Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts

Supporting Information for

Neutral Polyfluoroalkyl Substances in the Global Atmosphere

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Detailed Information on Methodology

Sampling Site Descriptions

Twenty-seven, 24-hour high volume AASs were collected in **Maun, Botswana** every two weeks between May 2006 and May 2007.[1] During that one year period, duplicate XAD resin-based PASs were deployed at ten sites within or near to the Okavango Delta in Northwestern Botswana, with five more in the more populated East of the country.[1] Located in southern Africa, Botswana's climate is semiarid with consistently high temperatures throughout the year. Rainfall varies, being heaviest in the Northeast (~650mm) and sparse (~<250mm) in the Kalahari Desert to the Southwest. Detailed description of the sites is given in Figure 1 and in ref. [1]

Eight 24-hour high volume AASs were taken in **San Antonio de Belen** in Costa Rica's heavily populated central valley between October 2005 and October 2006. At the same time, duplicate XAD resin-based PASs were deployed across the country at seven sites in remote or agricultural areas.[2] Concurrently, five duplicate sets of PAS collected air in Belen for variable lengths of time, ranging from four months to somewhat more than one year, in order to determine the uptake of nPFAS in XAD-2 based samplers in tropical zones.[3] Costa Rica, a mountainous Central American country situated near the equator, has a tropical climate with consistently high temperatures throughout the year and a distinct rainy season.

Twenty-one low volume AAS sampled continuously for consecutive two-week periods between March 2006 and March 2007 in **Egbert, Ontario, Canada**. Similar to the study in Costa Rica, five duplicate sets of PAS collected air for variable lengths of time, ranging from three months to one year. Egbert is in rural southern Ontario, approximately 100 kilometers north of Toronto. The region has continental temperate climate, with very large seasonal temperature variations.

Within the **GAPS Network** scientists from around the globe collaborate to monitor concentrations of Persistent Organic Pollutants (POPs) in air.[4-8] The data will aid in evaluating the effectiveness of the restrictions imposed on POPs under the Stockholm Convention. Two types of PASs are used in GAPS; polyurethane foams (PUFs) or sorbent-impregnated PUFs (SIPs) are deployed at a seasonal resolution, whereas XAD-PASs yield annual averaged air concentrations. Specifically, such PASs were deployed at 34, 46, 33, 34, 22, and 17 sites during each of six sampling years, which roughly correspond to calendar years 2006 to 2011. Samples from the first year of the GAPS study, in 2005, were not included because extract clean-up with alumina columns compromised the analysis for the analytes of interest. Because previous sampling campaigns showed generally good agreement between replicates[3,9-11] XAD-PASs within GAPS are not duplicated. A variety of stations participated each year, including 13 stations that were continuously part of the campaign. Previously, GAPS sites had been categorized into five types. As population density and proximity to industrial

activity are influential factors for the presence of nPFAS in the atmosphere[12-14] sites categorized as 'agricultural', 'rural', or 'background' were reclassified as either 'remote' or 'urban', so that a simplified categorization only distinguished between urban, remote, and polar sites (Table 1, Figure 1). For geographic comparisons, sites were also grouped into four regions:[5] North America (9-18 samples), South (5-11), Europe (5-8), and Asia (2-12) (Figure 1).

Sample Preparation and Collection

Preparation and collection of the samples have been described in detail elsewhere.[15] In the case of PAS, 10 cm (Botswana, Ontario) or 20 cm (GAPS, Costa Rica) long mesh cylinders (diameter: 2 cm) were filled with pre-cleaned XAD-2 resin (Supelpak 2, Supelco, Bellefonte, PA). Mesh cylinders were placed into stainless cylinder tubes closed with stoppers, sealed in plastic bags, and shipped to the sites. Field blanks were treated in the same manner as the samples, except that the blanks were not exposed to air. The high volume AAS used in the Costa Rica and Botswana campaigns consisted of 10 g XAD-2 sandwiched between two large (width w_{PUF} 6 cm, length l_{PUF} 3 cm) PUF plugs. The low volume AAS used in the Egbert campaign was comprised of 5 g XAD-2 between two small (w_{PUF} 2 cm, l_{PUF} 3 cm) PUF plugs.

Sample Extraction and Analysis

Target analytes in these four campaigns were the following seven chemicals: three fluorotelomer alcohols (6:2, 8:2, 10:2 FTOH), two perfluorooctane sulfonamides (MeFOSA, EtFOSA) and two perfluorooctane sulfonamidoethanols (MeFOSE, EtFOSE). Additionally, 8 isotope labeled nPFAS were analyzed for recovery and volume correction (Table S1).

Samples from Botswana,[1] Costa Rica,[3,2] Ontario[16] and 2006-2008 GAP samples[5] underwent Soxhlet extraction overnight with dichloromethane. These samples had not been spiked with isotope labeled nPFAS prior to extraction. Recoveries of laboratory spikes (n=6) were on average between 77-96%, 111-124% and 113-115% for FTOHs, FOSAs and FOSEs, respectively. As these recoveries were judged acceptable, samples were not recovery-corrected, aside from adjustment for any detector response differences during gas chromatography-mass spectrometry (GC-MS) determination. This correction was made by spiking 5-12 ng of isotope labeled nPFAS prior to analysis on the GC-MS.

2009-2011 samples within GAPS were extracted using pressurized liquid extraction (Dionex ASE®350) with 1:1 (v/v) acetone:hexane at 75 °C, adapted from Dionex's protocol.[17] Primbs et al.[18] further investigated and confirmed the applicability of this extraction technique for sorbents used in air sampling. Prior to extraction, these samples were spiked with 5-12 ng of the labeled nPFAS. Average recoveries for these samples were as follows: 6:2 FTOH (39%), 8:2 FTOH (74%), 10:2 FTOH (107%), MeFOSA (111%), EtFOSA (114%), MeFOSE (241%) and EtFOSE (251%). Relatively

high volatility of 6:2 FTOH and high pressure applied during the extraction can explain the lower recovery for this compound. Altering the method for more volatile compounds might affect the recoveries for other sets of chemicals monitored within GAPS. Elevated recoveries for the FOSEs have previously been reported,[19-23] and are likely due to matrix effects and solvent enhancement, especially given the long periods of deployment. Spiked laboratory blanks showed similar recoveries (FOSA: 106-108%; FOSE: 146-152%). Given the low and high recoveries for some of the FTOHs and FOSEs, 2009-2011 GAPS samples were recovery-corrected.

After extraction, all samples were volume reduced using either a rotary evaporator or Turbovap, further concentrated to 500 µl under nitrogen, and then solvent-exchanged into iso-octane. Aside from passing the samples through ~1.0 g of sodium sulfate to remove moisture, no clean-up was done on the extracts. Additionally, prior to injection, 10 ng of N,N-Me_2FOSA was added into the samples for volume correction.

Analysis of the samples was performed using GC-MS in selected ion monitoring mode using positive chemical ionization (ions in Table S1). Aliquots of 2 µL were injected and separated on a 30 m DB-WAX column with a 0.25 mm inner diameter and 0.25 µm film thickness. Helium was the carrier gas at a flow of 1.2 $mL \cdot min^{-1}$. Temperature program was as follows: 60-65 °C (held for 3 min), ramped at 2 $°C \cdot min^{-1}$ to 70 °C, then ramped at 8 $°C \cdot min^{-1}$ to 120 °C, and finally ramped at 10 $°C \cdot min^{-1}$ to 220 °C with a post run at 230 °C for 3 min. A 5-10 point calibration curve (0.48-96 $pg \cdot \mu l^{-1}$) was used for quantification, using the isotope dilution method.

Table S1. nPFAS analytes, acronyms, and target and qualifier ions for GC/MS detection. Supplier of the compounds was Wellington Laboratories (Purity >98%).

Analyte	Acronym	Target Ion	Qualifier Ion
Perfluorohexyl ethanol	6:2 FTOH	365	327
2-perfluorohexyl-($^{13}C_2$)-ethanol	^{13}C 6:2 FTOH	369	331
Perfluorooctyl ethanol	8:2 FTOH	465	427
2-perfluorooctyl-($^{13}C_2$)-ethanol	^{13}C 8:2 FTOH	469	497
Perfluorodecl ethanol	10:2 FTOH	565	427
2-perfluorodecyl-($^{13}C_2$)-ethanol	^{13}C 10:2 FTOH	569	531
N-methyl perfluorooctane sulfonamide	MeFOSA	514	
Methyl-d_3-perfluorooctane sulfonamide	d_3 MeFOSA	517	
N-ethyl perfluorooctane sulfonamide	EtFOSA	528	
Ethyl-d_5-perfluorooctane sulfonamide	d_5 EtFOSA	533	
N-methyl perfluorooctane sulfonamidoethanol	MeFOSE	540	558
Methyl-d_7-perfluorooctane sulfonamidoethanol	d_7 MeFOSE	547	565
N-ethyl perfluorooctane sulfonamidoethanol	EtFOSE	554	572
Ethyl-d_9-perfluorooctane sulfonamidoethanol	d_9 EtFOSE	563	581
N,N-dimethylperfluoro-1-octanesulfonamide	N,N-Me_2FOSA	528	

Table S2. Concentrations of nPFAS sequestered on XAD-PAS (averaged duplicates with standard deviation, ng.PAS^{-1}) deployed in San Antonio de Belen (Part 1) and Egbert (Part 2).

Part 1 *San Antonio de Belen, Costa Rica*

Deployment:	Oct 10, 2005	Oct 10, 2005	Oct 10, 2005	Oct 10, 2005	Oct 10, 2005
Retrieval:	Feb 25, 2006	May 19, 2006	Jul 28, 2006	Sept 11, 2006	Oct 24, 2006
Compound					
6:2 FTOH	1.11 ± 0.21	3.43 ± 0.04	4.96 ± 0.10	6.52 ± 0.27	4.85 ± 0.11
8:2 FTOH	5.59 ± 0.19	11.09 ± 0.24	16.18 ± 0.37	21.41 ± 1.27	15.05 ± 1.02
10:2 FTOH	2.04 ± 0.10	2.82 ± 0.06	4.38 ± 0.27	5.40 ± 0.66	3.86 ± 0.25
MeFOSA	0.25 ± 0.00	0.44 ± 0.07	0.63 ± 0.01	0.76 ± 0.07	0.58 ± 0.02
EtFOSA	1.05 ± 0.06	2.53 ± 0.02	4.57 ± 0.27	5.48 ± 0.37	4.41 ± 0.11
MeFOSE	0.39 ± 0.02	0.58 ± 0.03	0.79 ± 0.06	0.92 ± 0.13	0.77 ± 0.11
EtFOSE	0.22 ± 0.02	0.23 ± 0.06	0.31 ± 0.02	0.38 ± 0.03	0.30 ± 0.02

Part 2 *Egbert, Ontario, Canada*

Deployment:	Mar 1, 2006	Mar 1, 2006	Mar 1, 2006	Mar 1, 2006	Mar 1, 2006
Retrieval:	Apr 25, 2006	Jun 30, 2006	Sept 1, 2006	Oct 27, 2006	Feb 28, 2007
Compound					
6:2 FTOH	0 ± 0	0 ± 0	0 ± 0	0 ± 0	3.1 ± 3.1
8:2 FTOH	0 ± 0	0 ± 0	0 ± 0	3.9 ± 3.9	10 ± 3
10:2 FTOH	0.9 ± 0.3	2.1 ± 0.3	2.5 ± 0.4	3.0 ± 0.3	3.5 ± 0.4
MeFOSA	0.0 ± 0.0	0.2 ± 0.1	0.3 ± 0.0	0.3 ± 0.1	0.3 ± 0.0
EtFOSA	0.2 ± 0.1	0.3 ± 0.1	0.5 ± 0.1	0.5 ± 0.0	0.5 ± 0.1
MeFOSE	0.2 ± 0.1	0.5 ± 0.2	0.8 ± 0.1	1.0 ± 0.1	1.0 ± 0.2

Table S3. Statistical results for the sampling uptake curves

	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE
San Antonio de Belen, Costa Rica						
p-value:	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	
R^2:	0.84	0.83	0.87	0.86	0.89	
Egbert, Ontario, Canada						
p-value:		< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001
R^2:		0.83	0.92	0.94	0.86	0.96

Table S4. Concentrations and method detection limits (MDL) in pg·m^{-3} of selected nPFASs in active air samples (AAS) taken in Maun (Part 1), Egbert (Part 2), and San Antonio de Belen (Part 3). ND: Not detected (below the instrumental detection limit), BDL: below MDL.

Part 1: *Maun, Botswana*

Dates			6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE
		MDL	0.54	0.20	0.19	0.05	0.06	0.42	0.53
07/13/06	-	07/14/06	ND	7.1	1.9	0.09	0.13	BDL	ND
08/02/06	-	08/03/06	ND	3.2	1.0	BDL	0.06	BDL	ND
08/11/06	-	08/12/06	ND	2.1	0.8	0.06	BDL	BDL	ND
08/30/06	-	08/31/06	ND	1.1	1.2	0.08	0.13	0.51	ND
09/21/06	-	09/22/06	ND	0.70	1.0	0.06	0.15	0.43	ND
10/06/06	-	10/07/06	ND	3.2	1.1	0.07	0.07	0.48	ND
10/20/06	-	10/21/06	ND	3.2	1.5	0.07	0.07	0.51	ND
11/02/06	-	11/03/06	ND	0.92	0.59	0.08	0.12	0.43	ND
11/17/06	-	11/18/06	ND	1.2	1.6	0.13	0.08	BDL	ND
12/15/06	-	12/16/06	ND	0.55	1.0	0.09	0.12	BDL	ND
01/05/07	-	01/06/07	ND	0.77	0.84	0.07	0.07	0.57	ND
01/19/07	-	01/20/07	ND	1.2	0.91	0.08	0.17	BDL	ND
01/26/07	-	01/27/07	ND	1.0	0.66	0.09	0.10	0.47	ND
02/08/07	-	02/09/07	ND	1.1	0.83	0.10	0.11	BDL	ND
02/23/07	-	02/24/07	ND	2.9	6.2	0.16	0.28	0.77	ND
03/09/07	-	03/10/07	ND	3.6	7.4	0.21	0.28	0.55	ND
03/23/07	-	03/24/07	ND	0.91	1.4	0.11	0.17	0.73	ND
04/06/07	-	04/07/07	ND	2.9	3.6	0.10	0.19	0.50	ND
04/20/07	-	04/21/07	ND	1.6	2.1	0.10	0.17	BDL	ND
05/04/07	-	05/05/07	ND	3.6	5.1	0.11	0.18	BDL	ND
05/18/07	-	05/19/07	ND	1.4	1.0	0.06	0.10	ND	ND
06/01/07	-	06/02/07	ND	2.4	3.6	0.12	0.18	BDL	ND
06/15/07	-	06/16/07	ND	2.0	2.6	0.15	0.30	BDL	ND
06/29/07	-	06/30/07	ND	1.2	1.6	0.11	0.17	BDL	ND
07/13/07	-	07/14/07	ND	1.7	1.1	0.09	0.11	ND	ND
07/27/07	-	07/28/07	ND	1.8	1.3	0.08	0.11	BDL	ND
08/10/07	-	08/11/07	ND	1.6	1.1	0.10	0.16	ND	ND

Part 2: *Egbert, Ontario, Canada*

Dates			6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE
		MDL	0.38	0.49	1.52	0.39	1.57	0.32	0.48
03/01/06	-	03/15/06	ND	ND	ND	ND	ND	ND	ND
03/15/06	-	03/29/06	ND	ND	ND	ND	ND	ND	ND
03/29/06	-	04/13/06	ND	ND	ND	ND	ND	ND	ND
04/13/06	-	04/27/06	ND	ND	ND	ND	ND	ND	ND
04/27/06	-	05/12/06	ND	ND	9.9	0.92	2.1	ND	23
05/12/06	-	05/31/06	ND	67	31	2.5	ND	18	43
05/31/06	-	06/15/06	ND	81	30	3.0	ND	16	27
06/15/06	-	06/30/06	ND	48	30	7.6	31	59	125
06/30/06	-	07/20/06	ND	66	27	3.5	3.3	12	10
07/20/06	-	08/03/06	ND	14	11	0.74	ND	13	ND
08/03/06	-	08/17/06	ND	51	16	1.2	ND	12	6.7
08/17/06	-	08/31/06	ND	74	26	0.99	3.0	18	ND
08/31/06	-	09/14/06	ND	33	20	0.49	ND	7.1	ND
09/14/06	-	09/27/06	ND	92	24	1.6	ND	18	ND
09/27/06	-	10/10/06	ND	57	18	ND	ND	15	ND
10/10/06	-	10/27/06	ND	17	7.9	ND	ND	9.1	ND
10/27/06	-	11/21/06	ND	9.1	7.0	ND	ND	3.3	ND
11/21/06	-	12/08/06	ND	34	13	0.41	ND	ND	ND
12/08/07	-	01/03/07	ND	2.7	4.5	ND	ND	4.4	ND
01/03/07	-	02/07/07	ND	13	10	ND	ND	4.5	4.2
02/07/06	-	02/27/07	ND	16	6.7	ND	ND	5.0	ND

Part 3: *San Antonio de Belen, Costa Rica.*

Dates			6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE
		MDL	0.75	0.28	0.27	0.06	0.09	0.58	0.73
11/28/05	-	11/29/05	ND	10	3.0	0.44	2.0	3.6	ND
12/22/05	-	12/23/05	ND	8.6	2.7	0.52	0.74	9.5	ND
02/02/06	-	02/03/06	ND	17	7.0	0.82	13	6.6	ND
03/21/06	-	03/22/06	ND	2.7	1.3	0.28	0.55	1.5	ND
05/19/06	-	05/20/06	ND	5.9	2.1	0.35	4.1	3.5	ND
06/30/06	-	07/01/06	ND	2.2	0.82	0.15	0.51	4.6	ND
07/28/06	-	07/29/06	ND	10	3.9	0.41	6.3	5.5	ND
09/11/06	-	09/12/06	ND	7.0	2.8	0.36	6.4	4.2	ND

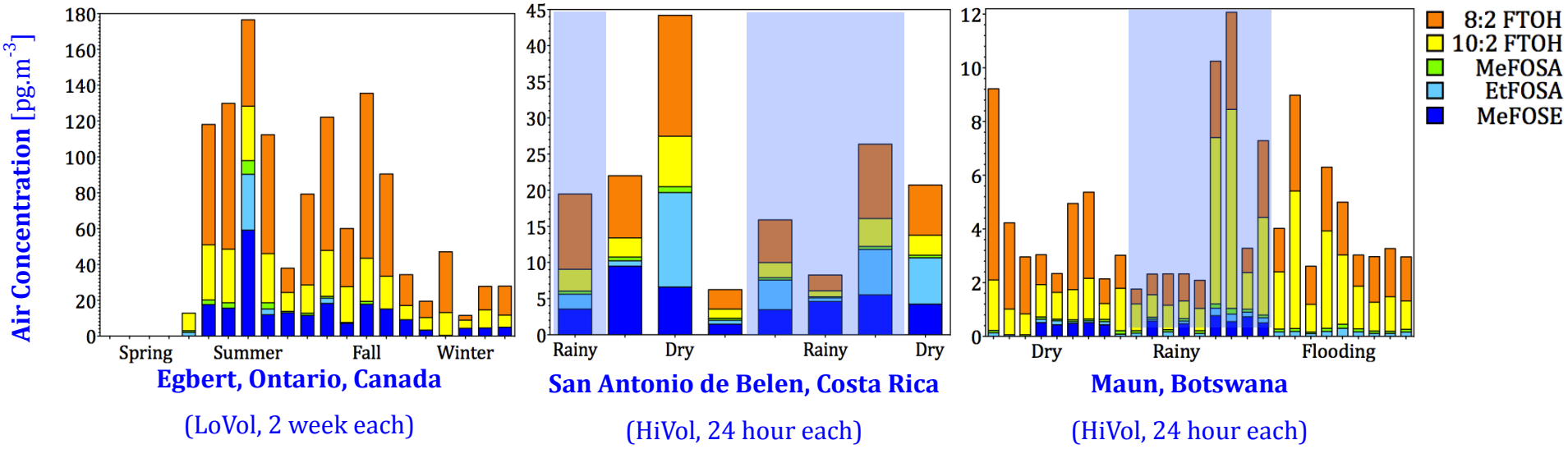

Figure S1. Seasonal variability of nPFAS concentrations during the 3 active air-sampling campaigns. Note the different scales on the y-axis. Blue shading indicates rainy seasons in Costa Rica and Botswana.

Table S5. Results from 1-way ANOVA test for nPFAS concentrations between the three active air-sampling sites. Comparisons between sites used Tukey-Kramer's Multiple Comparison Test. NS = not significant.

	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE
All Sites	< 0.0001	< 0.0001	0.012	0.070	<0.01
Belen vs. Maun	NS	NS	NS	NS	NS
Belen vs. Egbert	<0.01	< 0.001	NS	NS	NS
Maun vs. Egbert	< 0.001	< 0.001	<0.01	NS	< 0.001

Table S2. Name, geographical coordinates (latitude, longitude), site classification (AG: Agricultural, BA: Background, PO: Polar, RU: Rural, and UR: Urban), and length of sampling period for GAPS sites that had XAD-PAS deployed between 2006 and 2010.

					Sampling Length (days)					
Country	**Location**	**Type**	**Latitude**	**Longitude**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**
North America										
Barbados	Ragged Point, St. Philip	BA	13° 10' N	59° 26' W				280		
Bermuda	Tudor Hill	BA	32° 22'N	64° 39' W	327	343	364	355	351	364
Canada	Alert	PO	82° 7'N	63° 30' W		365				
Canada	Bratt's Lake	AG	50° 12'N	104° 42' W	359	344	371	354	364	363
Canada	Fraserdale	BA	49° 53'N	81° 34' W		347	357	364		
Canada	Lasqueti Island	BA	49° 29'N	124° 21' W	397	323	355	380	347	358
Canada	Little Fox Lake	PO	61° 21'N	135° 38' W		227	387	352	374	353
Canada	Sable Island	BA	43° N	60° W		368	377	355		
Canada	Toronto	UR	43° 46'N	79° 28' W	380	350	362	364	366	365
Canada	Ucluelet	BA	48° 54'N	125° 32' W		292	375	368		
Canada	Whistler	BA	50° 03'N	122° 57' W	315	344	375	361	358	362
Costa Rica	Tapanti National Park	BA	9° 46'N	83° 47' W	365	351	356	452	475	
Mexico	Tlahuac	UR	19° 14'N	99° 00' W		183	355			
USA	Barrow	PO	71° 18' N	156° 44' W	367	359		369	302	367
USA	Dyea	BA	59° 31' N	135° 21' W	372	98	391	348	373	
USA	Mauna	BA	19.54° N	155.58° W		325	362	364		
USA	Point Reyes	BA	33° 14'N	122° 19' W		341	366	364		
USA	Sydney	UR	27° 57' N	82° 12' W		296	370	365	365	
USA	Tula	BA	14.24° S	170.57° W		299	341	364		
Asia										
China	Nam Co, Tibet		30° 46' N	90° 57' E		180	366	364		
India	Delhi Site C	AG	28° 40' N	77° 14' E	317	319				
India	Delhi Site D	AG	28° 40'N	77° 14' E	317	319				
India	Coimbatore	BA	11° N	77° E		353				
Indonesia	Bukit Kototabang	BA	0.20° S	100.32o E	365	281	345	365	365	363
Korea	Pohang	RU	36° 0' N	129° 19' E		352				
Korea	Seoul	UR	37° 35' N	127° 10' E		346				
Korea	Gosan, Jeju Island	BA	33° 24' N	126° 00' E		205				
Kuwait	Abdaly	BA	29° 58' N	47° 42' E		344	382	351		
Kuwait	Kuwait City	UR	29° 34' N	47° 90' E	358					
Malaysia	Danum Valley	BA	4° 95' N	117° 85' E	363	329	364	364	364	360
Nepal	Dhulikhel	BA	27° 37' N	75° 32' E		145		364		
Philippines	Tagaytay City	BA	14° 08' N	121° 00' E		352	368	364		
Philippines	Manila	UR	14° 39' N	121° 04' E	351					

					Sampling Length (days)					
Country	**Location**	**Type**	**Latitude**	**Longitude**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**
South										
Australia	Cape Grim	BA	40° 41' S	144° 41' E	295	342	391	344	358	365
Australia	Darwin	RU	12° 22' S	130° 51' E	343	358	362	367	364	360
New Zealand	Temple Basin, Arthur's Pass	BA	42° 54’ S	171° 34’E				345		
Colombia	Arauca	RU	7° 00' N	70° 44' W	368	290	624		363	
Ecuador	Santa Cruz Island, Galapagos	BA	0° 43' N	90° 17'W				332		
Bolivia	Huayna Potosi La Paz	BA	16° 16' S	68° 08' W	380					
Brazil	Puruzinho	UR	07° 22' S	63° 03'W				328		
Brazil	St. Peter & St. Paul Rocks	BA	17° 37' S	47° 47' W			369			
Brazil	Indaiatuba	RU	23° 09' S	47° 10' W	366	295	316			
Argentina	Bahai Blanca	AG	38° 45' S	62° 15' W	326					
Chile	Coyhaique	BA	45°35' S	72° 02' W		365				
Spain	Teide, Las Palmas	RU	28° 59' S	15° 22' W	370	275			370	
Egypt	Cairo	RU	30° 08' N	31° 37' E	398					
Ghana	Accra	RU	8° 00' N	2° 00' W	365					
Kenya	Mt. Kenya	BA	0.062° S	37.297° E				356		
Botswana	Kalahari	BA	25° 52' S	22° 54' E	482	250	366			
South Africa	DeAar	BA	30° 40' S	24° 00' E	364	346	364	367	365	368
South Africa	Vanderbijlpark	UR	26.70° S	27.82° E				324		
Europe										
Czech Rep.	Košetice	BA	49° 35' N	15° 05' E	354	347	369	365	363	360
Finland	Pallas	BA	68° 00' N	24° 14' E	365	351	362	370	359	359
France	Paris	UR	48° 51' N	2° 21' E	321	363	362	365	365	361
Iceland	Stórhöfði	BA	63° 24' N	20° 17' W	361	366	359	365	365	360
Ireland	Malin Head	BA	55° 23' N	7° 22' W	363	343	365	370		360
Norway	Ny Ålesund	PO	78° 54' N	11° 53' E	272				340	346
Poland	Pomlewo	RU	54° 12' N	18° 22' E	365	348				
Russia	Danki	RU	54° 54' N	37° 48' E	343	355	367	361		
Turkey	Izmir	UR	38° 25' N	27° 08' E	372					

Table S3. Concentrations and method detection limits (MDL) in ng·PAS^{-1} of selected neutral polyfluoroalkyl substances (nPFAS) at GAPS sites. Values were normalized to 365 days of sampling. ND = not detected (below instrument detection limit, IDL); BDL = below MDL. Questionable concentrations, which were not included in the figures and statistical analyses have * next to the numbers. Additional sampling site information can be found in Table S1 in Shunthirasingham et al.[5] First sampling year (late 2004 to late 2005) not included due to loss of analytes.

Part 1 *Second sampling year (late 2005 to late 2006)*

Location	6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE
MDL	0.43	0.15	0.14	0.04	0.04	0.30	0.29
North America							
Bratt's Lake, Canada	0.75	2.13	0.95	0.26	0.22	0.66	ND
Toronto, Canada	2.49	9.85	7.58	0.51	0.34	1.03	0.39
Whistler, Canada	0.89	3.03	1.08	0.32	0.16	ND	ND
Lasqueti Island, Canada	0.67	2.06	0.84	0.23	0.16	ND	ND
Barrow, USA	BDL	1.79	0.39	0.11	0.08	ND	ND
Dyea, USA	BDL	36.28*	7.01	0.15	0.08	ND	ND
Tudor Hill, Bermuda	BDL	13.98	2.26	0.23	0.14	ND	ND
Tapanti, Costa Rica	0.70	0.98	0.22	0.08	ND	ND	ND
Mexico, Tlahuac	3.35	14.81	5.15	0.55	0.45	1.24	0.59
South							
Arauca, Colombia	ND	1.21	0.34	0.07	0.10	ND	ND
Huayna Potosi, Bolivia	ND	47.47*	0.60	0.33	0.67	ND	ND
Indaiatuba, Brazil	ND	9.72	37.05*	0.26	3.5*	1.11	ND
Bahia Blanca, Argentina	0.58	1.45	0.69	0.16	0.09	BDL	ND
Cape Grim, Australia	ND	1.03	0.52	0.13	ND	ND	ND
Darwin, Australia	BDL	2.68	1.15	0.21	0.12	0.66	ND
Kalahari, Botswana	ND	0.71	0.56	BDL	0.05	BDL	BDL
DeAar, South Africa	ND	17.57*	9.38	0.26	0.16	ND	ND
Accra, Ghana	ND	2.11	0.73	0.16	0.14	0.75	ND
Teide, Canary Islands	0.62	3.66	1.42	0.31	0.19	0.85	ND
Cairo, Egypt	ND	6.69	2.41	0.34	0.39	0.85	0.32
Europe							
Pallas, Finland	ND	2.69	0.55	0.12	0.10	ND	ND
Košetice, Czech Republic	ND	19.59	11.33	0.46	0.23	ND	ND
Pomlewo, Poland	2.33	14.11	7.64	0.30	0.21	ND	ND
Izmir, Turkey	1.83	62.19	13.02	0.27	0.11	ND	ND
Stórhöfði, Iceland	ND	2.74	0.94	0.19	0.07	ND	ND
Malin Head, Ireland	1.20	4.14	2.02	0.39	0.18	1.04	ND
Paris, France	5.90	38.64	20.50	1.46	0.55	3.84	1.57
Danki, Russia	0.74	2.03	0.89	0.12	0.09	ND	ND
Asia							
Delhi Site C, India	ND	19.03	5.23	0.26	0.64	ND	ND
Delhi Site D, India	ND	18.71	6.45	0.32	0.28	1.28	ND
Danum Valley, Malaysia	ND	2.59	9.89	0.09	ND	0.68	ND
Kuwait City, Kuwait	ND	5.01	1.55	0.63	0.37	0.74	ND
Manila, The Philippines	2.18	10.13	3.49	0.20	0.25	1.04	0.75
Bukit Kototabang, Indonesia	ND	1.59	0.47	0.08	0.07	ND	ND

Part 2 *Third sampling year (late 2006 to late 2007)*

Location	6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE
MDL	0.25	0.11	0.05	0.02	0.02	0.26	0.24
North America							
Bratt's Lake, Canada	0.60	1.22	0.38	0.05	0.07	ND	ND
Toronto, Canada	3.15	9.75	2.88	0.32	0.25	0.53	0.32
Whistler, Canada	0.90	3.14	0.83	0.10	0.05	ND	ND
Lasqueti Island, Canada	0.93	2.03	0.40	0.04	0.02	ND	ND
Little Fox Lake, Canada	1.71	1.44	0.36	0.03	0.07	ND	ND
Sable Island, Canada	1.29	3.55	1.04	0.10	0.07	ND	ND
Fraserdale, Canada	0.64	1.00	0.26	0.08	0.05	ND	ND
Alert, Canada	ND	ND	ND	ND	ND	ND	ND
Ucluelet, Canada	1.49	1.52	0.29	0.02	BDL	ND	ND
Barrow, USA	ND	1.53	0.62	0.03	ND	ND	ND
Dyea, USA	1.53	17.31*	20.41*	0.10	0.07	ND	ND
Point Reyes, USA	ND	0.47	0.25	0.04	0.03	ND	ND
Mauna, USA	0.96	ND	0.20	ND	ND	ND	ND
Tula, USA	1.49	ND	0.68	BDL	ND	ND	ND
Sydney, USA	0.97	5.12	1.30	0.27	0.17	0.31	ND
Tudor Hill, Bermuda	0.93	2.36	0.59	0.07	0.06	BDL	ND
Tapanti, Costa Rica	1.16	0.73	0.18	BDL	0.03	ND	ND
Tlahuac, Mexico	3.29	7.53	2.30	0.28	0.22	0.41	0.27
South							
Arauca, Colombia	0.96	1.77	0.51	0.06	ND	BDL	ND
Coyhaique, Chile	BDL	1.19	0.78	0.05	0.06	BDL	ND
Indaiatuba, Brazil	1.80	4.51	1.72	0.07	3.24*	BDL	ND
Cape Grim, Australia	ND	0.44	ND	0.02	ND	ND	ND
Darwin, Australia	0.78	3.45	0.55	0.06	0.04	BDL	ND
Kalahari, Botswana	ND	1.25	1.36	0.03	0.06	ND	ND
DeAar, South Africa	ND	0.52	0.18	0.05	ND	ND	ND
Teide, Canary Islands	0.76	2.25	0.63	0.07	0.07	BDL	ND
Europe							
Pallas, Finland	1.01	0.55	0.44	0.05	0.03	ND	ND
Košetice, Czech Republic	1.93	21.56*	1.59	0.16	0.08	ND	ND
Ny Ålesund, Norway	1.59	1.13	0.27	0.03	ND	ND	ND
Pomlewo, Poland	1.11	0.76	1.44	0.10	0.07	ND	ND
Stórhöfði, Iceland	0.52	0.80	0.45	0.04	0.04	ND	ND
Malin Head, Ireland	0.64	1.06	0.55	0.05	0.04	BDL	ND
Paris, France	2.23	16.98	7.66	0.47	0.27	1.33	0.53
Danki, Russia	1.03	2.02	0.77	0.06	ND	ND	ND
Asia							
Delhi Site C, India	ND	10.21	3.12	0.16	0.21	0.37	0.26
Delhi Site D, India	ND	14.90	2.14	0.10	0.19	0.27	BDL
Coimbatore, India	ND	2.23	0.79	0.03	0.20	ND	ND
Dhulikhel, Nepal	ND	0.84	0.37	0.11	ND	0.29	ND
Danum Valley, Malaysia	0.56	2.20	0.30	BDL	ND	ND	ND
Abdaly, Kuwait	BDL	0.90	0.57	0.06	0.11	ND	ND
Tagaytay City, Philippines	ND	1.12	0.63	0.04	0.07	ND	ND
Bukit Kototabang, Indonesia	2.08	1.51	0.42	BDL	ND	ND	ND

Pohang, Korea	2.00	21.19	8.33	0.14	0.26	BDL	BDL
Seoul, Korea	3.70	31.06	14.00	1.03	0.70	2.05	1.12
Gosan, Korea	1.21	14.30	1.67	0.05	0.04	ND	ND
Nam Co, Tibet, China	1.95	3.93	1.11	BDL	ND	ND	ND

Part 3 *Fourth sampling year (late 2007 to late 2008)*

Location	**6:2 FTOH**	**8:2 FTOH**	**10:2 FTOH**	**MeFOSA**	**EtFOSA**	**MeFOSE**	**EtFOSE**
MDL	0.33	0.16	0.08	0.02	0.02	0.19	0.33
North America							
Bratt's Lake, Canada	1.40	0.44	0.09	ND	ND	ND	ND
Toronto, Canada	2.26	6.41	2.30	0.38	0.25	0.54	ND
Whistler, Canada	ND	1.18	0.32	ND	ND	ND	ND
Lasqueti Island, Canada	0.51	0.74	0.09	ND	ND	ND	ND
Little Fox Lake, Canada	ND	0.89	ND	ND	ND	ND	ND
Sable Island, Canada	0.67	4.20	0.87	ND	0.07	ND	ND
Fraserdale, Canada	BDL	0.88	BDL	ND	0.09	ND	ND
Ucluelet, Canada	ND	0.49	0.34	ND	0.05	0.92	0.46
Dyea, USA	ND	0.45	BDL	ND	ND	ND	ND
Point Reyes, USA	ND	1.91	0.86	ND	ND	ND	0.34
Mauna, USA	0.35	0.98	BDL	ND	ND	ND	ND
Tula, USA	ND	ND	0.85	ND	ND	ND	ND
Sydney, USA	1.01	3.65	1.20	0.35	0.17	ND	ND
Tudor Hill, Bermuda	ND	1.83	0.93	ND	0.06	ND	ND
Tapanti, Costa Rica	ND	ND	0.18	ND	ND	ND	ND
South							
Arauca, Colombia	BDL	2.06	1.19	ND	ND	2.09	2.04
Indaiatuba, Brazil	ND	3.10	1.45	ND	3.33	ND	ND
St. Peter, Brazil	ND	ND	1.38	ND	2.24	ND	ND
Cape Grim, Australia	ND	ND	0.28	ND	ND	ND	ND
Darwin, Australia	ND	1.22	0.46	ND	ND	ND	ND
Kalahari, Botswana	ND	0.28	0.11	0.05	ND	ND	ND
DeAar, South Africa	ND	1.15	0.83	ND	ND	ND	ND
Europe							
Pallas, Finland	ND	13.52*	BDL	ND	ND	ND	ND
Košetice, Czech Republic	2.16	5.94	1.74	ND	ND	ND	ND
Stórhöfði, Iceland	ND	0.63	0.60	ND	ND	ND	ND
Malin Head, Ireland	BDL	1.31	0.16	ND	ND	ND	ND
Paris, France	0.67	17.10	6.46	0.62	0.24	1.38	0.55
Danki, Russia	0.57	1.63	0.39	ND	ND	ND	ND
Asia							
Danum Valley, Malaysia	1.90	2.49	0.96	ND	ND	ND	ND
Abdaly, Kuwait	2.42	6.83	1.04	0.19	0.11	2.18	1.96
Tagaytay City, Philippines	ND	0.94	0.48	ND	0.09	ND	ND
Bukit Kototabang, Indonesia	ND	ND	ND	ND	ND	ND	ND
Nam Co, Tibet, China	ND	ND	0.71	ND	ND	ND	ND

Part 4 *Fifth sampling year (late 2008 to late 2009)*

Location	**6:2 FTOH**	**8:2 FTOH**	**10:2 FTOH**	**MeFOSA**	**EtFOSA**	**MeFOSE**	**EtFOSE**
MDL	0.41*	0.42	0.18	0.12	0.043*	0.17*	0.21*

North America							
Bratt's Lake, Canada	0.80	1.65	0.19	ND	BDL	ND	ND
Whistler, Canada	BDL	4.29	1.36	ND	0.05	ND	ND
Lasqueti Island, Canada	0.58	1.23	BDL	ND	ND	ND	ND
Little Fox Lake, Canada	BDL	2.50	BDL	ND	BDL	ND	ND
Sable Island, Canada	2.72	6.05	2.02	0.13	BDL	BDL	ND
Ucluelet, Canada	0.53	1.61	0.27	ND	ND	ND	ND
Barrow, USA	0.59	2.12	0.22	ND	ND	ND	ND
Dyea, USA	BDL	1.53	BDL	ND	ND	ND	ND
Point Reyes, USA	0.88	1.32	0.19	ND	BDL	ND	ND
Mauna, USA	ND	BDL	BDL	ND	BDL	ND	ND
Tula, USA	ND	73.29*	7.27	ND	ND	0.30	ND
Sydney, USA	3.16	9.96	3.44	0.36	0.33	ND	BDL
Tudor Hill, Bermuda	0.88	3.74	1.00	ND	0.05	ND	ND
Tapanti, Costa Rica	0.81	BDL	ND	ND	0.06	ND	ND
Ragged Point, California	0.62	0.61	BDL	ND	ND	ND	ND
South							
Galapagos, Ecuador	ND	ND	ND	ND	ND	ND	ND
Puruzinho, Brazil	BDL	7.88	2.60	ND	0.17	ND	ND
Cape Grim, Australia	BDL	0.66	BDL	ND	ND	ND	ND
Darwin, Australia	0.90	5.75	1.46	ND	0.13	BDL	ND
Temple Basin, New Zealand	ND	1.65	0.26	ND	ND	ND	ND
Vanderbijlpark, South Africa	0.97	3.66	1.15	0.17	0.13	0.25	ND
DeAar, South Africa	ND	0.74	0.29	ND	ND	ND	ND
Mount Kenya, Kenya	ND	BDL	ND	ND	ND	ND	ND
Europe							
Pallas, Finland	ND	1.53	0.31	ND	BDL	ND	ND
Košetice, Czech Republic	5.47*	10.92	3.30	BDL	0.11	0.25	ND
Stórhöfði, Iceland	1.04	2.17	0.77	ND	ND	ND	ND
Malin Head, Ireland	1.22	3.28	1.00	ND	BDL	ND	ND
Paris, France	8.33	28.22	12.60	0.67	0.41	1.61	0.44
Danki, Russia	BDL	1.82	0.35	ND	ND	ND	ND
Asia							
Dhulikhel, Nepal	ND	19.88*	14.97*	ND	BDL	ND	BDL
Danum Valley, Malaysia	ND	ND	ND	ND	ND	ND	ND
Tagaytay City, Philippines	ND	25.46*	4.53	ND	0.06	0.26	ND
Bukit Kototabang, Indonesia	ND	21.26*	6.12	ND	ND	ND	BDL
Nam Co, Tibet, China	ND	BDL	BDL	ND	0.44*	ND	ND

Part 5 *Sixth sampling year (late 2009 to late 2010)*

Location	**6:2 FTOH**	**8:2 FTOH**	**10:2 FTOH**	**MeFOSA**	**EtFOSA**	**MeFOSE**	**EtFOSE**
MDL	0.89*	0.11	0.058	0.015	0.035	0.099*	0.15*
North America							
Bratt's Lake, Canada	BDL	1.05	0.32	ND	BDL	ND	ND
Toronto, Canada	1.92	5.33	6.43	0.23	0.24	0.24	0.20
Whistler, Canada	BDL	11.49	1.35	ND	BDL	ND	ND
Lasqueti Island, Canada	ND	1.38	0.33	ND	ND	ND	ND
Little Fox Lake, Canada	ND	1.56	0.23	ND	BDL	ND	ND
Barrow, USA	ND	2.52	0.37	ND	BDL	ND	BDL

Dyea, USA	ND	3.17	0.50	ND	BDL	BDL	ND
Sydney, USA	3.93	7.56	2.58	ND	0.24	0.10	BDL
Tudor Hill, Bermuda	BDL	2.05	0.55	ND	BDL	ND	BDL
Tapanti, Costa Rica	ND	0.45	0.07	ND	BDL	0.13	ND
South							
Arauca, Colombia	1.05	1.44	0.43	ND	0.14	0.11	BDL
Cape Grim, Australia	ND	0.24	0.12	ND	ND	ND	ND
Darwin, Australia	ND	4.30	1.39	ND	0.06	BDL	ND
DeAar, South Africa	ND	1.23	0.28	ND	BDL	BDL	BDL
Teide, Canary Islands	1.09	5.68	1.87	ND	0.15	0.41	BDL
Europe							
Pallas, Finland	ND	2.64	0.55	ND	BDL	ND	ND
Košetice, Czech Republic	5.13*	8.75	2.70	0.06	0.09	ND	ND
Ny Ålesund, Norway	0.99	2.05	0.40	ND	ND	ND	ND
Stórhöfði, Iceland	ND	5.51	0.59	ND	ND	ND	ND
Paris, France	3.25	17.72	6.38	0.33	0.21	0.64	0.20
Asia							
Danum Valley, Malaysia	ND	0.52	0.24	ND	BDL	ND	ND
Bukit Kototabang, Indonesia	ND	0.91	1.43	ND	BDL	ND	ND

Part 6 *Seventh sampling year (late 2010 to late 2011)*

Location	**6:2 FTOH**	**8:2 FTOH**	**10:2 FTOH**	**MeFOSA**	**EtFOSA**	**MeFOSE**	**EtFOSE**
MDL	1.24	0.89	0.26	0.26	0.08	0.07	0.58
North America							
Bratt's Lake, Canada	BDL	1.88	BDL	ND	BDL	ND	BDL
Toronto, Canada	17.04*	21.09	5.89	0.30	0.32	0.31	BDL
Whistler, Canada	ND	7.63	1.60	ND	ND	BDL	BDL
Lasqueti Island, Canada	2.30	3.73	0.47	ND	0.17	BDL	BDL
Barrow, USA	BDL	1.83	0.41	ND	BDL	BDL	BDL
Tudor Hill, Bermuda	1.77	2.17	0.60	ND	0.14	BDL	BDL
South							
Cape Grim, Australia	BDL	BDL	BDL	ND	0.13	ND	BDL
Darwin, Australia	2.12	10.67	2.31	BDL	BDL	0.13	BDL
DeAar, South Africa	BDL	BDL	0.74	ND	BDL	0.09	BDL
Europe							
Pallas, Finland	1.47	2.09	0.47	ND	BDL	BDL	BDL
Košetice, Czech Republic	5.59	10.65	3.44	BDL	0.09	ND	BDL
Ny Ålesund, Norway	BDL	2.35	0.39	ND	BDL	BDL	BDL
Stórhöfði, Iceland	1.72	2.59	0.53	ND	BDL	BDL	BDL
Malin Head, Ireland	2.91	4.33	1.02	ND	BDL	BDL	BDL
Paris, France	14.12	48.19	15.81	0.73	0.36	1.21	BDL
Asia							
Danum Valley, Malaysia	BDL	4.25	ND	7.48*	0.58	0.08	BDL
Bukit Kototabang, Indonesia	ND	1.42	0.31	ND	BDL	BDL	BDL

Table S4. Percentage of individual nPFAS detected per year with number of sites for that year.

	# of Sites	6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE
2006	34	41	100	100	97	91	41	15
2007	46	72	93	96	85	70	17	11
2008	33	33	82	82	15	33	15	15
2009	34	16	28	23	4	11	5	1
2010	22	32	100	100	14	32	27	9
2011	17	53	88	82	18	41	29	0

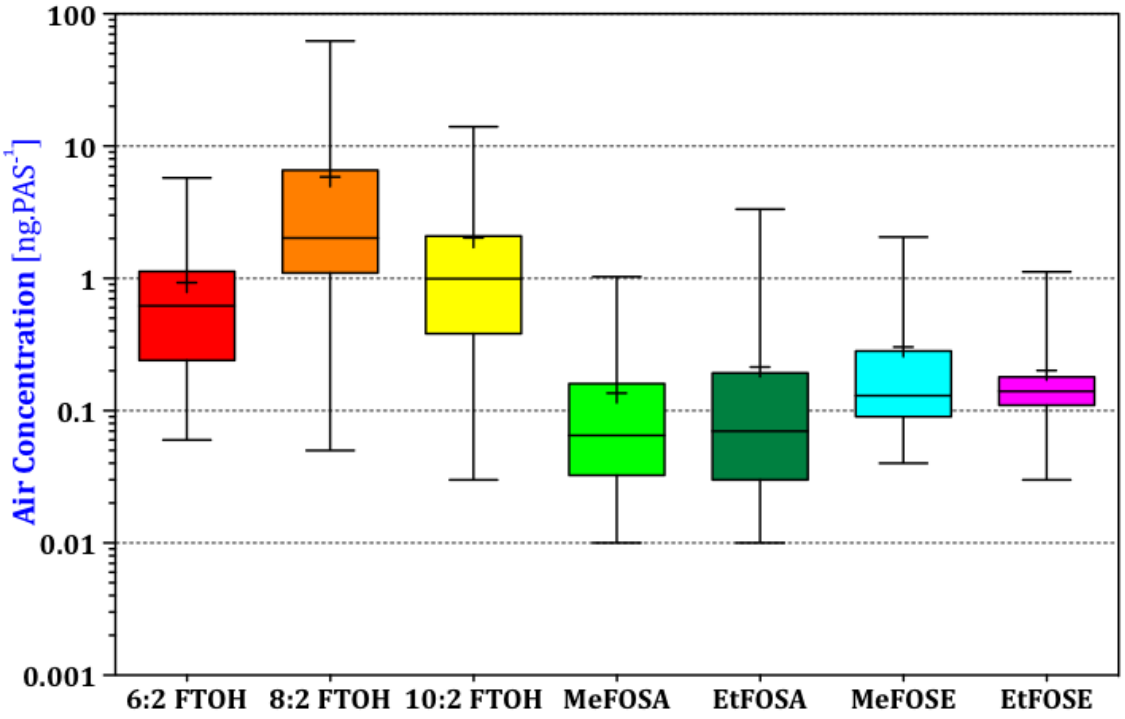

Figure S2. Relative abundance of nPFAS on a global scale.

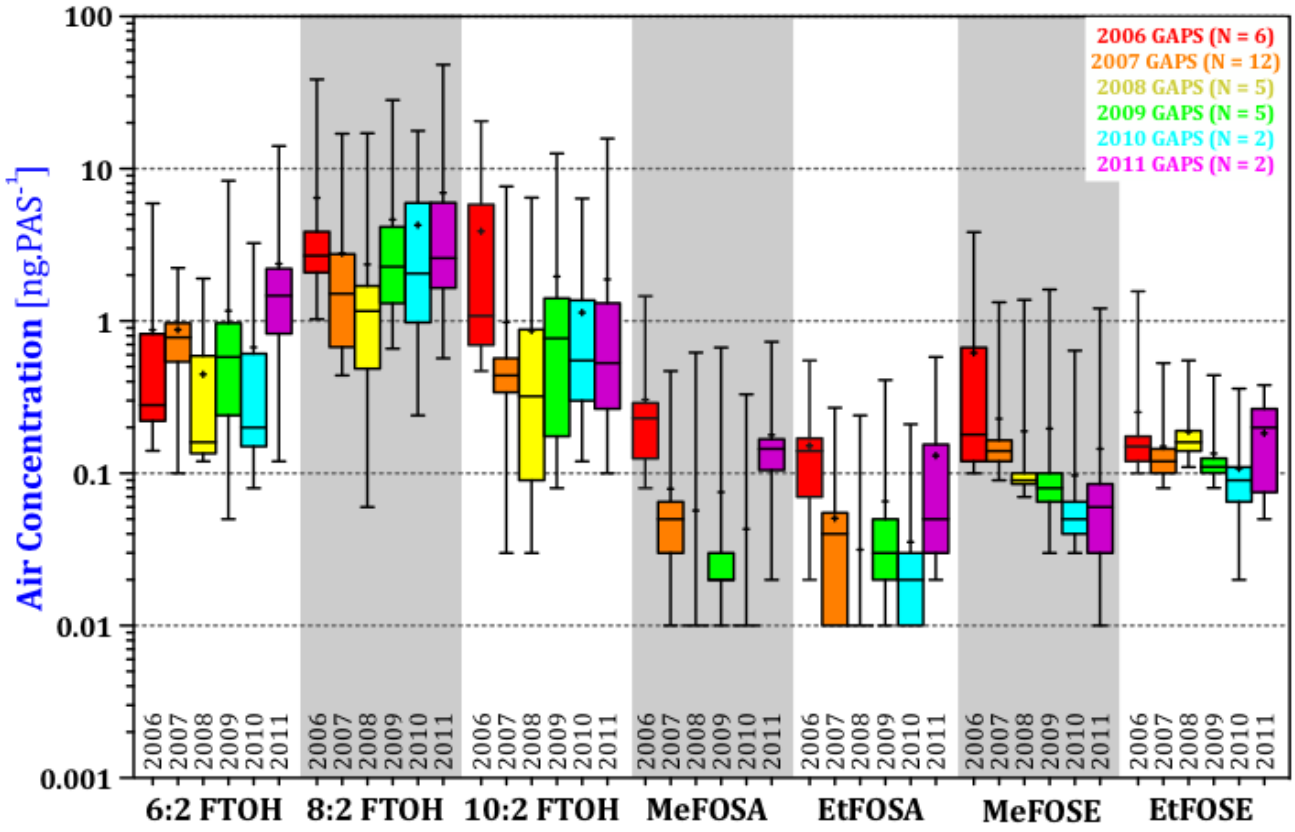

Figure S3. Temporal trends (2006-2011) of nPFASs in XAD-PAS at the 13 sites that were consistently part of the GAPS program.

Table S5. Results from 1-way ANOVA test investigating the differences in concentrations between site types.

	6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE
p-value:	0.00020	< 0.0001	< 0.0001	0.0003	0.025	< 0.0001	0.029
R^2:	0.26	0.32	0.34	0.25	0.12	0.37	0.13
			Arithmetic Means [ng.PAS^{-1}]				
Polar	0.61	1.5	0.24	0.045	0.02	0.09	0.13
Remote	0.66	3.0	1.2	0.10	0.13	0.19	0.17
Urban	2.1	16	5.2	0.38	0.55	0.75	0.34

Table S6. 1-way randomized block design ANOVA result for the concentrations of individual nPFAS between years 2006-2011. P-values <0.05 suggest nPFAS concentrations are significantly different between sampling years. Between two years, used post-test to compare statistically significance within the five years of sampling (post-test using Tukey-Kramer's Multiple Comparison Test.). NS = not significant.

Location	Year		p-values and post-test						
	From	To	6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE
North America	All five years		0.31	0.036	0.053	< 0.0001	0.011	0.0025	0.0003
	2006	2007	NS	NS	<0.05	<0.01	<0.05	<0.05	NS
		2008	NS	NS	<0.05	<0.001	<0.05	<0.05	NS
		2009	NS	NS	NS	<0.001	<0.05	<0.01	<0.05
		2010	NS	NS	NS	<0.001	NS	<0.01	<0.05
		2011	NS	NS	NS	NS	NS	<0.01	NS
	2007	2008	NS	NS	NS	NS	NS	NS	NS
		2009	NS	NS	NS	NS	NS	NS	NS
		2010	NS	NS	NS	NS	NS	NS	NS
		2011	NS	NS	NS	NS	NS	NS	NS
	2008	2009	NS	NS	NS	NS	NS	NS	<0.05
		2010	NS	NS	NS	NS	NS	NS	<0.01
		2011	NS	NS	NS	NS	NS	NS	NS
	2009	2010	NS	NS	NS	NS	NS	NS	NS
		2011	NS	NS	NS	NS	NS	NS	NS
	2010	2011	NS	NS	NS	NS	NS	NS	NS
South	All five years		0.0075	0.58	0.66	< 0.0001	0.16	0.25	0.2
	2006	2007	NS	NS	NS	<0.001	NS	NS	NS
		2008	NS	NS	NS	<0.001	NS	NS	NS
		2009	NS	NS	NS	<0.001	NS	NS	NS
		2010	NS	NS	NS	<0.001	NS	NS	NS
		2011	<0.01	NS	NS	NS	NS	NS	NS
	2007	2008	NS	NS	NS	NS	NS	NS	NS
		2009	NS	NS	NS	NS	NS	NS	NS
		2010	NS	NS	NS	NS	NS	NS	NS
		2011	NS	NS	NS	NS	NS	NS	NS
	2008	2009	NS	NS	NS	NS	NS	NS	NS
		2010	NS	NS	NS	NS	NS	NS	NS
		2011	<0.01	NS	NS	NS	NS	NS	NS
	2009	2010	NS	NS	NS	NS	NS	NS	NS
		2011	<0.05	NS	NS	NS	NS	NS	NS
	2010	2011	NS	NS	NS	NS	NS	NS	NS
Europe	All five years		0.17	0.38	0.24	0.22	0.27	0.72	0.74
	2006	2007	NS	NS	NS	NS	NS	NS	NS
		2008	NS	NS	NS	NS	NS	NS	NS
		2009	NS	NS	NS	NS	NS	NS	NS
		2010	NS	NS	NS	NS	NS	NS	NS
		2011	NS	NS	NS	NS	NS	NS	NS

	2007	2008	NS	NS	NS	NS	NS	NS	NS
		2009	NS	NS	NS	NS	NS	NS	NS
		2010	NS	NS	NS	NS	NS	NS	NS
		2011	NS	NS	NS	NS	NS	NS	NS
	2008	2009	NS	NS	NS	NS	NS	NS	NS
		2010	NS	NS	NS	NS	NS	NS	NS
		2011	NS	NS	NS	NS	NS	NS	NS
	2009	2010	NS	NS	NS	NS	NS	NS	NS
		2011	NS	NS	NS	NS	NS	NS	NS
	2010	2011	NS	NS	NS	NS	NS	NS	NS
Asia	All five years		0.56	0.36	0.41	0.33	0.18	0.71	0.56
	2006	2007	NS	NS	NS	N/A	NS	N/A	NS
		2008	NS	NS	NS	N/A	NS	N/A	NS
		2009	NS	NS	NS	N/A	NS	N/A	NS
		2010	NS	NS	NS	N/A	NS	N/A	NS
		2011	NS	NS	NS	N/A	NS	N/A	NS
	2007	2008	NS	NS	NS	N/A	NS	NS	NS
		2009	NS	NS	NS	N/A	NS	NS	NS
		2010	NS	NS	NS	N/A	NS	NS	NS
		2011	NS	NS	NS	N/A	NS	NS	NS
	2008	2009	NS	NS	NS	N/A	NS	NS	NS
		2010	NS	NS	NS	N/A	NS	NS	NS
		2011	NS	NS	NS	N/A	NS	NS	NS
	2009	2010	NS	NS	NS	N/A	NS	NS	NS
		2011	NS	NS	NS	N/A	NS	NS	NS
	2010	2011	NS	NS	NS	N/A	NS	NS	NS
Overall	All five years		< 0.0001	0.0097	0.0012	0.0095	0.18	0.0009	0.0085
	2006	2007	NS	NS	<0.01	NS	NS	<0.05	NS
		2008	NS	<0.01	<0.001	NS	NS	NS	NS
		2009	NS	NS	<0.05	NS	NS	<0.01	NS
		2010	NS	NS	<0.05	NS	NS	<0.01	NS
		2011	< 0.001	NS	NS	NS	NS	<0.05	NS
	2007	2008	NS	NS	NS	NS	NS	NS	NS
		2009	NS	NS	NS	NS	NS	NS	NS
		2010	NS	NS	NS	NS	NS	NS	NS
		2011	< 0.001	NS	NS	<0.05	NS	NS	NS
	2008	2009	NS	NS	NS	NS	NS	NS	<0.05
		2010	NS	NS	NS	NS	NS	NS	<0.05
		2011	< 0.001	NS	NS	<0.05	NS	NS	NS
	2009	2010	NS	NS	NS	NS	NS	NS	NS
		2011	< 0.001	NS	NS	<0.05	NS	NS	NS
	2010	2011	<0.01	NS	NS	<0.05	NS	NS	NS

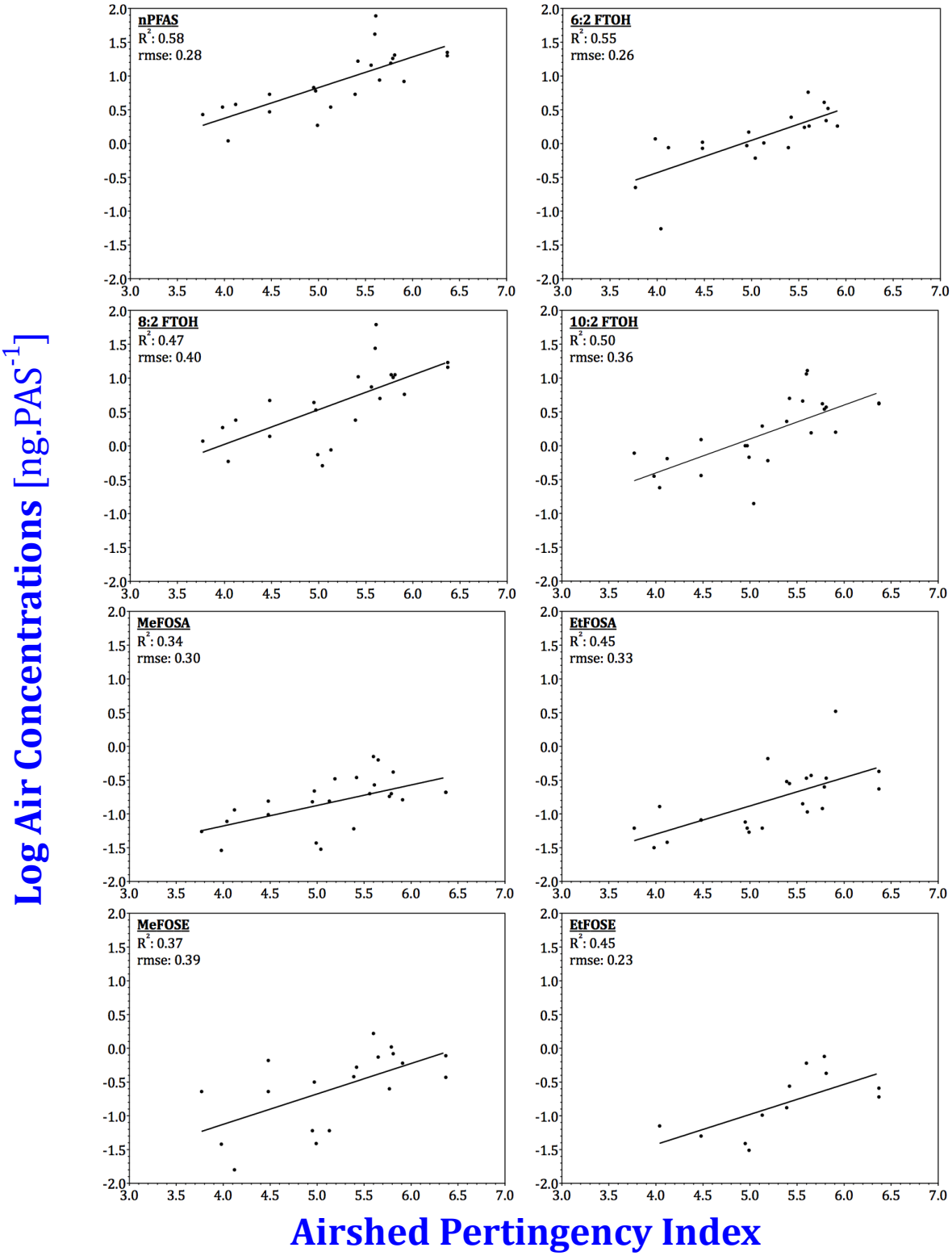

Figure S4. Pearson Correlation between the concentrations of the nPFASs in XAD-PAS and the pertingency index of the sampling site, which expresses the proximity to people. In the case of the plot for sum of nPFAS, levels below the IDL were assigned values between 1/3-2/3 of IDL, which adds uncertainty to this regression.

Regional Differences in nPFAS Levels

Figure S3 compares the levels of the seven analytes in four world regions. Given that nPFAS levels were correlated with proximity to people, sites are separated based on region and site type (remote vs. urban). Because of their limited number, the urban sites can hardly be considered representative for all urban areas in a region. Polar sites were not included in this analysis at all because of their small number. At the remote sites, the order of total nPFAS concentrations from lowest to highest generally is: South $\leq$ North America < Europe < Asia. Lower nPFAS levels in the southern hemisphere might be expected, considering that use of nPFAS is much lower.[24] On the other hand, Asian countries, namely China, still manufacture PFOS and its derivatives, including perfluorooctane sulfonyl fluoride.[25] However, statistically, none of the differences between the four regions is significant (Table S11).

Pearson correlation statistics of individual compounds was conducted for the global environment and also for the four regions (Table S12). It was suggested previously that correlations between compounds imply similar sources and fates.[26,27] In North America, correlations were highly significant ($R>0.61$, $p<0.01$) for all compounds, in Asia and Europe, approximately half of the compounds correlate with one another, whereas in the South correlations between the nPFASs were weakest. Aside from EtFOSA, all the compounds were correlated with one another on a global scale. As the emissions of all of the analytes are concentrated in urban areas, the correlations are likely just another indication that sites with high PI have elevated nPFAS levels.

At a regional scale (Figure S6), both North America and Europe showed a remarkable nPFAS decrease between 2006 and 2007. After 2007, levels increase again, although not as high as those measured in 2006. Ahrens et al.[28] have observed an increase in FTOH amounts in the Canadian Archipelago between 2005 and 2007/2008. Interestingly, efforts since 2005 have been made to reduce fluorotelomer-based residuals in Canada[29] and the United States [30]. However, due to long product lifetimes, it will take some time for households to switch to newer products that contain fewer FTOH residuals.[31] Levels of all FTOHs in the South have remained steady, whereas in Asia, FTOH levels have been declining, although not significantly.

As for the FOSAs and FOSEs, there are no observable declines, aside from North America where after 2006 levels have dropped significantly ($p<0.05$, Table S9). The phase-out of perfluorooctane sulfonates and related compounds[25] occurred already in 2000-2002 in most parts of the world (aside from China[25] and Brazil[32]). It thus comes as no surprise that the FOSA and FOSE concentrations are near detection limits and show no significant decline during the period of sampling.

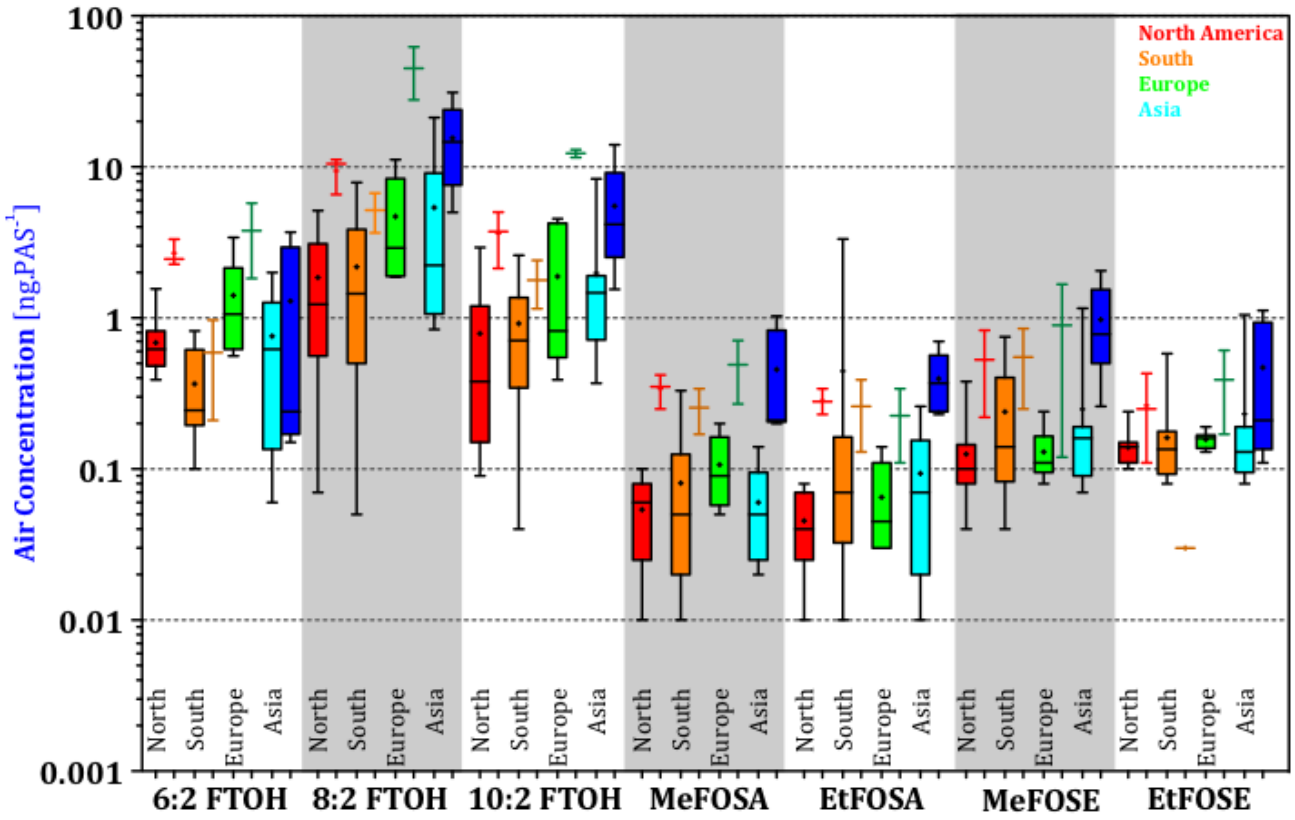

Figure S5. Box and whiskers plots for nPFAS separated according to the four major world regions and proximity to emissions (i.e. "remote" and "urban"). Polar sites were not included due to their small number.

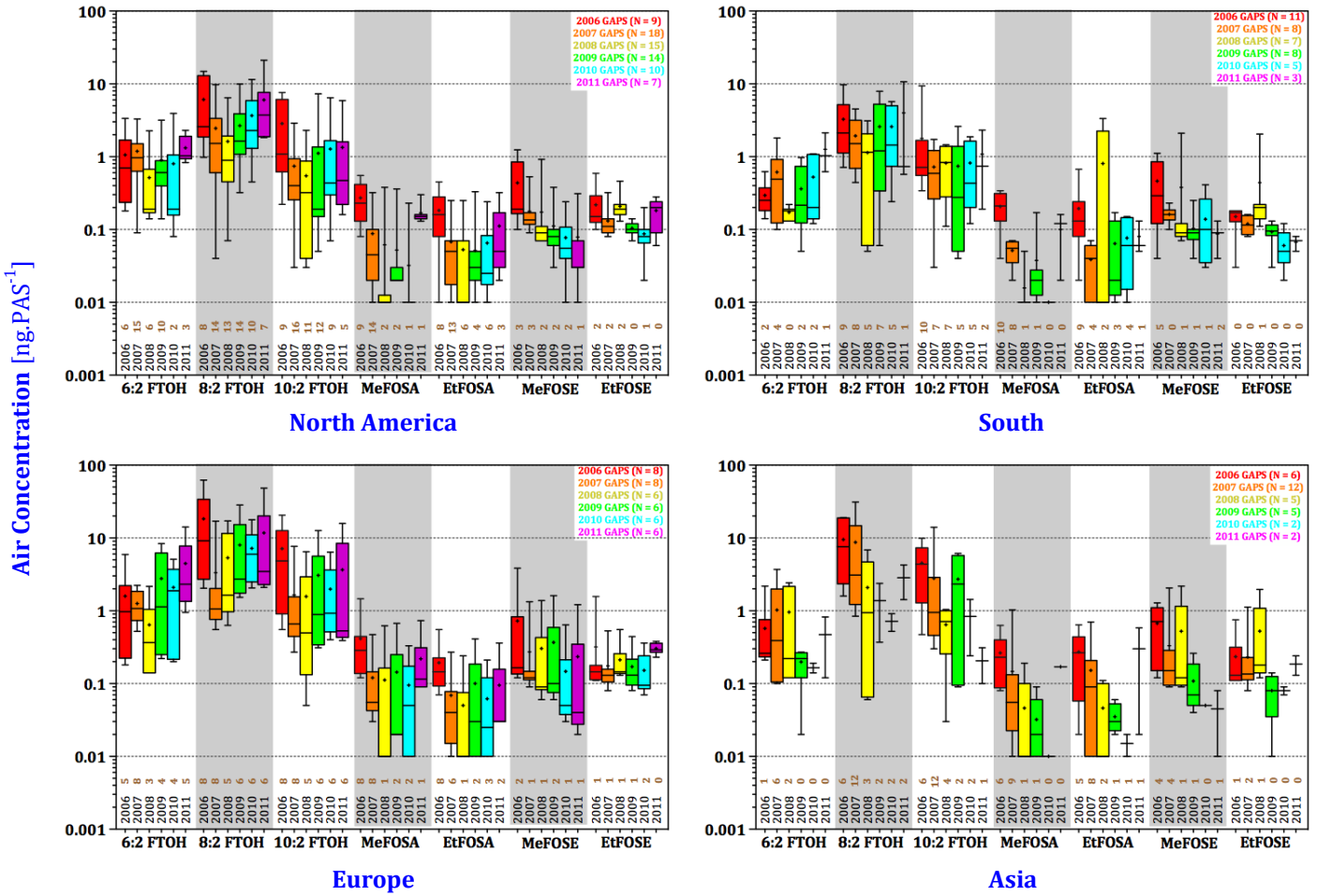

Figure S6. Temporal trends (2006-2011) of nPFASs in XAD-PAS across the four global regions.

Table S7. 1-way ANOVA on nPFAS concentrations based on region. This analysis only considered sampling sites located in remote locations.

	6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE
p-value:	0.0026	0.12	0.14	0.31	0.24	0.36	0.59
R^2:	0.30	0.14	0.13	0.084	0.099	0.076	0.046
North America vs. South	NS	NS	NS	NS	NS	NS	NS
North America vs. Europe	<0.05	NS	NS	NS	NS	NS	NS
North America vs. Asia	NS	NS	NS	NS	NS	NS	NS
South vs. Europe	<0.01	NS	NS	NS	NS	NS	NS
South vs. Asia	NS	NS	NS	NS	NS	NS	NS
Europe vs. Asia	NS	NS	NS	NS	NS	NS	NS
Arithmetic Means [ng.PAS^{-1}]							
North America	0.69	1.9	0.79	0.054	0.045	0.13	0.14
South	0.37	2.1	0.92	0.081	0.45	0.24	0.16
Europe	1.4	4.7	1.9	0.11	0.065	0.13	0.16
Asia	0.76	5.4	2.0	0.060	0.093	0.25	0.23

Table S8. nPFAS correlations (Pearson, r) among all samples in the global environment and region, where *P<0.05*, *P<0.01*, and *P<0.0001*.

		6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE
Global (all 4 regions)	6:2 FTOH						
	8:2 FTOH	***0.57***					
	10:2 FTOH	***0.71***	***0.90***				
	MeFOSA	***0.66***	***0.58***	***0.72***			
	EtFOSA	0.05	0.09	0.13	0.18		
	MeFOSE	***0.60***	***0.41***	***0.59***	***0.82***	0.18	
	EtFOSE	***0.55***	***0.34***	***0.49***	***0.59***	0.12	***0.85***
North America	6:2 FTOH						
	8:2 FTOH	***0.91***					
	10:2 FTOH	***0.77***	***0.79***				
	MeFOSA	***0.94***	***0.95***	***0.79***			
	EtFOSA	***0.95***	***0.93***	***0.78***	***0.99***		
	MeFOSE	***0.82***	***0.76***	***0.72***	***0.83***	***0.83***	
	EtFOSE	***0.69***	***0.66***	***0.58***	***0.71***	***0.69***	***0.91***
South	6:2 FTOH						
	8:2 FTOH	0.27					
	10:2 FTOH	0.07	***0.77***				
	MeFOSA	0.15	0.44	0.25			
	EtFOSA	0.13	0.21	0.28	0.05		
	MeFOSE	0.30	0.39	0.26	*0.57*	0.08	
	EtFOSE	0.07	-0.19	-0.11	-0.04	0.08	*0.51*
Europe	6:2 FTOH						
	8:2 FTOH	0.39					
	10:2 FTOH	*0.68*	***0.92***				
	MeFOSA	***0.91***	0.54	*0.81*			
	EtFOSA	***0.92***	0.45	*0.76*	***0.98***		
	MeFOSE	***0.86***	0.27	0.57	***0.94***	***0.91***	
	EtFOSE	***0.87***	0.30	0.60	***0.95***	***0.92***	***1.00***
Asia	6:2 FTOH						
	8:2 FTOH	***0.72***					
	10:2 FTOH	***0.79***	***0.91***				
	MeFOSA	*0.61*	*0.66*	***0.74***			
	EtFOSA	*0.55*	***0.77***	***0.81***	***0.88***		
	MeFOSE	***0.72***	*0.59*	*0.66*	***0.82***	***0.72***	
	EtFOSE	***0.78***	0.45	0.53	*0.56*	0.51	***0.88***

Table S9. Average concentrations of nPFAS in duplicate XAD-PAS [ng.PAS^{-1}] deployed across Costa Rica (Part 1) and Botswana (Part 2). Samples were normalized to 365 days of sampling. MDL = method detection limit; ND = not detected (below instrumental detection limit); BDL = below MDL. Additional sample site information for Botswana can be found in Table S1 in Shunthirasingham et al.[1].

Part 1 Costa Rica

City	Sampling Length		6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE
	days	MDL	0.33	1.97	0.74	.029	0.029	0.34	0.33
Santa Rosa	379		ND	0.70 ± 0.020	0.11 ± 0.080	ND	ND	ND	ND
Palo Verde	379		ND	0.17 ± 0.12	0.14 ± 0.10	ND	0.12 ± 0.010	ND	ND
Monteverde	379		ND	0.06*	ND	ND	ND	ND	ND
EARTH	379		ND	1.8 ± 0.30	0.68 ± 0.26	ND	2.0 ± 0.090	ND	ND
La Selva	379		ND	1.2 ± 0.44	0.87 ± 0.080	ND	0.10*	ND	ND
Carrara	379		ND	ND	0.08*	ND	0.35 ± 0.080	ND	0.92*
Belen	379		5.0±0.39	9.2 ± 0.64	1.8 ± 0.31	0.50 ± 0.080	3.8 ± 0.040	0.87 ± 0.080	0.49 ± 0.030

Part 2 Botswana

City	Sampling Length		6:2 FTOH	8:2 FTOH	10:2 FTOH	MeFOSA	EtFOSA	MeFOSE	EtFOSE
	Days	MDL	0.45	0.16	0.090	0.023	0.038	0.34	0.38
Kasane	371		ND	9.4 ± 1.5	7.7 ± 1.6	0.25 ± 0.02	0.14 ± 0.04	1.5 ± 0.40	ND
Guma	370		ND	7.9 ± 0.30	3.8 ± 0.70	0.21 ± 0.04	0.16 ± 0.00	BDL	ND
Francistown	330		ND	23.2 ± 0.90	20.4 ± 1.5	0.27 ± 0.06	0.4 ± 0.1	ND	ND
Mahalapye	331		ND	8.8 ± 0.50	0.7 ± 0.10	4.4 ± 0.60	ND	1.9 ± 0.40	ND
Sehitwa	307		ND	1.16 ± 0.09	3.0 ± 0.50	0.16 ± 0.01	ND	ND	ND
Eagle Island	299		ND	8.8 ± 0.20	6.5 ± 0.70	2.9 ± 0.70	0.08 ± 0.00	5.7±1.1	ND
Maun	370		ND	ND	2.7 ± 0.20	ND	ND	ND	ND
Xakanaxa	370		ND	1.9 ± 0.10	0.8 ± 0.10	0.15 ± 0.02	ND	ND	ND
Gaborone	370		ND	5.9 ± 0.40	2.7 ± 0.50	0.28 ± 0.03	0.15*	ND	ND
Nokaneng	307		ND	6.6 ± 0.60	2.9 ± 0.70	ND	0.07*	ND	ND
Seronga	370		ND	4.9 ± 0.30	4.1 ± 0.50	0.30 ± 0.03	0.14 ± 0.020	2.2±0.30	ND
Stanley	295		ND	ND	3.9 ± 0.70	0.81 ± 0.01	0.76 ± 0.040	1.1±0.20	ND
Pandamatenga	370		ND	9.2 ± 0.70	ND	BDL	BDL	BDL	ND
Nxaraga	370		ND	ND	ND	ND	ND	ND	ND
Maun Airport	341		ND	6.7 ± 0.40	9.6 ± 1.1	0.37 ± 0.05	0.18 ± 0.020	ND	ND

* Detected in one of the two samples

International Partners

We appreciate the efforts of our collaborators from all around the globe for setting up and retrieving the XAD-resin based passive air samplers. Listed below are additional collaborators, which have deployed XAD-PAS between 2009-2011. The original list of partners can be found in the supplemental information of Shunthirasingham et al.[5].

Mt. Kenya, Kenya
Vincent Madadi, GAW Station, Department of Chemistry, University of Nairobi, Nairobi, Kenya

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Ragged Point, St. Philip, Barbados
Shaina Goodridge, Environmental Protection Department, Dalkeith, St. Michael, Barbados; Allison Reeves and Justin Yearwood

Santa Cruz Island, Galapagos Islands, Ecuador
Maricruz Hernandez, Ministerio del Ambiente de Ecuador, Quito, Ecuador

Temple Basin, Arthur's Pass, New Zealand
Kimberly Hageman, Department of Chemistry, University of Otago, Dunedin, New Zealand

Vanderbijlpark, South Africa
Henk Bouwman and Laura Quinn, Logistics Department, North-West University, Potchefstroom, South Africa

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