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Results of Water Monitoring on Persistent Organic Pollutants

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ABBREVIATIONS

GEF	Global Environment Facility
GMP	Global monitoring plan
GNI	Gross national income
GRULAC	Group of Latin American and Caribbean countries
HDPE	High-density polyethylene
MS	Mass spectrometer/spectrometry
MTM	Man Technology Environment of School of Science and Technology, Örebro University
PAC	Pacific Islands countries
PopDen	Population density
PFAS	Per- and polyfluoroalkyl substances
PFHxS	Perfluorohexane sulfonic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
SPE	Solid-phase extraction
UPLC	Ultraperformance liquid chromatograph(y)
UN	United Nations
UNEP	United Nations Environment Programme
WBC	World Bank classification (of income groups)

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Background and context

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BACKGROUND AND CONTEXT

Persistent organic pollutants (POPs) represent a class of chemical compounds known for their toxicity and ability to persist in the environment without breaking down easily. These substances tend to bioaccumulate in living organisms through the food chain and can travel long distances through air masses, water currents, and the movement of migratory species, transcending national borders (United Nations Environment Program [UNEP] and Secretariat of the Stockholm Convention 2017).

The impact of POPs extends beyond their threat to the ecosystem. They also pose significant risks to human populations, causing a variety of health problems. The effects of exposure to these hazardous chemicals can vary based on gender and age, with men and women, as well as adults and children, displaying differing levels of physiological susceptibility (Secretariat of the Strategic Approach to International Chemicals Management 2018). Notably, women and children are particularly vulnerable during certain life stages, such as pregnancy and lactation, as toxic substances can be transferred from mother to child during these critical periods. Future monitoring and mitigation strategies must include the incorporation of gender-disaggregated data collection and analysis. (UNEP and Secretariat of the Stockholm Convention 2017).

The global monitoring plan (GMP) of the Stockholm Convention in POPs defines ambient air and human milk (or human blood) as core matrices recommended to be sampled and analyzed for all POPs listed in either of the Annexes A, B, or C of the Convention (UNEP 2021).

The GMP defined water as a core matrix to evaluate changes over time caused by Party action to eliminate POPs according to the goals of the Stockholm Convention (Fiedler *et al.* 2019; Fiedler *et al.* 2020). It shall be noted that water was designated as a core matrix for perfluorooctane sulfonic acid (PFOS) (Secretariat of the Stockholm Convention 2009; Secretariat of the Stockholm Convention 2019a), perfluorooctanoic acid (PFOA) (Secretariat of the Stockholm Convention 2019b), and perfluorohexane sulfonic acid (PFHxS) (UNEP 2022) after their listings. It shall be noted that chlorinated or brominated POPs were not recommended for analysis in water as a core matrix (UNEP 2019; UNEP 2021). The UNEP-coordinated GMP2 projects took note of these recommendations and tested the suitability of the guidance document, developed in 2015 (Weiss *et al.* 2015), and investigate the levels of PFOS, PFOA and PFHxS in surface water samples collected in selected developing countries in Africa, Asia-Pacific, and Group of Latin America and Caribbean (GRULAC) countries. In addition, although the country was not selected for the GMP2 water network, some countries collected water samples under the 'national samples component' of the projects and sent them for analysis. These samples are included in this report as well.

This report summarizes and assesses the results from the four regional UNEP/GEF GMP2 projects coordinated and implemented by the United Nations Environment Programme (UNEP) to support implementation of the global monitoring plan (GMP) in developing countries. The projects and the regional reports referred to are for the African region with 15 participating countries (UNEP 2024a; UNEP 2014a), Asian region with seven countries (UNEP 2024b; UNEP 2014b), Pacific Islands (PAC) region with nine countries (UNEP 2024c; UNEP 2014c), and the Latin American and Caribbean region (GRULAC) with nine participating countries (UNEP 2024d; UNEP 2014d).

Separated reports were prepared for the core matrices human milk (UNEP 2024e) and air where the results of the measured data from pssive and active air samples have been summarized (UNEP 2024f).

SECTION 1

Methodology

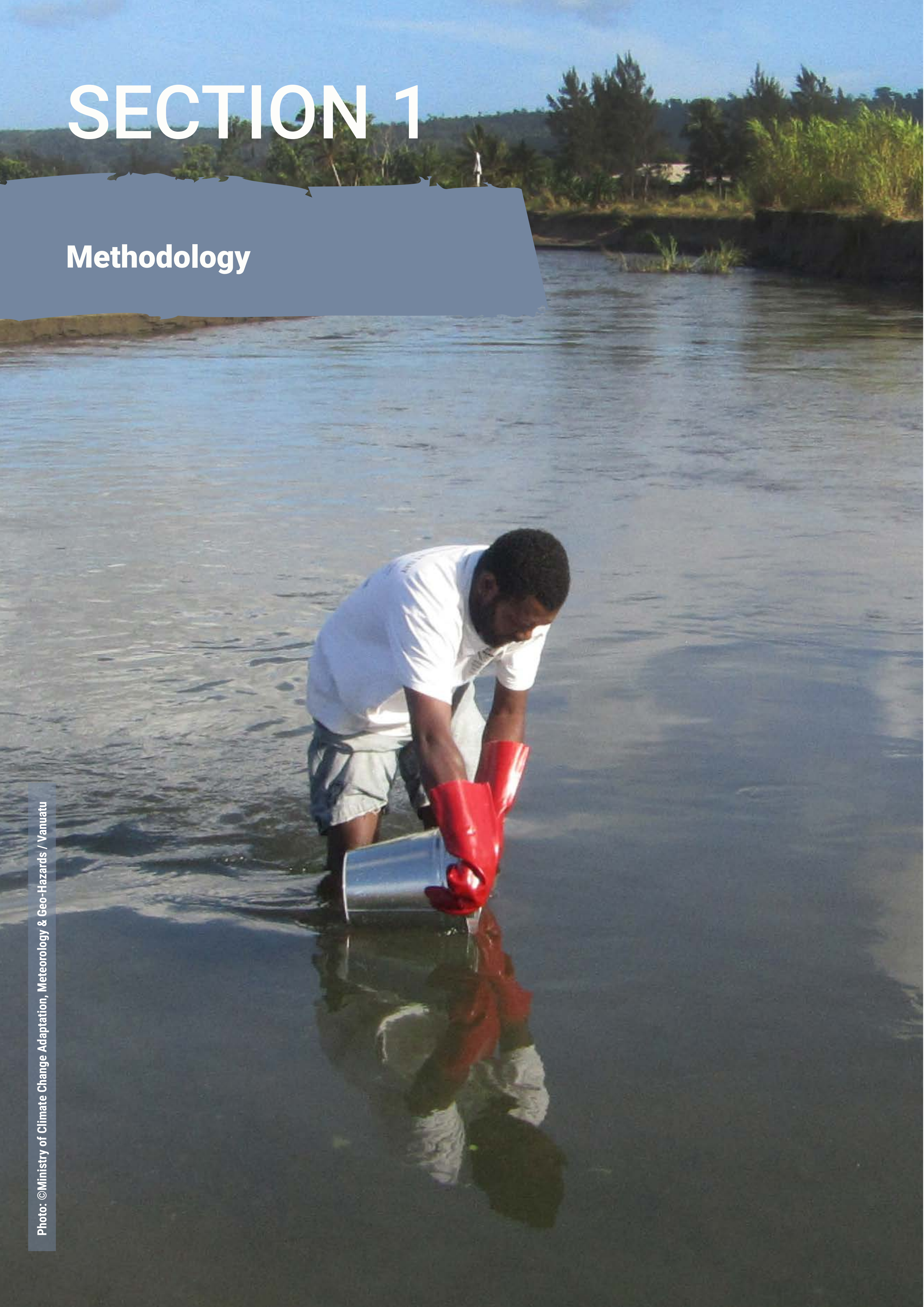

Photo: ©Ministry of Climate Change Adaptation, Meteorology & Geo-Hazards / Vanuatu

1. METHODOLOGY

1.1. Origin and characterization of samples

For the sampling at national level, a guidance document was developed to contain the recommended requirements for the selection of sampling sites (Weiss *et al.* 2015). The guidance document recommended active sampling, *i.e.*, punctual at a defined integrative location, often at the mouth of large rivers or at estuaries. Time-integrative sampling, *i.e.*, using passive samplers, was not recommended. Sampling should occur once every three months, so that four samples are obtained *per* year. This number was thought to be sufficient for an annual coverage of changes that may occur at a sampling location.

A standard operational procedure (SOP) document was developed and made available in English, Spanish and French for the core matrix water (UNEP 2017). Briefly, surface water samples were collected at the designated locations, often at the mouth of large rivers or at estuaries. Collection was done with a bucket and 1 liter (L) of water was filled into a 1-L HDPE bottle. The water samples were stored in fridges until shipment to the expert laboratory for analysis of per- and polyfluoroalkyl substances (PFAS).

Although a total of 42 countries participated in the four regional projects, only 22 countries fulfilled the criteria as stipulated in the guidance document (Weiss *et al.* 2015) and were selected to participate in the 'water network'. Their geographic location is displayed in Table 2 and they are designated as 'GMP2'. An additional six countries sent water samples for PFAS analysis as part of their national samples (indicated as 'Nat"). Finally, three countries from the GMP2 water network sent additional samples as part of their national samples. Thus, in total, samples from 28 countries were available. Further information is shown in the results sections in chapters 3 and 4.

1.2. Chemical analysis

A generic protocol for the analysis of PFAS was developed (UNEP 2015). The SOP used in this GMP2 project recommended PFAS to be analyzed using UPLC/MSMS after solid-phase extraction (SPE).

Table 1: POPs analyzed and reported

POP / Listing	Abbreviation	Analyte
Perfluorooctane sulfonic acid (Secretariat of the Stockholm Convention 2009a; Secretariat of the Stockholm Convention 2019a)	PFOS	L- and br-PFOS
Perfluorooctanoic acid (Secretariat of the Stockholm Convention 2019b)	PFOA	L-PFOA
Perfluorohexane sulfonic acid (UNEP 2022)	PFHxS	L-PFHxS

Note: L = Linear; br=branched.

Chemical analysis of all samples collected in the individual projects were shipped to and analyzed by MTM Örebro University, Sweden. PFAS in water were reported in ng/L.

1.3. Samples planned vs. results reported

The following graphic shows the efficiency of the project as the number of samples planned for analysis to be collected and contracted to the participating country *vs*. the number of samples received at and analyzed by the expert laboratory. These samples were reported for PFAS concentrations. The graphs contain the number of water samples planned/reported according to UN region.

The planned number of samples in each country consists of four samples per year and two years of sampling. Thus, the base number for samples is eight per country for PFAS in water.

GRULAC was the only project region that sent all water samples as planned; for PAC, there was quite a large difference between the targeted number and the effective number of samples (72 targeted, 46 achieved). One sample from SEN (Africa) did leak out of the HDPE bottle and could not be analyzed; otherwise, the target was almost reached like for Asia (Figure 1).

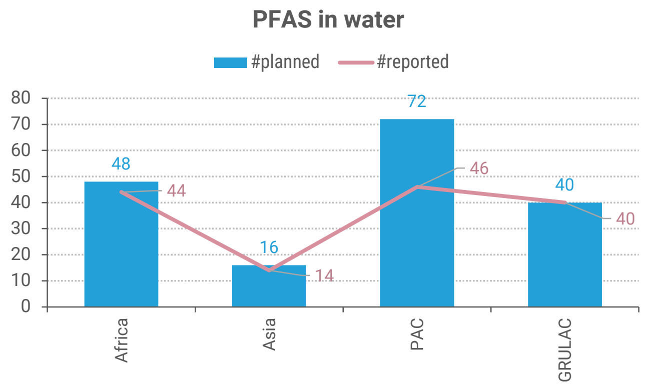

Figure 1: Water samples planned vs. analyzed/reported

1.4. Characteristics of the participating countries

The occurrence of PFAS in water samples is assessed on a regional basis and by country (see section 3) but also for metadata, such as wealth and population (section 4).

For the assessment of lifestyle factors, global indicators as established by the World Bank have been used. These include the economic situation in a country using the World Bank classification (WBC) defining the four income groups low-, lower-middle-, upper-middle- and high-income groups (L, LM, UM, H) as the gross national income (GNI) per capita in US$ according to the Atlas methodology (World Bank n.d. a). The classification of the participating countries in the respective years are shown in Table 3. It can be seen that all WBC were represented in these UNEP/GMP2 projects; however, the number of low-income countries (L) was very low and only in the group of the national samples, except for Senegal, which was assigned L in 2017 but not in 2018.

The second parameter is the population density (PD), which is defined as population per square kilometer of land area (pop/km²) (World Bank n.d. b). There is no internationally accepted scheme and therefore we defined population density codes as shown in Table 4. There were some least densely populated countries with population density of less than 25 inhabitants *per* km²; the least densely populated country was Mongolia with 2 inhabitants *per* km². The most densely populated country was Tuvalu with 379 inhabitants per km².

Table 2: Origin and type of water samples received and analyzed

Region	ISO3	GMP2	Nat
Africa		**6**	**2**
Egypt	EGY	X	
Ghana	GHA	X	
Kenya	KEN	X	
Nigeria	NGA		X
Senegal	SEN	X	
Tunisia	TUN	X	
Uganda	UGA		X
Zambia	ZMB	X	
GRULAC		**5**	**2+1**
Argentina	ARG	X	
Antigua and Barbuda	ATG		X
Brazil	BRA	X	
Ecuador	ECU	X	
Jamaica	JAM	X	X
Mexico	MEX	X	
Uruguay	URY		X
Region	**ISO3**	**GMP2**	**Nat**
Asia		**2**	**2+2**
Indonesia	IDN		X
Mongolia	MNG	X	X
Thailand	THA		X
Viet Nam	VNM	X	X
PAC		**9**	**0**
Fiji	FJI	X	
Kiribati	KIR	X	
Marshall Islands	MHL	X	
Niue	NIU	X	
Palau	PLW	X	
Solomon Islands	SLB	X	
Tuvalu	TUV	X	
Vanuatu	VUT	X	
Samoa	WSM	X	
Total		22	6+3

Table 3: Assignment of countries to WBC codes for the sampling year (Historical classification by income) (World Bank n.d. c)

Region	ISO-3	WBC 2017	WBC 2018	WBC 2019
Africa	EGY	LM	LM	LM
Africa	GHA	LM	LM	LM
Africa	KEN	LM	LM	LM
Africa	NGA	LM	LM	LM
Africa	SEN	L	LM	LM
Africa	TUN	LM	LM	LM
Africa	UGA	L	L	L
Africa	ZMB	LM	LM	LM
Asia	IDN	LM	LM	UM
Asia	MNG	LM	LM	LM
Asia	THA	UM	UM	UM
Asia	VNM	LM	LM	LM
GRULAC	ARG	H	UM	UM
GRULAC	ATG	H	H	H
GRULAC	BRA	UM	UM	UM
GRULAC	JAM	UM	UM	UM
GRULAC	MEX	UM	UM	UM
GRULAC	URY	H	H	H
PAC	FJI	UM	UM	UM
PAC	KIR	LM	LM	LM
PAC	MHL	UM	UM	UM
PAC	NIU	UM	UM	UM
PAC	PLW	H	H	H
PAC	SLB	LM	LM	LM
PAC	TUV	UM	UM	UM
PAC	VUT	LM	LM	LM
PAC	WSM	UM	UM	UM

Table 4: Assignment of countries to population density (as PD_Codes) for the sampling year

Region	ISO-3	Pop/km2 2017	PD 2017	Pop/km2 2018	PD 2018	Pop/km2 2019	PD 2019
Africa	EGY	97	PD_90-200	99	PD_90-200	101	PD_90-200
Africa	GHA	128	PD_90-200	131	PD_90-200	134	PD_90-200
Africa	KEN	88	PD_25-90	90	PD_90-200	92	PD_90-200
Africa	NGA	210	PD_200-330	215	PD_200-330	221	PD_200-330
Africa	SEN	80	PD_25-90	82	PD_25-90	85	PD_25-90
Africa	TUN	74	PD_25-90	74	PD_25-90	75	PD_25-90
Africa	UGA	205	PD_200-330	213	PD_200-330	221	PD_200-330
Africa	ZMB	23	PD<25	23	PD<25	24	PD<25
Asia	IDN	146	PD_90-200	148	PD_90-200	144	PD_90-200
Asia	MNG	2	PD<25	2	PD<25	2	PD<25
Asia	THA	135	PD_90-200	136	PD_90-200	136	PD_90-200
Asia	VNM	305	PD_200-330	308	PD_200-330	311	PD_200-330
PAC	FJI	48	PD_25-90	48	PD_25-90	49	PD_25-90
PAC	KIR	141	PD_90-200	143	PD_90-200	145	PD_90-200
PAC	MHL	323	PD_200-330	325	PD_200-330	327	PD_200-330
PAC	NIU	6	PD<25	6	PD<25	6	PD<25
PAC	PLW	39	PD_25-90	39	PD_25-90	39	PD_25-90
PAC	WSM	69	PD_25-90	69	PD_25-90	70	PD_25-90
PAC	SLB	23	PD<25	23	PD<25	24	PD<25
PAC	TUV	379	PD_330-2000	384	PD_330-2000	389	PD_330-2000
PAC	VUT	23	PD<25	24	PD<25	25	PD<25
GRULAC	ARG	16	PD<25	16	PD<25	16	PD<25
GRULAC	ATG	217	PD_200-330	219	PD_200-330	221	PD_200-330
GRULAC	BRA	25	PD<25	25	PD_25-90	25	PD_25-90
GRULAC	JAM	270	PD_200-330	271	PD_200-330	272	PD_200-330
GRULAC	MEX	64	PD_25-90	65	PD_25-90	66	PD_25-90
GRULAC	URY	20	PD<25	20	PD<25	20	PD<25

1.5. Assessment and visualization of results

All data were maintained in Microsoft Office 365 Excel®; statistical evaluations were made using R packages with R-Studio. The Kruskal-Wallis H test was used to determine if there are statistically significant differences between the independent variables and dependent variables. Post-hoc analysis was performed using the pairwise Wilcoxon test. Adjustment of the p-value was made using the Benjamini-Hochberg method. Significance level was set to p=0.05. The below the LOQ were replaced by 0.

Multivariate analysis such as principal component analysis (PCA) was used for visualization and interpretation of results.

SECTION 2

Results from water monitoring by region and country

Photo: ©Unsplash / Jason Cooper

2. RESULTS FROM WATER MONITORING BY REGION AND COUNTRY

2.1. Overview

A total of 165 samples were analyzed for PFAS; of these, 144 samples were GMP2 samples and an additional 21 were national samples (Table 5). Most samples were collected in 2018 (N=89) followed by 2017 (N=64). The three regions, Africa, PAC, and GRULAC contributed almost the same number of samples (28%-30% of total); Asia had less (23 samples or 14%). It is noteworthy that GRULAC submitted all 40 planned GMP2 samples; *i.e.*, each of the five participating countries the recommended number of eight samples (see also Figure 1).

Table 6 summarizes the overall results by source. It can be seen that the national samples had similar values for PFOS but higher values for PFOA and PFHxS when assessing the mean values. The median values were very comparable across all cells. In general, the concentrations were quite low and none of the mean or median values were greater than 1 ng/L. The graphical overview is shown in Figure 2.

Table 5: Overview on number of water samples analyzed for PFAS

	2017 (N=64)	2018 (N=89)	2019 (N=11)	2020 (N=1)	Overall (N=165)
Region					
Africa	24	25	0	1	50 (30.3%)
Asia	6	12	5	0	23 (13.9%)
PAC	14	30	2	0	46 (27.9%)
GRULAC	20	22	4	0	46 (27.9%)
Source					
GMP2	64	77	3	0	144 (87.3%)
Nat	0	12	8	1	21 (12.7%)
WBC					
H	8	2	4	0	14 (8.5%)
UM	21	38	0	0	59 (35.8%)
LM	31	44	7	1	83 (50.3%)
L	4	5	0	0	9 (5.5%)
PD_Code					
PD<25	20	20	6	0	46 (27.9%)
PD_25-90	27	28	0	0	55 (33.3%)
PD_90-200	10	21	0	0	31 (18.8%)
PD_200-330	6	17	5	1	29 (17.6%)
PD_330-2000	1	3	0	0	4 (2.4%)

Table 6: Water: Descriptive statistics by source (concentrations in ng/L)

PFAS	Central tendencies	GMP2 (N=144)	Nat (N=21)	Overall (N=165)
PFOS	Mean (SD)	0.985 (1.39)	0.771 (0.833)	0.958 (1.33)
	Median [Min, Max]	0.370 [0, 6.23]	0.444 [0.0343, 2.68]	0.410 [0, 6.23]
PFOA	Mean (SD)	0.464 (0.599)	0.917 (0.910)	0.521 (0.661)
	Median [Min, Max]	0.225 [0, 4.02]	0.259 [0, 2.33]	0.239 [0, 4.02]
PFHxS	Mean (SD)	0.329 (0.670)	0.158 (0.190)	0.307 (0.632)
	Median [Min, Max]	0.055 [0, 3.51]	0.102 [0, 0.740]	0.066 [0, 3.51]

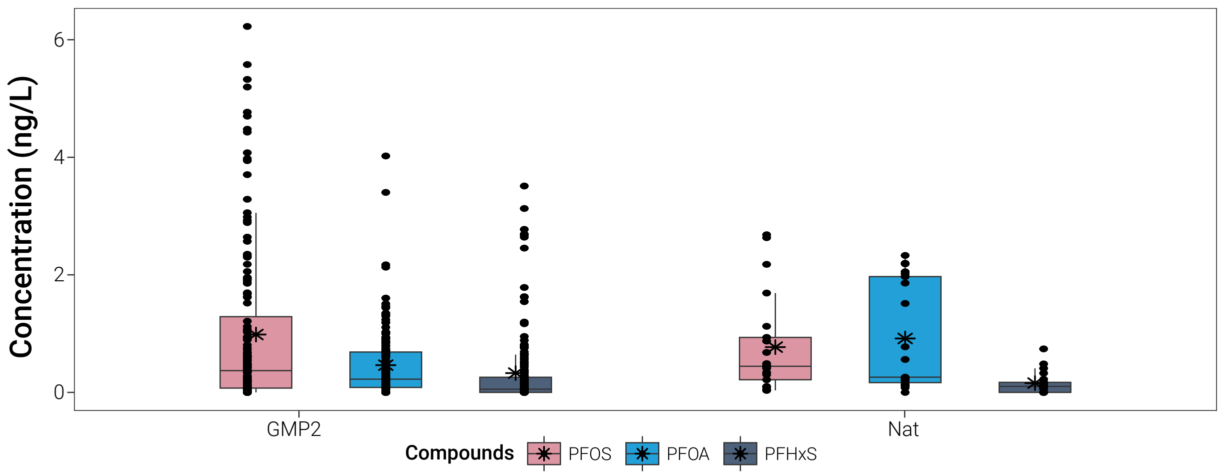

Figure 2: Unscaled box whisker plots to compare PFAS values by source (ng/L) (n=165)

Box 1 for all the box and whiskers plots in this report:

The whiskers represent the minimum and maximum concentrations without the outliers. The lower border of the box represents the first quartile (25%), the line inside the box the median and the upper border is the third quartile (75%). The dots outside the whiskers are outliers, which were defined as all concentrations greater or smaller the interquartile range multiplied by 1.5.

2.2. Assessment by region

In this chapter, the results for PFAS analyzed in water are summarized with an emphasis on the region.

More details at a higher level of disaggregation are provided in Table 7. For the GMP2 samples, the highest overall mean and median values were for PFOS (0.99 ng/L; 0.37 ng/L); the maximum value was found in PAC (6.23 ng/L in Vanuatu, VUT) followed by GRULAC (5.32 ng/L in Argentina). PFOA had lower mean and median values, with the maximum was found in Africa (4.02 ng/L in Kenya). PFHXs had much lower median values than PFOS and PFOA and the highest value was found in PAC (3.51 ng/L in VUT). The graphical summary is shown in Figure 3. The analytes were highly correlated (Figure 4).

Within the national samples (Nat), the highest PFOS, PFOA, and PFHxS values were 2.68 ng/L, 2.33 ng/L, and 0.41 ng/L, all of them in Asia. The graphical summary by region and source is provided in Figure 3.

The frequency distribution, in number of samples within a concentration bin (range in ng/L), of the three PFAS according to region is shown in Figure 4, 5, and 6.

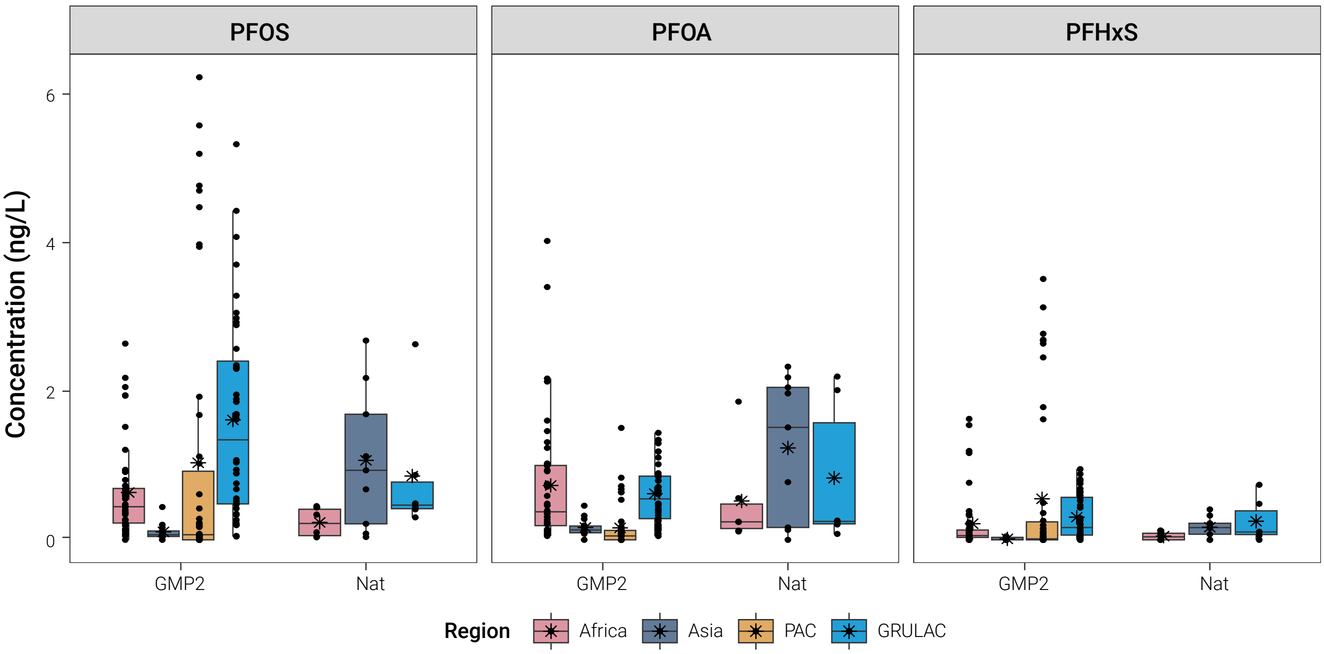

Figure 3: Unscaled boxplots for three PFAS by source colored by region (ng/L) (n=165)

Table 7: Descriptive statistics for water samples by region and source of sample (concentrations in ng/L)

PFAS	Central tendencies	Africa		Asia		PAC	GRULAC		Overall	
		GMP2 (N=44)	Nat (N=6)	GMP2 (N=14)	Nat (N=9)	GMP2 (N=46)	GMP2 (N=40)	Nat (N=6)	GMP2 (N=144)	Nat (N=21)
PFOS	Mean (SD)	0.637 (0.637)	0.234 (0.197)	0.107 (0.111)	1.07 (0.946)	1.04 (1.85)	1.61 (1.35)	0.859 (0.890)	0.985 (1.39)	0.771 (0.833)
	Median [Min, Max]	0.446 [0, 2.64]	0.220 [0.034, 0.454]	0.069 [0, 0.441]	0.936 [0.038, 2.68]	0.069 [0, 6.23]	1.35 [0.044, 5.32]	0.467 [0.303, 2.63]	0.370 [0, 6.23]	0.444 [0.034, 2.68]
PFOA	Mean (SD)	0.732 (0.854)	0.523 (0.675)	0.166 (0.118)	1.24 (0.967)	0.161 (0.302)	0.621 (0.396)	0.832 (0.990)	0.464 (0.599)	0.917 (0.910)
	Median [Min, Max]	0.377 [0.052, 4.02]	0.242 [0.112, 1.86]	0.132 [0, 0.459]	1.51 [0, 2.33]	0.0526 [0, 1.51]	0.551 [0.051, 1.44]	0.248 [0.080, 2.20]	0.225 [0, 4.02]	0.259 [0, 2.33]
PFHxS	Mean (SD)	0.217 (0.403)	0.050 (0.056)	0.013 (0.019)	0.170 (0.138)	0.552 (1.05)	0.305 (0.295)	0.249 (0.295)	0.329 (0.670)	0.158 (0.190)
	Median [Min, Max]	0.0570 [0, 1.63]	0.0403 [0, 0.126]	0 [0, 0.047]	0.164 [0, 0.409]	0.0139 [0, 3.51]	0.166 [0, 0.952]	0.106 [0, 0.740]	0.055 [0, 3.51]	0.102 [0, 0.740]

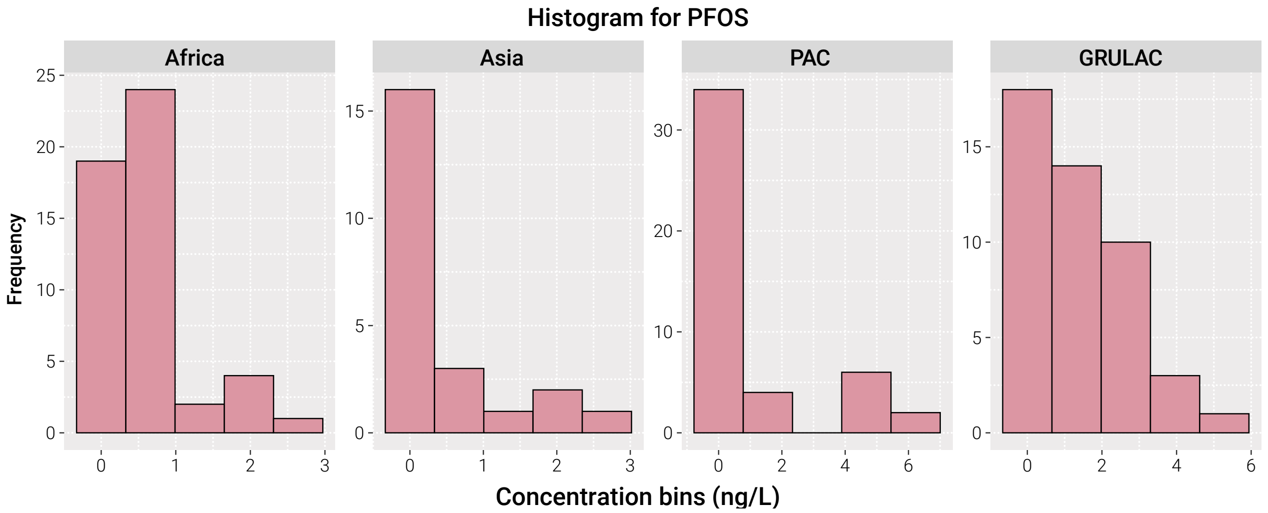

Figure 4: Frequency distribution of PFOS according to the region (n=165)

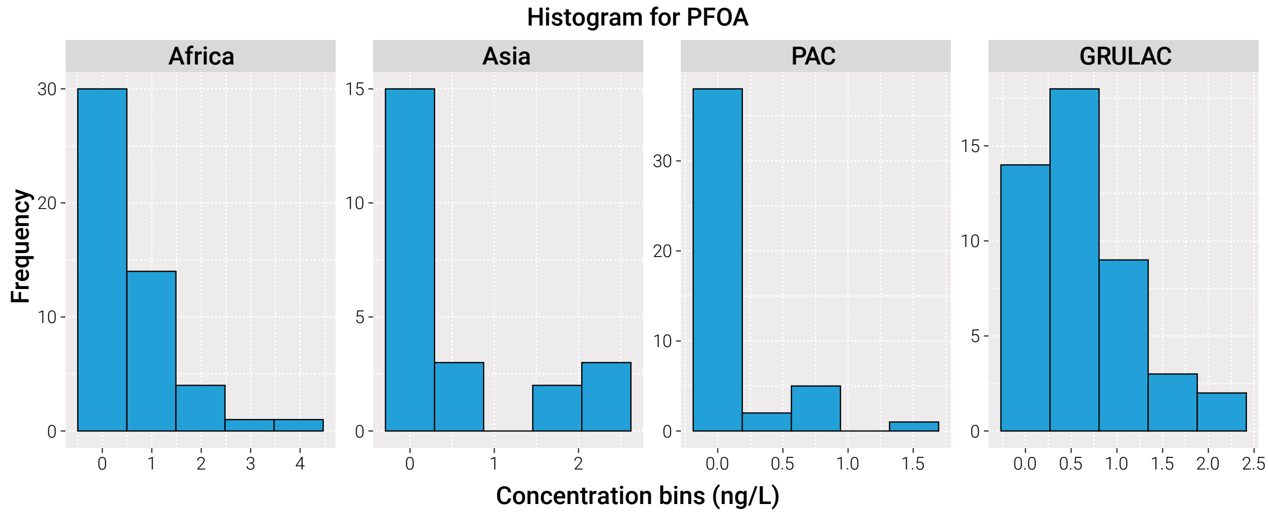

Figure 5: Frequency distribution of PFOA according to the region (n=165)

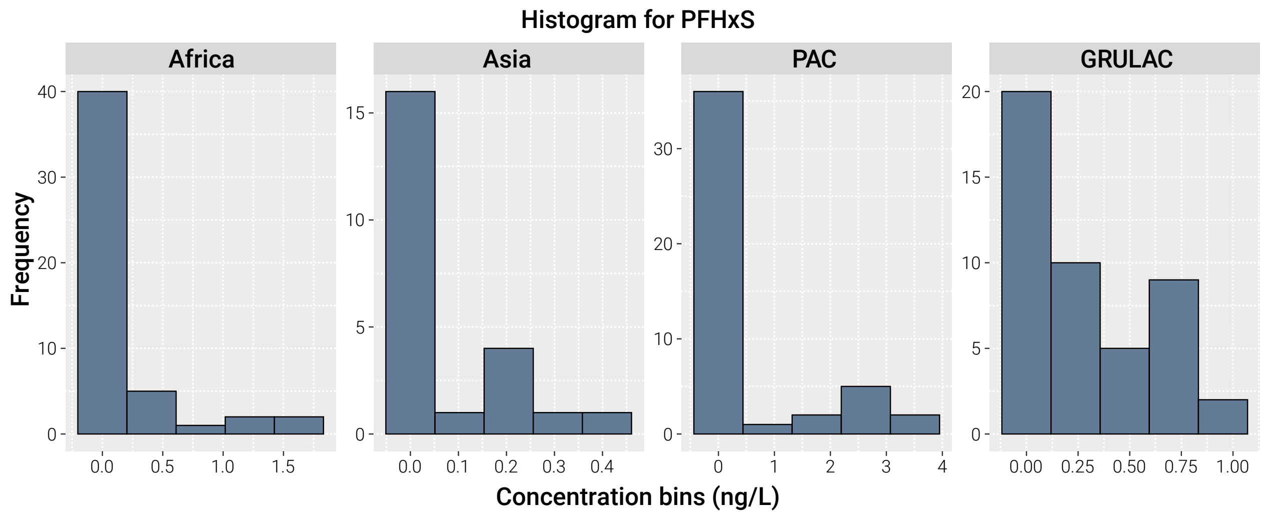

Figure 6: Frequency distribution of PFHxS according to the region (n=165)

The mean values of the three PFAS and their standard deviations according to region are shown in Figure 7. The highest mean value was found in GRULAC, followed by the Pacific Islands.

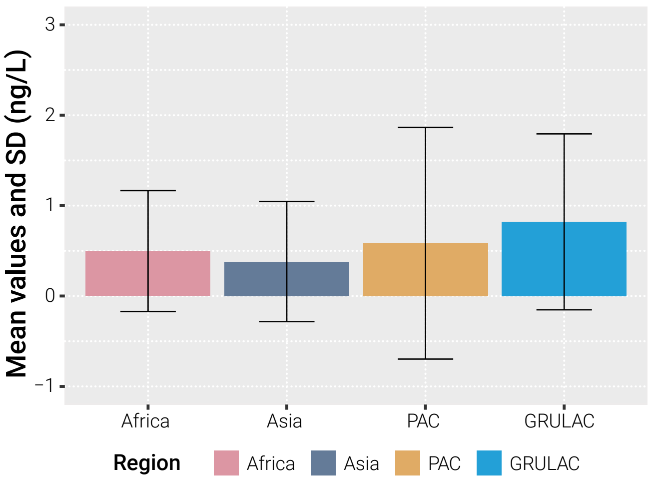

Figure 7: Mean values of three PFAS by region (ng/L) (n=165)

Boxplots for each region and differentiated between GMP2 and Nat samples are shown in Figure 8. Please note that there were no national samples from PAC. Within the GMP2 samples, the highest median values for PFOS, PFOA, and PFOS were found in GRULAC samples. It should be noticed that among the 40 GRULAC samples, there was only one outlier for PFOS, all other concentrations were within 1.5-times the interquartile range. This indicates that the concentrations in GRULAC were very homogeneous whereas in the other regions, many outliers were registered. The high abundance of outliers within the PAC GMP2 samples is noteworthy; also, African samples had many outliers, indicating high variation within the "regular" sampling network activities.

The national samples from Asia showed higher median values than the GMP2 samples but no outliers.

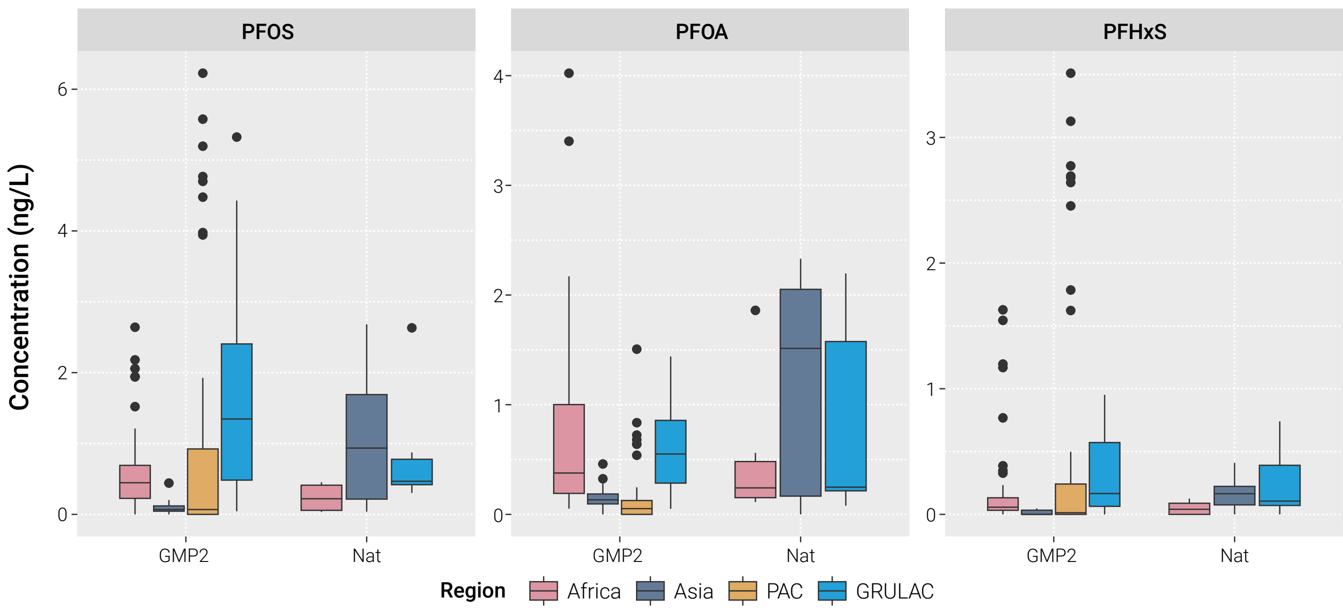

Figure 8: PFAS in water: Scaled boxplots for three PFAS and region (ng/L) (n=165)

Statistically for the three PFAS together and all 165 samples, the GMP2 samples were not significantly different from the Nat samples (p=0.14). On a regional basis, the results were significantly different ($p=1.9 \times 10^{-15}$) with pairwise statistically significant differences between all regions except for Asia with PAC (p=0.052).

Therefore, Figure 9 shows the concentrations of the three PFAS in each region without further differentiation.

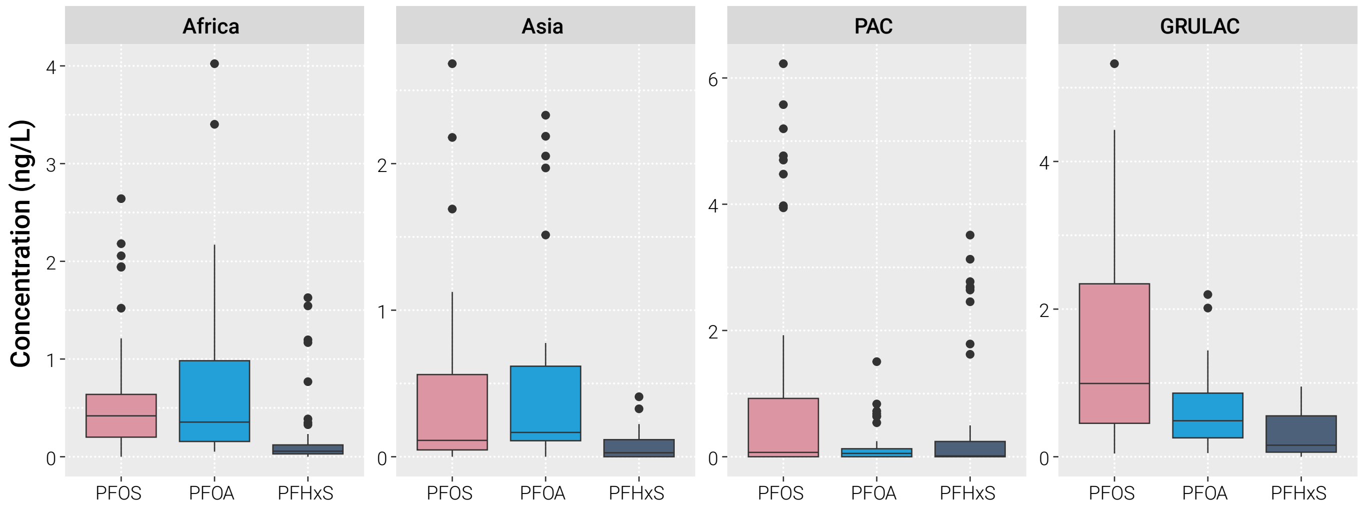

Figure 9: PFAS in water: Scaled boxplots for three PFAS within project region (ng/L) (n=165)

2.3. By country

The GMP2 water network samples can be identified by the Sample ID, which contains the ISO3 code followed by the year (YYYY) and the sampling quarter (1, 2, 3, or 4). The national samples were the sample name as assigned by the country of origin.

Figure 10 shows the occurrence of the three PFAS by country as box whisker plots. For some countries the up to eight measurements gave quite homogeneous results and only a few outliers were seen.

Brazil was the only country that changed the sampling location: in 2017, water samples were collected at the mouth of the Amazon River but due to long travel distances and low concentrations, the location was changed to the São Paulo Channel in 2018. The increase in concentrations in the year 2018 can be seen in Figure 11.

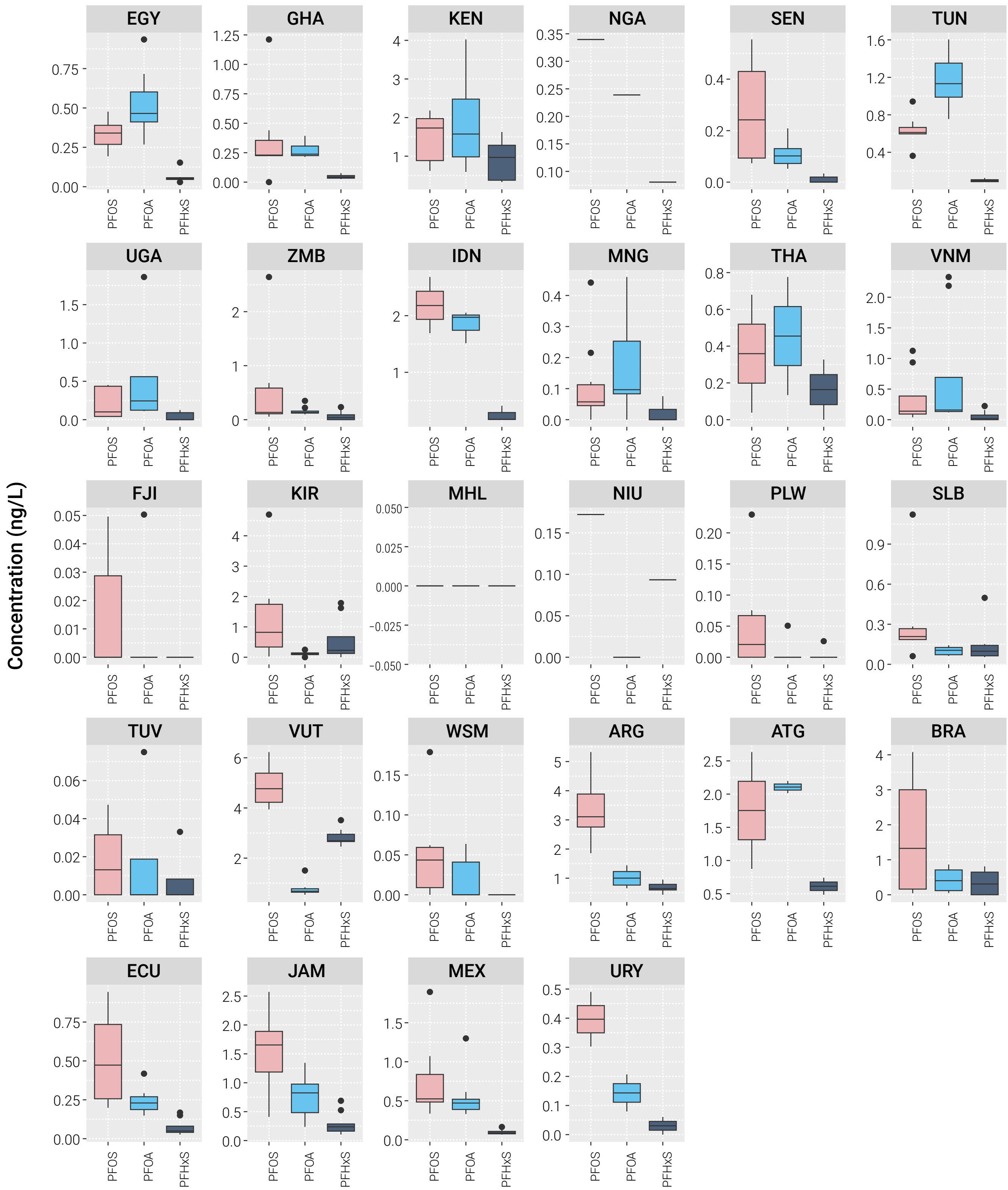

Figure 10: PFAS in water: Scaled boxplots three PFAS by country in each project region (ng/L) (n=165)

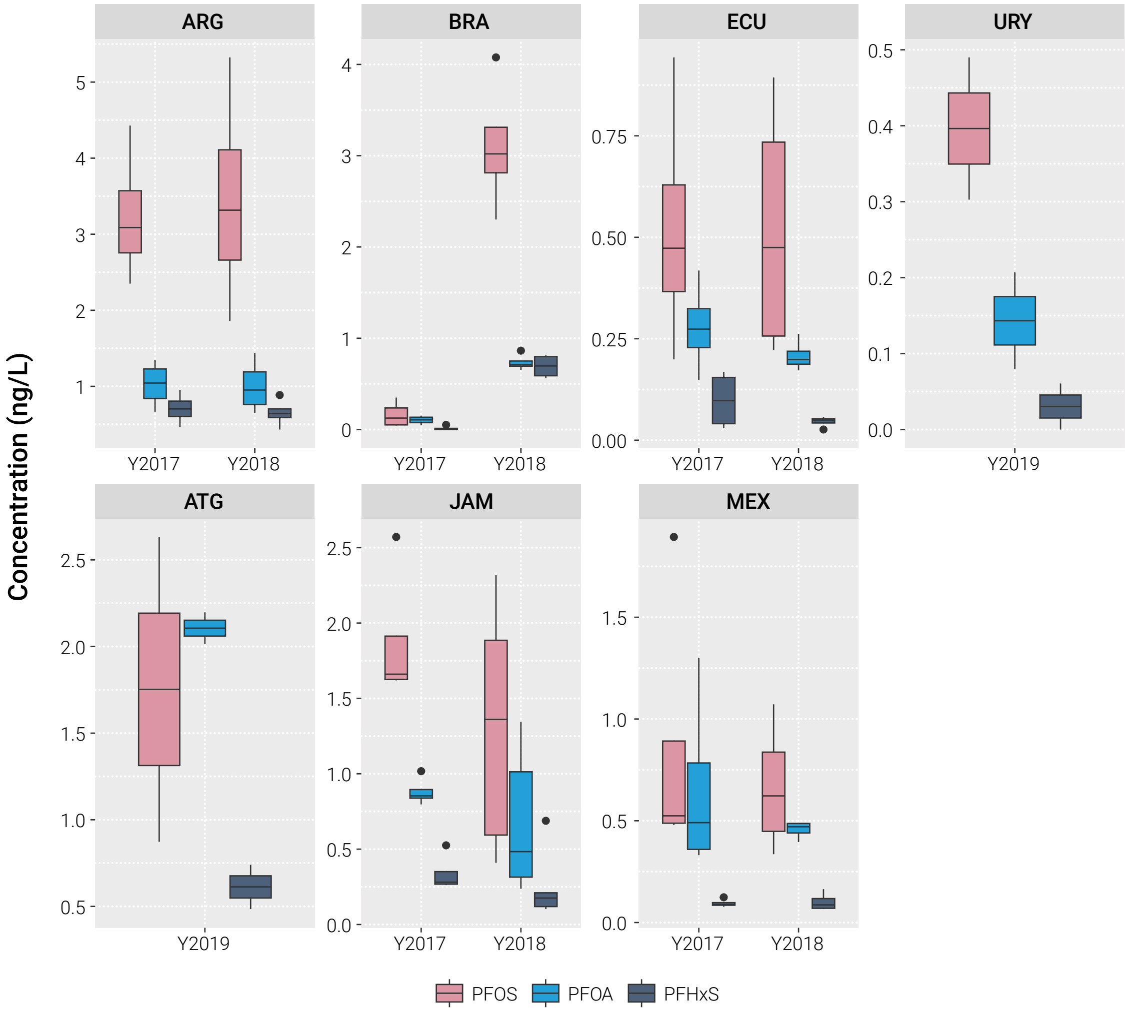

Figure 11: PFAS in GRULAC: Scaled boxplots for three PFAS by country and year (ng/L) (N=46)

Figure 12 shows the quantitative results of all samples for the three PFAS by country and Figure 13 displays the pattern as stacked bars at 100%. The change in scale for the Brazilian samples in 2017 and 2018 can be clearly identified; also, the patten in 2018 had less PFOA than in 2017.

Quite large differences in scale between the samplings were seen in Kenya and Kiribati; however, the pattern was quite stable. Very stable pattern was found in Argentina and Vanuatu.

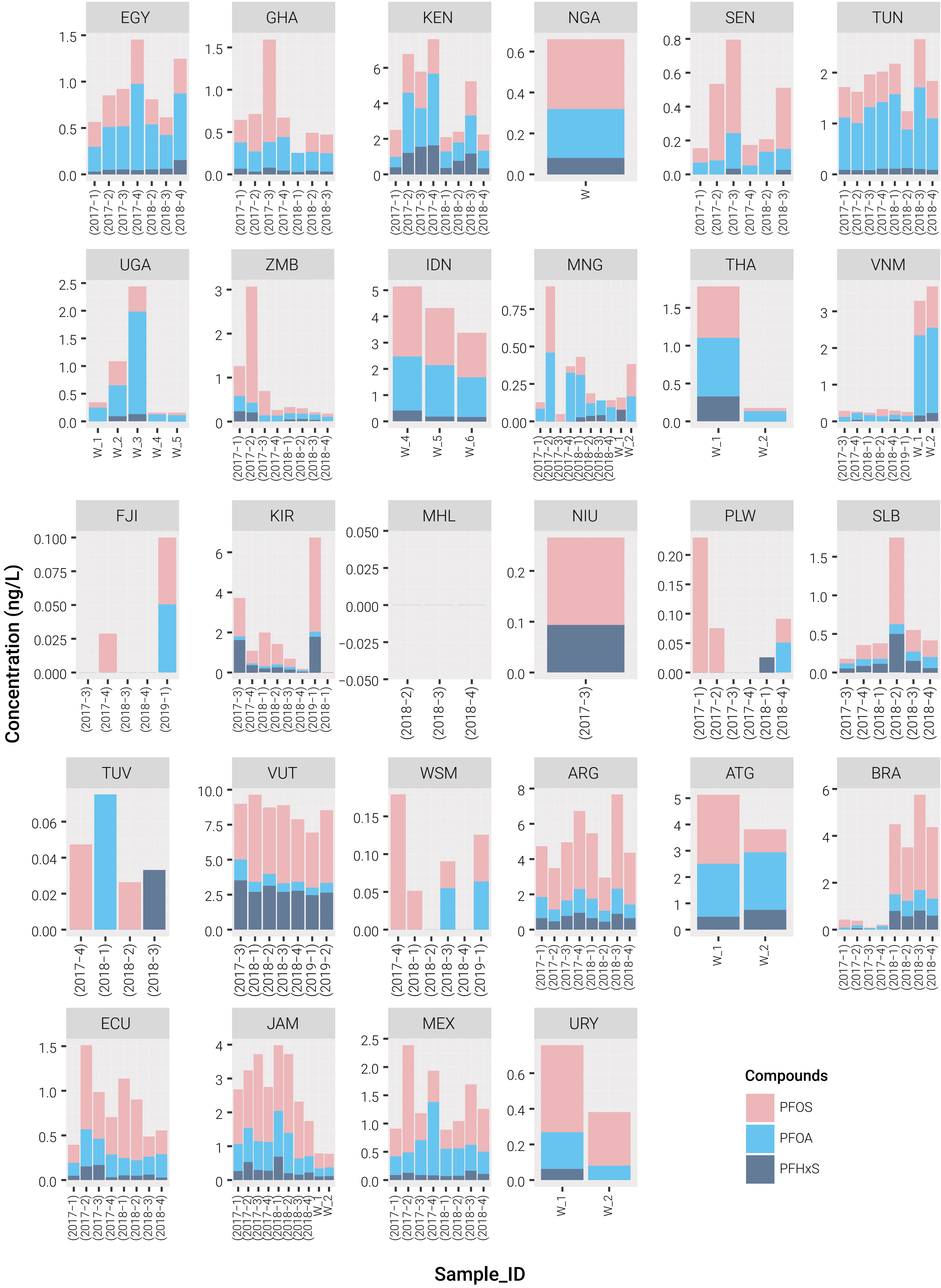

Figure 12: Three PFAS as stacked bars by country (N=165)

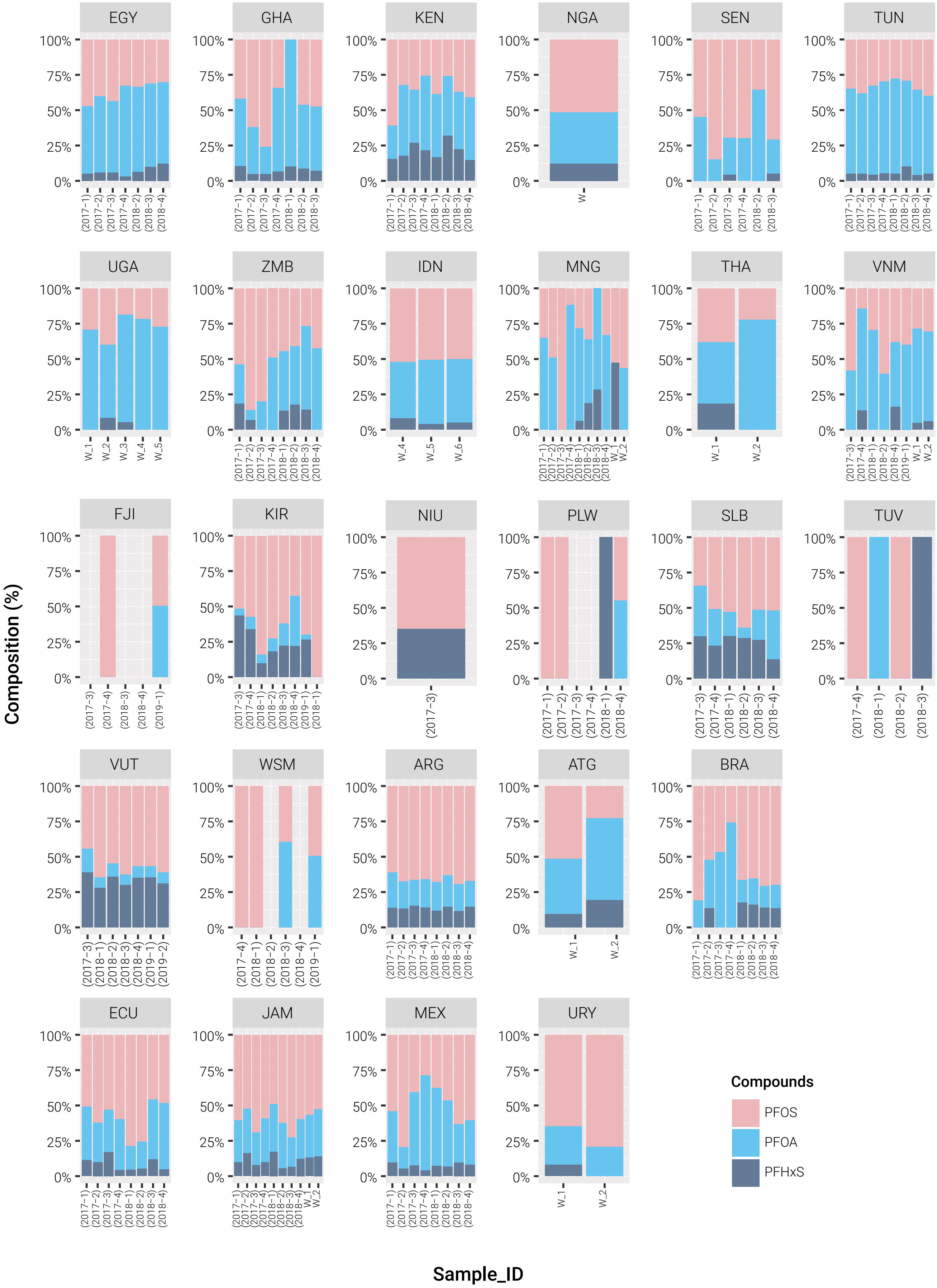

Figure 13: Pattern of the three PFAS by country and Sample_ID

SECTION 3

Results in relation to metadata (Income and population density)

Photo: ©UNEP / Victor Estellano

3. RESULTS IN RELATION TO METADATA (INCOME AND POPULATION DENSITY)

Lifestyle factors include wealth, with WBC used as an indicator, and population density as an indicator for urban or rural settings. Is important to note that the classification of the World Bank is used and applies to the whole country and not to the specific location of the sampling sites.

3.1. Income

Quite a clear picture is seen in such manner that the mean and median values for PFHxS in the low-income countries is much lower than in the three other WBC groups. The difference is statistically significant (p=0.004); however, the pairwise ranking test confirms that only the pairs L to LM and LM to UM are statistically significantly different (p=0.016 and p=0.017).

Table 8: Descriptive statistics for three PFAS grouped by income (WBC)

PFAS	Central tendencies	H (N=14)	UM (N=59)	LM (N=83)	L (N=9)	Overall (N=165)
PFOS	Mean (SD)	1.26 (1.53)	0.912 (1.20)	1.02 (1.44)	0.253 (0.214)	0.958 (1.33)
	Median [Min, Max]	0.396 [0, 4.43]	0.422 [0, 5.32]	0.401 [0, 6.23]	0.121 [0.034, 0.554]	0.410 [0, 6.23]
PFOA	Mean (SD)	0.618 (0.788)	0.380 (0.401)	0.622 (0.775)	0.368 (0.581)	0.521 (0.661)
	Median [Min, Max]	0.143 [0, 2.20]	0.255 [0, 1.44]	0.268 [0, 4.02]	0.123 [0.052, 1.86]	0.239 [0, 4.02]
PF-HxS	Mean (SD)	0.295 (0.360)	0.170 (0.243)	0.436 (0.835)	0.028 (0.048)	0.307 (0.632)
	Median [Min, Max]	0.043 [0, 0.952]	0.066 [0, 0.886]	0.081 [0, 3.51]	0 [0, 0.126]	0.066 [0, 3.51]

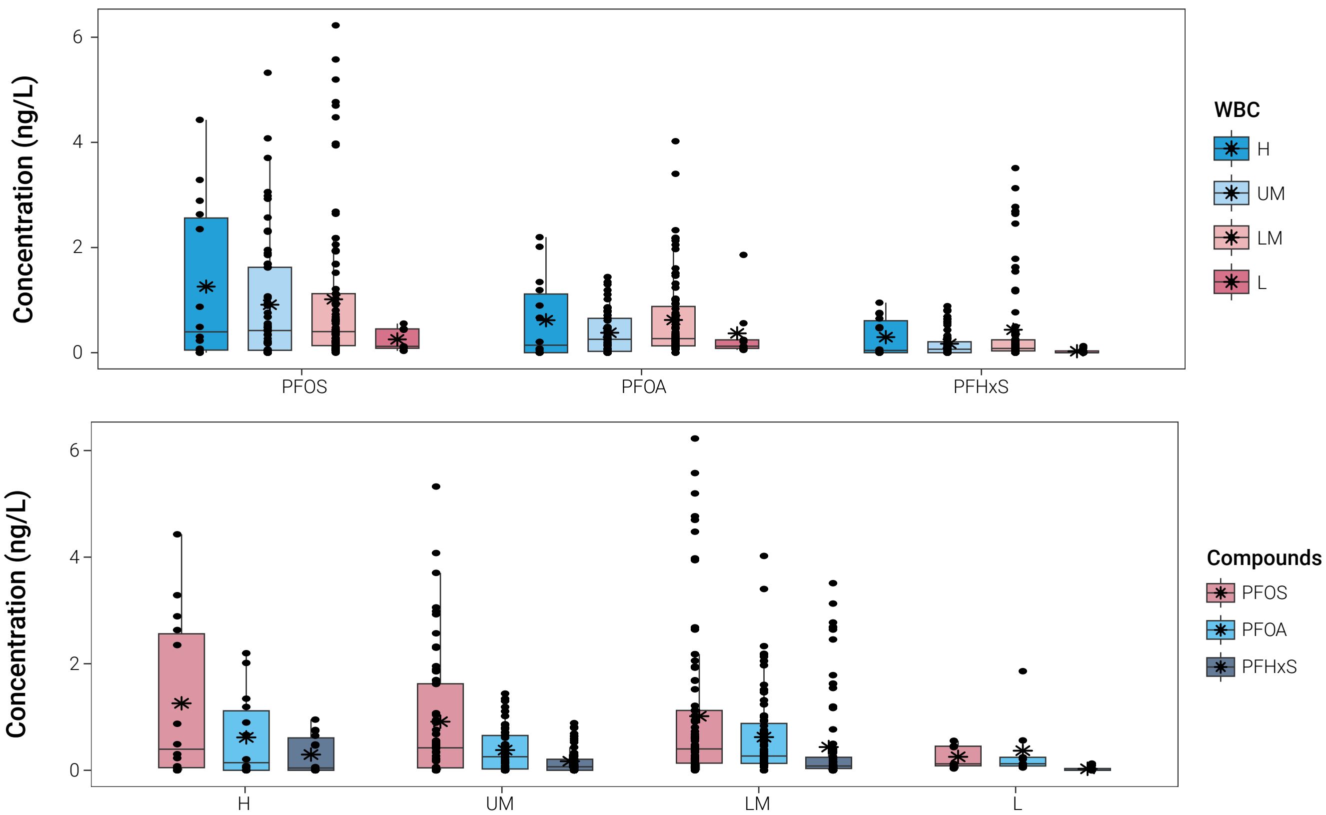

Figure 14: Unscaled boxplots for PFAS in water by WBC at global level (concentration in ng/L) (n=165)

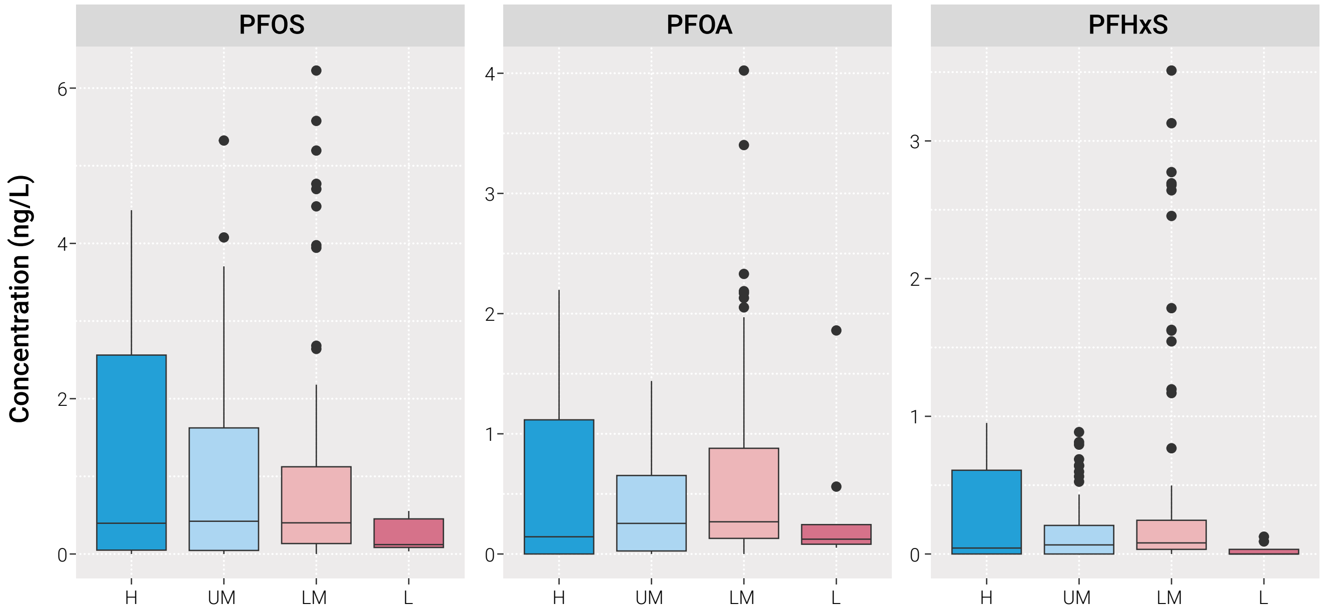

Figure 15: Scaled boxplots for PFAS in water by WBC at global level (concentration in ng/L) (n=165)

Photo: ©Environmental Management Agency / Zambia

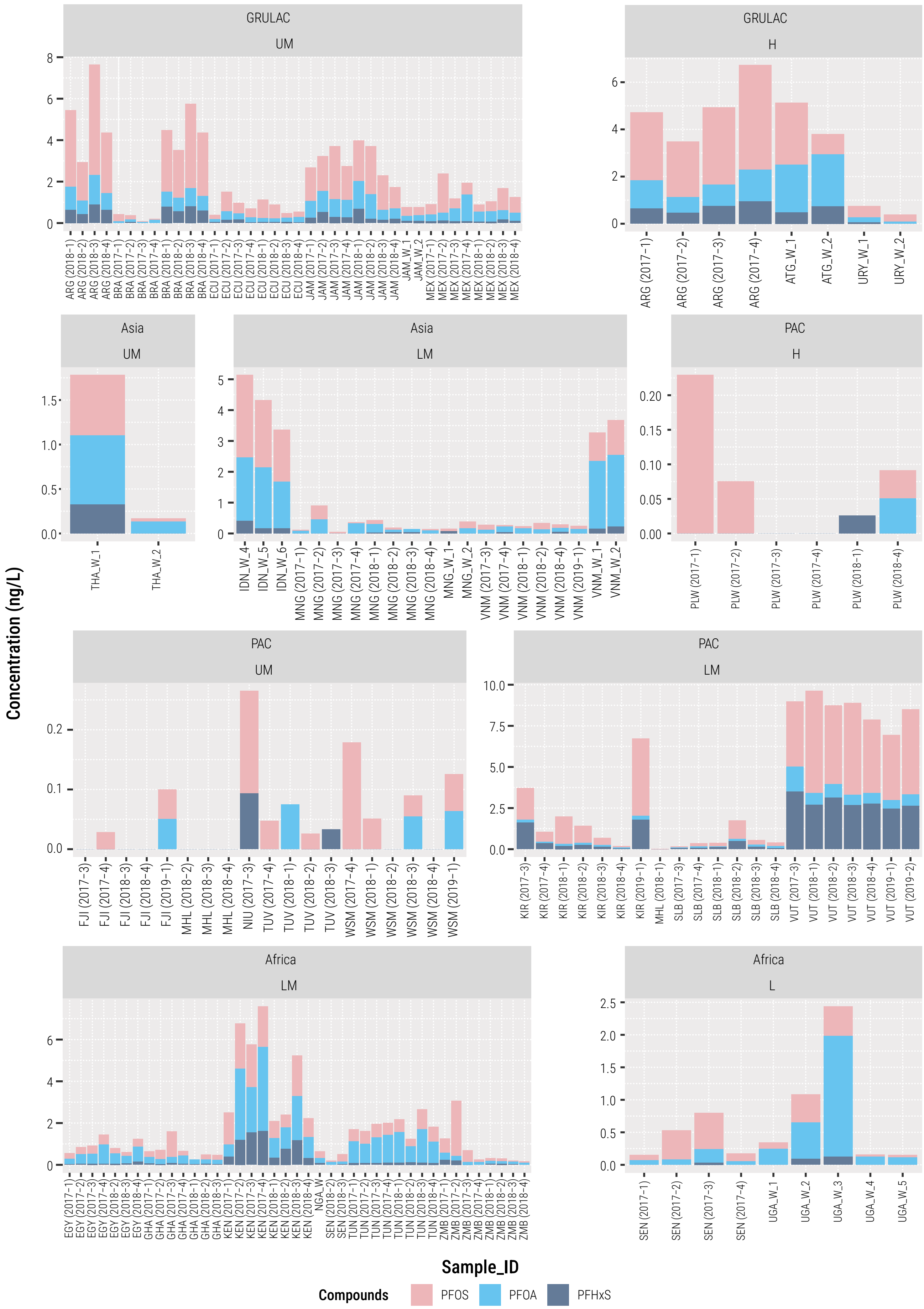

Figure 16: Stacked bars for three PFAS in water grouped by region and WBC (n=165)4

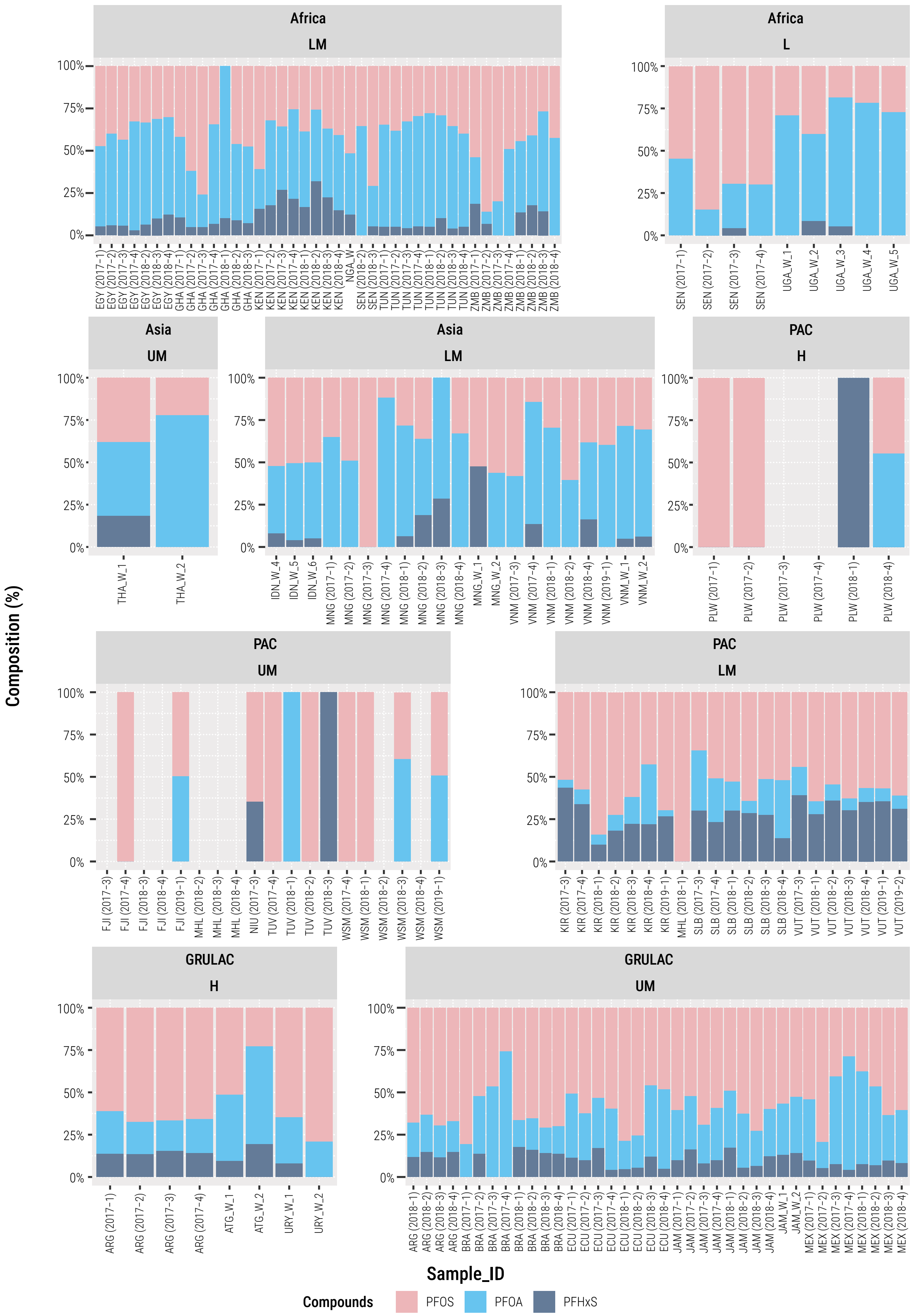

Figure 16: Stacked bars for three PFAS in water grouped by region and WBC (n=165)4

3.2. Population density

The difference is statistically significant ($p=8 \times 10^{-6}$); however, the pairwise ranking test showed that only the most densely populated group PD_330-2000 is significantly different from all other groups: with PD<25 ($p=2.6 \times 10^{-5}$), with PD_25-90 ($p=0.0006$), with PD_90-200 ($p=6.2 \times 10^{-6}$), and with PD_200-330 ($p=0.0001$) and PD_25-90 with PD_90-200 ($p=0.010$).

Table 9: Descriptive statistics for three PFAS grouped by population density (PD_Code)

PFAS	Central tendencies	PD<25 (N=46)	PD_25-90 (N=55)	PD_90-200 (N=31)	PD_200-330 (N=29)	PD_330-2000 (N=4)	Overall (N=165)
PFOS	Mean (SD)	1.52 (1.96)	0.688 (0.888)	0.869 (1.01)	0.794 (0.854)	0.018 (0.023)	0.958 (1.33)
	Median [Min, Max]	0.293 [0, 6.23]	0.452 [0, 4.08]	0.440 [0, 4.70]	0.436 [0, 2.63]	0.013 [0, 0.]	0.410 [0, 6.23]
PFOA	Mean (SD)	0.389 (0.417)	0.541 (0.796)	0.583 (0.602)	0.699 (0.754)	0.019 (0.038)	0.521 (0.661)
	Median [Min, Max]	0.147 [0, 1.51]	0.255 [0, 4.02]	0.307 [0, 2.13]	0.259 [0, 2.33]	0 [0, 0.075]	0.239 [0, 4.02]
PFHxS	Mean (SD)	0.591 (1.01)	0.177 (0.362)	0.286 (0.452)	0.165 (0.207)	0.008 (0.017)	0.307 (0.632)
	Median [Min, Max]	0.068 [0, 3.51]	0.051 [0, 1.63]	0.077 [0, 1.79]	0.102 [0, 0.740]	0 [0, 0.033]	0.066 [0, 3.51]

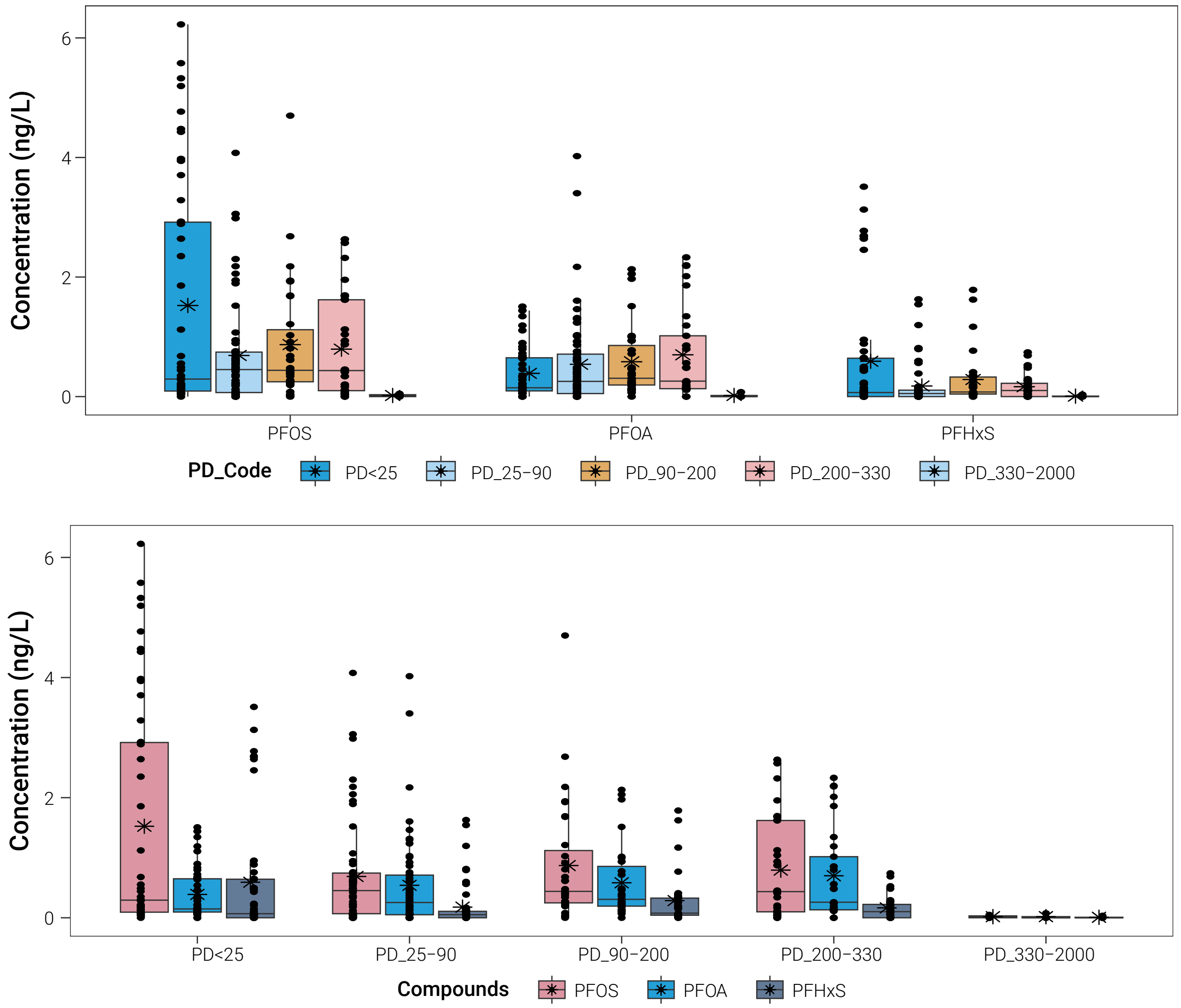

Figure 17: Unscaled boxplots for PFAS in water by PD_Code at global level (concentration in ng/L) (n=165)

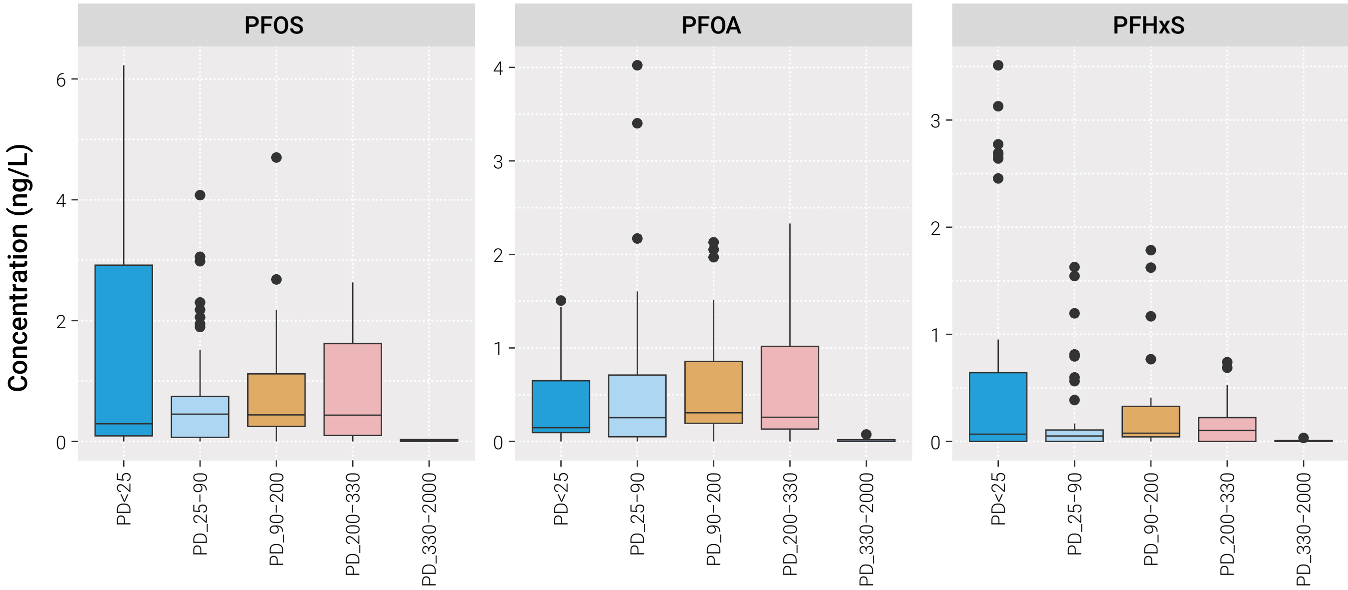

Figure 18: Scaled boxplots for PFAS in water by PD_Code at global level (concentration in ng/L) (n=165)

Photo: ©Unsplash / Nathan Cima

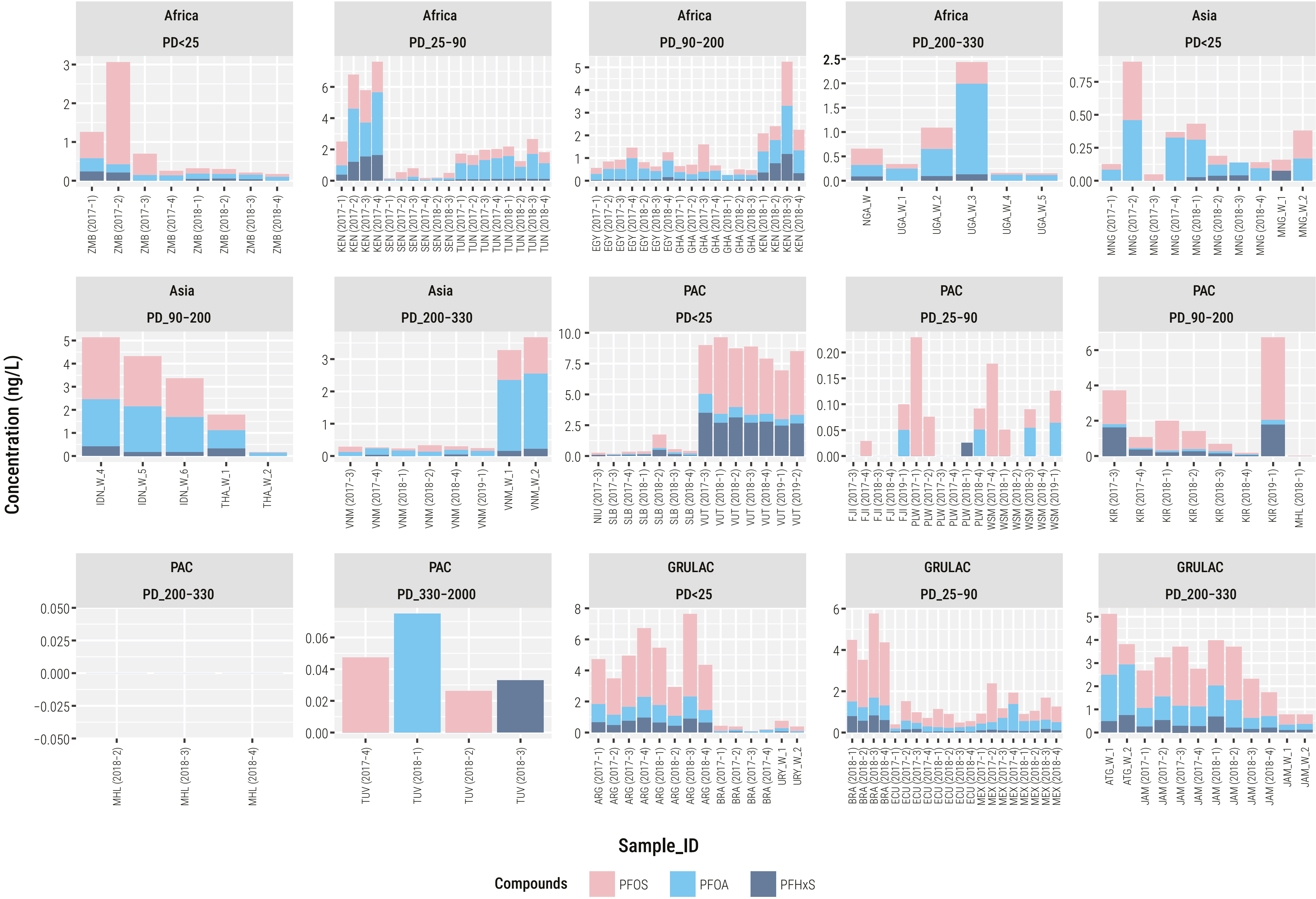

Figure 19: Stacked bars for three PFAS in water grouped by region and PD_Code (n=165)

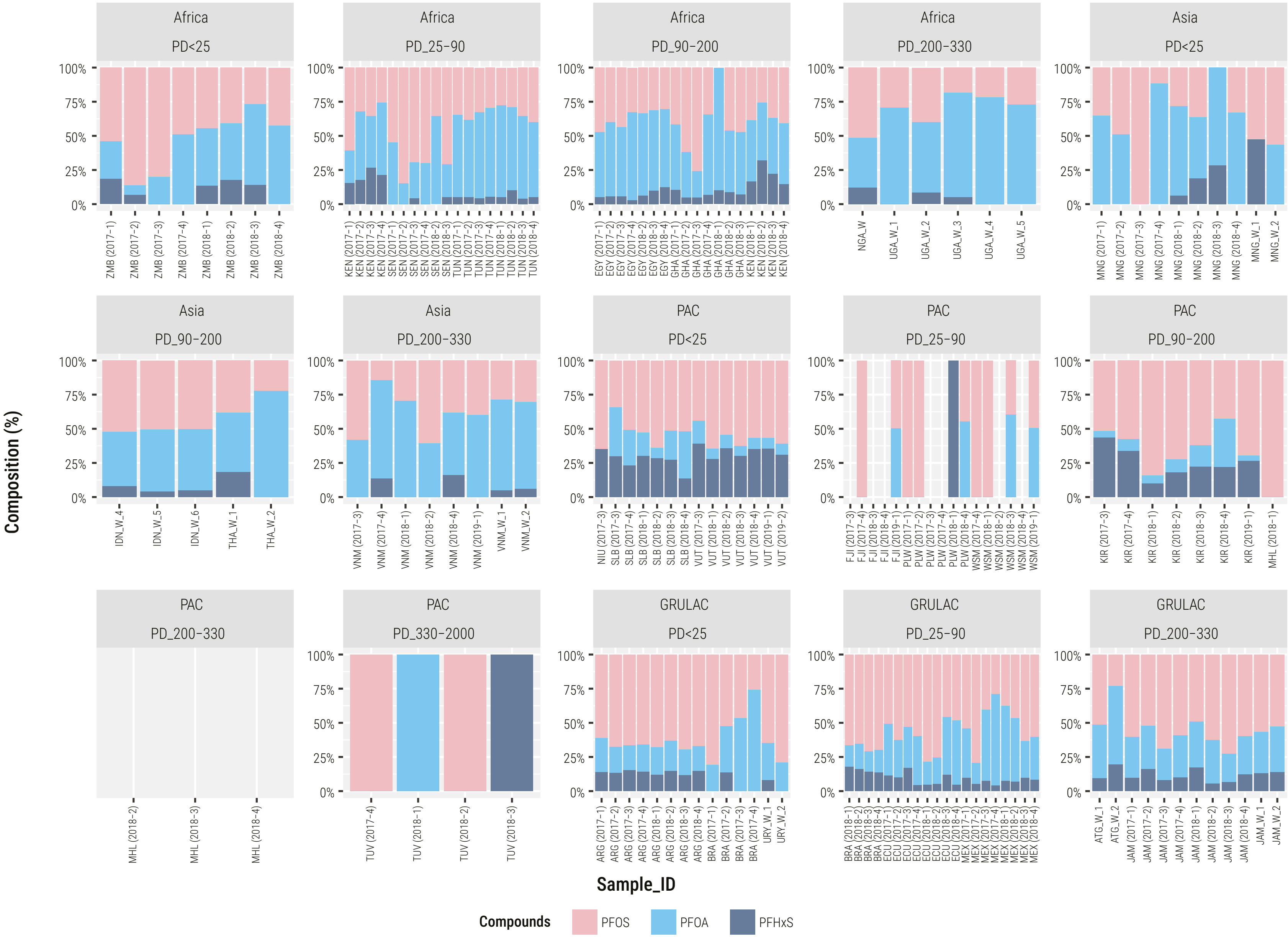

Figure 19: Stacked bars for three PFAS in water grouped by region and PD_Code (n=165)

SECTION 4

Discussion and conclusions

Photo: ©UNEP / Victor Estellano

4. DISCUSSION AND CONCLUSIONS

4.1. Correlation

The 165 samples were assessed for Pearson correlation between the variables using Euclidean distances and the Ward method, which optimizes similarities. It was found that across all samples, the two sulfonic acids, PFOS and PFHxS were highly correlated (r=0.83) but correlations for PFOA with PFOS and PFHxS were weak (r=0.46 and r=0.40) (Figure 20). All correlations were significant with p-values <<0.05.

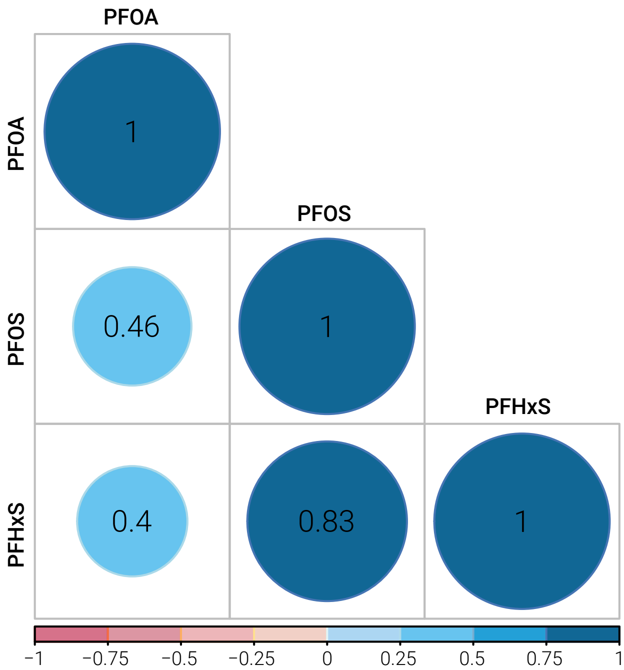

Figure 20: Correlation coefficients for the three PFAS in 165 surface water samples

4.2. Multivariate analysis

Multivariate analysis, such as principal component analysis (PCA) was applied to extract important information from large datasets (multivariate tables; here: three PFAS as variables) and express the information as a set of new variables, the principal components (Kassambara 2017). The principal components correspond to a linear combination of the original variables. The goal of the PCA is to identify directions or principal components along which variation in the data is maximal. Thus, PCA reduces the dimensionality of multivariate data to two (here; otherwise more) principal components, that can be visualized graphically, with minimal loss of information.

The location of the 165 water samples in the PCA and the contribution of the individuals to the PCAs are shown in Figure 21. The first principal component (as Dim1) is the first principal direction along which the samples show the largest variation. Dim1 represents 71.5% of the total variation among samples. The second PC explains 23% of the total variation; thus, the first two dimensions explain 94.4% of the total variation in the samples. The samples in orange colors in Figure 21 have the largest contributions; these are samples from Kenya from the year 2017 and the Vanuatu samples.

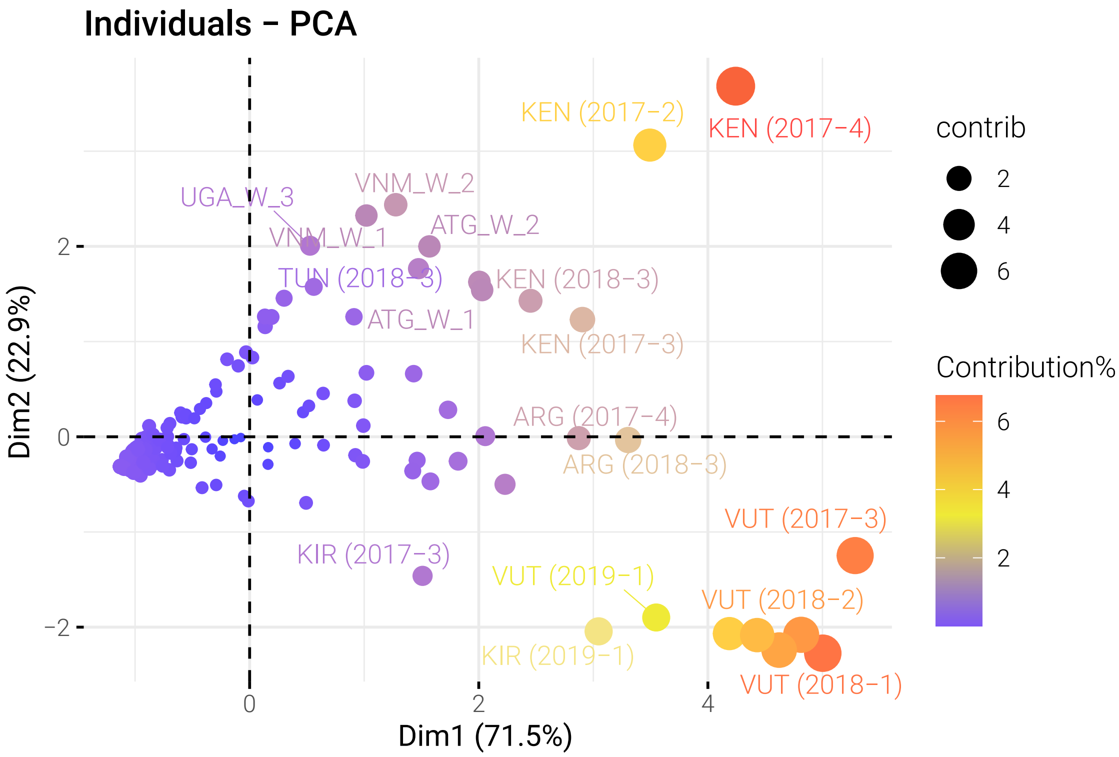

Figure 21: Location of the samples in the PCA for three PFAS and contribution of individuals

A graphical sketch for a grouping optimized to largest differences along the two first dimensions is shown in Figure 22. The PCA at left shows concentration ellipses around the samples colored according to the source: for most samples an overlap of the GMP2 and the Nat ellipse can be seen; thus, there were no differences between the GMP and the national samples. At right, the ellipses are around the four regions. It can be seen that the GRULAC samples tend to be arranged more symmetrically around the origin; thus, not having strong scales to any of the three PFAS. The PAC samples form a relatively narrow ellipse in the 3rd and 4th quartile with high values for PFOS and PFHxS but negatively correlated to PFHxS (located in the 1st quartile). African samples are more abundant in the 1st quartile.

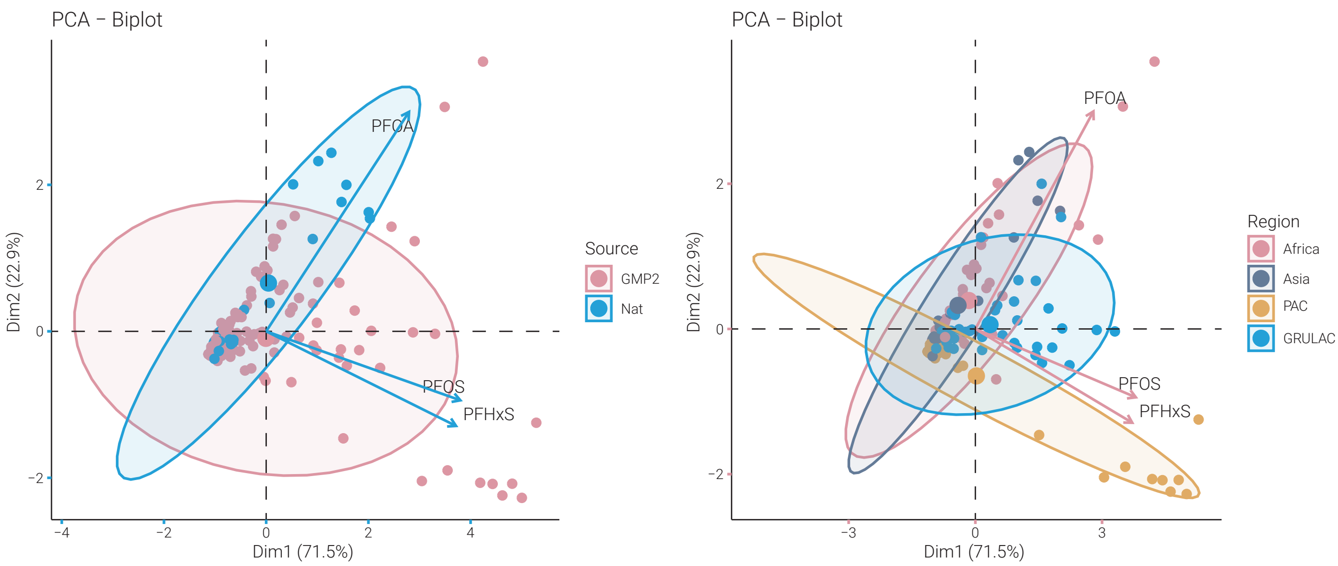

Figure 22: PFAS in water: PCA for three PFAS with ellipse around source (left) around regions (right)

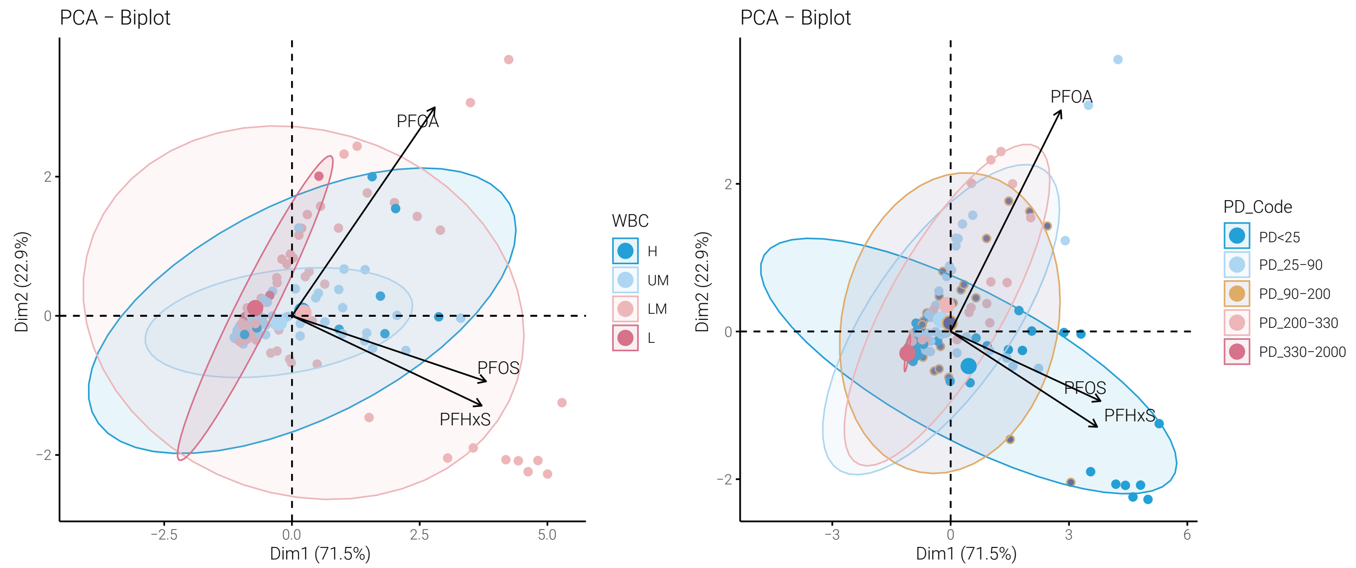

Figure 23: PCA by PD_Code at global (n=165)

With respect to the indicators of income and population density, the low-income countries (dark pink color) tend to have lower concentrations than countries with higher incomes (light blue - dark blue colors) (Figure 23). Population density does not seem to be a suitable indicator to predict PFAS concentrations in surface waters.

4.3. Recommendations

The testing of the SOPs developed for the collection of water samples (Weiss et al. 2015; UNEP 2017) and their analysis (UNEP 2015) was proven successful. The procedures were also recommended for future GMP projects (see para 48 of [UNEP 2023]).

Sustainable monitoring of POPs including close collaboration and continuity in study design is recommended to be maintained. Data generation and interpretation must remain robust and constant.

The SOPs allow for inclusion of other water samples, such as national samples in the UNEP/GEF GMP2 projects, however, for interpretation information as to the sampling objectives and site characterizations are necessary.

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