent Profiles. To evaluate generally whether vents supply TFA-enriched water to world oceans, we obtained profiles over three active vent areas. One such site, near Easter Island in the South Pacific, showed low TFA concentration levels throughout the water column (Figure 3, site 9). At maximum depths, higher TFA values were detected (17 ng/L). At the other nearby South Pacific profile site 8, higher concentrations of TFA were measured in the samples collected near maximum depth (>3800 m).

A series of two sample collections were made at a vent area in the NE Pacific Ocean, near Vancouver Island. One was over a deep-sea vent (4000 m) and the other, directly over a volcanic vent. Over the deep-sea vent, down to a depth of 800 m, the TFA concentrations were low (Figure 3, site 10). From 1000 m to 1500 m the TFA concentrations increased to 100 ng/L and then decreased to <10 ng/L. Low values (<10 ng/L) were measured down to 4000 m with exceptions of a major increase at 2000 m (200 ng/L) and an another concentration increase at 3000 m. At the other site over a volcanic vent, samples were collected at the top of the plume (1900 m), the bottom of the plume (2050 m), and within the core of the plume at 1980 to 2010 m. The maximum TFA concentration occurred at about 2100 m, where a concentration of 140 ng/L (Figure 3, site 11) was observed, much higher than surface waters that had concentrations of 3 ng/L.

A depth profile was also taken over a vent in the Mediterranean Sea. The results showed relatively low concentrations of TFA, often <1 ng/L. Near the surface, values of ~15 ng/L were measured, and at two other depths higher values (100 ng/L) were found (Supporting Information, Figure IIIj).

Salinity and temperature were measured at the sampling depths for the northern Pacific deep profile (Figure 2, site 10) and the Atlantic return current profiles (Supporting Information, Figure Ia–c). These parameters are plotted with the TFA values where both the temperature and salinity describe smooth functions and do not correlate with the TFA values.

Discusssion

The results reported here suggest considerable heterogeneity of TFA in the marine environment, something that cannot occur without active sources or sinks. Surface waters interact with the atmosphere and the hydrosphere rapidly (weeks to years), allowing spatial heterogeneity to develop where modern (anthropogenic) sources are unevenly distributed. In contrast, the deep ocean has a ventilation or circulation time scale measured in centuries to millenia (*19*).

Water in the Canada Basin (Arctic Ocean) would not be influenced by local human activities. Vertical variation in TFA in the upper waters of the Canada Basin, therefore, is likely supported by strong stratification together with three different sources of water (freshwater runoff (~top 50 m), Pacific (~top 200 m), Atlantic (>200 m). The deep water (>700 m) is not influenced by Pacific contributions. Water in the Nares Strait had consistently high values indicating surface waters originating either in the Canada Basin to the west or from the return Atlantic flow from the Eurasian Basin in the Arctic. There are insufficient data to choose between these options. As the ^{14}C age of the deep water in the Canadian Basin is ~1000 years (*19*), only a natural, preanthropogenic, source of TFA could explain the observed high values. Underwater vents have been suggested as a possible natural source of the TFA (*20*), and in this light, it should be noted that the geochemical imprint of active vents has recently been found over the Gakkel Ridge in the Arctic Ocean (*21*).

In Table 2, maximum and minimum estimates of the TFA inventories in the major ocean basins have been calculated. For the Pacific Ocean, values measured to depths down to 4000 m have been used, but the lower 5000 m of the depth has been give a minimal value of 10 ng/L and a maximum value of 175 ng/L. The maximum value for the Atlantic Ocean is calculated by assigning the entire water column a TFA concentration of 175 ng/L. The minimum value is derived by assigning the upper 4000 m a TFA concentration of 175 ng/L and deeper waters, a value of 10 ng/L. The TFA estimates

TABLE 2. Inventories of TFA in Ocean Waters

ocean	total volume (*23*) (km^3) × 10^6	depth (*23*) (m)	volume (*24*) (km^3) × 10^6	average concn (ng/L)	amount TFA kg × 10^{15}	max subtotal 10^6 tonne	min subtotal 10^6 tonne
Atlantic	337	0−4000	155	175	27		
		4000−10000	182	175	32	59	
		4000−10000	182	10	1.8		29
Pacific	714	0−200	53	9	0.4		
		200−1000	32	31	0.6		
		1000−2000	31	31	0.9		
		2000−3000	60	7.1	0.4		
		3000−4000	150	40	6.9		
		4000−10000	386	175	68	77	
		4000−10000	386	10	3.9		13
Indian	284	0−10000	285	175	50	50	
		0−10000	285	10	2.8		20
Canada Basin	4	0−4000	4	175	0.7	0.7	0.7
total						205	61

for the Indian Ocean are derived by assuming the entire water column has either a maximum concentration, similar to the Atlantic Ocean, or minimum concentration, similar to the Pacific Ocean. The maximum value of TFA in the ocean water is 187 million tonnes (Mt) and a minimum value of 63 Mt. From the profiles reported here, it is clear that the Pacific Ocean, which generally contains water with longest ventilation times, has lower concentrations of TFA than the Atlantic Ocean. There is precedent for differing geochemical properties of the Atlantic and Pacific Oceans, supported by long residence times together with large-scale thermohaline circulation producing newly ventilated bottom water in the North Atlantic and Southern Ocean and the oldest bottom water in the North Pacific (cf. ref *22*). Accordingly, for surface waters net moisture flux via the atmosphere from Atlantic to Pacific basins sustains a fresher Pacific Ocean (*23*), while for intermediate and deep waters, silicate (*24*) and cadmium (*25*) are both enriched in the Pacific Ocean through cumulative inputs from land together with biological cycling and remineralization operating over the circulation time scale of the global ocean. There is no evidence in the profiles presented here that TFA enters the biological cycle (i.e., enrichments coincident with nutrient maxima), which implies that higher concentrations of TFA in the Atlantic Ocean must be sustained by sources there and lower values in the Pacific Ocean by losses operating at least on time scales less than a millennium. We presently have insufficient evidence to define these sources and sinks. Of the three major ocean basins (Pacific, Atlantic, and Indian), no information has been published on the waters of the Indian Ocean. Also, no data exist for samples at depths greater than 5300 m, which represents about half the volume of the world's oceans (*26*). Therefore the estimate of the total TFA presented here remains preliminary. Our estimate, which provides a range of 20−75% of the previous estimate (*11*), is based on a far larger number of samples with wider oceanic distribution.

The variation of TFA levels in the surface waters implies a heterogeneous distribution of this compound, which can be partially explained by recent anthropogenic sources. However the total inventory in the oceans cannot be explained entirely by human activities (*11*). The data for deep ocean waters display a degree of heterogeneity between oceans with high homogeneous values in the waters of the Atlantic and Arctic Oceans but lower and less homogeneous values in the Pacific Ocean. A very approximate estimate of 6000 kg/yr of TFA from an ocean vent can be calculated (*27*). At this rate of input, it would take 330 million years to account for the present inventories. Given ocean mixing times on the order of millennia, it would be impossible to support the observed interocean heterogeneity with such large residence times suggesting that other sources and sinks must operate within the global ocean.

Acknowledgments

The authors appreciate the assistance and cooperation of the captains and crews of the research vessels (Table 1) that participated in this study. J. Prach and F. Kepplerare are thanked for providing the southern Pacific Ocean samples as well as the Mediterranean profile samples. Isabelle Fahimi's (University of Heidelberg) assistance in analyzing the South Pacific samples is also appreciated. Discussions of southern Pacific profiles with H. Schoeler are valued.

Supporting Information Available

Site locations, sampling dates, and research vessels (Table 1), TFA concentrations (ng/L), salinity (ppt), and temperature (°C) as a function of depth (m) for Nares Strait (Figure Ia−c), TFA concentrations (ng/L) as a function of depth (m) for surface water profiles for northwestern Pacific Ocean (Figure IId−i), TFA concentrations (ng/L) as a function of depth (m) for the Mediterranean Sea site over the surface active zone (Figure IIIj), and the chromatogram of the TFA parent ion abundance for (i) the South Atlantic sample and (ii) the laboratory blank (Figure IV). This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review December 21, 2004. Revised manuscript received May 16, 2005. Accepted June 9, 2005.

ES047975U