

Sectoral Report

Results of

# Air Monitoring

## on Persistent Organic Pollutants



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# ABBREVIATIONS

AAS	Active air sampler(s)/sampling
CSIC	Consejo superior de investigaciones científicas (Spanish Research Council)
dl-POPs	Dioxin-like persistent organic pollutants
DDT	Dichlorodiphenyltrichloroethane; DDD and DDE are transformation products of DDT
Drins	aldrin, dieldrin, and endrin as a sum
E&H VU	Environment and Health Department, Vrije universiteit
GC	Gas chromatograph
GEF	Global Environment Facility
GNI	Gross national income
FOSA	Perfluorooctanesulfonamide
NMeFOSA	N-Methyl Perfluorooctanesulfonamide
NEtFOSA	N-Ethyl Perfluorooctanesulfonamide
FOSE	Perfluorooctanesulfonamido Ethanol
NMeFOSE	N-Methyl Perfluorooctanesulfonamido Ethanol
NEtFOSE	N-Ethyl Perfluorooctanesulfonamido Ethanol
GMP	Global monitoring plan
GRULAC	Group of Latin American and Caribbean countries
HBCD	Hexabromocyclododecane
HCBD	Hexachlorobutadiene
HCH(s)	Hexachlorocyclohexane (s)
HRMS	High resolution mass spectrometer
LC	Liquid chromatograph
MS	Mass spectrometer
MTM	Man Technology Environment of School of Science and Technology, Örebro University, Sweden
OCPs	Organochlorine pesticides
PAS	Passive air sampler(s)
PBB153	Hexabromobiphenyl, IUPAC No. 153
PBDE	Polybrominated diphenylether(s)
PCB	Polychlorinated biphenyl(s)
PCDD	Polychlorinated dibenzodioxins
PCDF	Polychlorinated dibenzofurans
PeCBz	Pentachlorobenzene
PopDen	Population density
PFAS	Perfluoroalkane substances
PFHxS	Perfluorohexanesulfonic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PUF	polyurethane foam
TEF	Toxicity equivalency factor
TEQ	Toxic equivalent
TEQ_DF	Toxic equivalent composed of 17 PCDD and PCDF
TEQ_PCB	Toxic equivalent composed of 12 PCB
UN	United Nations
UNEP	United Nations Environment Programme
VU	Vrije Universiteit, Amsterdam, The Netherlands
WBC	World Bank classification (of income groups)
WEOG	Western European and Other Groups
WHO	World Health Organization

## Units

nanogram ng	= $10 \times 10^{-9}$ g
picogram pg	= $10 \times 10^{-12}$ g
femtogram fg	= $10 \times 10^{-15}$ g

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# SECTION 1

## Background and context





# 1. BACKGROUND AND CONTEXT

Persistent organic pollutants (POPs) are a group of chemicals that have toxic properties, resist degradation in the environment, bioaccumulate through food chains and are transported long distances through moving air masses, water currents and migratory species, within and across national boundaries (United Nations Environment Programme [UNEP] and Secretariat of the Stockholm Convention 2017). In addition to being hazardous to our ecosystem, POPs affect human populations adversely leading to various health problems. Men and women as well as adults and children differ in their physiological susceptibility to the effects of exposure to hazardous chemicals. For example, pregnancy, and lactation are periods of susceptibility for women and children where the transfer of toxic chemicals can occur (Secretariat of the Strategic Approach to International Chemicals Management 2018).

The Global Monitoring Plan (GMP) under the Stockholm Convention on POPs is a tool that collects information on POPs in the environment and in humans. The GMP is a key component of the effectiveness evaluation of the convention and provides a harmonized framework to identify changes in concentrations of POPs over time, as well as information on their regional and global environmental transport. This report summarizes and assesses the results of POP concentration in air from the four regional UNEP/ Global Environment Facility (UNEP/GEF) GMP2 projects.

The projects and the regional reports referred to are for the African region with 15 participating countries (United Nations Environment Programme [UNEP] 2015a, UNEP 2024a), Asian region with 7 countries (UNEP 2015b; UNEP 2024b), Pacific Islands (PAC) region with 9 countries (UNEP 2015c; UNEP 2024c), and the Latin American and Caribbean region (GRULAC) with 11 participating countries (UNEP 2015d; UNEP 2024d).

## 1.1. Methodology: Core matrices, analytes and chemical analytical laboratories

The global monitoring plan of the Stockholm Convention on Persistent Organic Pollutants (POPs) defines ambient air and human milk (or human blood) as core matrices rec-

ommended to be sampled and analyzed for all POPs listed in either of the Annexes A, B, or C of the Convention. Water is a core matrix only for perfluorinated substances (PFAS) but not for chlorinated or brominated POPs (UNEP 2021).

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.). The second parameter is the population density (PopDen), which is defined as population *per square kilometer* of land area (pop/km<sup>2</sup>). Population densities have been grouped into ranges (referred to as PD\_Code), which are indicated by the lower and the upper number of the range. The least densely populated countries are referred to as PD<25.

### 1.1.1. Sampling of core matrix air

For the sampling at national level, standard operational procedure (SOP) documents were developed and made available in English, Spanish and French for the core matrices air using passive samplers (PAS) (UNEP 2017) and active samplers (UNEP 2018).

#### Passive air samplers

Air monitoring was performed using passive air samplers equipped with polyurethane foam (PUF) disks. At each site, a maximum of 12 PAS were set up, in order to monitor different POPs groups, whereby each PUF from PAS with odd numbers were shipped to the expert laboratories and PUFs from even-number PAS should be analyzed in a national laboratory if capacity existed. Each PUF should be exposed for one season, *i.e.*, three months, and be analyzed for the respective POP group. For dl-POPs and toxaphene, since analysis is complex and expensive and concentrations were expected to be low, four PUFs should be combined for one annual sample. National coordinators sent the PUFs to the expert laboratory assigned (see Table 2) once *per year*; some sent individual PUFs directly after collection. In a few cases, the PUFs were sent to one laboratory, which then forwarded to the partner laboratories. To compare measurements having different exposure times or analyses of coextracted/combined PUFs, air measurement results were reported *per PUF* and three months exposure time.

## Active air samplers

Identification of sites for active air sampling was determined to take as follows:

1. Africa: Planned for Ghana and Kenya using the existing equipment from MONET Africa. According to the project document. Chemical analysis should be shared between three laboratories: E&H VU universiteit Amsterdam, MTM Research Centre Örebro University, RECETOX Masaryk University.
2. Asia: Viet Nam using the existing sampling site and equipment from the POPsEastAsia project and Mongolia: to be newly established
3. GRULAC: Brazil: new site at CETESB to be established.

The two sampling sites in Africa were withdrawn from the active project and a new site was established in Mauritius. Measurement results for Ghana and Kenya had been submitted by Recetox, Masaryk University, and are contained in section 3.

A protocol was developed for this project to be applied in Mongolia, Mauritius, and Brazil (UNEP 2018).

### 1.1.2. Chemical analysis

Generic protocols for the analysis of POPs had been developed in a previous GEF project for organochlorine pesticides (OCPs) and indicator PCB (PCB<sub>6</sub>) (UNEP 2014a), polybrominated diphenyl ether (PBDE) (UNEP 2014b), and perfluoroalkane substances (UNEP 2015e). They were used in this GMP2 project. In brief, brominated and chlorinated POPs were analyzed using GC/MS instrumentation whereby dl-POPs were detected with high resolution mass spectrometers (HRMS), *i.e.*, sector-field instruments. PFAS were analyzed using liquid chromatographs (LC) equipped with ultra-performance LC columns (UPLC) coupled to tandem mass spectrometers (MS/MS), the combination is referred to as UPLC/MSMS.

POPs were determined as the mass concentration (ng or pg) based on one PUF and three months of exposure. For active air samplers (AAS), the reporting unit is pg or fg per cubic meter (m<sup>3</sup>).

For certain groups of POPs, such as dl-POPs or toxaphene, it was recommended to combine four PUFs to an annual sample. For comparison of results, all data were normalized to one PUF and a 3-months exposure time.

For presentation and in graphics, certain POPs were combined into the groups as shown in Table 1. Dicofol, chlordecone, pentachlorophenol and related compounds, polychlorinated naphthalenes (PCNs) are not included in this report since they were not or only occasionally measured in the projects.

**Table 1:** POPs and POPs groups analyzed and reported

POP Group	POP	Compounds Analyzed
Br-POPs also BFR	PBDE *	PBDE 47, PBDE 99, PBDE 153, PBDE 154, PBDE 175; Optional: PBDE 17, PBDE 28, PBDE 100
	HBCD	a-HBCD, b-HBCD, g-HBCD
	HBB	PBB 153
	deca-BDE	PBDE 209
Cl-POPs	drins**	aldrin, dieldrin, endrin
	DDT	o,p'-DDT; p,p'-DDT; o,p'-DDD; p,p'-DDD; o,p'-DDE; p,p'-DDE
	chlordane	cis-, trans-chlordane; cis-, trans-nonachlor, oxychlordane
	heptachlor	heptachlor, heptachlorepoxi
	endosulfan	α-, β-endosulfan; and endosulfan sulfate
	toxaphene	P26, P50, P62
	HCHs**	a-HCH, b-HCH, lindane (g-HCH)
	PCB <sub>6</sub>	PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180
	SCCP	
		mirex, chlordecone, HCB, PeCBz, HCBd
dl-POPs	PCDD/PCDF***	7 PCDD and 10 PCDF congeners
	PCB****	4 non-ortho- and 8 mono-ortho-chlorinated PCB
PFAS	PFOS	L- and br-PFOS precursor compounds: FOSA, NMeFOSA, NEtFOSA, NMeFOSE, NEtFOSE
	PFOA, PFHxS	L-PFOA, L-PFHxS

\* not differentiated into tetra-/penta- and hexa-/hepta-BDE as listed in the Stockholm Convention

\*\* although listed as three entries, combined into one result

\*\*\* although listed as two entries, combined and presented as TEQ, using TEFs (van den Berg et al. 2006)

\*\*\*\* presented as TEQ, using TEFs (van den Berg et al. 2006)

Chemical analysis of all samples collected in the individual projects were shipped to and analyzed by so-called 'expert laboratories' with the assignments according to POPs group and both, the PAS and AAS matrix or region as shown in Table 2. The laboratories had successfully participated in the two rounds of the interlaboratory assessments that were implemented during the GMP2 period; for references see the UNEP reports (UNEP 2023; Fiedler, van der Veen and de Boer 2017; Fiedler, van der Veen and de Boer 2021) and relevant publications (van der Veen and de Boer 2020; de Boer, van der Veen and Fiedler 2022; Fiedler, van der Veen and de Boer 2022a; Fiedler, van der Veen and de Boer 2022b; van der Veen, Fiedler and de Boer 2023)

**Table 2:** Expert laboratories delivering results for the core matrix air

Laboratory	Matrix	Region	POPs Group
E&H VU Vrije Universiteit	Air	Africa	Organochlorine pesticides (OCPs), toxaphene, indicator PCB (PCB <sub>6</sub> ), HCB, PeCBz, HCBd, PBDE, HBCD isomers, HBB,
		Asia	
		PAC	
		GRULAC	HBCD isomers
MTM Örebro University	Air	Africa, Asia, PAC	PCDD/PCDF, dl-PCB (dl-POPs) handling
		Africa, Asia, PAC, GRULAC	PFOS, PFOA, PFHxS
CSIC	Air	GRULAC	OCPs, indicator PCB (PCB <sub>6</sub> ), HCB, PeCBz, PBDE, PCDD/PCDF, dl-PCB (dl-POPs)
		Africa, Asia, PAC	PCDD/PCDF, dl-PCB (dl-POPs) from MTM Örebro University

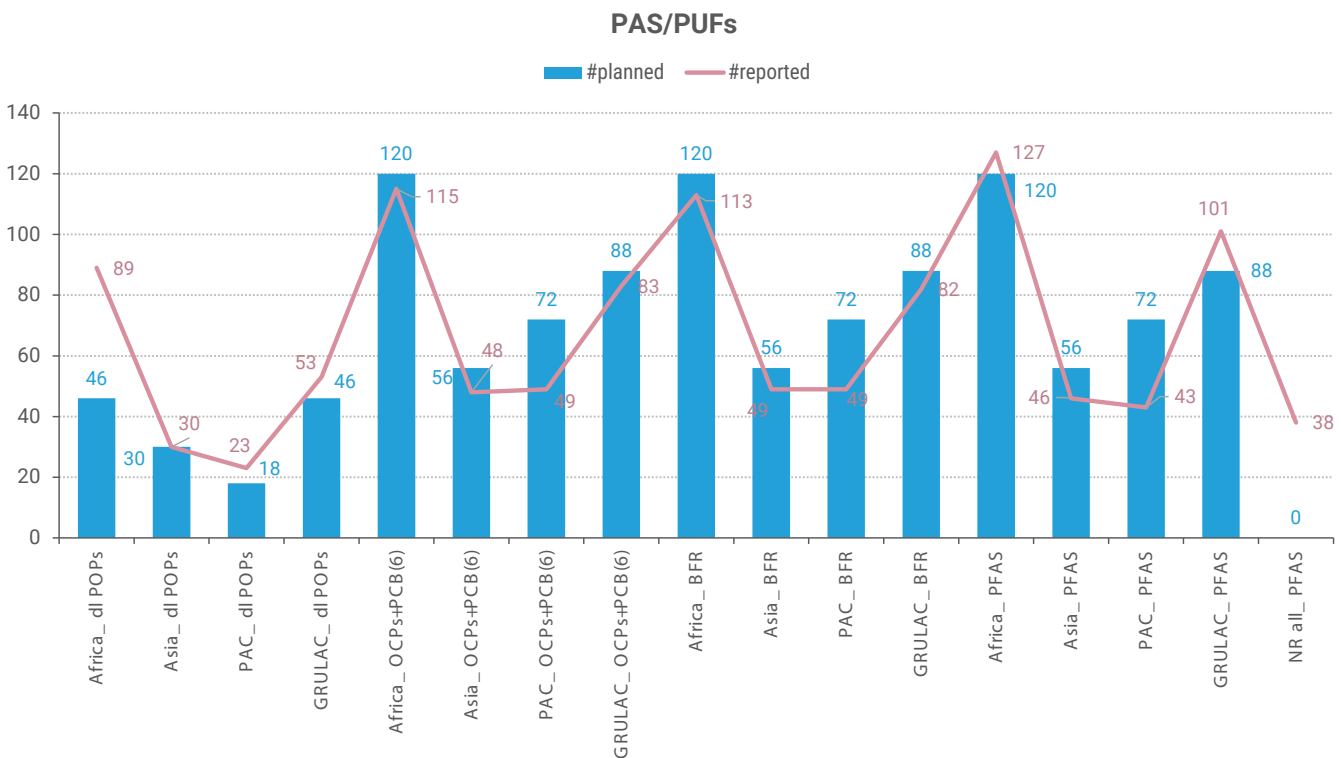
## 1.2. Samples planned vs. results reported

The following graphics show the efficiency of the project as number of samples planned for analysis (and contracted to the expert laboratories) vs. the number of samples reported for POPs concentrations. The graph is grouped according to PAS/PUF and contain the analytes planned/ reported according to region and POPs. For the overview, groups of similar POPs were grouped together. It shall be

noted that for PFAS in PAS/PUFs, there were 38 samples that did undergo the analytical steps, but it was not possible to quantify any compound. All other samples that were received have been analyzed.

The planned number of samples consists of four samples *per* year and exposures of two years. Thus, the base number for samples is eight *per* country for OCPs+PCB<sub>6</sub>, PBDE+PBB153+HBCD, and PFAS in PAS/PUFs as well as PFAS in water. For dl-POPs the base number is one annual sample, which adds up to two samples *per* country for PAS/PUFs. In addition, four countries in GRULAC (Brazil, Barbados, Mexico, Uruguay), two countries in Asia (Mongolia, Viet Nam), and two countries in Africa (Egypt, Tunisia) planned to analyze quarterly samples, thus, eight samples for two years. In addition, due to the differentiation of the expert laboratories, there were eight samples for each of the GRULAC countries.

In the projects, there were a total of 42. For PAS/PUFs, the target numbers were exceeded for dl-POPs and PFAS; however, not in Asia and PAC. For OCPs+PCB<sub>6</sub> and brominated POPs, the planned numbers could not be achieved with major gaps in Africa and PAC (Figure 1).



**Figure 1:** PAS/PUF samples planned vs. analyzed/reported

# SECTION 2

**Air monitoring using passive air samplers with polyurethane foam disks (PAS/PUF)**



## 2. AIR MONITORING USING PASSIVE AIR SAMPLERS WITH POLYURETHANE FOAM DISKS (PAS/PUF)

In this chapter 2, the results for brominated, chlorinated and fluorinated POPs analyzed in the PAS/PUFs, are summarized with an emphasis on the region. Information relevant to the lifestyle factors are presented in the summarizing tables as follows: Table 3 for chlorinated POPs, Table 5 for dl-POPs, Table 7 for brominated POPs, and Table 9 for PFAS. The assessment itself and visualization are contained in chapter 4.

For presentation and assessment, chlorinated POPs include all POPs listed in Annex A or B having a chlorine atom in the molecule, except PCDD, PCDF, and dl-PCB. Not included are the POPs that were not addressed in the air monitoring subprojects, such as short-chain chlorinated paraffins (SCCP), pentachlorophenol (PCP), its salts, and esters, dicofol or polychlorinated naphthalenes (PCN).

For endosulfan, only the  $\alpha$ -isomer is included since not all samples contained the  $\beta$ -isomer or the sulfate. For PFOA and PFHxS, only the linear isomer was analyzed (L-PFOA, L-PFHxS).

In this assessment, the following individually listed POPs were grouped as follows:

- Aldrin, dieldrin, and endrin as 'drins'
- $\alpha$ -HCH,  $\beta$ -HCH, and lindane were grouped as 'HCHs',
- PCDD and PCDF (values shown as TEQs) combined as TEQ\_DF.

Further, no differentiation is made for POPs that are listed as one entry but consisted of more than one recommended isomer or congeners as shown in Table 1.

### 2.1. Chlorinated POPs

The terms, chlorinated POPs refer to the organochlorine pesticides (OCPs) and the industrial chemicals, PCB<sub>s</sub>, HCB, and PeCBz. In total, results were available from 294 PAS/PUF samples. For toxaphene, no quarterly samples were available from GRULAC, but 21 annual samples (combination of 4 PUFs into one annual result); thus, 232 toxaphene results were assessed. Further, HCBd was not analyzed in GRULAC; thus, reducing the number of these results to 211 in total. The distribution of the samples to the project regions, sampling year, income group, and population density together with the respective percentages are shown in Table 3. Africa contributed with the largest share of samples (36%) and that best coverage across all samples was for 2018 (52%). It can also be seen that most samples were from countries belonging to the middle-income groups: 32% of results were from upper middle countries (UM) and 38% were from lower-middle (LM). The two extremes had almost the same percentage with 16% in the high (H) and 14% in the low (L) income groups. All countries from GRULAC belonged to either H or UM; there were no LM or L countries in this project. On the other hand, the African project did not have any high-income country (note: MUS became H only in 2019); in the Asia project, all countries were either UM or LM; PAC did not have any L country.

The countries in the different project varied highly as to population density: overall, sampling sites in countries with less than 90 inhabitants *per km*<sup>2</sup> dominated and covered 60% of all sampling sites. More specifically, PD<25 had 29% of the samples and PD\_25-90 had 30% of the samples. Countries in GRULAC were low densely populated (43% of the results were from sites assigned PD<25).





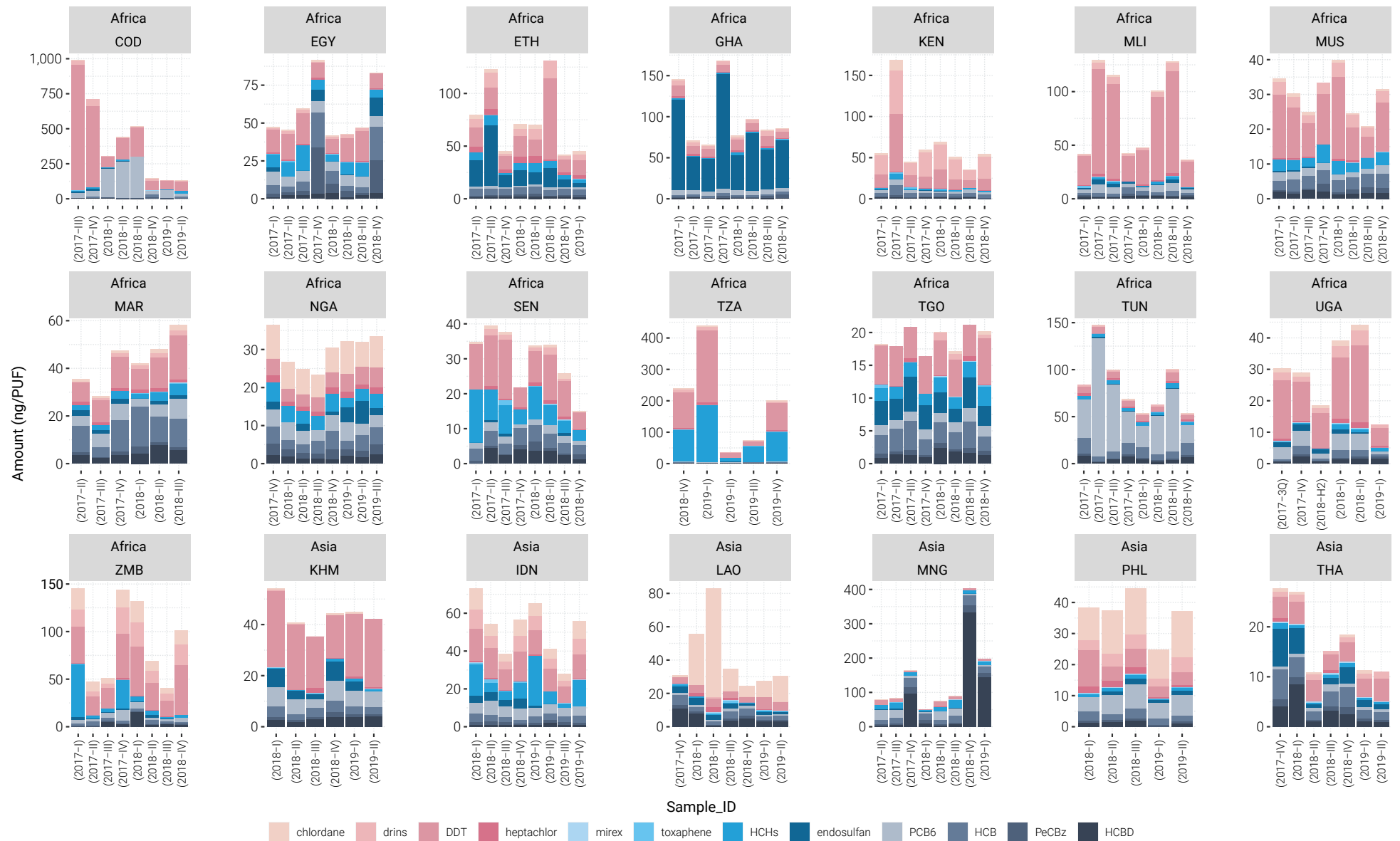
**Table 3:** Overview on number of PUFs analyzed for chlorinated POPs

Region	Africa (N=113)	Asia (N=49)	PAC (N=49)	GRULAC (N=104)	Overall (N=315)
	113 (35.9%)	49 (15.6%)	49 (15.6%)	104 (33.0%)	315 (100%)
Year					
2017	47 (41.6%)	8 (16.3%)	11 (22.4%)	49 (47.1%)	115 (36.5%)
2018	55 (48.7%)	27 (55.1%)	28 (57.1%)	53 (51.0%)	163 (51.7%)
2019	11 (9.7%)	14 (28.6%)	10 (20.4%)	2 (1.9%)	37 (11.7%)
WBC					
H	0 (0%)	0 (0%)	6 (12.2%)	44 (42.3%)	50 (15.9%)
UM	8 (7.1%)	11 (22.4%)	23 (46.9%)	60 (57.7%)	102 (32.4%)
LM	62 (54.9%)	38 (77.6%)	20 (40.8%)	0 (0%)	120 (38.1%)
L	43 (38.1%)	0 (0%)	0 (0%)	0 (0%)	43 (13.7%)
PD_Code					
PD<25	16 (14.2%)	8 (16.3%)	21 (42.9%)	45 (43.3%)	90 (28.6%)
PD_25-90	43 (38.1%)	7 (14.3%)	15 (30.6%)	30 (28.8%)	95 (30.2%)
PD_90-200	32 (28.3%)	21 (42.9%)	7 (14.3%)	0 (0%)	60 (19.0%)
PD_200-330	14 (12.4%)	8 (16.3%)	2 (4.1%)	19 (18.3%)	43 (13.7%)
PD_330-2000	8 (7.1%)	5 (10.2%)	4 (8.2%)	10 (9.6%)	27 (8.6%)

The amounts of the OCPs and industrial POPs measured in the individual samples in each country are displayed as stacked bars in Figure 2. The countries are grouped by project region, starting with Africa. It can be seen that in many countries, especially in Africa but also in the Solomon Islands and Peru, DDT is the dominating POP. PCB<sub>6</sub> is dominating in Tunisia, Samoa, Vanuatu, and in GRULAC countries such as Argentina and Peru. Other POPs, such as HCB are very abundant in Mongolia, Viet Nam Egypt, Tunisia, Argentina, and Peru, whereas PeCBz was abundant GRULAC, e.g., in Antigua and Barbuda, Argentina, Ecuador, and Uruguay. HCBd had a high abundance and

high amounts in Mongolia whereas in Kiribati and the Marshall Islands, abundance was high, but the amounts were low. Exceptional since detected only once is endosulfan in Ghana; some presence was also found in Ethiopia.

The descriptive statistics for chlorinated POPs in each region and across all samples are provided in Table 4. HCBd was not analyzed in GRULAC; indicated as NA in Table 4. Toxaphene was analyzed as annual samples in GRULAC but as quarterly samples in the other three project regions. All results were adjusted to one PUF and three months exposure time



**Figure 2:** PAS/PUFs: OCPs+industrial POPs measured in each sample. Amounts in ng/PUF (N=294 for most OCPs, N=323 for toxaphene, N=211 for HCBd)

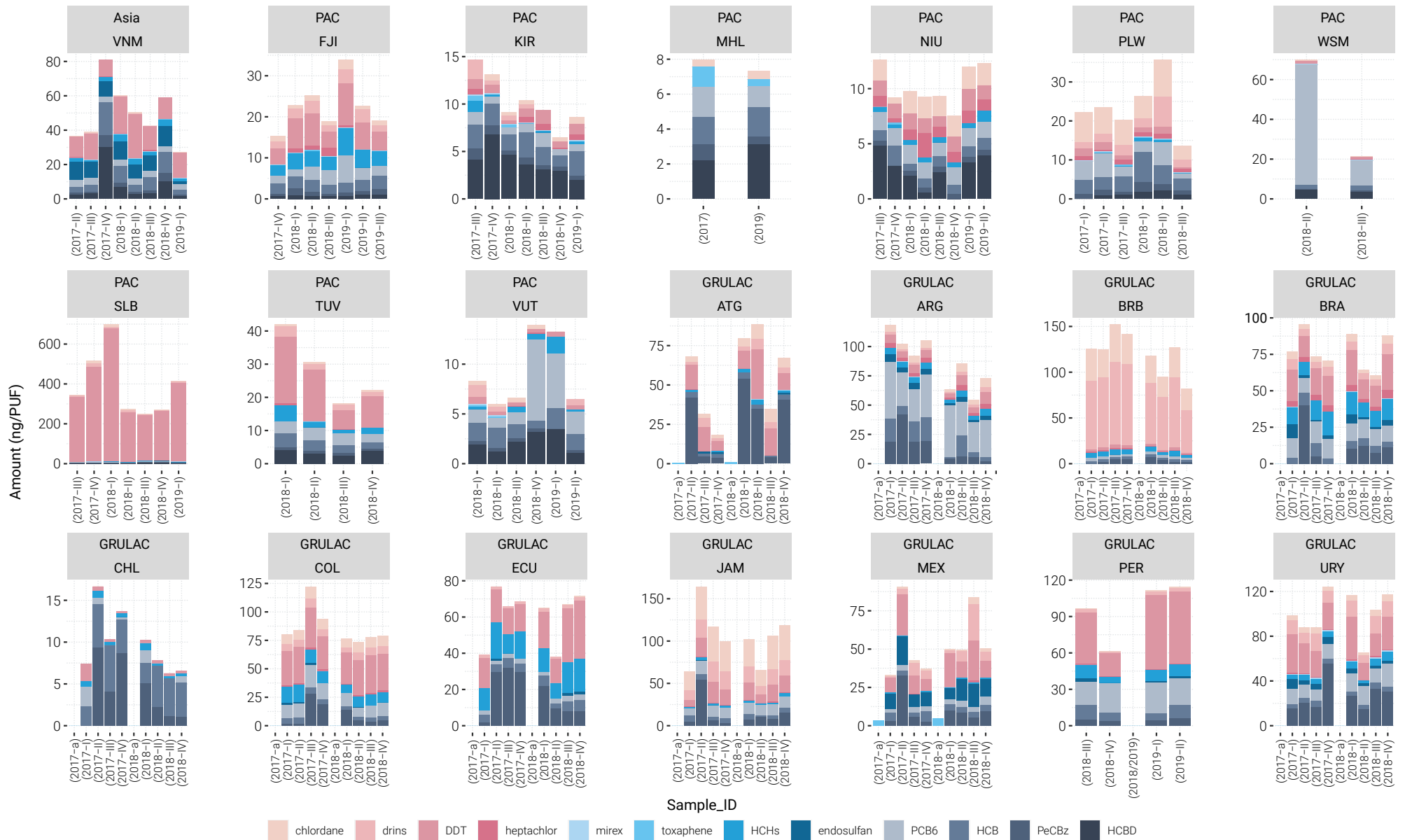


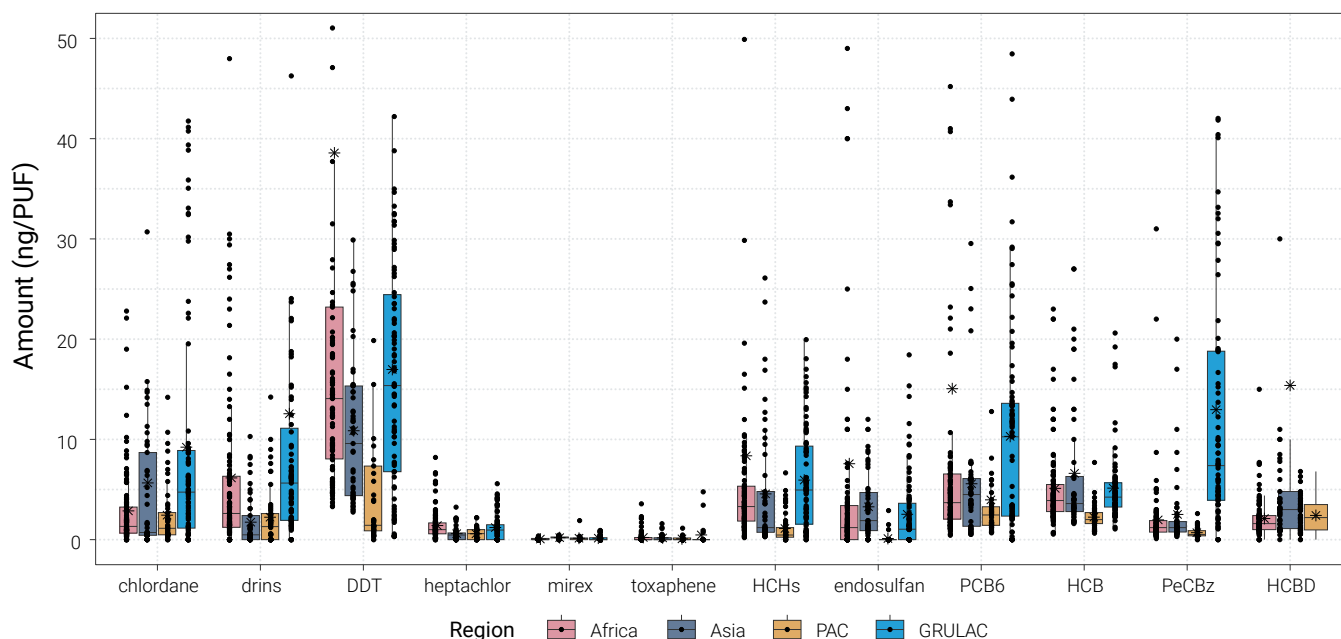
Figure 2: Continued

The visual representation of the chlorinated POPs in air (PAS/PUFs) as boxplots colored according to the region is shown in Figure 3. Detailed graphics by OCPs including countries are shown in Figure 4. Overall, it is evident that DDT was the dominating POP: Across all regions, the absolute maximum value was found in the Democratic Republic of the Congo with 895 ng/PUF (Africa) followed by the Solomon Islands with 667 ng/PUF (PAC). The mean and median values for Solomon Islands (370 ng/PUF and 325 ng/PUF) were higher than for Democratic Republic of the Con-

go (240 ng/PUF and 79 ng/PUF). Further, the results show that chlordane was dominating in GRULAC and some Asian countries. Drins had the highest median value in Barbados whereas heptachlor peaked in some African and GRULAC countries. Endosulfan was mainly found in Ghana. Highest PCB<sub>6</sub> values were found in D.R of the Congo. HCB was scattered in certain countries and found in all regions except PAC. Pentachlorobenzene (PeCBz) was most abundant in GRULAC. HCHs peaked in United Republic of Tanzania.

**Table 4:** PAS/PUFs chlorinated POPs: descriptive statistics by region (amounts in ng/PUF)

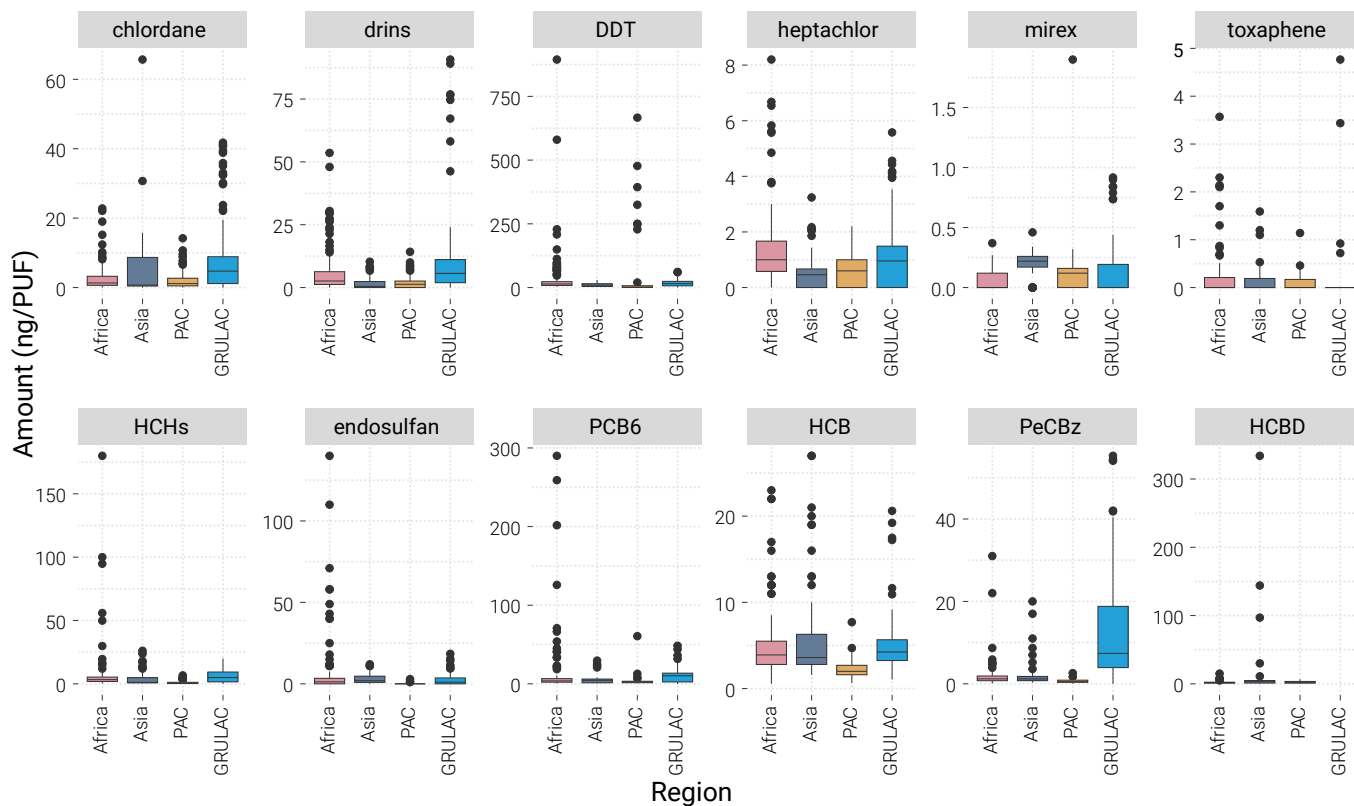
	Central tendencies	Africa (N=113)	Asia (N=49)	PAC (N=49)	GRULAC (N=104)	Overall (N=315)
<b>Chlordane</b>	Mean (SD)	2.87 (4.12)	5.66 (10.8)	2.44 (3.18)	9.22 (12.2)	5.06 (8.75)
	Median [Min, Max]	1.32 [0, 22.8]	0.710 [0, 65.7]	1.13 [0, 14.2]	4.74 [0, 41.8]	1.74 [0, 65.7]
<b>Sum of drins (Aldrin, Endrin and Dieldrin)</b>	Mean (SD)	6.16 (9.46)	1.74 (2.66)	2.24 (3.16)	12.6 (21.0)	6.57 (13.3)
	Median [Min, Max]	2.61 [0, 53.6]	0.480 [0, 10.3]	1.30 [0, 14.2]	5.64 [0, 90.7]	2.20 [0, 90.7]
<b>DDT</b>	Mean (SD)	38.6 (103)	10.9 (7.33)	55.4 (141)	17.0 (12.9)	30.7 (87.5)
	Median [Min, Max]	14.1 [3.29, 895]	9.59 [2.75, 29.9]	1.43 [0, 667]	15.4 [0.303, 61.1]	11.8 [0, 895]
<b>Sum of heptachlor</b>	Mean (SD)	1.40 (1.48)	0.596 (0.728)	0.584 (0.553)	1.21 (1.38)	1.08 (1.28)
	Median [Min, Max]	1.00 [0, 8.20]	0.460 [0, 3.24]	0.600 [0, 2.20]	0.957 [0, 5.58]	0.775 [0, 8.20]
<b>mirex</b>	Mean (SD)	0.0583 (0.0743)	0.199 (0.100)	0.138 (0.274)	0.146 (0.244)	0.120 (0.188)
	Median [Min, Max]	0 [0, 0.370]	0.220 [0, 0.460]	0.120 [0, 1.90]	0 [0, 0.917]	0.100 [0, 1.90]
<b>toxaphene</b>	Mean (SD)	0.218 (0.528)	0.173 (0.329)	0.0796 (0.190)	0.460 (1.25)	0.201 (0.557)
	Median [Min, Max]	0 [0, 3.57]	0 [0, 1.59]	0 [0, 1.14]	0 [0, 4.77]	0 [0, 4.77]
<b>Sum of HCHs</b>	Mean (SD)	8.36 (21.8)	4.56 (6.29)	1.11 (1.52)	5.94 (5.12)	5.84 (14.2)
	Median [Min, Max]	3.30 [0.197, 180]	1.20 [0.290, 26.1]	0.460 [0, 6.66]	4.95 [0, 20.0]	2.79 [0, 180]
<b>Sum fo endo-sulfan</b>	Mean (SD)	7.57 (20.4)	3.27 (3.39)	0.110 (0.480)	2.53 (3.86)	4.19 (13.2)
	Median [Min, Max]	1.20 [0, 140]	1.90 [0, 12.0]	0 [0, 2.90]	1.04 [0, 18.4]	0.925 [0, 140]
<b>PCB6</b>	Mean (SD)	15.1 (42.8)	5.57 (6.22)	3.97 (8.55)	10.3 (10.4)	10.3 (27.7)
	Median [Min, Max]	3.69 [0.440, 290]	4.50 [0.520, 29.5]	2.46 [0.680, 60.6]	10.3 [0, 48.5]	3.49 [0, 290]
<b>HCB</b>	Mean (SD)	5.11 (4.19)	6.61 (6.78)	2.24 (1.21)	5.14 (3.60)	4.89 (4.45)
	Median [Min, Max]	3.90 [0.550, 23.0]	3.60 [1.60, 27.0]	2.00 [0.640, 7.70]	4.24 [1.06, 20.6]	3.59 [0.550, 27.0]
<b>PeCBz</b>	Mean (SD)	1.97 (3.60)	2.51 (3.94)	0.695 (0.470)	13.0 (13.8)	4.95 (9.31)
	Median [Min, Max]	1.20 [0.100, 31.0]	1.20 [0.310, 20.0]	0.520 [0, 2.60]	7.38 [0, 55.3]	1.37 [0, 55.3]
<b>HCBd</b>	Mean (SD)	2.11 (1.93)	15.4 (52.4)	2.41 (1.65)	NA (NA)	5.26 (25.7)
	Median [Min, Max]	1.60 [0, 15.0]	3.00 [0, 334]	2.20 [0, 6.80]	NA [NA, NA]	2.00 [0, 334]



**Figure 3:** PAS/PUFs: Box plots for OCPs colored by region (unscaled boxplots, y-axis zoomed to 50 ng/PUF); values normalized to 1 PUF and 3 months exposure (N=294 for most OCPs, N=323 for toxaphene, N=211 for HCBd)

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

The whiskers represent the minimum and maximum amounts 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 asterisk represents the mean value. The dots outside the whiskers are outliers, which were defined as all amounts greater or smaller the interquartile range multiplied by 1.5.



**Figure 4:** PAS/PUFs: Scaled box plots by chlorinated POP colored for region; values normalized to 1 PUF and 3 months exposure (N=294 for most OCPs, N=323 for toxaphene, N=211 for HCBd)

The occurrence of the OCPs in each region is shown in the Annex, Figure S 1.

Figure 5 details the CI-POPs in each country as boxplots. In many countries, such as Mali, Mauritius, Senegal, Uganda, Cambodia, Solomon Islands, Tuvalu, Colombia or Peru, DDTs are the predominant POP in the air although at different scales. Other POPs had the highest median values as follows:

- Chlordane in Nigeria and the Philippines,
- Endosulfan in Ghana,
- PCB<sub>6</sub> in Tunisia, Samoa, and Argentina
- PeCBz in Antigua and Barbuda and Ecuador but also in Chile and Uruguay

- HCHs were predominant in U.R. of Tanzania but also in Brazil and Ecuador

- HCBd was dominant in Mongolia, Kiribati, Marshall Islands, Niue but also in Thailand and Vanuatu

Figure 6 shows scaled box plots for each country by POPs. On this comparative basis and with coloring the region, POPs countries and regions with high or very varying amounts can be easily identified. Whereas often, one country is dominating in one region, in GRULAC, the situation is much more complex and often more than one country has high values. Especially striking is the result for PeCBz where uniformly in almost all GRULAC countries the values are higher than for any other country in the other regions.



Photo: © Flickr / US Government



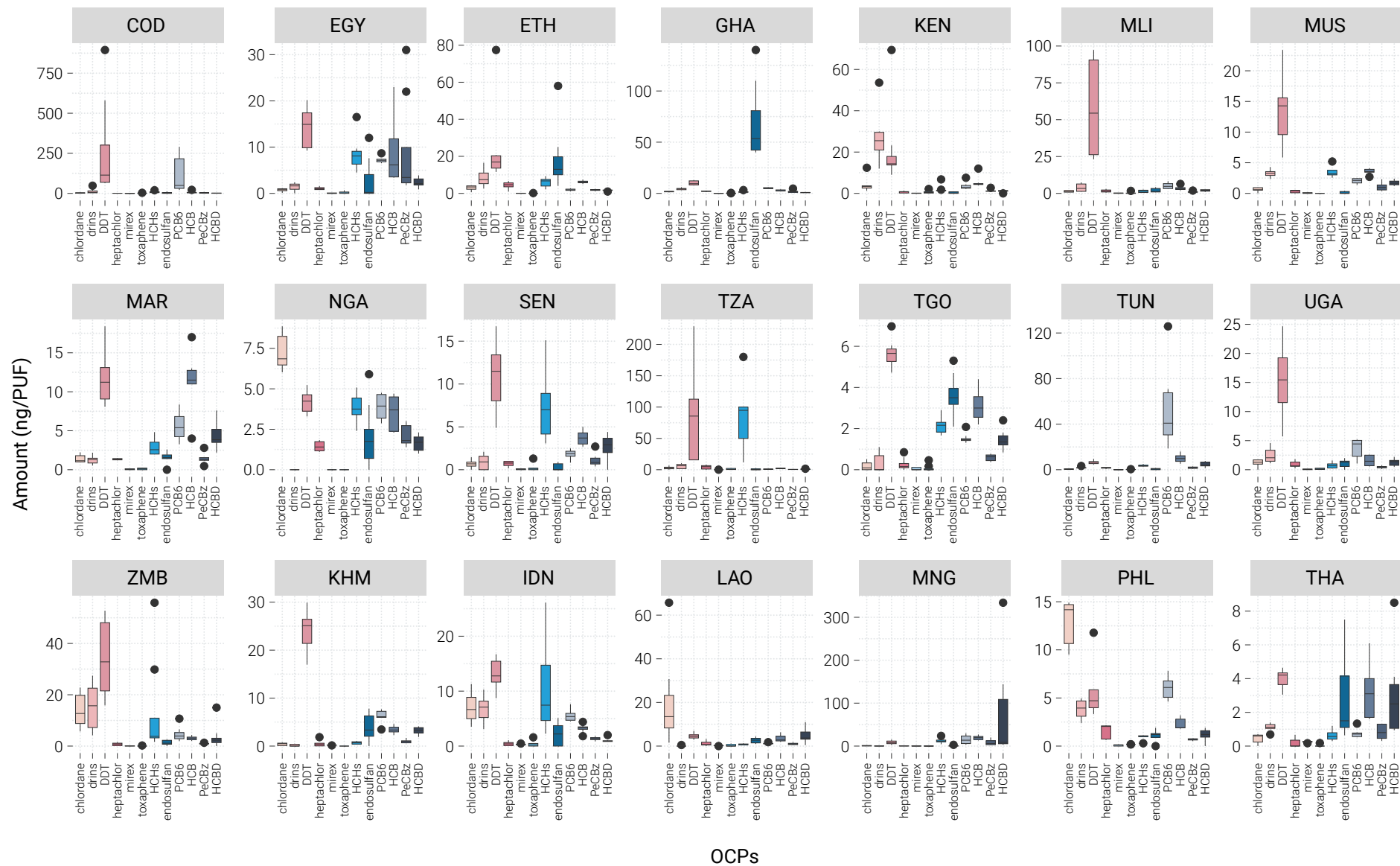


Figure 5: PAS/PUFs: Scaled box plots by country for CI-POPs; values normalized to 1 PUF and 3 months exposure (N=294 for most OCPs, N=323 for toxaphene, N=211 for HCBd)

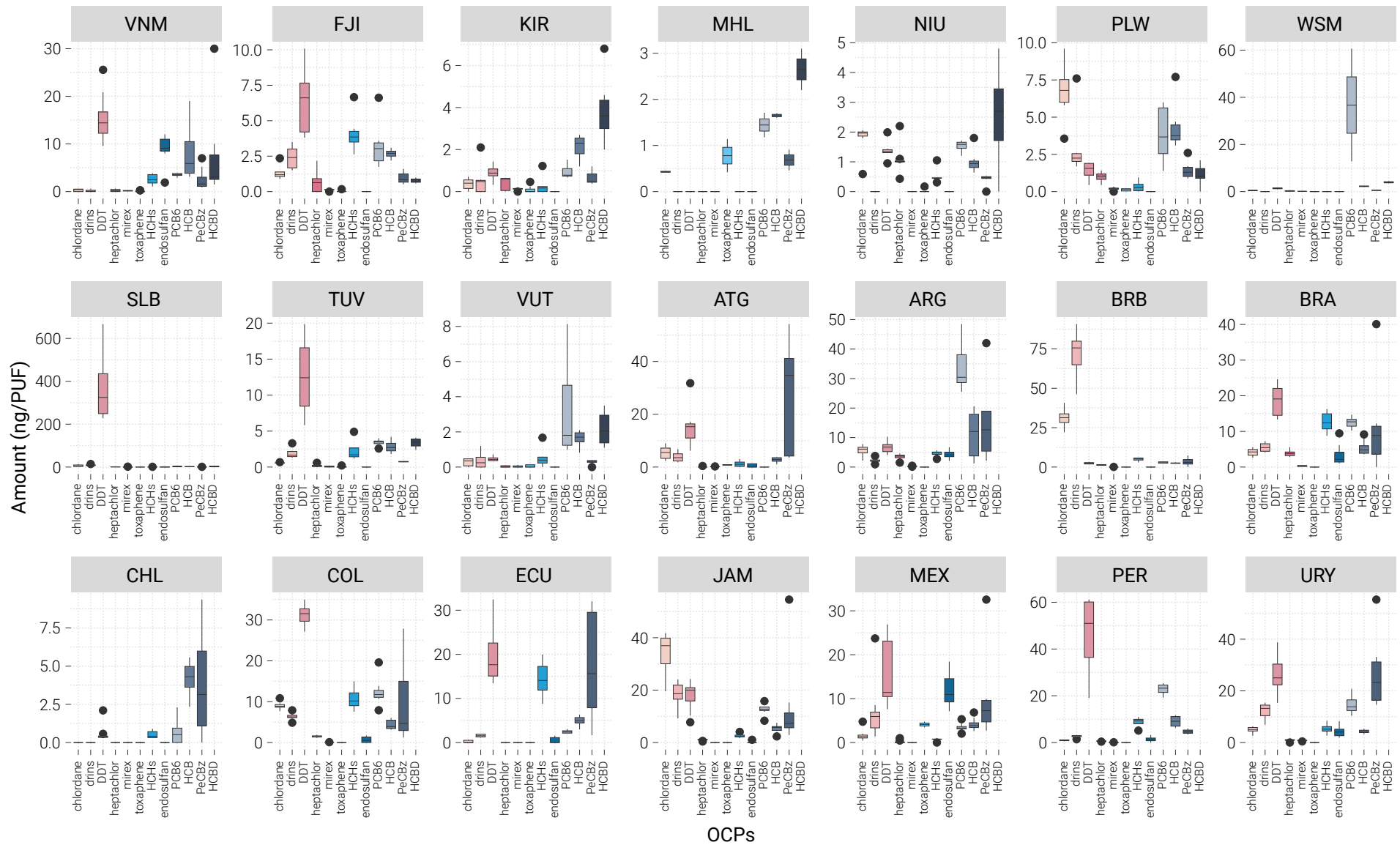
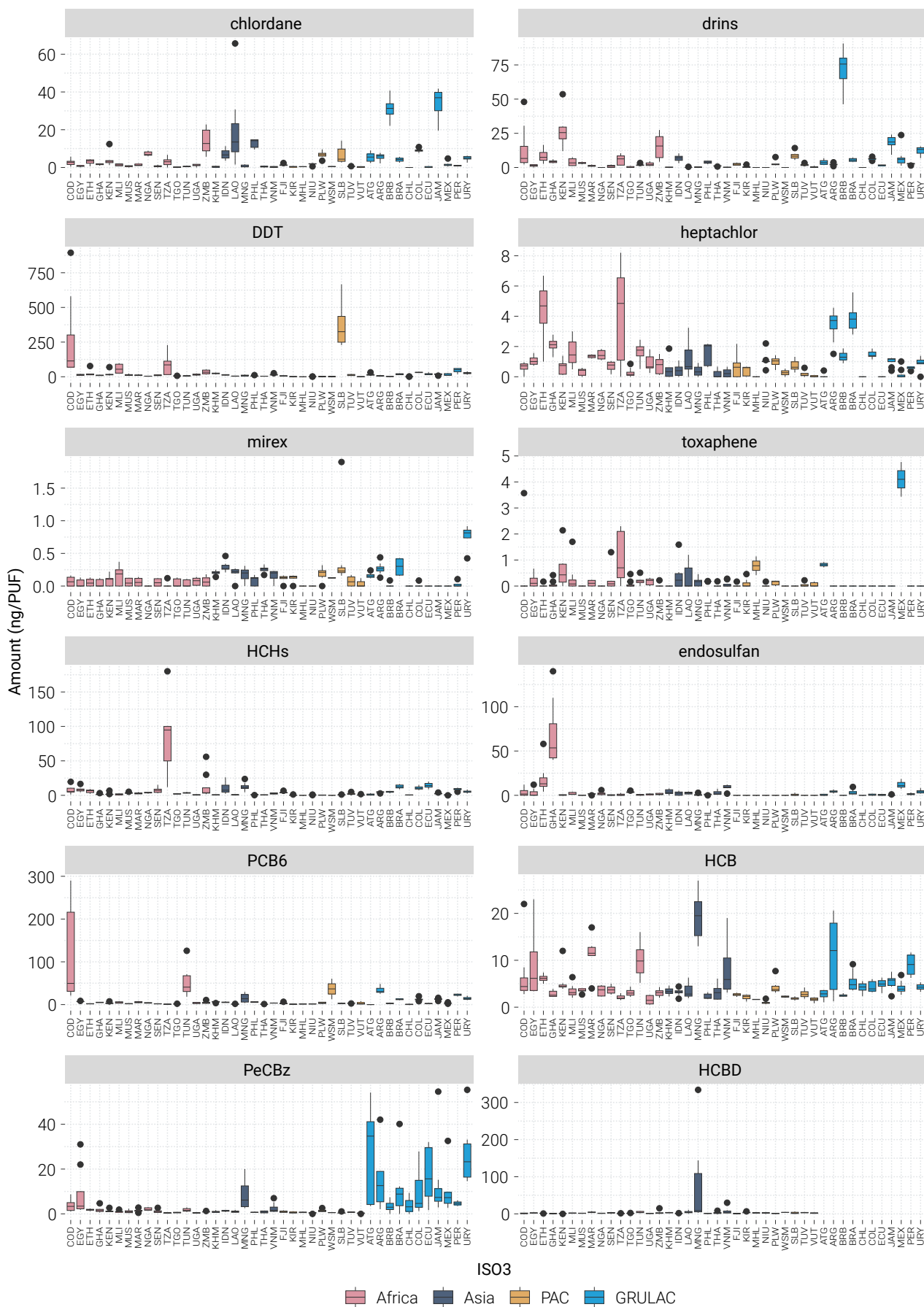
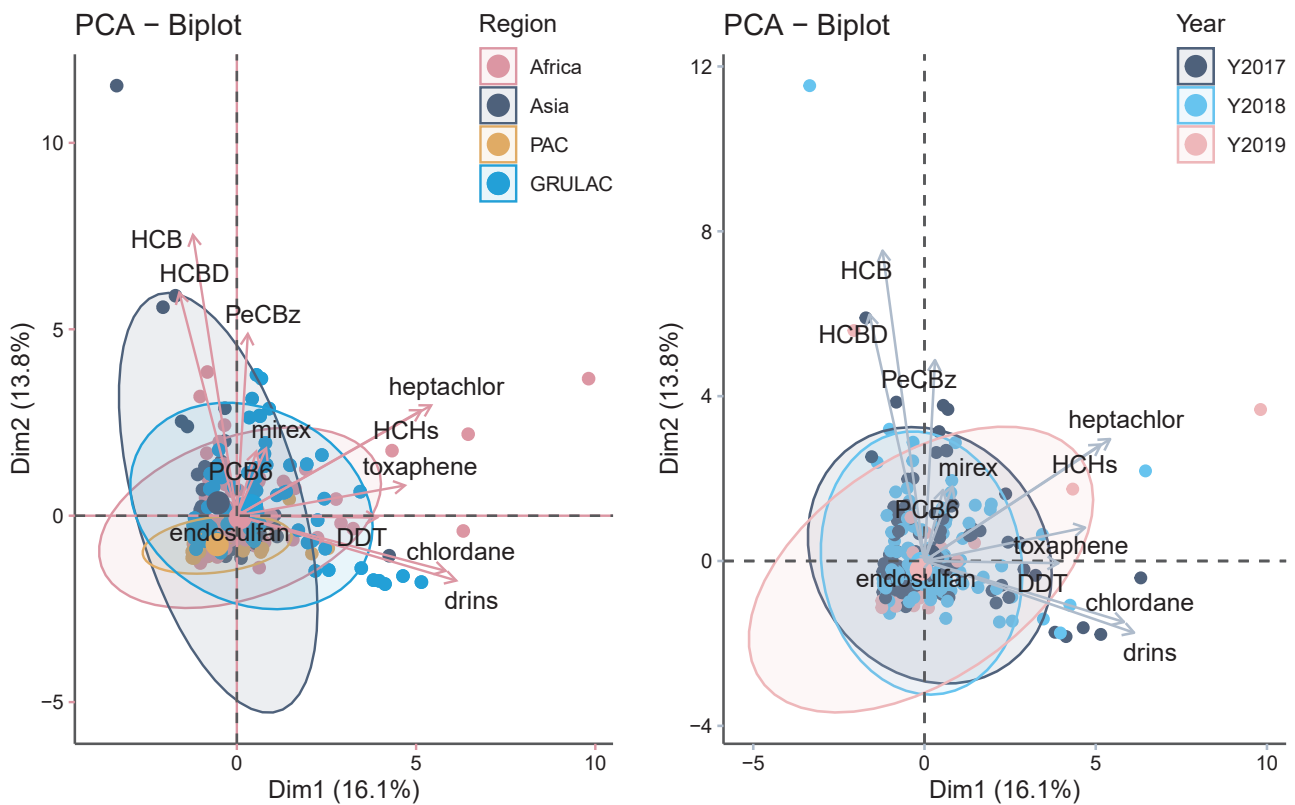


Figure 5: Continued





**Figure 6:** PAS/PUFs: Scaled box plots with facet for CI POPs and countries on bottom; values normalized to 1 PUF and 3 months exposure (N=294 for most OCPs, N=323 for toxaphene, N=211 for HCBd)



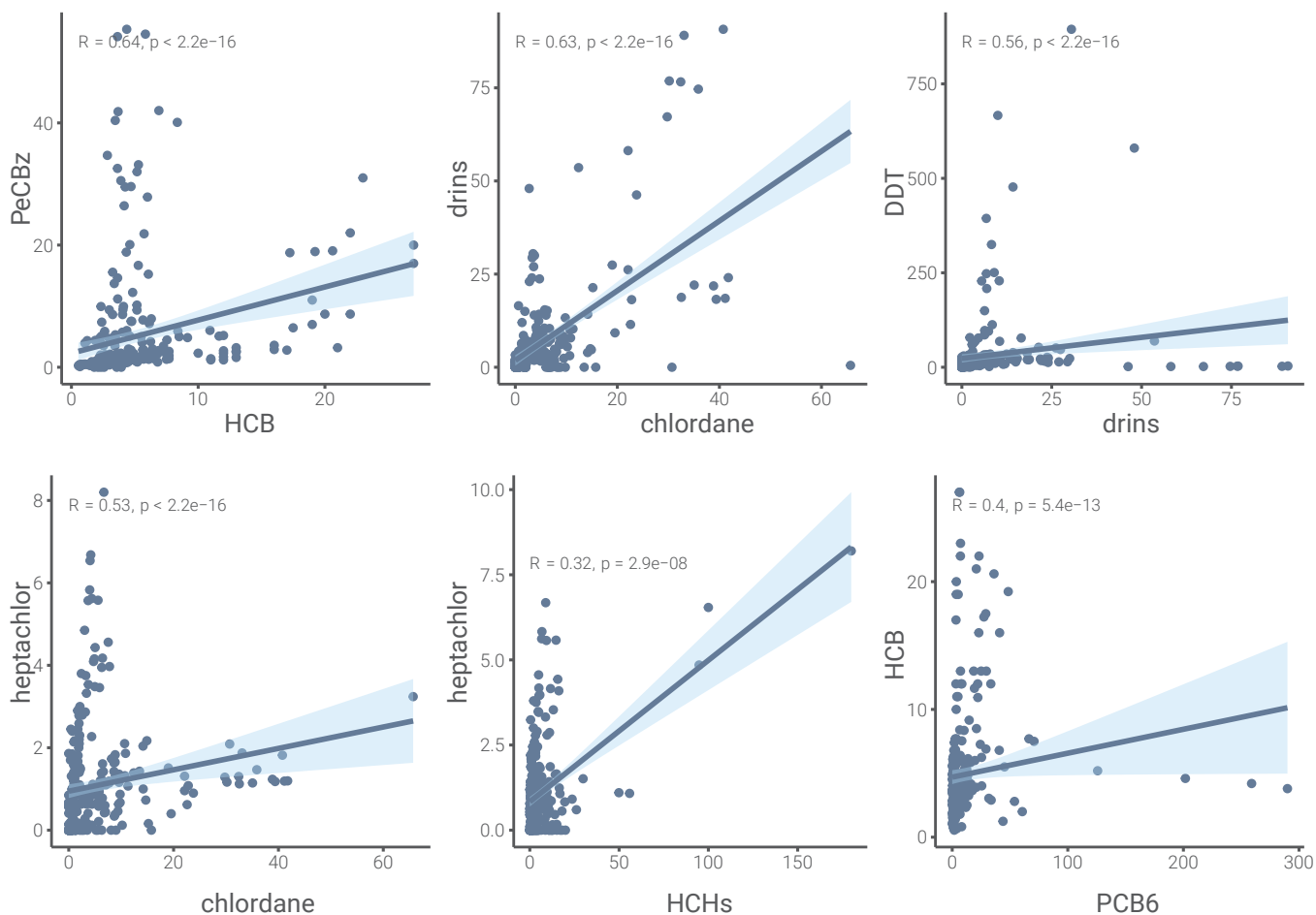
**Figure 7:** PAS/PUFs: PCA biplot for chlorinated POPs with ellipse around region (left) and year (right). All values are normalized to 1 PUF and 3-months exposure

The Principal Component Analyses (PCA) in Figure 7 displays the heterogeneity of the sample patterns and scales: The first and second dimensions only represent 30% of the samples. A distinct pattern can be seen only in the 4<sup>th</sup> quartile where samples with high amounts of chlordane and drins are located. These are mainly from GRULAC (Figure 7, left). Figure 7, right, shows that there was large overlap between the years.

Non-parametric tests reveal that the values – taken all together – are significantly different between regions ( $p=2.2 \times 10^{-16}$ ). Pairwise correlations were significant for all

combinations ( $p < 3 \times 10^{-9}$ ), except for Asia-Africa, which had a p-value of 0.99. With respect to years, they were all significantly different ( $p=2 \times 10^{-5}$ ).

Spearman correlation for the chlorinated POPs in PAS/PUFs has moderate correlation for HCB with PeCBz ( $r=0.64$ ), drins with chlordane ( $r=0.63$ ), drins with DDT ( $r=0.56$ ), and chlordane with heptachlor ( $r=0.53$ ). All other correlations are weak (Figure 8).



**Figure 8:** PAS/PUFs: Spearman correlation for selected CI-POPs

## 2.2. Dioxin-like POPs

The availability of results of dl-POPs analysis in PAS/PUFs on a regional basis is shown in Table 5 and the summarizing results in Table 6. The results have been published in the scientific literature (Abad, Abalos and Fiedler 2022). Extracts from single PUFs, named quarterly samples, resulting from 1 PUF and 3 months exposure, have been combined to annual samples or two parallel exposures from one quarter. Annual samples are designated as “-A” after the year. For comparison, all results were reported based on 1 PUF and 3 months of exposure. Results are presented in pg TEQ per PUF and 3 months exposure.

Overall, there are 195 results available, which are presented as TEQ for PCDD/PCDF (TEQ\_DF) and for dl-PCB (TEQ\_PCB). Figure 9 shows these 195 samples as stacked bars colored according to the POPs as TEQ\_PCDD (pink color)

and TEQ\_PCB (blue color). It can be seen that overall, the amounts of TEQ\_DF were about 3-times higher than the values for TEQ\_PCB. A few exceptions occurred in Tunisia, Zambia and Samoa. Interpretation of the amounts found in samples from the Marshall Islands and Tuvalu should not be made since the values were so low that such conclusion cannot be supported (Figure 9). From Table 6, it can be seen that often, mean and median values differ quite largely (except for GRULAC), indicating a high variability. The boxplots are shown in Figure 10 grouped by POPs and with the regions on the x-axis. The occurrence by region is shown in Figure S 2.

Highest median values for TEQ\_DF were found in Africa, Egypt and Mali but also Indonesia and Jamaica had high values. For TEQ\_PCB, the highest value was for Egypt (Figure 11).

**Table 5:** Overview on number of PUFs analyzed for dl-POPs by region

	Africa (N=89)	Asia (N=30)	PAC (N=23)	GRULAC (N=53)	Overall (N=195)
<b>Region</b>	89 (45.6%)	30 (15.4%)	23 (11.8%)	53 (27.2%)	195 (100%)
<b>Year</b>					
<b>2017</b>	62 (69.7%)	9 (30.0%)	11 (47.8%)	26 (49.1%)	108 (55.4%)
<b>2018</b>	22 (24.7%)	13 (43.3%)	10 (43.5%)	27 (50.9%)	72 (36.9%)
<b>2019</b>	5 (5.6%)	8 (26.7%)	2 (8.7%)	0 (0%)	15 (7.7%)
<b>WBC</b>					
<b>H</b>	0 (0%)	0 (0%)	5 (21.7%)	25 (47.2%)	30 (15.4%)
<b>UM</b>	6 (6.7%)	6 (20.0%)	11 (47.8%)	28 (52.8%)	51 (26.2%)
<b>LM</b>	50 (56.2%)	24 (80.0%)	7 (30.4%)	0 (0%)	81 (41.5%)
<b>L</b>	33 (37.1%)	0 (0%)	0 (0%)	0 (0%)	33 (16.9%)
<b>PopDen</b>					
<b>PD&lt;25</b>	12 (13.5%)	6 (20.0%)	8 (34.8%)	25 (47.2%)	51 (26.2%)
<b>PD_25-90</b>	37 (41.6%)	3 (10.0%)	10 (43.5%)	14 (26.4%)	64 (32.8%)
<b>PD_90-200</b>	27 (30.3%)	9 (30.0%)	2 (8.7%)	0 (0%)	38 (19.5%)
<b>PD_200-330</b>	7 (7.9%)	10 (33.3%)	1 (4.3%)	4 (7.5%)	22 (11.3%)
<b>PD_330-2000</b>	6 (6.7%)	2 (6.7%)	2 (8.7%)	10 (18.9%)	20 (10.3%)

**Table 6:** PAS/PUFs TEQ: Descriptive statistics by region (amounts in pg TEQ/PUF)

	Central tendencies	Africa (N=89)	Asia (N=30)	PAC (N=23)	GRULAC (N=53)	Overall (N=195)
<b>TEQ_DF</b>	Mean (SD)	13.3 (18.3)	13.6 (12.6)	4.79 (7.34)	10.4 (6.98)	11.5 (14.2)
	Median [Min, Max]	4.07 [0.0552, 77.7]	9.80 [0.162, 40.3]	1.01 [0.000495, 27.0]	10.4 [0.141, 33.5]	6.41 [0.000495, 77.7]
<b>TEQ_PCB</b>	Mean (SD)	3.53 (3.78)	3.30 (2.55)	1.15 (1.23)	2.94 (2.16)	3.05 (3.07)
	Median [Min, Max]	2.17 [0.000374, 16.4]	3.10 [0.00305, 8.57]	0.675 [0.00234, 4.32]	2.62 [0.253, 11.0]	2.34 [0.000374, 16.4]

Figure 12 shows scaled box plots for each country change to: by TEQ-DF and TEQ-PCB. On the graphic the countries with high or very varying amounts can be easily identified. TEQ\_PCDD and TEQ\_PCB were highest in Africa and therein in Egypt and Mali.

The data for TEQ\_DF and TEQ\_PCB between regions is significantly different ( $p=1.43 \times 10^{-6}$ ). Statistically, dl-POPs in the PAC region are significantly different from all other

regions ( $p=7.5 \times 10^{-5}$  to Africa and Asia,  $p=6.2 \times 10^{-7}$  to GRULAC). Results for Asia with GRULAC ( $p=0.900$ ) are similar as are Africa to Asia ( $p=0.232$ ).

Measured values were not statistically different according to the year. Across all samples,  $p=0.277$  with pairwise significance of  $p=0.34$  and  $p=0.42$ .

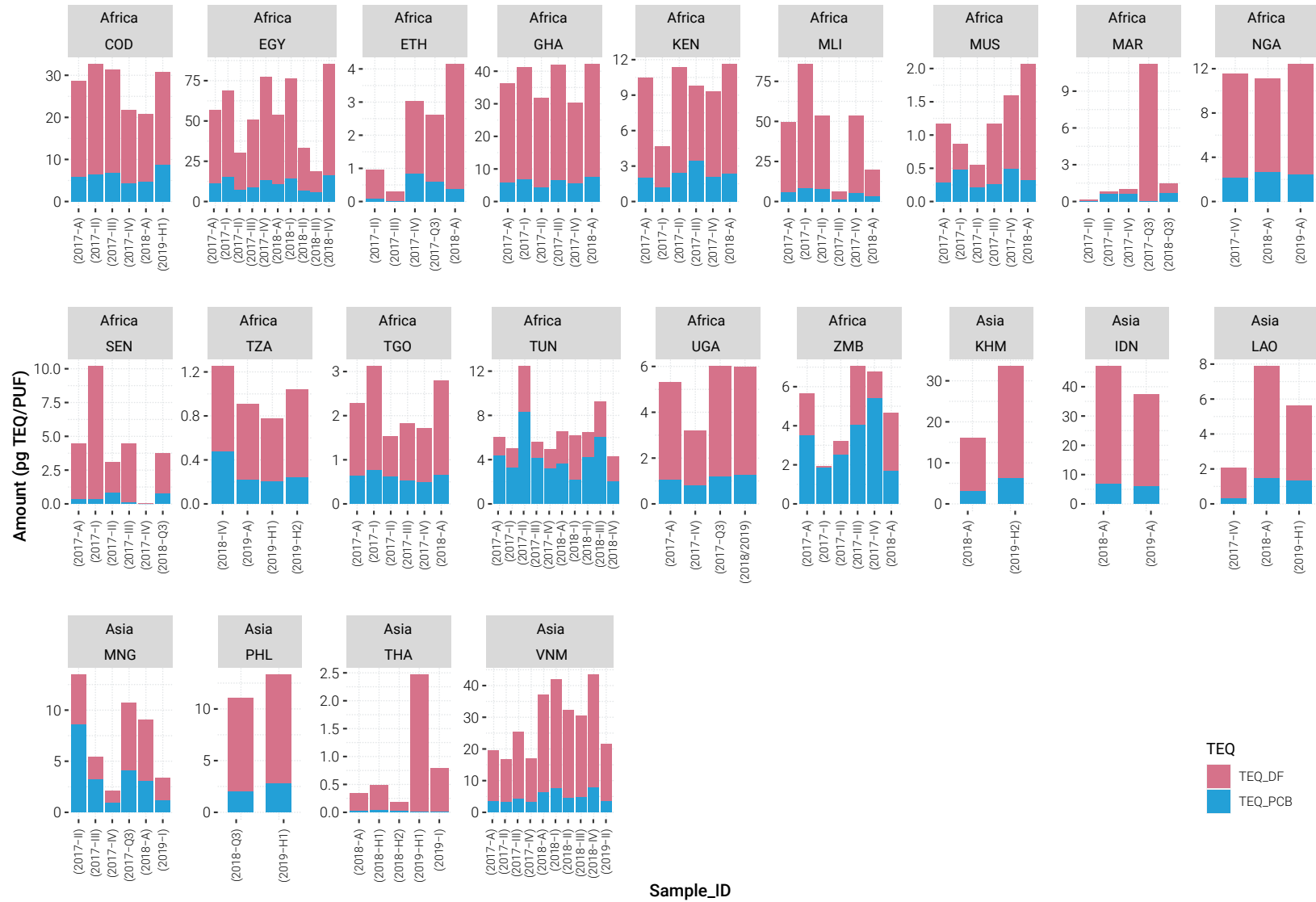


Figure 9: PAS/PUFs: dl-POPs measured in each sample. Amounts in pg TEQ/PUF (N=195)

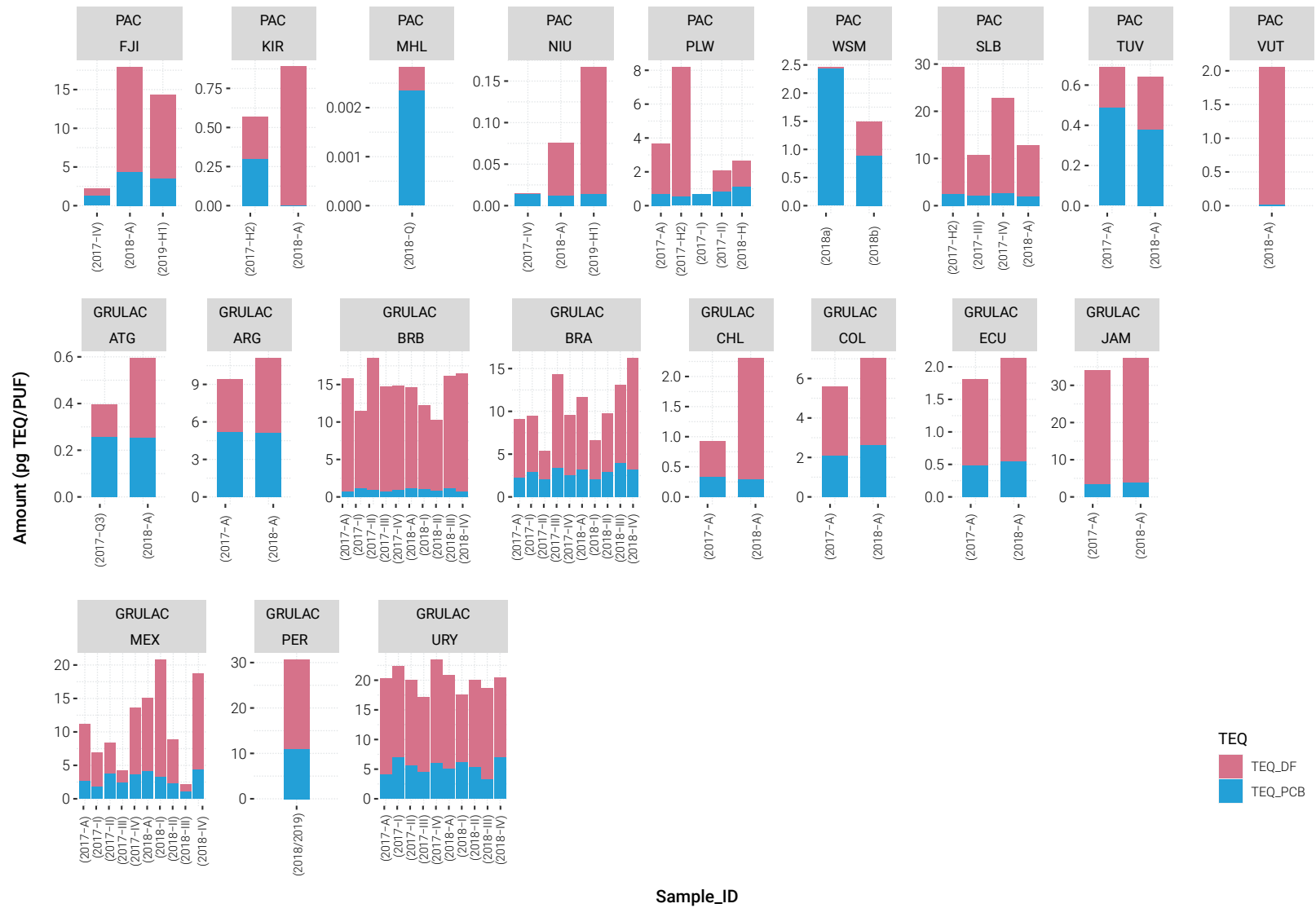


Figure 9: Continued



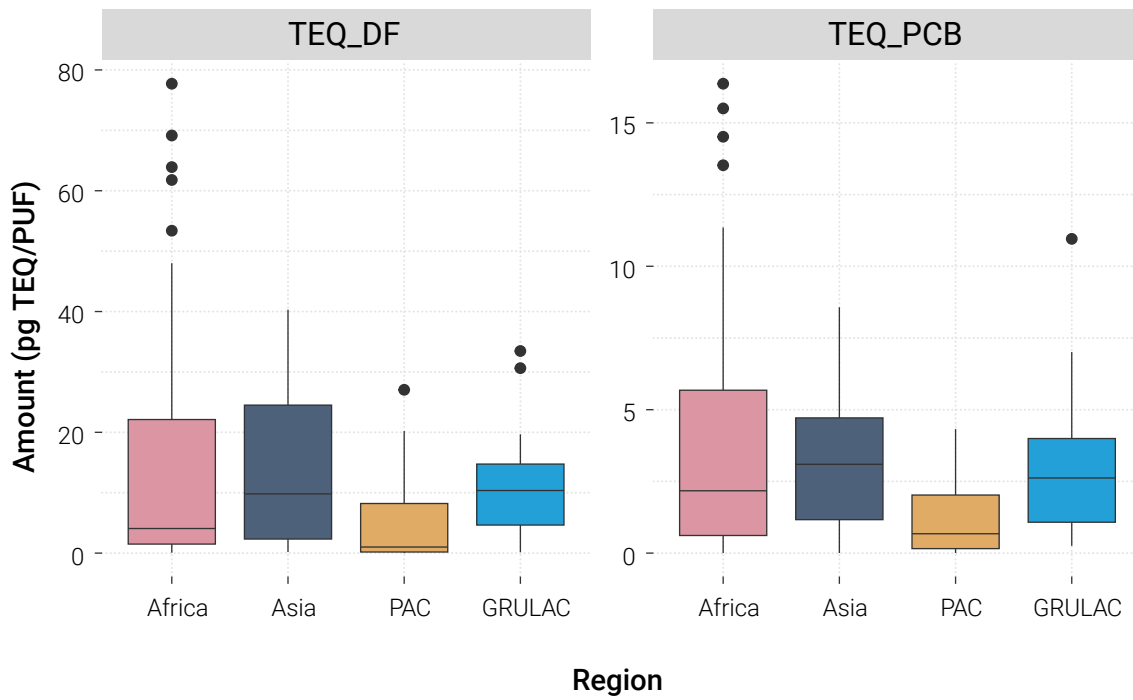


Figure 10: PAS/PUFs: Boxplots for two TEQ by region (left unscaled; right scaled); values normalized to 1 PUF and 3 months exposure (n=195)



Photo: © Unsplash / Carlos Gury Santos

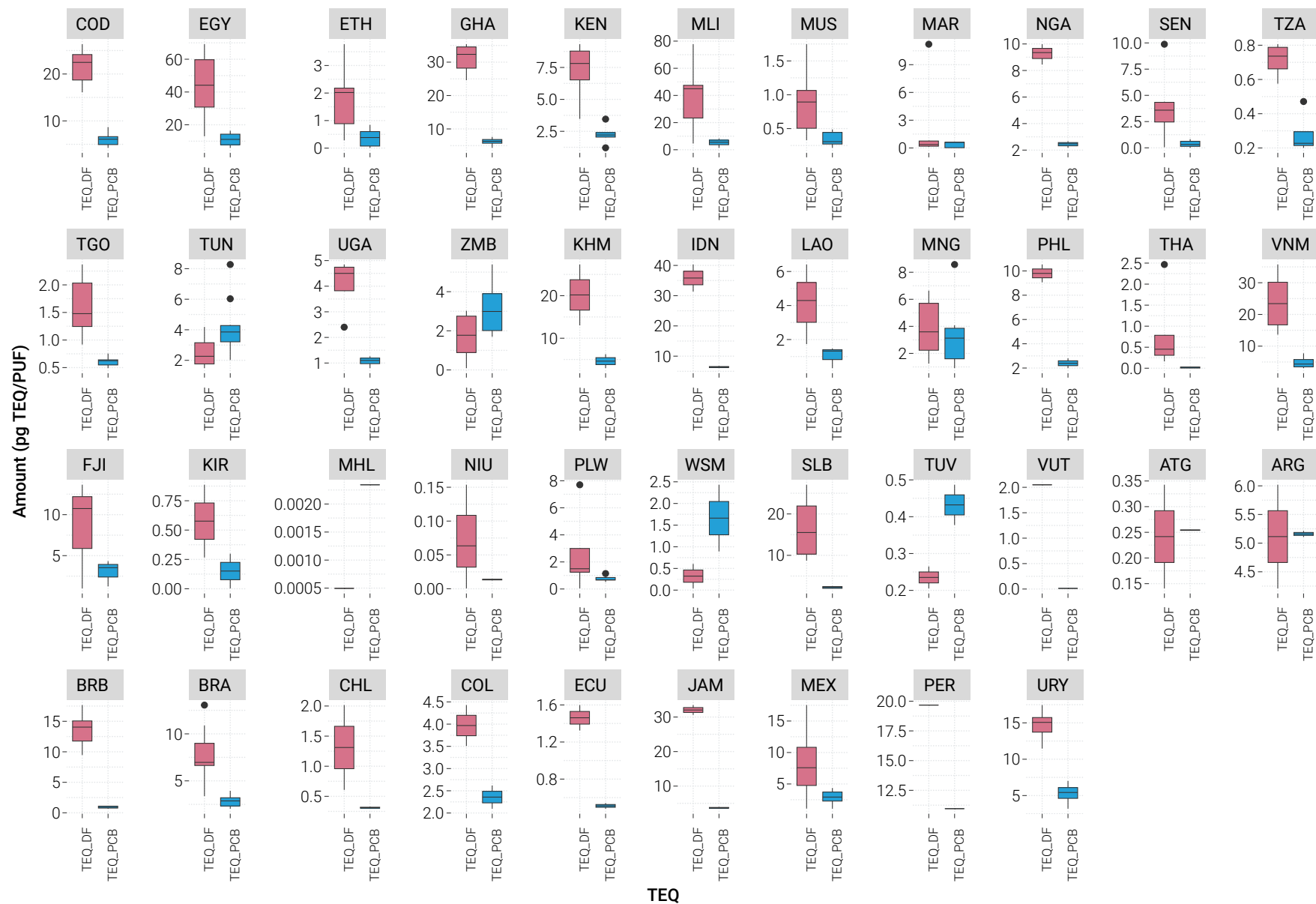


Figure 11: PAS/PUFs: Scaled box plots by 2 TEQs for country colored by POP (n=195); values normalized to 1 PUF and 3 months exposure.



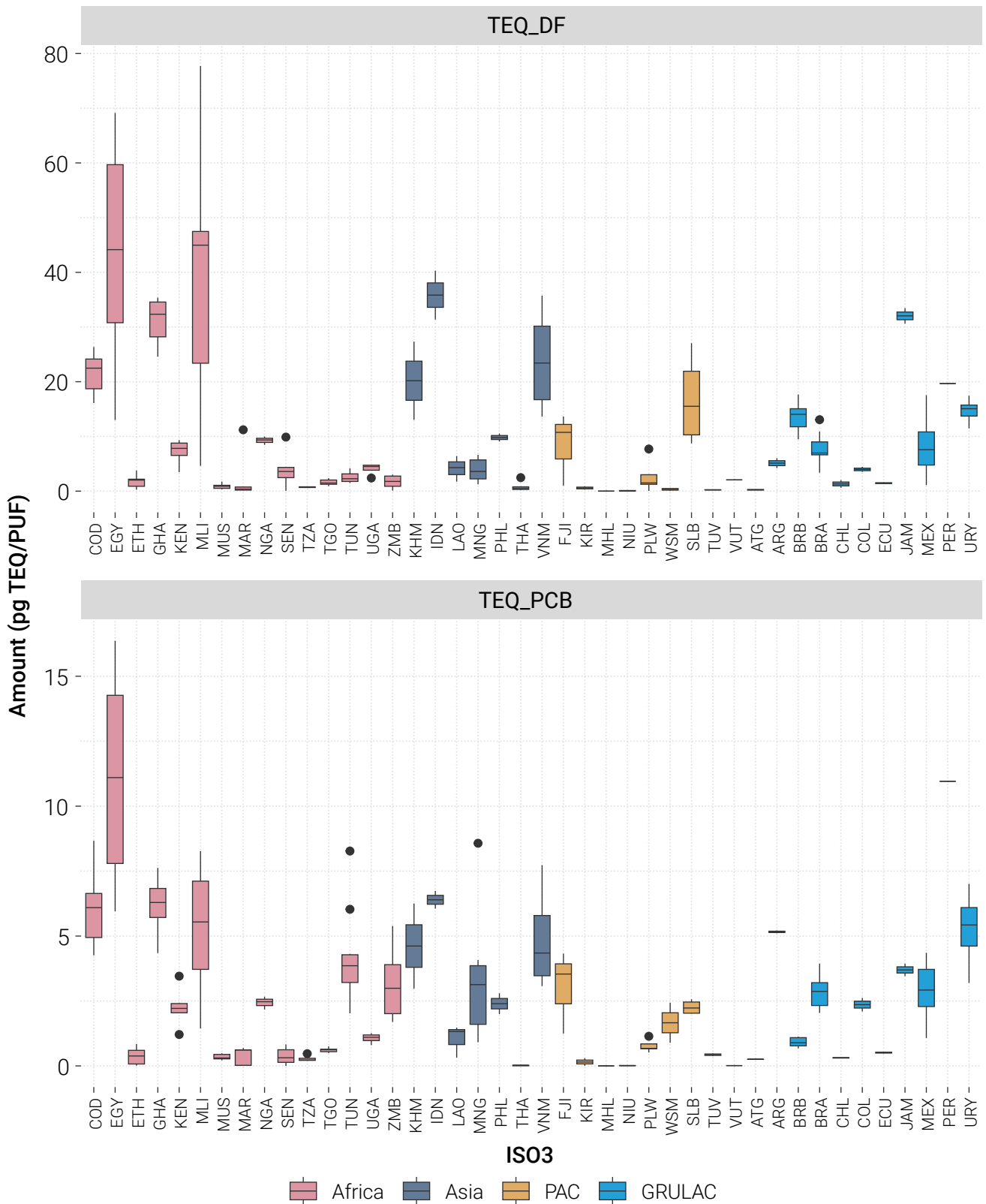
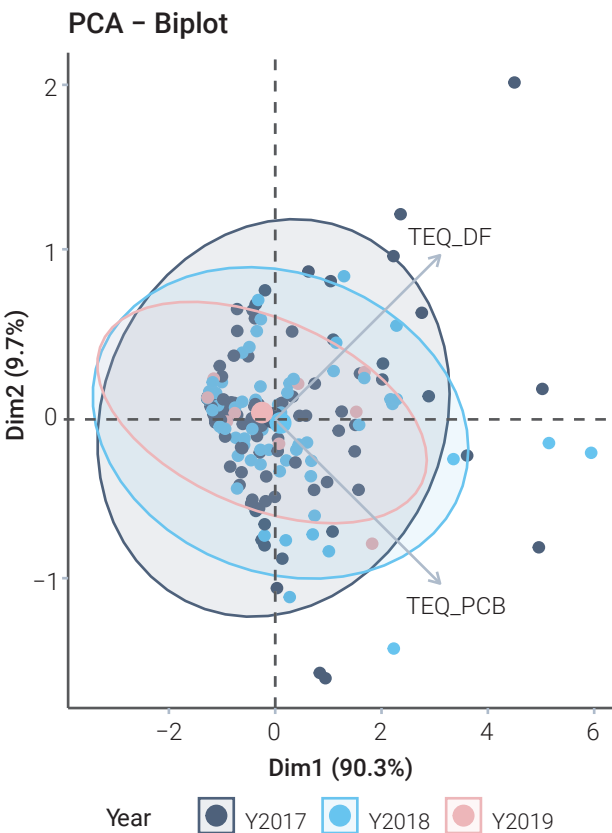
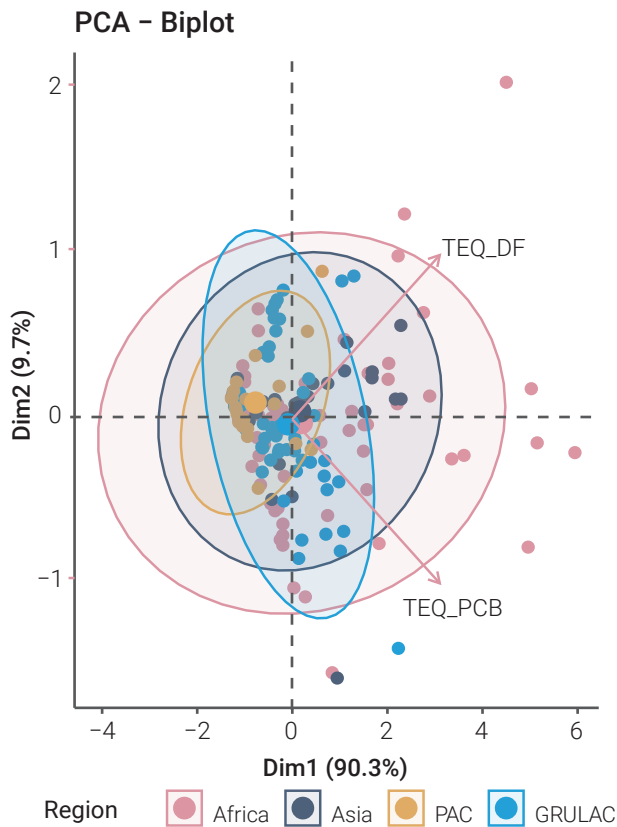


Figure 12: PAS/PUFs: Box plots by 2 TEQs for country colored by region (n=195); values normalized to 1 PUF and 3 months exposure.

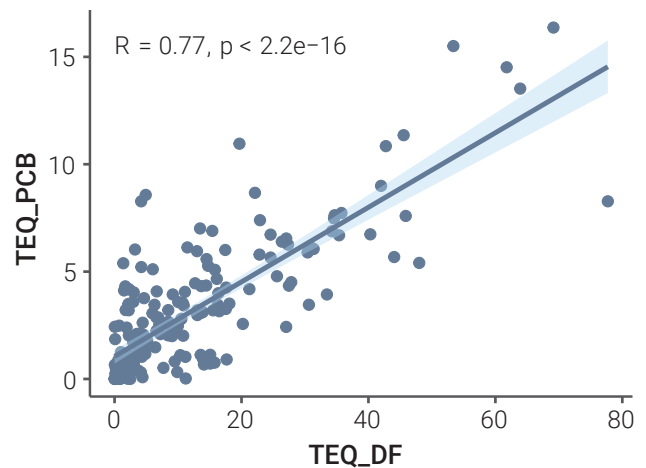
The PCA represents 100% of the samples and is dominated by the 1<sup>st</sup> dimension (x-axis), *i.e.*, the scale of the amounts (Figure 13). Highest values were found in Africa (samples from Egypt and one from Mali). At higher amounts, there are some

African samples in the 1<sup>st</sup> quartile, which were dominated by the TEQ\_DF and one African sample that was relatively high in TEQ\_PCB (Egypt (2017-I)). All other samples were close to the y-axis, *i.e.*, had lower amounts for both TEQs.



**Figure 13:** PAS/PUFs: PCA for dl-POPs (as two TEQs) according to region (above) and exposure year (below). All values are normalized to 1 PUF and 3-months exposure

Figure 14 shows that the TEQs for PCDD/PCDF and dl-PCB are highly correlated ( $r=0.77$ ).



**Figure 14:** PAS/PUFs: Spearman correlation for two TEQs

## 2.3. Brominated POPs

Results for brominated POPs were available from 293 PUFs. The number of PUFs analyzed within these UNEP/GEF GMP2 projects are summarized in Table 7 and the amounts in Table 8. For GRULAC, PBDE 209 was not analyzed and there were three samples less for HBCD (samples coming in late, e.g., from Peru). For PBDE<sub>8</sub>, the overall mean value was 2.1 ng/PUF and the median value was 1.0 ng/PUF. Especially countries from GRULAC and PAC were above these values. These values were lower than for deca-BDE, PBDE 209, which had an overall mean value of 6.6 ng/PUF and a median value of 1.5 ng/PUF.



**Table 7:** Overview on number of PUFs analyzed for brominated POPs

	Africa	Asia	PAC	GRULAC	Overall
<b>Region</b>	113 (38.6%)	49 (16.7%)	49 (16.7%)	82 (28.0%)	293 (100%)
<b>Year</b>					
<b>2017</b>	47 (41.6%)	8 (16.3%)	11 (22.4%)	39 (47.6%)	105 (35.8%)
<b>2018</b>	55 (48.7%)	27 (55.1%)	28 (57.1%)	41 (50.0%)	151 (51.5%)
<b>2019</b>	11 (9.7%)	14 (28.6%)	10 (20.4%)	2 (2.4%)	37 (12.6%)
<b>WBC</b>					
<b>H</b>			6 (12.2%)	35 (42.7%)	41 (14.0%)
<b>UM</b>	8 (7.1%)	11 (22.4%)	23 (46.9%)	47 (57.3%)	89 (30.4%)
<b>LM</b>	62 (54.9%)	38 (77.6%)	20 (40.8%)		120 (41.0%)
<b>L</b>	43 (38.1%)				43 (14.7%)
<b>PD_Code</b>					
<b>PD&lt;25</b>	16 (14.2%)	8 (16.3%)	21 (42.9%)	35 (42.7%)	80 (27.3%)
<b>PD_25-90</b>	43 (38.1%)	7 (14.3%)	15 (30.6%)	24 (29.3%)	89 (30.4%)
<b>PD_90-200</b>	32 (28.3%)	21 (42.9%)	7 (14.3%)	0 (0%)	60 (20.5%)
<b>PD_200-330</b>	14 (12.4%)	8 (16.3%)	2 (4.1%)	15 (18.3%)	39 (13.3%)
<b>PD_330-2000</b>	8 (7.1%)	5 (10.2%)	4 (8.2%)	8 (9.8%)	25 (8.5%)

**Table 8:** PAS/PUFs brominated POPs: descriptive statistics by region (amounts in ng/PUF)

Br-POPs	Central tendencies	Africa (N=113)	Asia (N=49)	PAC (N=49)	GRULAC (N=82)	Overall (N=293)
<b>PBDE8</b>	Mean (SD)	1.62 (2.68)	0.769 (0.847)	2.52 (3.11)	3.17 (3.57)	2.06 (2.96)
	Median [Min, Max]	0.580 [0, 16.3]	0.520 [0, 3.16]	1.08 [0, 14.9]	1.48 [0, 14.1]	0.980 [0, 16.3]
<b>PBDE209</b>	Mean (SD)	10.5 (21.2)	3.09 (7.07)	1.31 (2.82)	NA (NA)	6.64 (16.5)
	Median [Min, Max]	3.00 [0, 130]	0 [0, 39.0]	0 [0, 12.0]	NA [NA, NA]	1.50 [0, 130]
<b>PBB153</b>	Mean (SD)	0.024 (0.105)	0 (0)	0.0086 (0.0375)	0.0014 (0.009)	0.0111 (0.0680)
	Median [Min, Max]	0 [0, 0.870]	0 [0, 0]	0 [0, 0.230]	0 [0, 0.0670]	0 [0, 0.870]
<b>HBCD</b>	Mean (SD)	2.44 (5.72)	5.14 (14.2)	1.50 (6.97)	3.02 (5.22)	2.90 (7.94)
	Median [Min, Max]	0.440 [0, 39.4]	0.100 [0, 75.6]	0.0900 [0, 48.8]	1.38 [0, 35.7]	0.490 [0, 75.6]

The results as stacked bars for PBDE<sub>g</sub>, PBDE 209, PBB 153, and HBCD for each sample are shown in Figure 15. It can be seen that in some countries PBDE<sub>g</sub> dominates whereas in other countries, HBCD is most abundant. PBB153 is hardly quantified but the single POP, PBDE 209, was the dominant POP in almost all African countries.

The graphics showing box whisker plots demonstrate the large variation of the data, indicated by the many outliers for all BFR in all regions (Figure 16). The occurrence of the BFRs in the regions is contained in the Annex as Figure S 3.

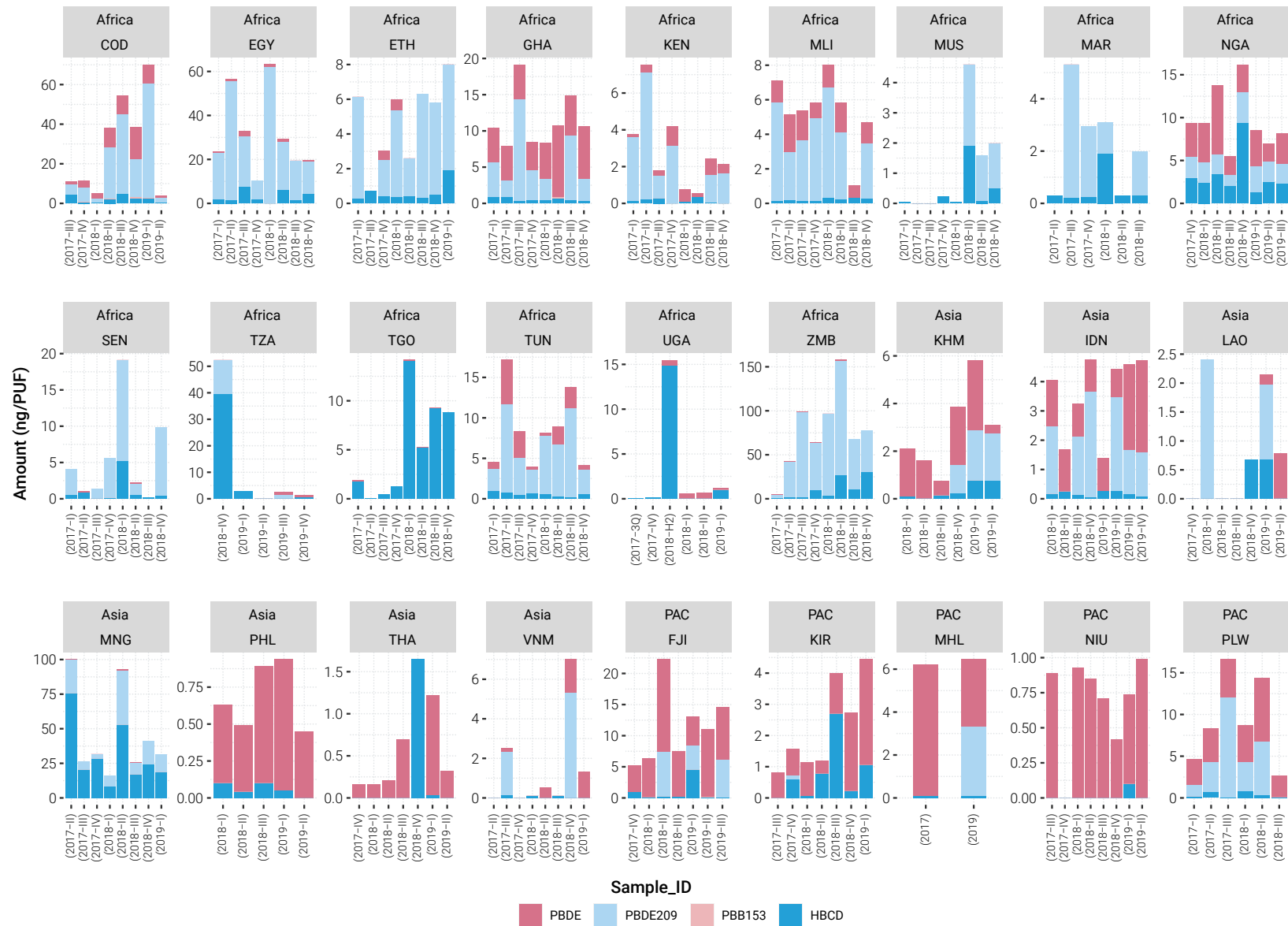


Figure 15: PAS/PUFs: Stacked bars of BFR measured in each sample. Amounts in ng/PUF

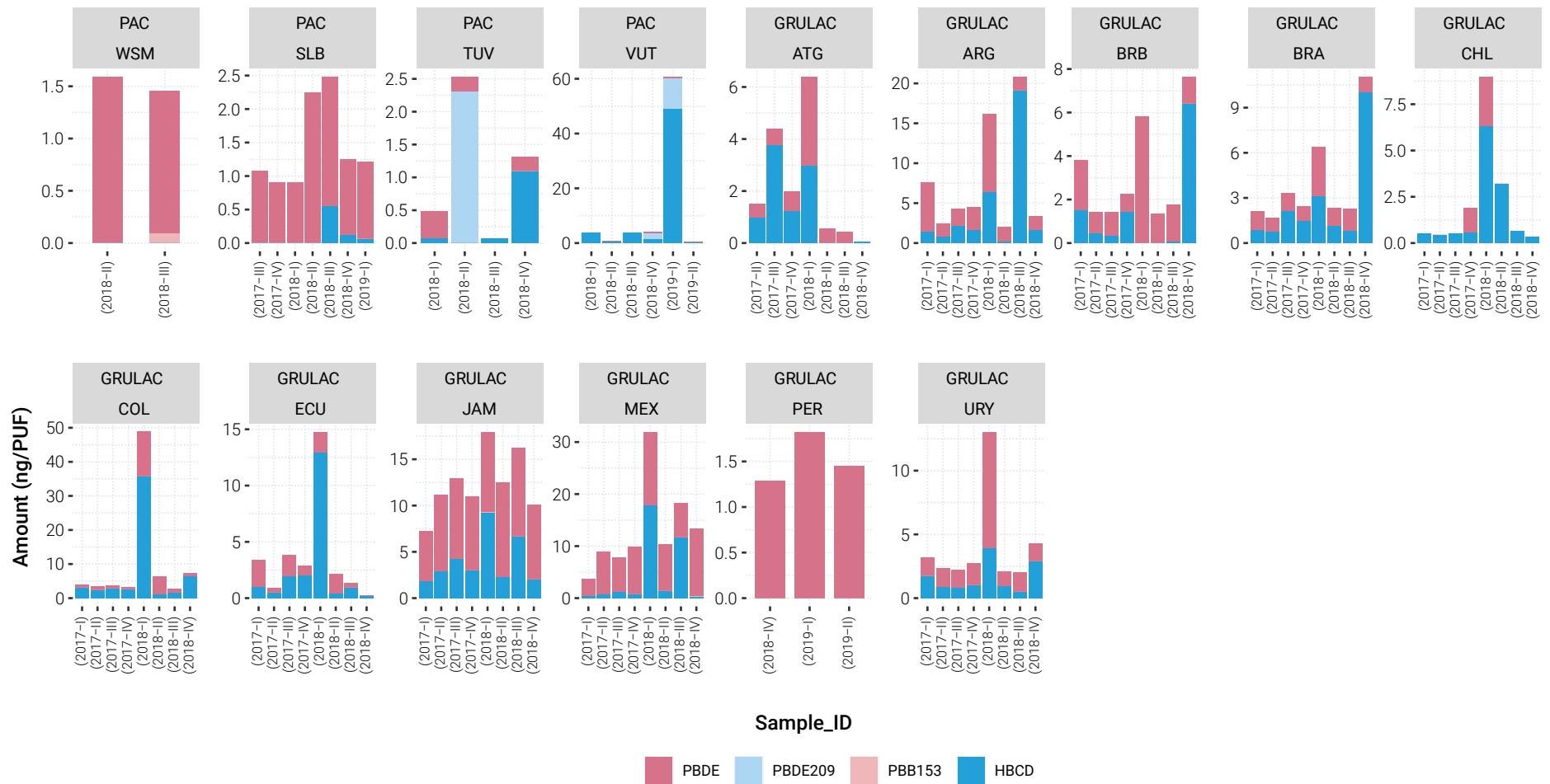


Figure 15: Continued



The highest value was measured in Africa, from Zambia. For HBCD, Asia had the highest mean and median values, driven by Mongolia (see Figure 17 and Figure 18). Both figures show that high amounts were also found in PAC (Fiji) and GRULAC (Jamaica, Mexico). It can also be seen that a substantial number of results were outliers.

For PBB153, all values were below 1 ng/PUF and most of them were <LOD.

HBCD had higher median values than PBDE<sub>8</sub> in Africa and Asia; in GRULAC, they were comparable. In PAC, PBDE<sub>8</sub> >HBCD.

The results for PBDE<sub>8</sub>, PBDE 209, PBB153, and HBCD by country are shown in Figure 17. Quite different results are obtained: for some countries PBDE<sub>8</sub>>HBCD, for others, HBCD>PBDE<sub>8</sub>. No uniform picture was obtained, not even within regions. It shall be noted that for most countries, the amounts were quite low except for Mongolia, Vanuatu, Colombia, and Mexico. PBDE 209 had high values in D.R. of the Congo, Egypt, and Zambia.

Figure 18 displays the results as box whisker plots for each country by Br-POPs. On this graphic the countries with high or very varying amounts can be easily identified.

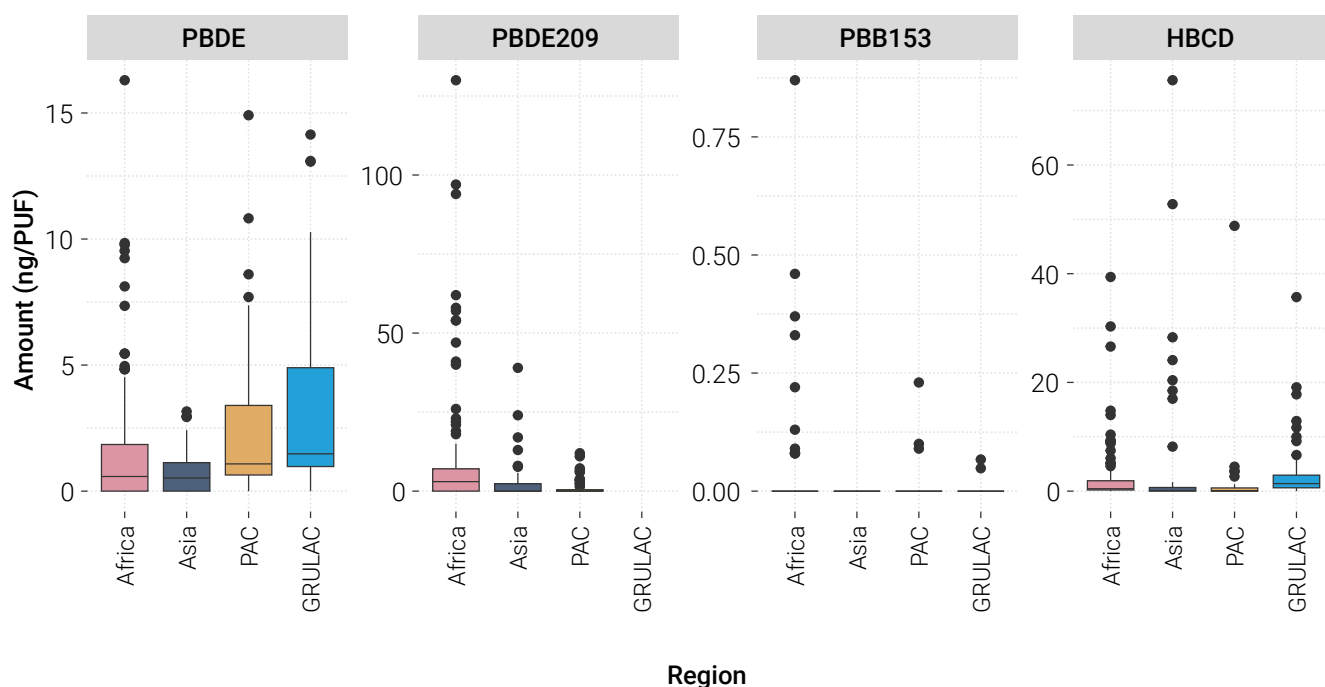


Figure 16: PAS/PUFs: Boxplots for brominated POPs by region (left unscaled; right scaled boxplot by POP); values normalized to 1 PUF and 3 months exposure (n=293)



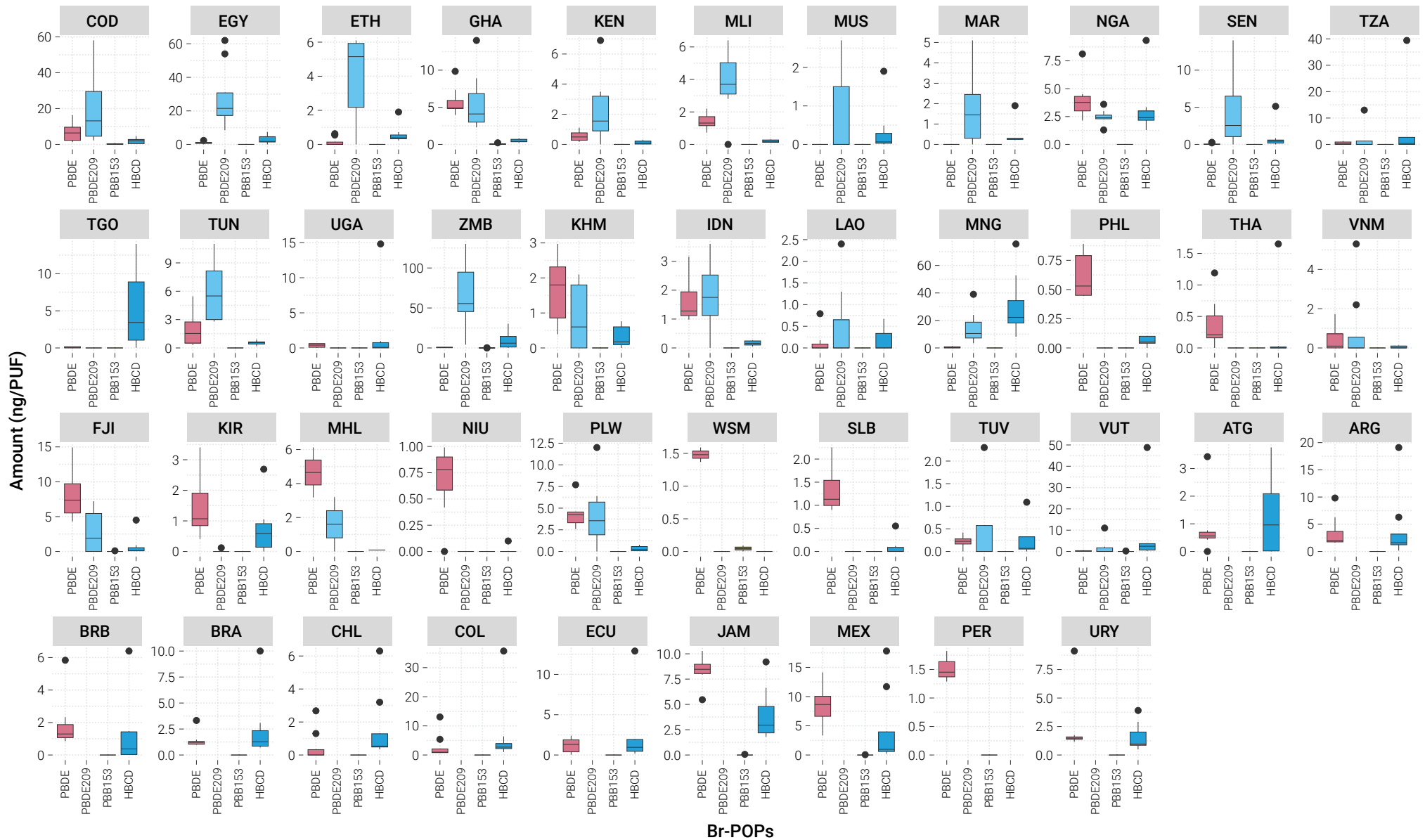


Figure 17: PAS/PUFs: Scaled box plots by country for Br-POPs; values normalized to 1 PUF and 3 months exposure (n=293)

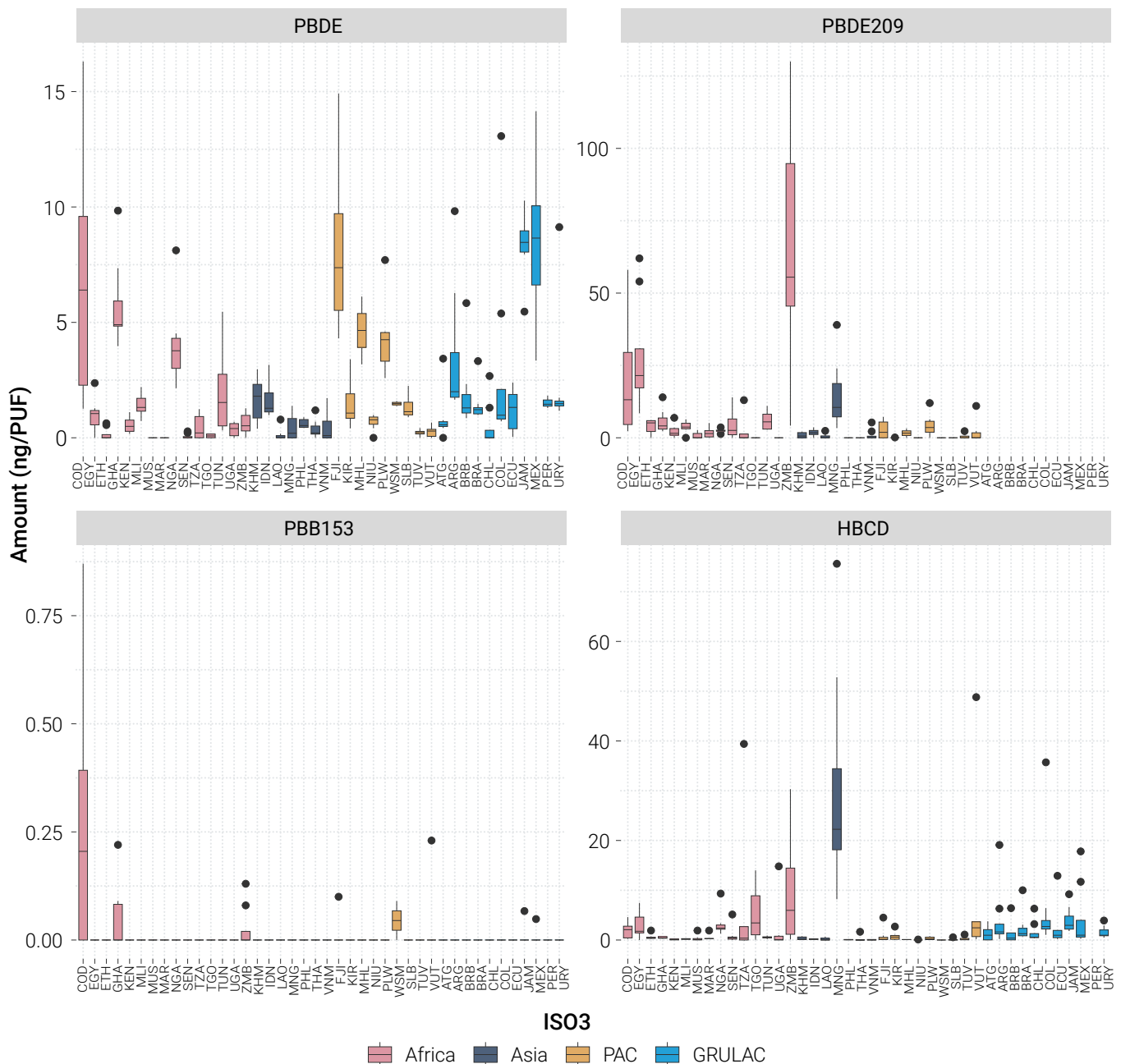


Figure 18: PAS/PUFs: Box plots by BFR for country; values normalized to 1 PUF and 3 months exposure (n=293)

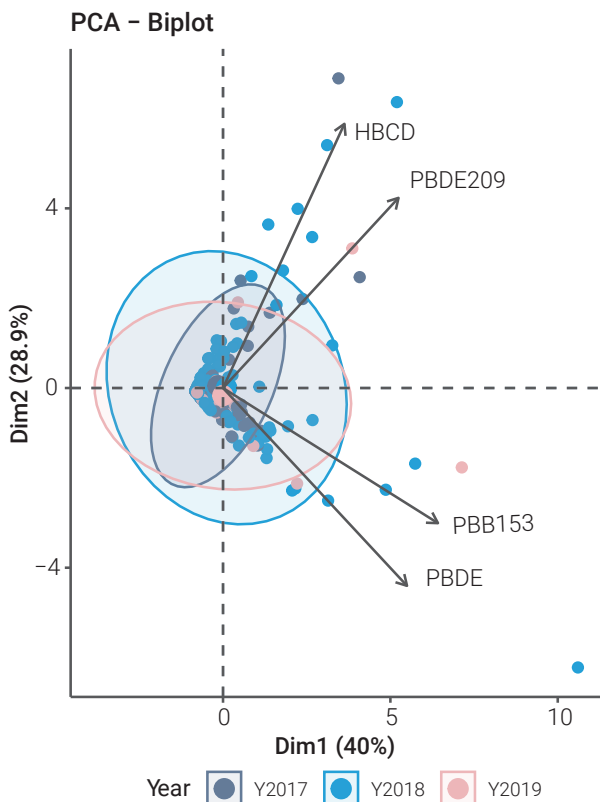
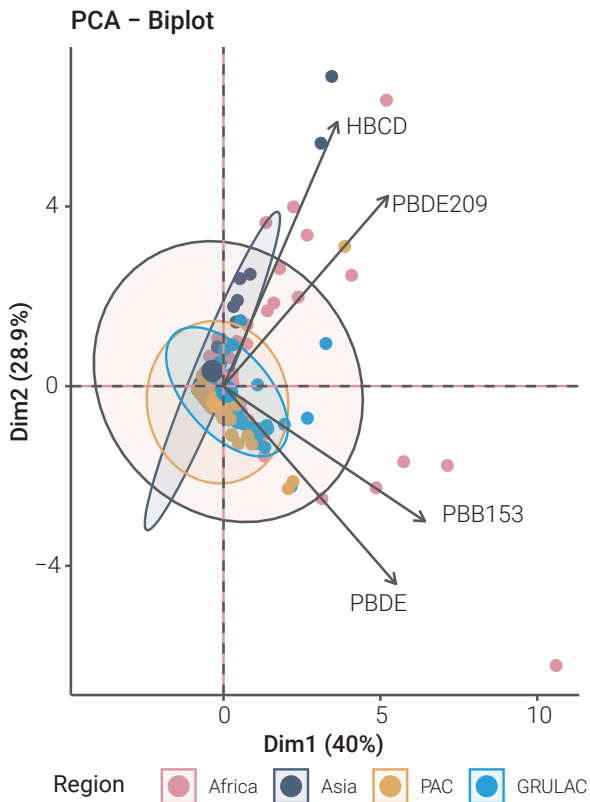
Very distinct pattern can be seen from the PCA, whereby the two first dimensions represent 69% of the variance: Samples with HBCD and PBDE 209 dominating are located in the 1<sup>st</sup> quartile whereas the samples dominated by PBDE<sub>8</sub> are located in the 4<sup>th</sup> quartile. HBCD was prevalent in samples from Asia and Africa whereas GRULAC and PAC samples were mainly present for PBDE<sub>8</sub> (Figure 19).

The non-parametric test with Kruskal Wallis gave  $p=8.55 \times 10^{-7}$ ; and pairwise significant differences between

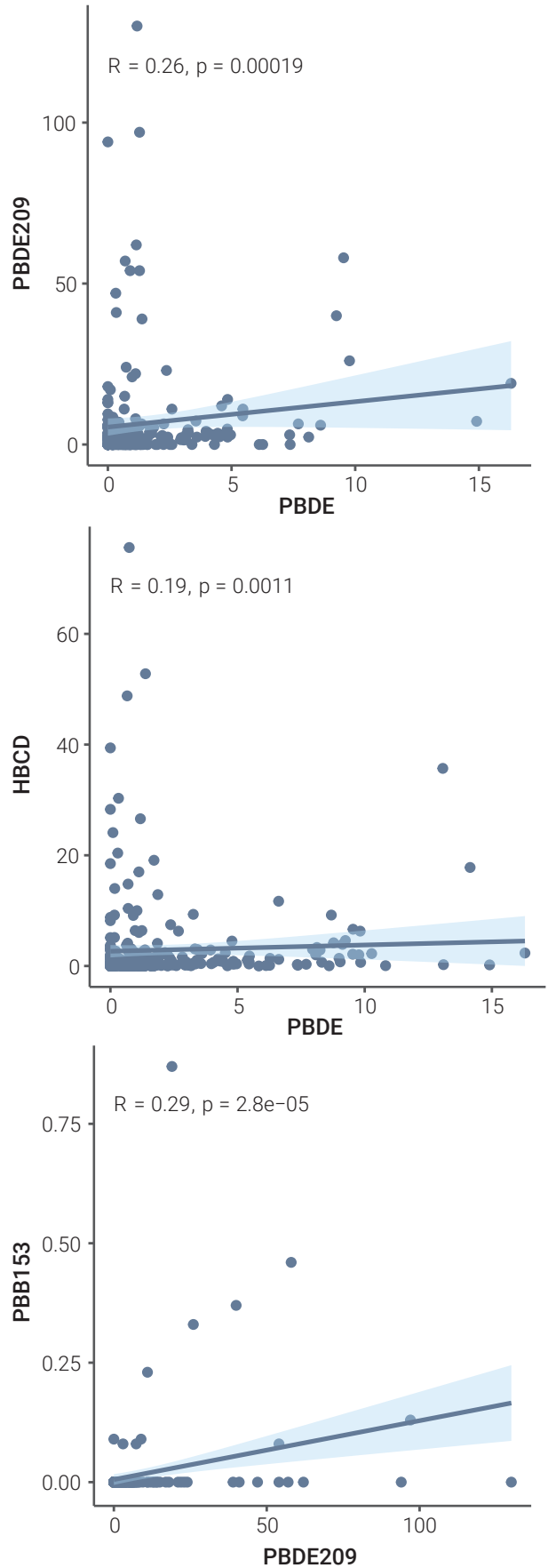
all regions with the exception between GRULAC and Africa ( $p=0.50$ ) and Asia and PAC ( $p=0.60$ ). Between years, no significant difference was found ( $p=0.98$ ).

Spearman correlation showed that PBDE<sub>8</sub> and HBCD are not correlated in the PAS/PUFs ( $r=0.19$  with high significance ( $p=0.001$ )). Further, no correlation was found between PBDE<sub>8</sub> and PCBE 209 ( $r=0.26$ ) (Figure 20).





**Figure 19:** PAS/PUFs: PCA for Br-POPs according to region (above) and year (below). All values are normalized to 1 PUF and 3-months exposure



**Figure 20:** PAS/PUFs: Spearman correlation for Br-POPs

## 2.4. Fluorinated POPs

No samples were obtained from U.R. of Tanzania, which did not expose methanol-pretreated PUFs and not from Samoa. In total, there were 355 PUFs analyzed for PFAS. However, 38 PUFs were so deteriorated that no PFAS could be quantified. Thus, leaving 317 PUFs for analysis. The number of samples and their classification is shown in Table 9.

In this report, all analyzed samples that gave quantifiable amounts, N=317, are assessed and the full set of 40 countries participating in the GMP2 project. Nine results from Zambia showed extremely high PFOS values because the sampling site was located at Kampala international airport and was affected by construction activities.

The overview of samples available for PFAS analysis is shown in Table 9 and the descriptive statistics in Table 10.

**Table 9:** Overview on number of PUFs analyzed for PFAS

	Africa (N=127)	Asia (N=46)	PAC (N=43)	GRULAC (N=101)	Overall (N=317)
<b>Region</b>	127 (40.1%)	46 (14.5%)	43 (13.6%)	101 (31.9%)	317 (100%)
<b>Year</b>					
<b>2017</b>	57 (44.9%)	9 (19.6%)	15 (34.9%)	47 (46.5%)	128 (40.4%)
<b>2018</b>	63 (49.6%)	29 (63.0%)	26 (60.5%)	52 (51.5%)	170 (53.6%)
<b>2019</b>	7 (5.5%)	8 (17.4%)	2 (4.7%)	2 (2.0%)	19 (6.0%)
<b>WBC</b>					
<b>H</b>	0 (0%)	0 (0%)	8 (18.6%)	43 (42.6%)	51 (16.1%)
<b>UM</b>	10 (7.9%)	9 (19.6%)	15 (34.9%)	58 (57.4%)	92 (29.0%)
<b>LM</b>	65 (51.2%)	37 (80.4%)	20 (46.5%)	0 (0%)	122 (38.5%)
<b>L</b>	52 (40.9%)	0 (0%)	0 (0%)	0 (0%)	52 (16.4%)
<b>PD_Code</b>					
<b>PD&lt;25</b>	19 (15.0%)	9 (19.6%)	18 (41.9%)	44 (43.6%)	90 (28.4%)
<b>PD_25-90</b>	47 (37.0%)	8 (17.4%)	13 (30.2%)	28 (27.7%)	96 (30.3%)
<b>PD_90-200</b>	37 (29.1%)	20 (43.5%)	8 (18.6%)	0 (0%)	65 (20.5%)
<b>PD_200-330</b>	14 (11.0%)	8 (17.4%)	1 (2.3%)	19 (18.8%)	42 (13.2%)
<b>PD_330-2000</b>	10 (7.9%)	1 (2.2%)	3 (7.0%)	10 (9.9%)	24 (7.6%)

The graphical sketch in Figure 21 shows the four PFAS as stacked bars. It can be seen that all samples were dominated by PFOS or PFOA. PFHxS was rarely quantified. FOSA was quantified in single countries such as Niue and Uruguay; also, in Togo, Brazil, and Ecuador. Whereas PFOS and PFOA had a detection frequency of 91% and 92%, respectively, PFHxS was found above the LOQ in 37% of the samples, and FOSA in only 17%. The occurrence of the PFAS in the regions is contained in the Annex, Figure S 4

The other four precursors of PFOS, NEtFOSA and NEtFOSE had only three values above LOQ (each) and NMeFO-SA and NMeFOSE did not show any quantifiable amounts.

The mean amounts for SPFOS varied highly between regions and peaked in Africa (Table 10). It shall be noted that the mean value in Africa was 1 640 pg/PUF whereas

the median value was 110 pg/PUF. The strong impact of the nine samples from Zambia can be seen in the mean value (without Zambia, the mean value was 185 pg/PUF, SD=289 pg/PUF) but does not have much weight on the median value (without Zambia, the median value was 97.7 pg/PUF). In GRULAC, a similar discrepancy between mean and median values was seen as well. Both mean values were accompanied with large SDs. Not expected was the finding that the highest median value for PFOS was found in the Pacific Islands countries (PAC; 266 pg/PUF). For PFOA, the values are more consistent for all regions and between regions. PFHxS showed many differences but homogenously median values of zero, except for the Pacific Islands.

As shown in Figure 25, 85% of the data were explained from the first two dimensions (Dim1 and Dim2). Despite the good representation explained by the two first dimension, the contribution of the individual samples to either Dim1 and or Dim2 varied highly, and each dimension was dominated by a few samples. For example, only 15 samples had a contribution of more than average (0.3%) to the PCA; of these, eight were from Zambia. Among the four PFAS, PFOS and PFOA are the main drivers into Dim1 whereas Dim2 had 80% from FOSA. With respect to the PCA, there was an almost even contribution of the four variables. The wide range of measured data, due to the samples from Zambia, can be seen in the wide ellipse for

Africa in Figure 25 at left and the years 2017 and 2018 at right. In 2019, there was no sample from Zambia. The samples from Asia, Pacific Islands, and GRULAC have very narrow and overlapping ellipses, which are centered around the origin (0,0); thus, are not dominated by any of the four PFAS. Outliers for FOSA along the y-axis in the 1<sup>st</sup> and 2<sup>nd</sup> quartiles are shown outside of the ellipses and for the regions contain African and GRULAC samples (three from Brazil, two from Uruguay, and one from Argentina). Along Dim1, all outliers are from Zambia. It is striking that FOSA and PFOS do not point into the same direction although FOSA is considered a precursor of PFOS.



Photo: © Unsplash / Annie Spratt

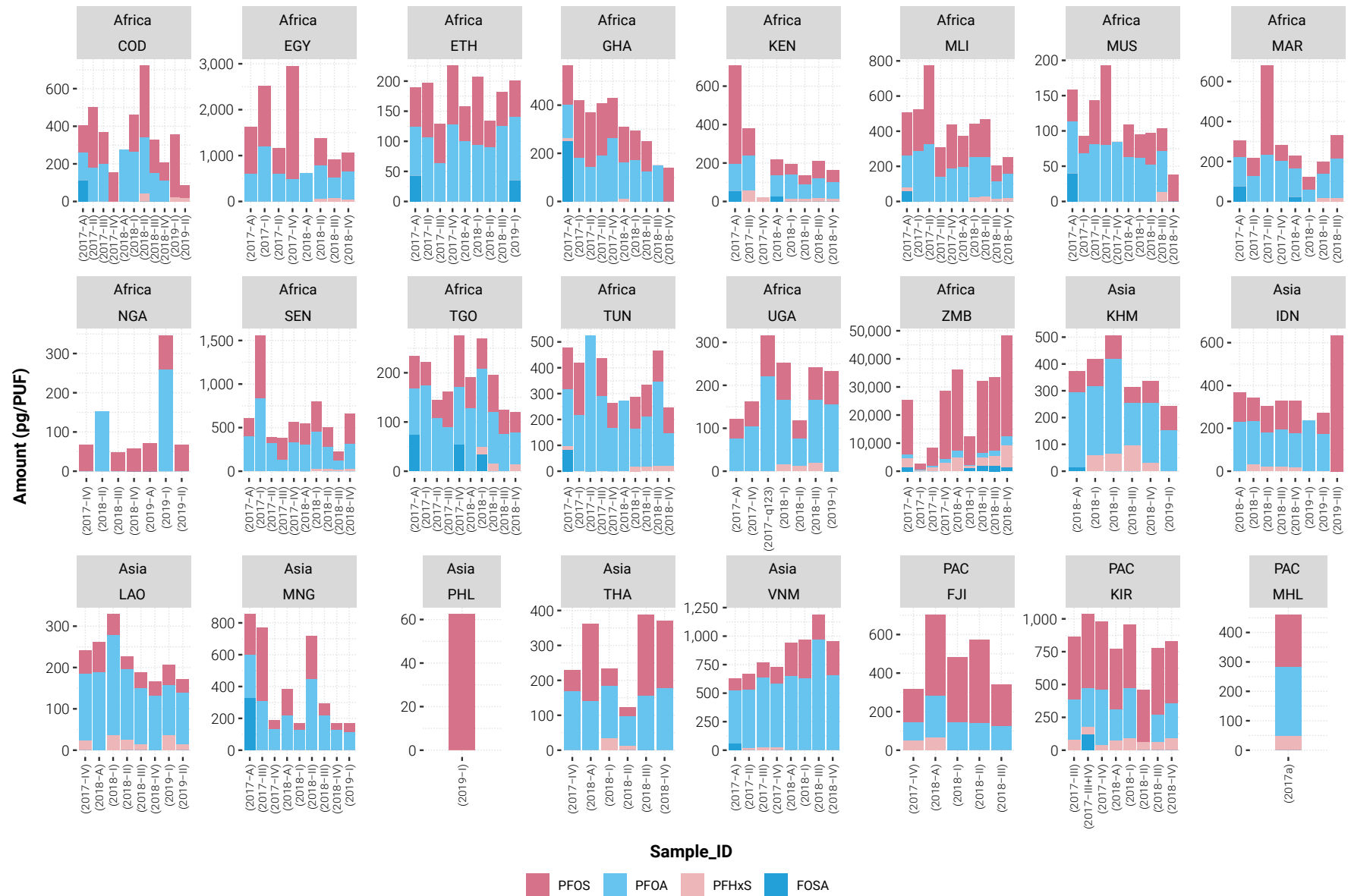


Figure 21: PFAS measured in each sample. Amounts in pg/PUF (n=317)

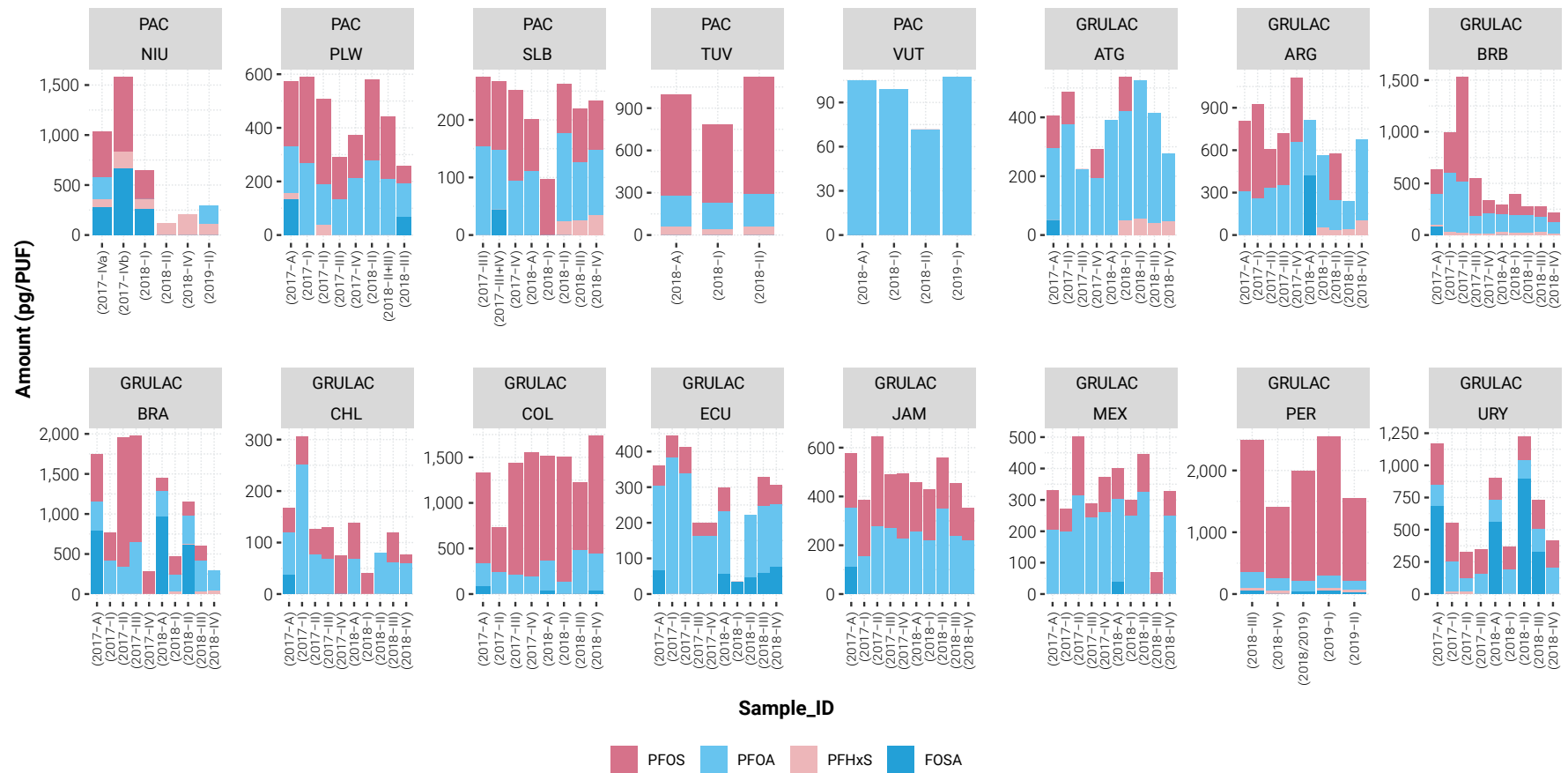
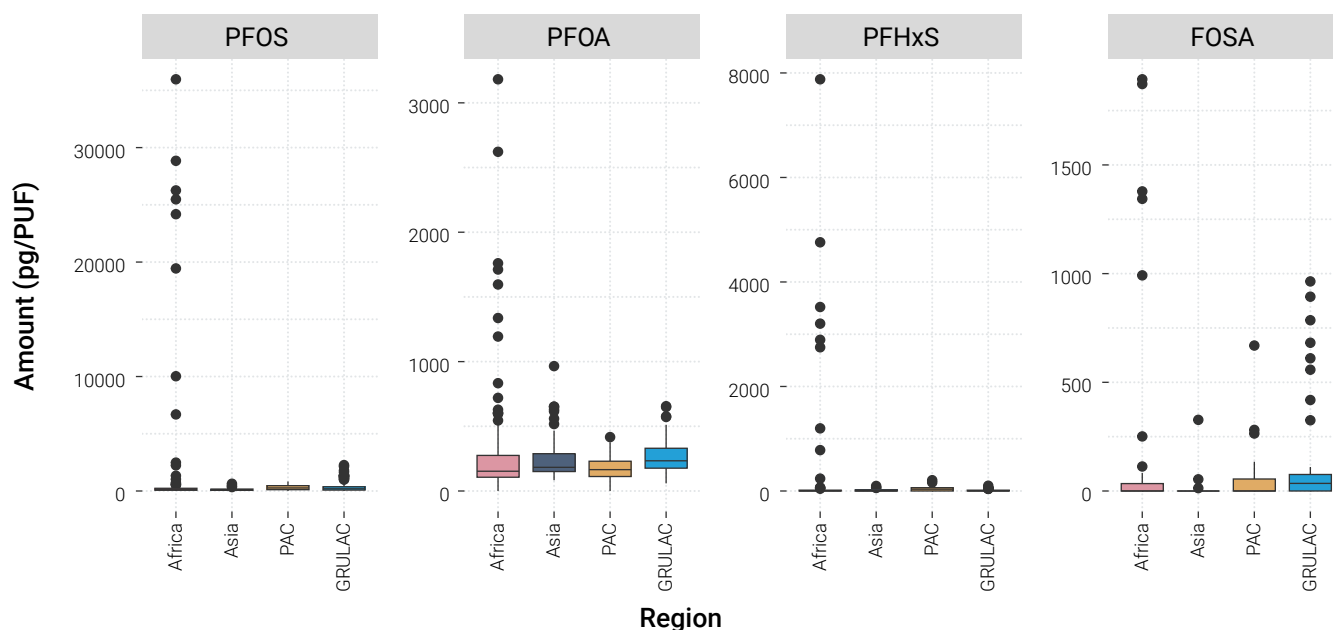


Figure 21: Continued



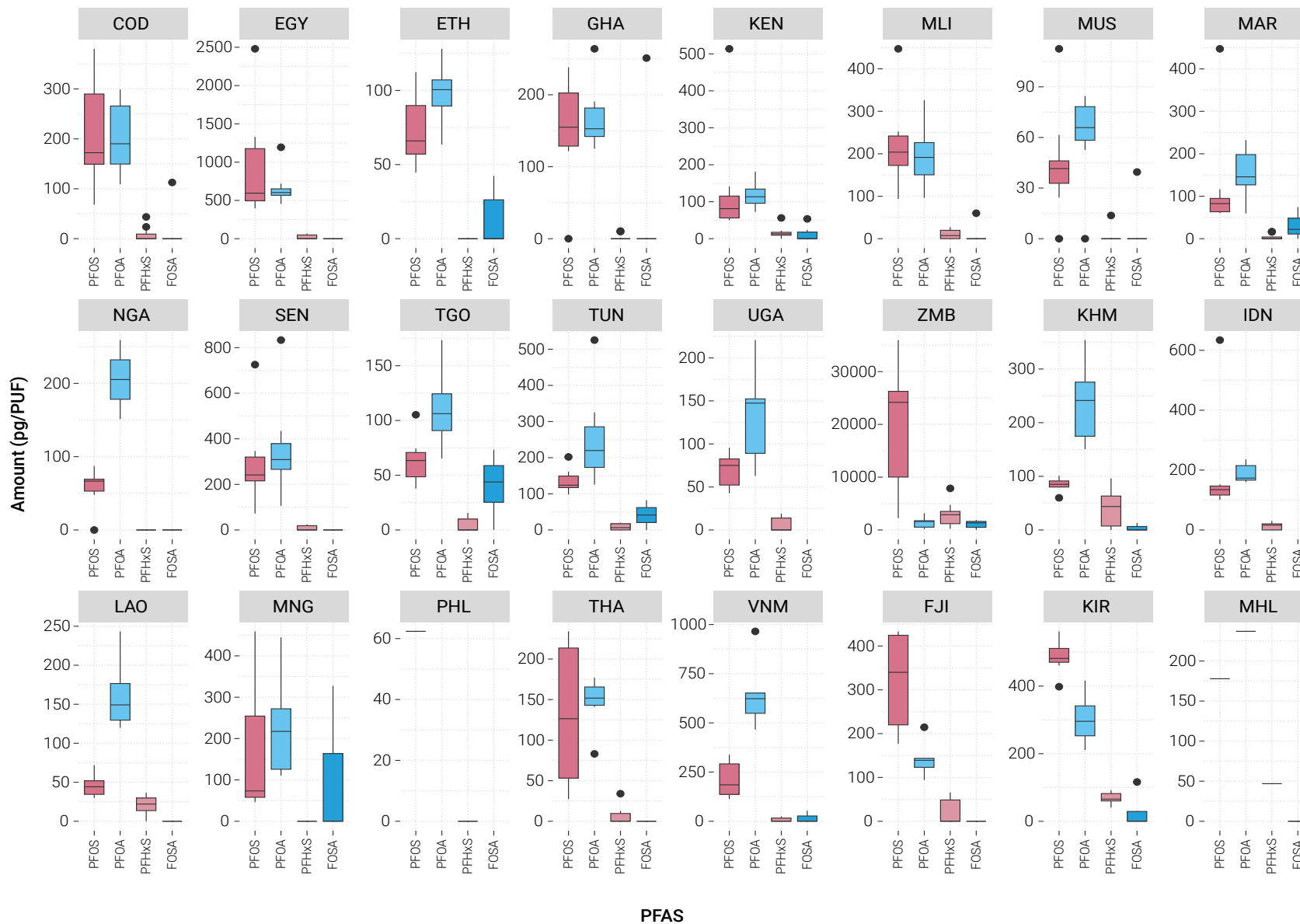
**Table 10:** PAS/PUFs PFAS: descriptive statistics by region (amounts in pg/PUF)

	Central tendencies	Africa (N=127)	Asia (N=46)	PAC (N=43)	GRULAC (N=101)	Overall (N=317)
<b>PFOS</b>	Mean (SD)	1640 (5940)	139 (122)	297 (219)	376 (497)	847 (3860)
	Median [Min, Max]	110 [0, 36000]	101 [27.3, 634]	266 [0, 827]	192 [0, 2260]	136 [0, 36000]
	Missing	5 (3.9%)	1 (2.2%)	3 (7.0%)	10 (9.9%)	19 (6.0%)
<b>PFOA</b>	Mean (SD)	305 (464)	271 (194)	181 (86.5)	257 (125)	268 (313)
	Median [Min, Max]	153 [0, 3180]	183 [83.1, 965]	165 [0, 417]	233 [58.9, 655]	192 [0, 3180]
	Missing	10 (7.9%)	2 (4.3%)	5 (11.6%)	5 (5.0%)	22 (6.9%)
<b>PFHxS</b>	Mean (SD)	224 (980)	13.4 (20.7)	41.6 (48.5)	9.72 (18.6)	101 (628)
	Median [Min, Max]	0 [0, 7880]	0 [0, 96.1]	34.7 [0, 206]	0 [0, 101]	0 [0, 7880]
	Missing	2 (1.6%)	2 (4.3%)	0 (0%)	1 (1.0%)	5 (1.6%)
<b>FOSA</b>	Mean (SD)	132 (414)	24.6 (81.8)	68.5 (155)	138 (260)	112 (315)
	Median [Min, Max]	0 [0, 1890]	0 [0, 327]	0 [0, 669]	34.9 [0, 964]	0 [0, 1890]
	Missing	63 (49.6%)	30 (65.2%)	20 (46.5%)	56 (55.4%)	169 (53.3%)



**Figure 22:** PAS/PUFs: Box plots for 4 PFAS colored by region (left, unscaled but zoomed to 1 500 pg/PUF) and with the regions (right, scaled); values normalized to 1 PUF and 3 months exposure (n=317)





**Figure 23:** PAS/PUFs: Box plots by country for 4 PFAS (n=317); values normalized to 1 PUF and 3 months exposure.

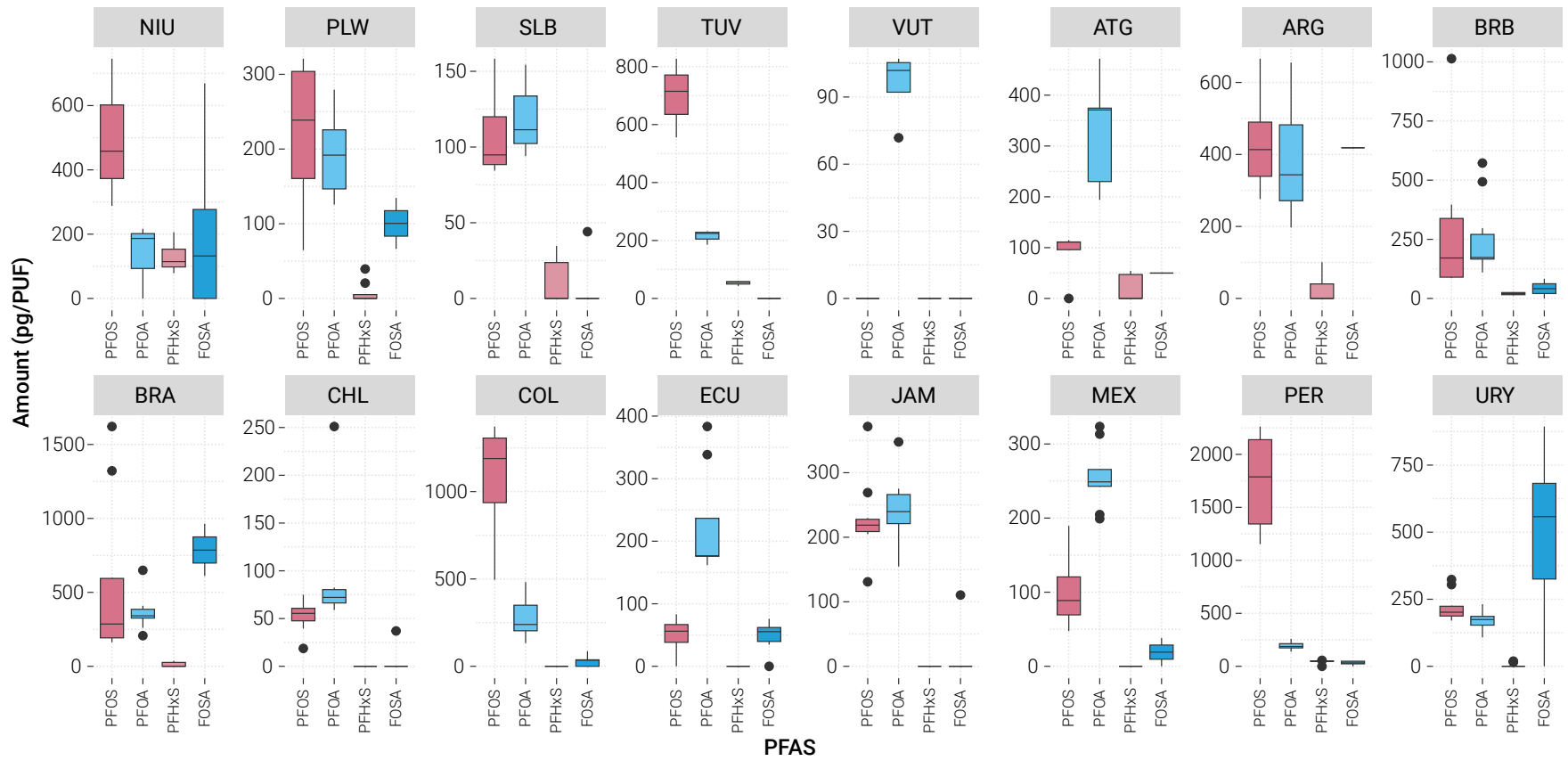


Figure 23: Continued

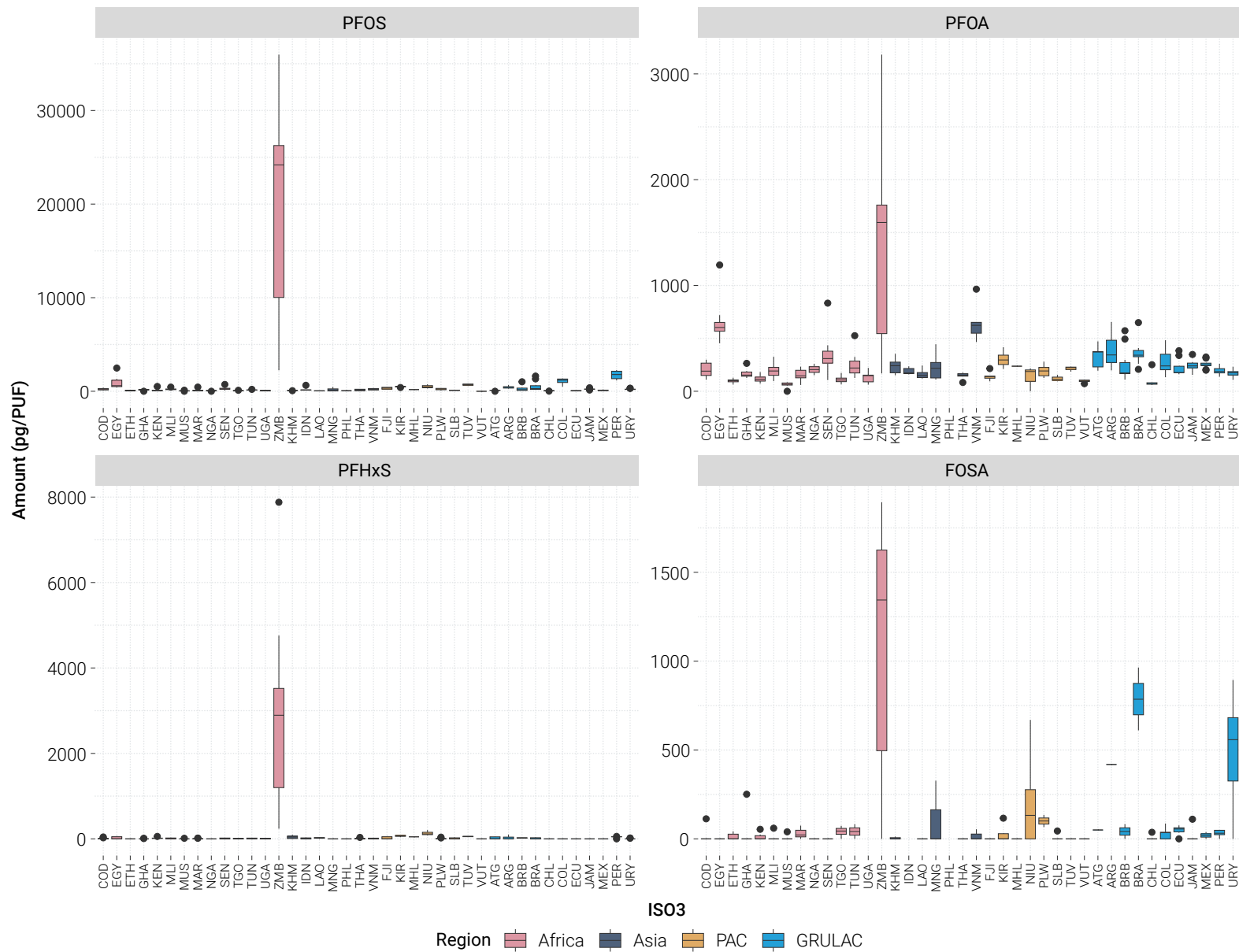
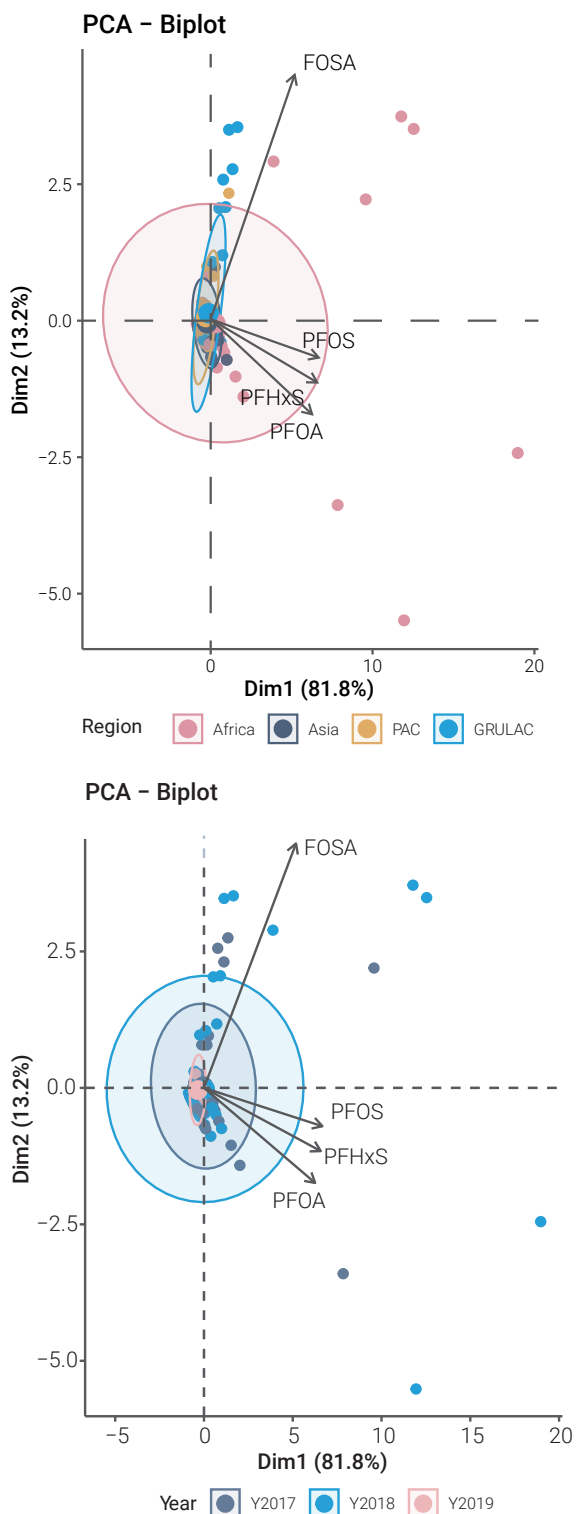


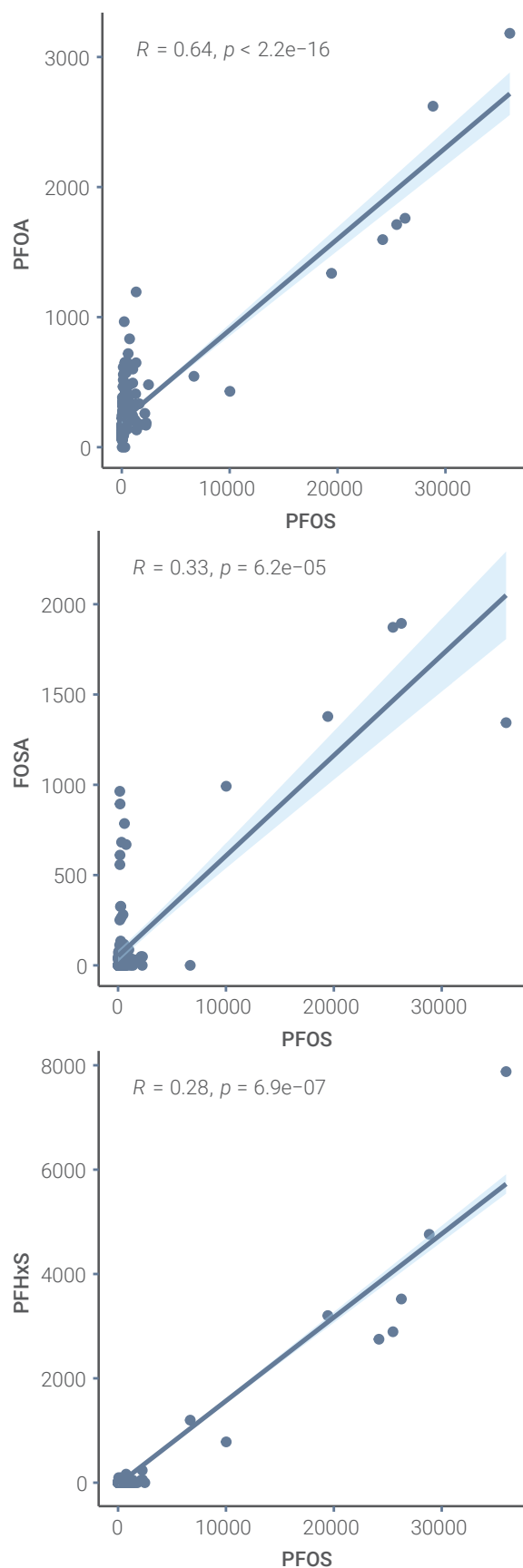
Figure 24: PAS/PUFs: Box plots by 4 PFAS by country colored for region (n=317); values normalized to 1 PUF and 3 months exposure.

PFOS was moderately correlated with PFOA ( $r=0.64$ ) but not with FOSA ( $r=0.33$ ) or PFHxS ( $r=0.28$ ) (Figure 26).

The Kruskal Wallis test did not show any significant differences between the regions ( $p=0.151$ ) but significant difference was found with respect to the years ( $p=0.014$ ); no significant differences between 2018 and 2019 measurements ( $p=0.180$ ).



**Figure 25:** PAS/PUFs: PCA for 4 PFAS according to region. All values are normalized to 1 PUF and 3-months exposure (N=317)



**Figure 26:** PAS/PUFs: Spearman correlation for PFAS

# SECTION 3

**Air monitoring with active air samplers (AAS)**





### 3. AIR MONITORING WITH ACTIVE AIR SAMPLERS (AAS)

The implementation of the AAS component of the project was very scattered and not all samples could be collected. In addition, some samples were lost in the laboratory or were deteriorated so that no results could be obtained. A further limitation included that not all the listed POPs were analyzed by all laboratories.

The following figures provide the measured data as stacked columns for the four classes of POPs groups analyzed by individual sample and as 100% columns (left and right sites of the figures) whereby the latter represents the profile for the POPs group- and summarized as box whisker plots with median values and quartiles (25<sup>th</sup> and 75<sup>th</sup>). All amounts refer to 1 m<sup>3</sup> of air sampled.

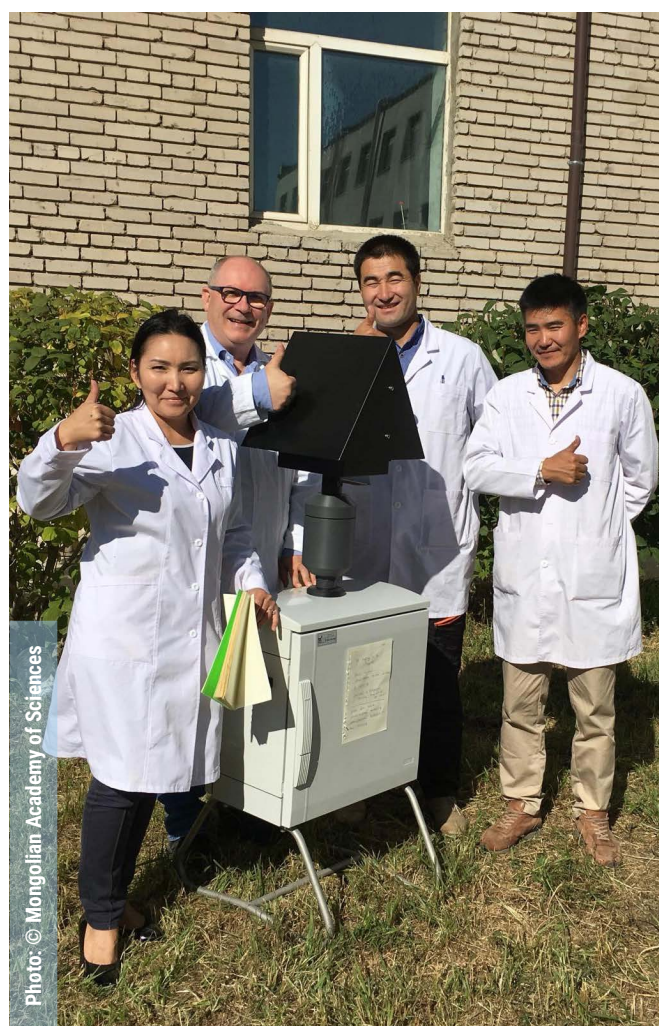
Figure 27 and Figure 28 refer to OCPs with the industrial POPs. It can be seen that the composition of the samples as well as the scale and the pattern are very different. Especially, the Ghana and the Kenya samples (analyzed by the same laboratory) showed very different composition: In Ghana, the whole pattern almost exclusively consisted of PCB<sub>6</sub> whereas in Kenya, PCB<sub>6</sub> and HCB played a minor role; instead, DDT was predominant. Whereas, the result for Kenya reflected the composition of Cl-POPs in the PAS/PUFs, the results for Ghana did not match (PAS/PUFs were dominated by endosulfan) (Figure 2). Also, Mauritius had higher percentages of PCB<sub>6</sub> and HCB in the PAS/PUFs than in the AAS sample. For Brazil, no OCPs could be measured due to interferences in the chromatogram.

With regards to dl-POPs, the pattern of the AAS were similar to the ones obtained for the PAS/PUFs (Figure 29); the pattern showed a clear dominance by PCDD/PCDF over the dl-PCB (Figure 9). As to scale, the amounts in the Mongolia samples had the highest median values (Figure 30).

For the Br-POPs, very few results were available and quite large differences as to the pattern between measurements in the same country or with respect to scale were found (Figure 31). With respect to overall scale, the highest values were found in Mongolia for AAS and PAS/PUFs (Figure 15).

Finally, the PFAS data in the AAS samples (Figure 33 and Figure 34) were hampered by the fact that for Viet Nam,

only the PUFs and XAD were available for analysis but not glass fiber filters (GFF). For Brazil, only the GFFs were analyzed. In order to obtain quantifiable results, GFFs from two sampling campaigns, each 3 days, were combined. Further it must be mentioned that two different laboratories analyzed the samples, which might explain the large differences in amounts but also in PFAS. Samples from Ghana and Kenya were analyzed by the same laboratory with large differences in scale: whereas the Ghana sample is comparable to the Brazil sample (analyzed by a different laboratory), the Kenya sample had much higher concentrations than the three other samples. PFOS was dominating over PFOA in all samples but Ghana. The Brazil sample is interesting in so far that the PFOS precursor FOSA was present at about 30% of the total. In the PAS/PUFs, Ghana and Kenya had similar scale and composition of the pattern whereas the Viet Nam samples were dominated by PFOA. The Brazil PAS/PUFs samples had FOSA present as well.





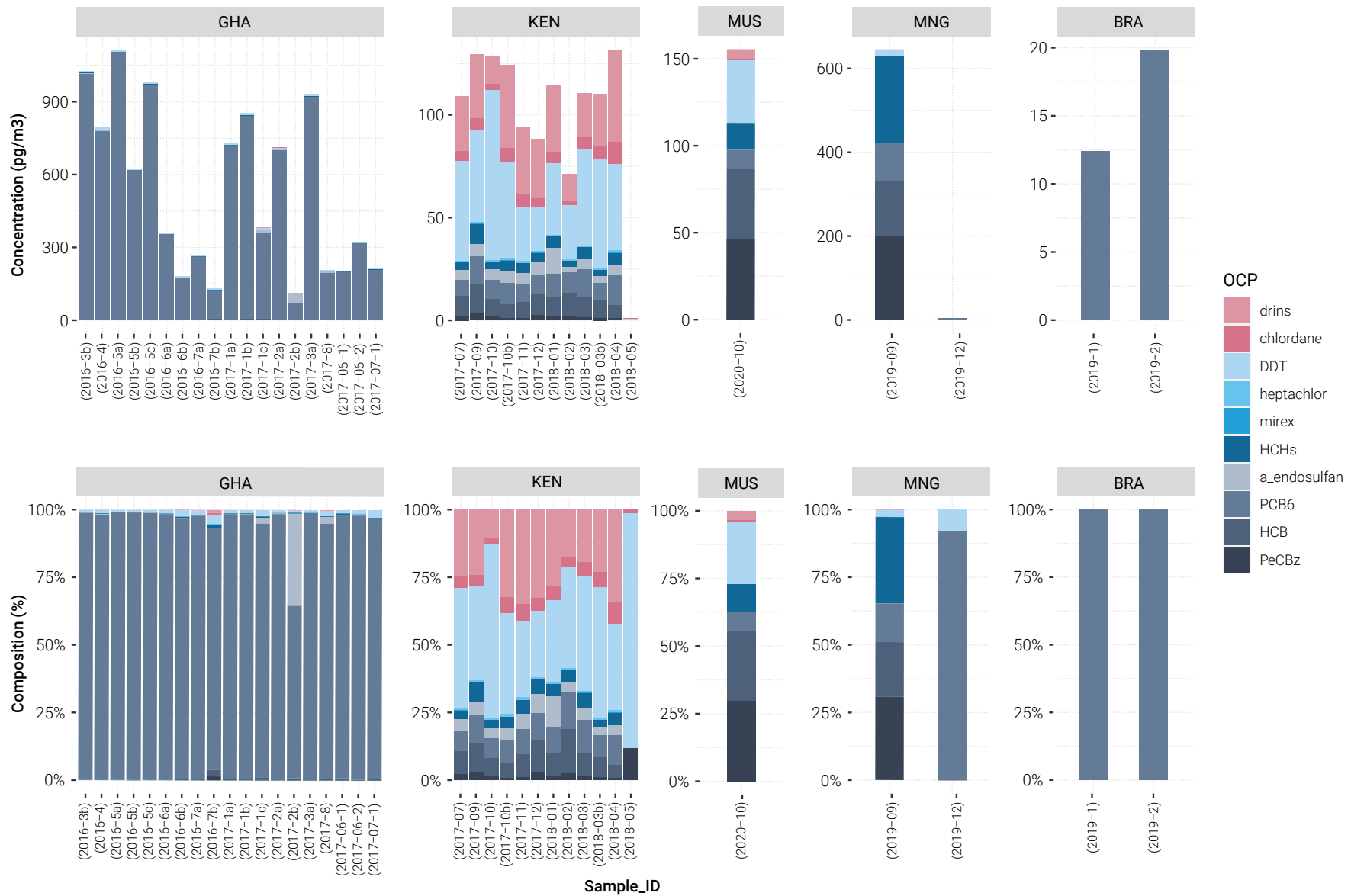


Figure 27: AAS: bar plots with stacked bars for OCPs+PCB6; left: scale, right: percentage of quantified POPs

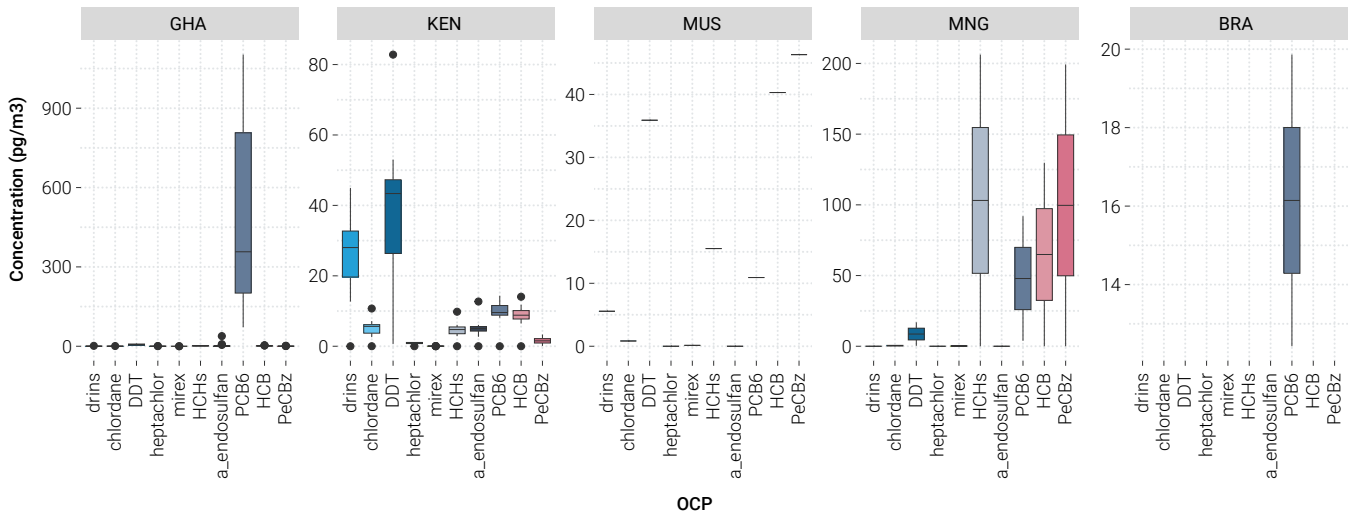


Figure 28: AAS: Box whisker plots for CI-POPs

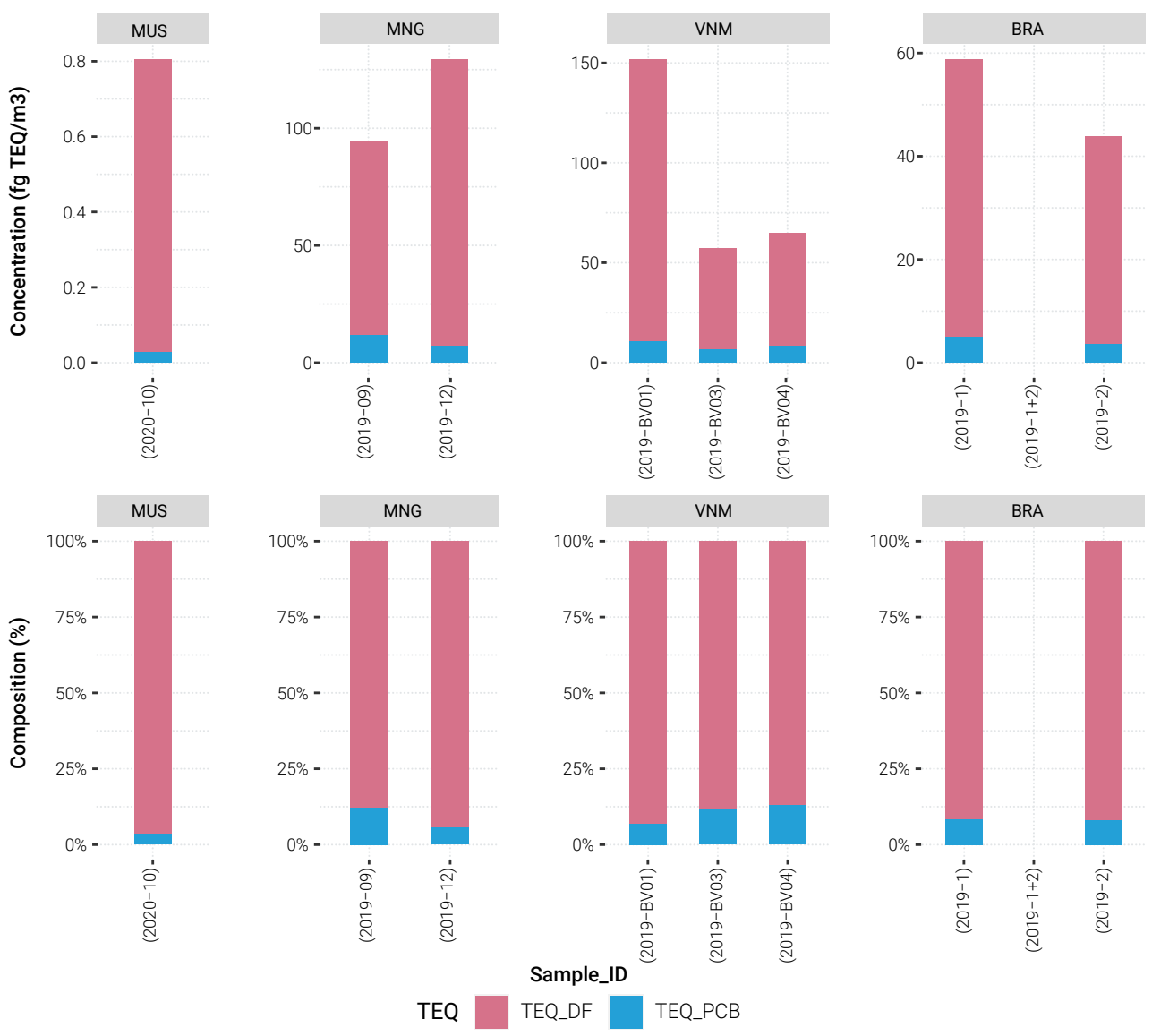


Figure 29: AAS: bar plots with stacked bars for dl-POPs; left: scale, right: percentage of quantified POPs

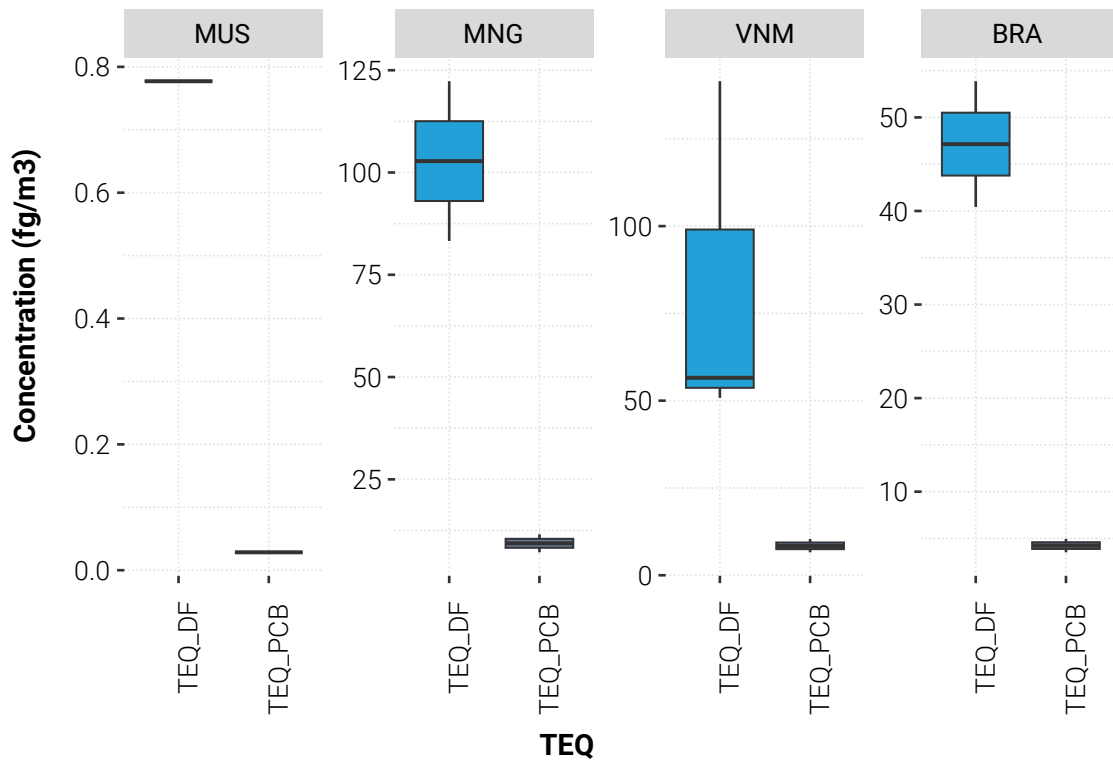


Figure 30: AAS: Box whisker plots for dl-POPs

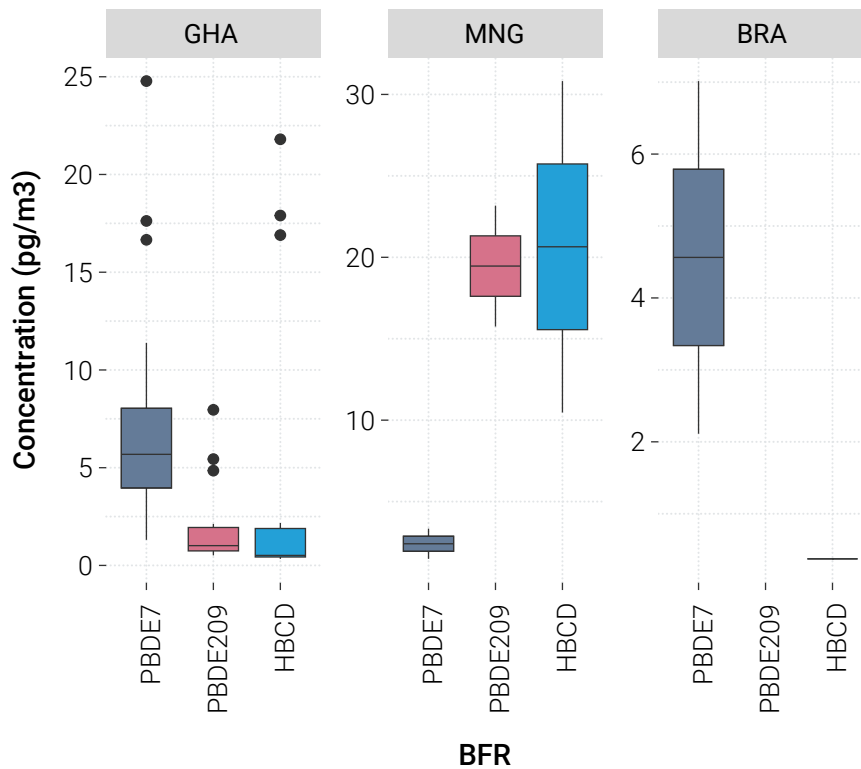


Figure 32: AAS: Box whisker plots for Br-POPs



Figure 33: AAS: bar plots with stacked bars for PFAS; left: scale, right: percentage of quantified POPs

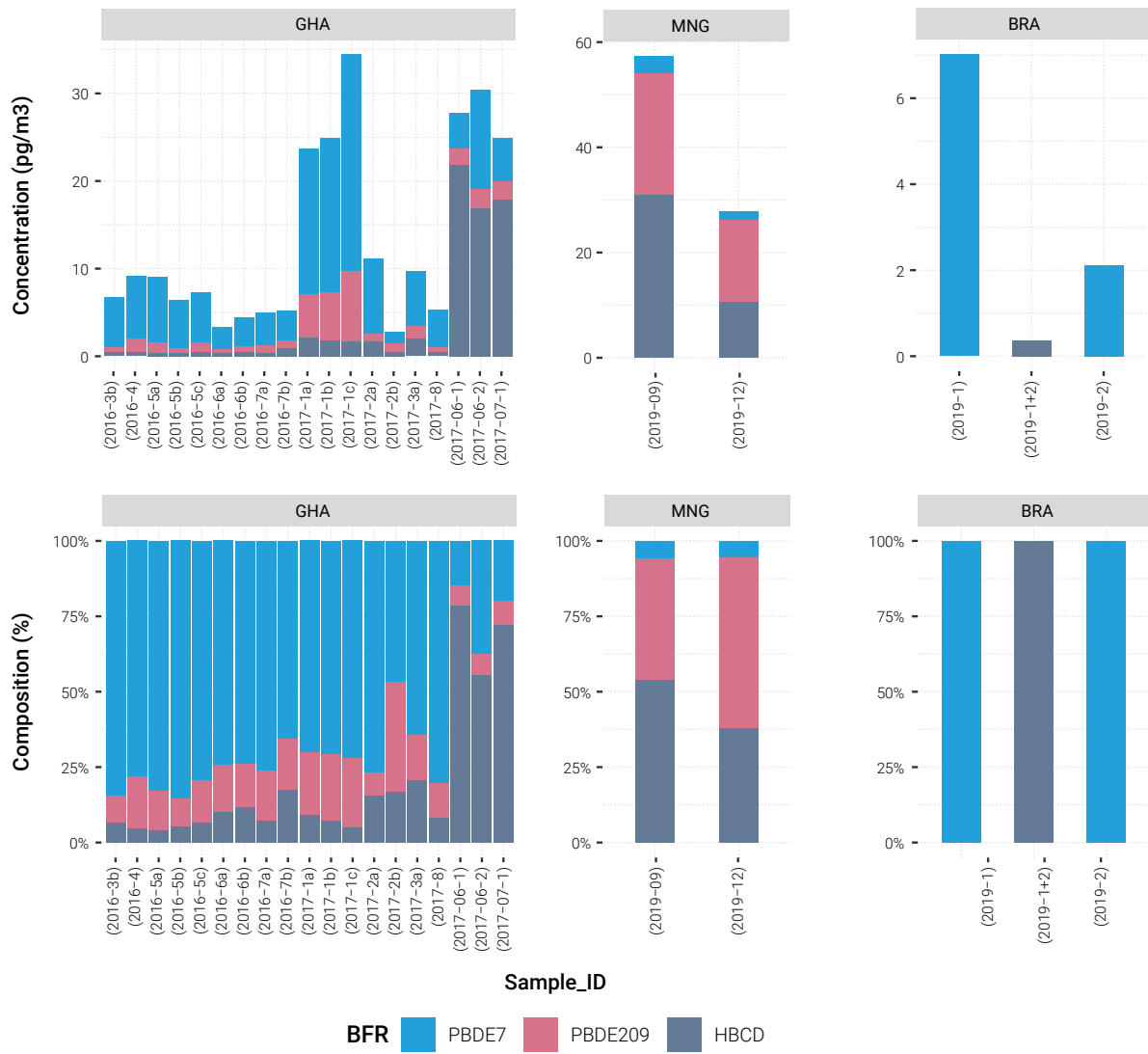


Figure 31: AAS: bar plots with stacked bars for Br-POPs; left: scale, right: percentage of quantified POPs

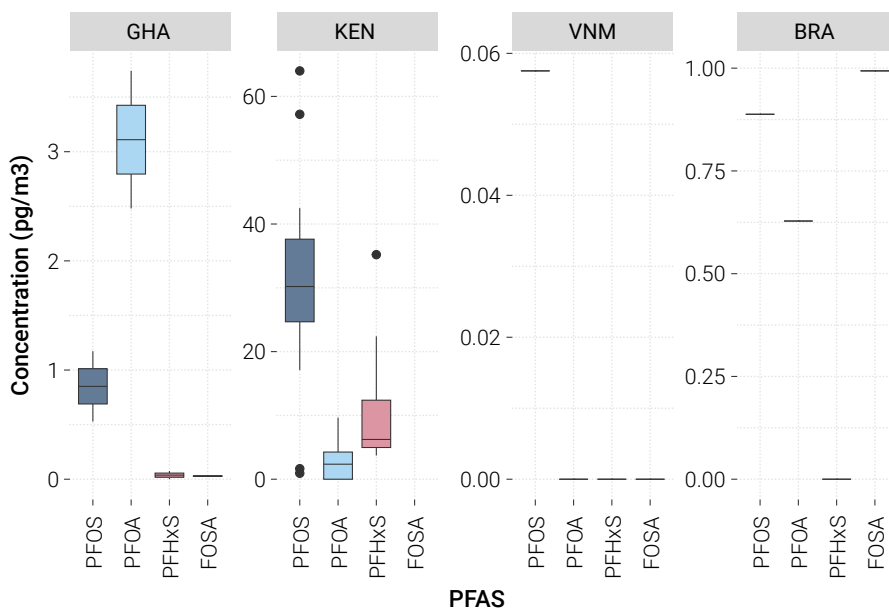


Figure 34: AAS: Box whisker plots for PFAS



# SECTION 4

PAS/PUF data in relation to metadata  
(income and population density)



# 4. PAS/PUF DATA IN RELATION TO METADATA (INCOME AND POPULATION DENSITY)

In the present section the lifestyle factors include wealth, with WBC used as an indicator, and population density as an indicator for urban or rural settings were used for further analyses. It is important to note that the classification of the World Bank and the population density are used and applies to the whole country and not to the specific location of the sampling sites.

As in previous sections, the POPs were grouped into chlorinated POPs, brominated POPs, dl-POPs and fluorinated POPs. The number of samples and their respective regions as to WBC or PD\_Code are contained in the tables for chlorinated POPs (Table 3), dl-POPs (Table 5), BFR (Table 7), and PFAS (Table 9).

The following tables provide the descriptive statistics for each POPs groups for WBC (Table 11, Table 13, Table 15, and Table 17) and for the PD\_Code (Table 12, Table 14, Table 16, and Table 18), respectively. The figures show the amounts of the quantified POPs colored by either income

group or population density. Some distinct pattern can be seen for individual POPs; however, statistical testing was not done for individual POPs rather for POPs groups.

## 4.1. Chlorinated POPs

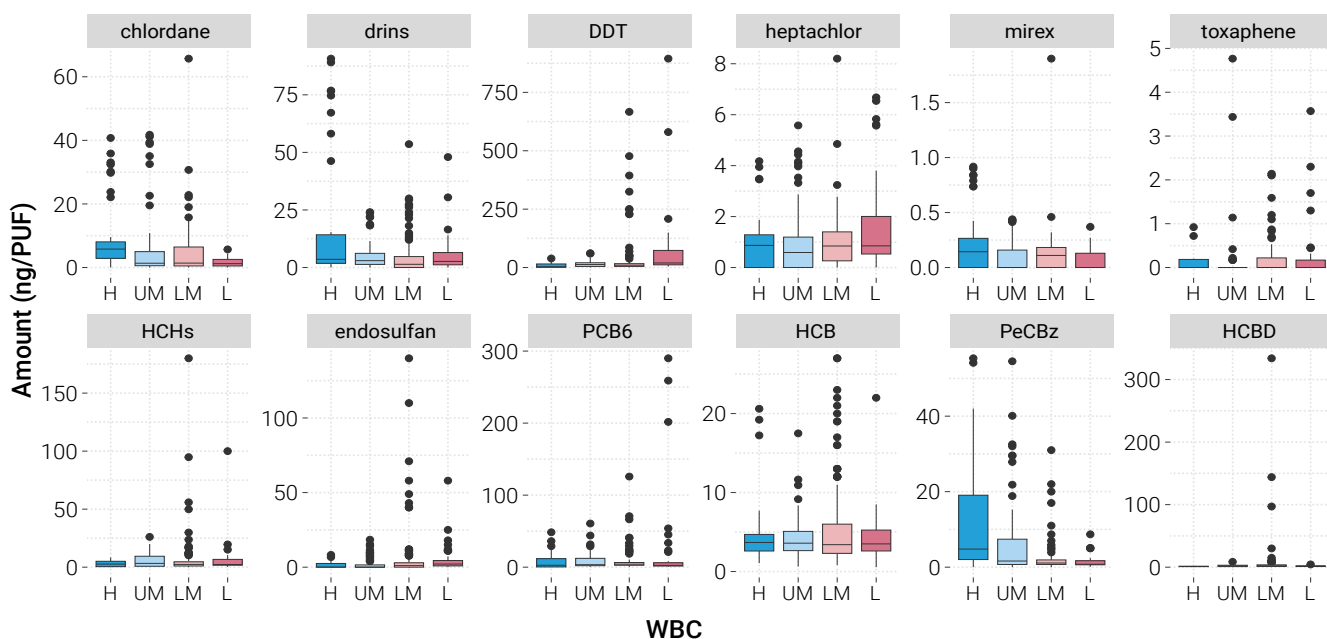
As was found for the regions, the scale of POPs in PAS/PUF was very different for the OCPs and industrial POPs. With respect to income, DDT values increase with decreasing income so that low-income countries had the highest values whereby the differences between the income groups were larger for the mean values than the median values (Table 11). Also, for PCB<sub>6</sub>, highest values were associated with low income. On the other hand, high income countries (H), from the present study, had highest amounts for chlordane, the drins, and PeCBz.

Figure 35 and Figure 36 show the WBC classification codes for each POP as scaled box plots for the overall samples and by country. Although there were many outliers found, the median values are very similar for all POPs. Subsequently, with respect to income, no significant differences were found (p=0.40).

A similar picture was obtained for population density, whereby densely populated countries had high values for chlordane and drins whereas least densely populated countries peaked for PCB<sub>6</sub> (Table 12) and Figure 37 and Figure 38.

No significant difference was found between the PD\_Codes; p-value = 0.099.

These similarities can also be seen in the PCAs for chlorinated POPs where ellipses largely overlap (Figure 39).

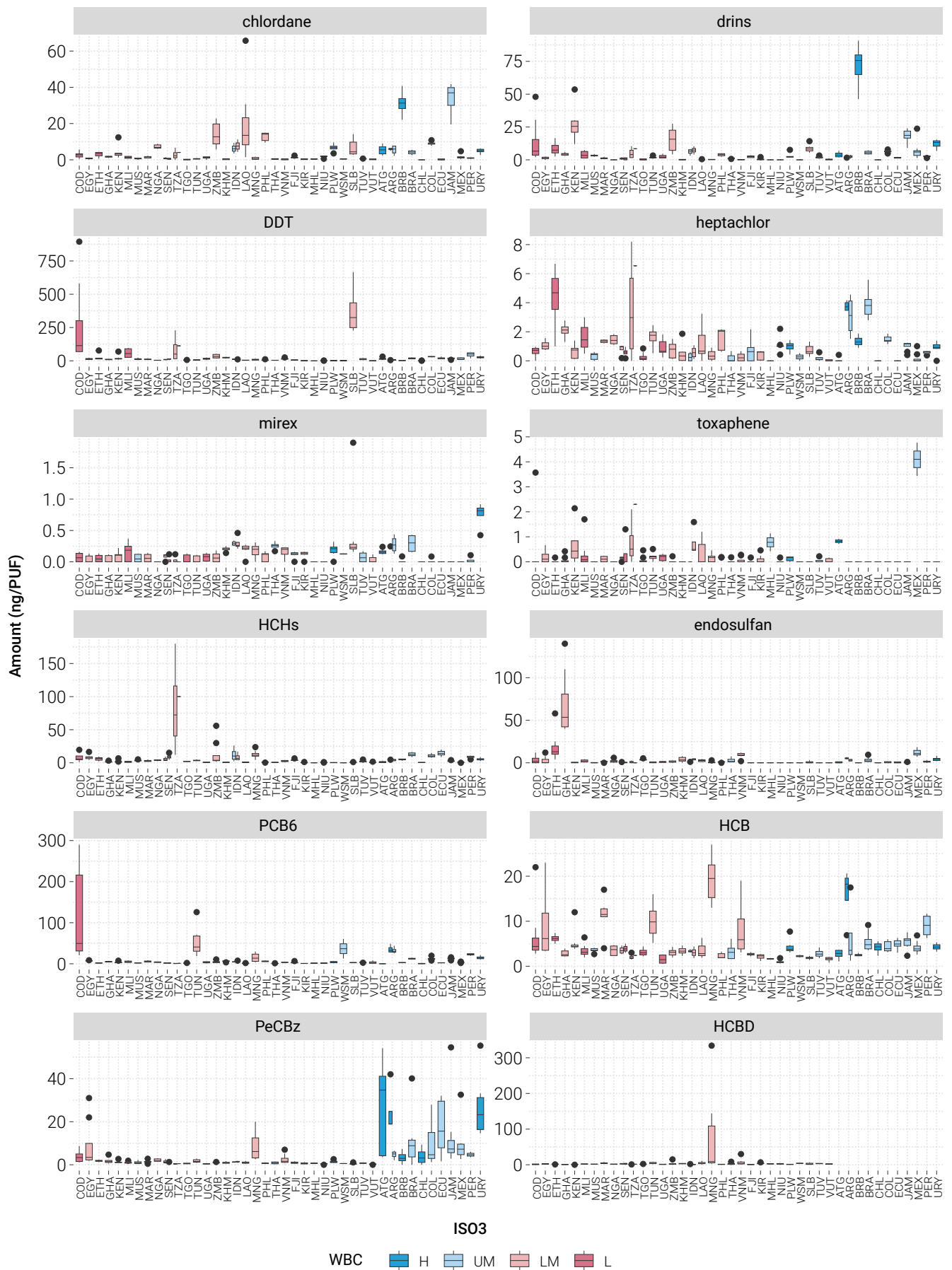


**Figure 35:** PAS/PUFs: Scaled boxplots for chlorinated POPs colored according to WBC (L=low, LM=lower-middle, UM=upper-middle, H=high) (N=294; N=211 for HCBd, N=232 for toxaphene)

**Table 11:** Descriptive statistics for OCPs+industrial POPs according to income (WBC) (Amounts in ng/PUF)

	Central tendencies	H (N=50)	UM (N=102)	LM (N=120)	L (N=43)	Overall (N=315)
<b>chlordane</b>	Mean (SD)	9.49 (11.3)	5.31 (9.69)	4.57 (7.94)	1.66 (1.46)	5.06 (8.75)
	Median [Min, Max]	5.80 [0, 40.8]	1.35 [0, 41.8]	1.39 [0, 65.7]	1.22 [0, 5.70]	1.74 [0, 65.7]
	Missing	9 (18.0%)	12 (11.8%)	0 (0%)	0 (0%)	21 (6.7%)
<b>drins</b>	Mean (SD)	17.8 (28.3)	4.59 (5.46)	4.59 (8.25)	5.55 (8.67)	6.57 (13.3)
	Median [Min, Max]	3.56 [0, 90.7]	2.98 [0, 24.1]	1.40 [0, 53.6]	2.65 [0, 48.0]	2.20 [0, 90.7]
<b>DDT</b>	Mean (SD)	9.22 (11.0)	14.8 (12.1)	35.3 (93.9)	71.3 (159)	30.7 (87.5)
	Median [Min, Max]	3.05 [0.303, 38.8]	12.8 [0, 61.1]	10.0 [0.320, 667]	19.5 [4.72, 895]	11.8 [0, 895]
<b>heptachlor</b>	Mean (SD)	0.958 (1.11)	0.960 (1.24)	1.01 (1.05)	1.62 (1.89)	1.08 (1.28)
	Median [Min, Max]	0.870 [0, 4.17]	0.590 [0, 5.58]	0.845 [0, 8.20]	0.850 [0, 6.68]	0.775 [0, 8.20]
<b>mirex</b>	Mean (SD)	0.233 (0.294)	0.0935 (0.128)	0.118 (0.192)	0.0731 (0.0904)	0.120 (0.188)
	Median [Min, Max]	0.144 [0, 0.917]	0 [0, 0.439]	0.110 [0, 1.90]	0 [0, 0.370]	0.100 [0, 1.90]
<b>toxaphene</b>	Mean (SD)	0.0854 (0.151)	0.212 (0.808)	0.188 (0.366)	0.266 (0.696)	0.201 (0.557)
	Median [Min, Max]	0 [0, 0.540]	0 [0, 4.77]	0 [0, 2.14]	0 [0, 3.57]	0 [0, 4.77]
<b>HCHs</b>	Mean (SD)	2.83 (2.45)	5.58 (5.71)	6.82 (19.6)	6.51 (15.2)	5.84 (14.2)
	Median [Min, Max]	2.66 [0, 8.41]	3.27 [0, 26.1]	2.38 [0, 180]	2.32 [0.197, 100]	2.79 [0, 180]
<b>endosul-fan</b>	Mean (SD)	1.44 (2.30)	1.92 (3.70)	6.40 (19.2)	5.39 (9.82)	4.19 (13.2)
	Median [Min, Max]	0 [0, 8.24]	0 [0, 18.4]	1.05 [0, 140]	2.10 [0, 58.0]	0.925 [0, 140]
<b>PCB<sub>6</sub></b>	Mean (SD)	7.55 (11.1)	8.15 (9.88)	7.95 (15.3)	23.9 (64.5)	10.3 (27.7)
	Median [Min, Max]	2.65 [0, 48.5]	3.45 [0.520, 60.6]	4.19 [0.440, 126]	2.49 [0.830, 290]	3.49 [0, 290]
<b>HCB</b>	Mean (SD)	4.81 (4.27)	4.07 (2.53)	5.76 (5.71)	4.28 (3.31)	4.89 (4.45)
	Median [Min, Max]	3.68 [1.06, 20.6]	3.59 [0.640, 17.5]	3.40 [0.820, 27.0]	3.50 [0.550, 22.0]	3.59 [0.550, 27.0]
<b>PeCBz</b>	Mean (SD)	13.7 (15.8)	6.22 (9.79)	2.27 (4.20)	1.47 (1.63)	4.95 (9.31)
	Median [Min, Max]	4.79 [0, 55.3]	1.63 [0, 54.5]	1.10 [0, 31.0]	0.780 [0.100, 8.70]	1.37 [0, 55.3]
<b>HCBD</b>	Mean (SD)	1.12 (0.726)	2.18 (1.60)	7.84 (33.9)	1.64 (0.906)	5.26 (25.7)
	Median [Min, Max]	1.04 [0, 2.10]	2.00 [0, 8.50]	2.25 [0, 334]	1.60 [0, 4.40]	2.00 [0, 334]





**Figure 36:** PAS/PUFs: Scaled boxplots for OCPs+industrial POPs with country and colored according to WBC (N=294; N=211 for HCBd, N=232 for toxaphene)

**Table 12:** Descriptive statistics for OCPs+industrial POPs to according to population density (PD\_Code) (Amounts in ng/PUF)

	Central tendencies	PD<25 (N=90)	PD_25-90 (N=91)	PD_90-200 (N=64)	PD_200-330 (N=43)	PD_330-2000 (N=27)	Overall (N=315)
<b>chlordane</b>	Mean (SD)	3.86 (4.73)	4.20 (8.22)	1.89 (2.43)	9.67 (13.3)	12.8 (14.0)	5.06 (8.75)
	Median [Min, Max]	2.06 [0, 22.8]	1.43 [0, 65.7]	0.735 [0, 11.3]	5.52 [0, 41.8]	9.50 [0, 40.8]	1.74 [0, 65.7]
<b>drins</b>	Mean (SD)	4.81 (6.10)	5.26 (9.20)	4.31 (6.29)	4.80 (7.36)	25.3 (34.0)	6.57 (13.3)
	Median [Min, Max]	2.22 [0, 27.4]	2.00 [0, 53.6]	1.77 [0, 30.0]	1.45 [0, 24.1]	3.70 [1.30, 90.7]	2.20 [0, 90.7]
<b>DDT</b>	Mean (SD)	49.5 (110)	41.4 (118)	12.1 (10.9)	12.8 (7.82)	8.39 (6.43)	30.7 (87.5)
	Median [Min, Max]	15.3 [0.303, 667]	13.0 [0.440, 895]	10.6 [0.320, 77.4]	12.3 [0, 31.8]	5.85 [1.72, 23.4]	11.8 [0, 895]
<b>heptachlor</b>	Mean (SD)	1.28 (1.38)	1.03 (1.30)	1.18 (1.53)	0.707 (0.626)	0.874 (0.712)	1.08 (1.28)
	Median [Min, Max]	0.910 [0, 5.58]	0.870 [0, 8.20]	0.665 [0, 6.68]	0.619 [0, 1.83]	0.630 [0, 2.17]	0.775 [0, 8.20]
<b>mirex</b>	Mean (SD)	0.215 (0.303)	0.0669 (0.0870)	0.126 (0.111)	0.072 (0.089)	0.050 (0.065)	0.120 (0.188)
	Median [Min, Max]	0.150 [0, 1.90]	0 [0, 0.320]	0.115 [0, 0.460]	0 [0, 0.239]	0 [0, 0.170]	0.100 [0, 1.90]
<b>toxaphene</b>	Mean (SD)	0.170 (0.684)	0.433 (0.925)	0.118 (0.255)	0.131 (0.251)	0.059 (0.090)	0.201 (0.557)
	Median [Min, Max]	0 [0, 4.77]	0 [0, 4.77]	0 [0, 1.59]	0 [0, 1.14]	0 [0, 0.220]	0 [0, 4.77]
<b>HCHs</b>	Mean (SD)	5.54 (8.07)	10.1 (24.3)	3.81 (4.84)	2.16 (1.45)	3.24 (1.79)	5.84 (14.2)
	Median [Min, Max]	2.84 [0, 55.9]	3.80 [0, 180]	1.72 [0, 26.1]	2.24 [0, 5.08]	3.13 [0.290, 5.86]	2.79 [0, 180]
<b>endosulfan</b>	Mean (SD)	1.70 (2.10)	2.05 (3.88)	12.7 (26.0)	2.52 (3.71)	0.257 (0.514)	4.19 (13.2)
	Median [Min, Max]	1.02 [0, 9.45]	0.630 [0, 18.4]	3.30 [0, 140]	1.17 [0, 12.0]	0 [0, 1.90]	0.925 [0, 140]
<b>PCB<sub>6</sub></b>	Mean (SD)	10.3 (10.9)	19.9 (49.0)	3.61 (2.48)	4.75 (4.44)	3.32 (1.63)	10.3 (27.7)
	Median [Min, Max]	5.92 [0, 48.5]	3.28 [0.440, 290]	2.64 [0.520, 8.67]	3.67 [0, 15.8]	2.70 [1.39, 7.82]	3.49 [0, 290]
<b>HCB</b>	Mean (SD)	5.88 (6.21)	5.31 (3.76)	4.27 (3.65)	4.25 (3.43)	2.87 (0.741)	4.89 (4.45)
	Median [Min, Max]	3.70 [0.640, 27.0]	4.20 [1.50, 22.0]	3.40 [1.20, 23.0]	3.46 [0.550, 19.0]	2.71 [1.80, 4.20]	3.59 [0.550, 27.0]
<b>PeCBz</b>	Mean (SD)	6.91 (10.8)	4.54 (7.52)	2.15 (4.59)	8.52 (14.8)	1.66 (1.75)	4.95 (9.31)
	Median [Min, Max]	1.30 [0, 55.3]	1.50 [0.290, 32.6]	1.20 [0.310, 31.0]	2.70 [0.100, 54.5]	0.770 [0, 7.38]	1.37 [0, 55.3]
<b>HCBD</b>	Mean (SD)	15.6 (54.7)	2.61 (2.32)	2.03 (1.51)	3.57 (5.99)	1.93 (1.02)	5.26 (25.7)
	Median [Min, Max]	2.40 [0, 334]	2.10 [0, 11.0]	1.60 [0, 8.50]	2.05 [0.500, 30.0]	1.70 [0, 4.10]	2.00 [0, 334]

For population density across all PD\_Codes, no significant difference was found (p=0.099).



Photo: © JNEP / Victor Estellano La Paz, Bolivia



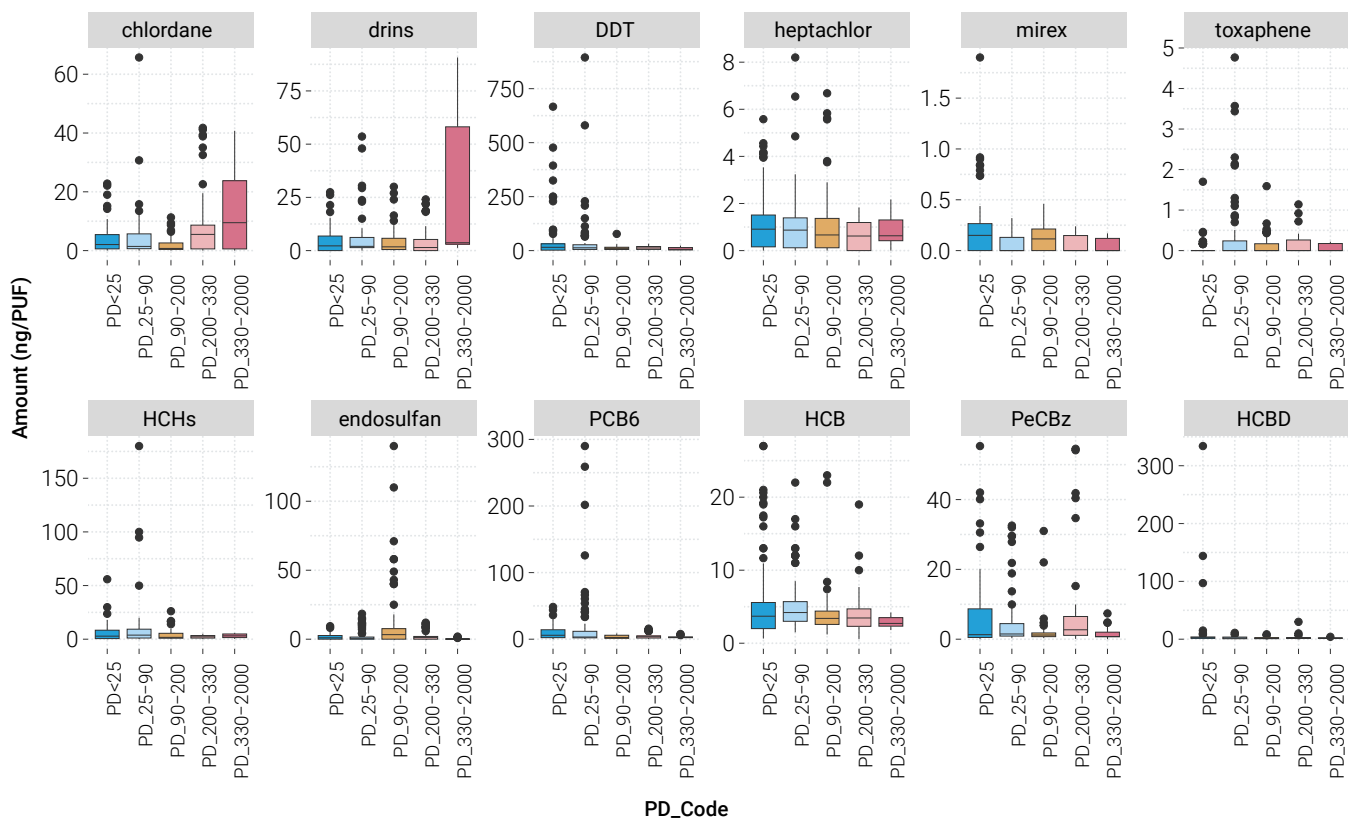
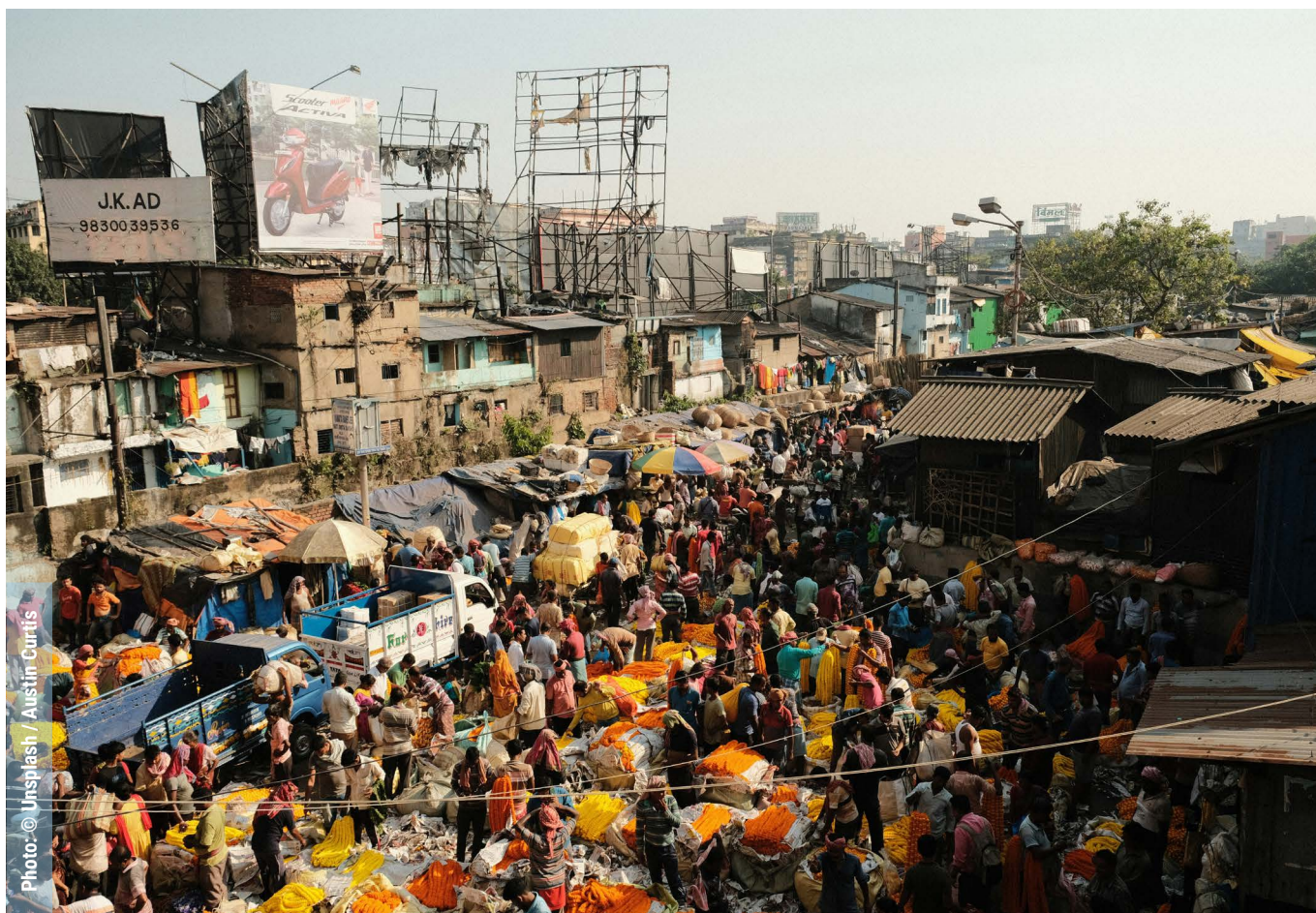
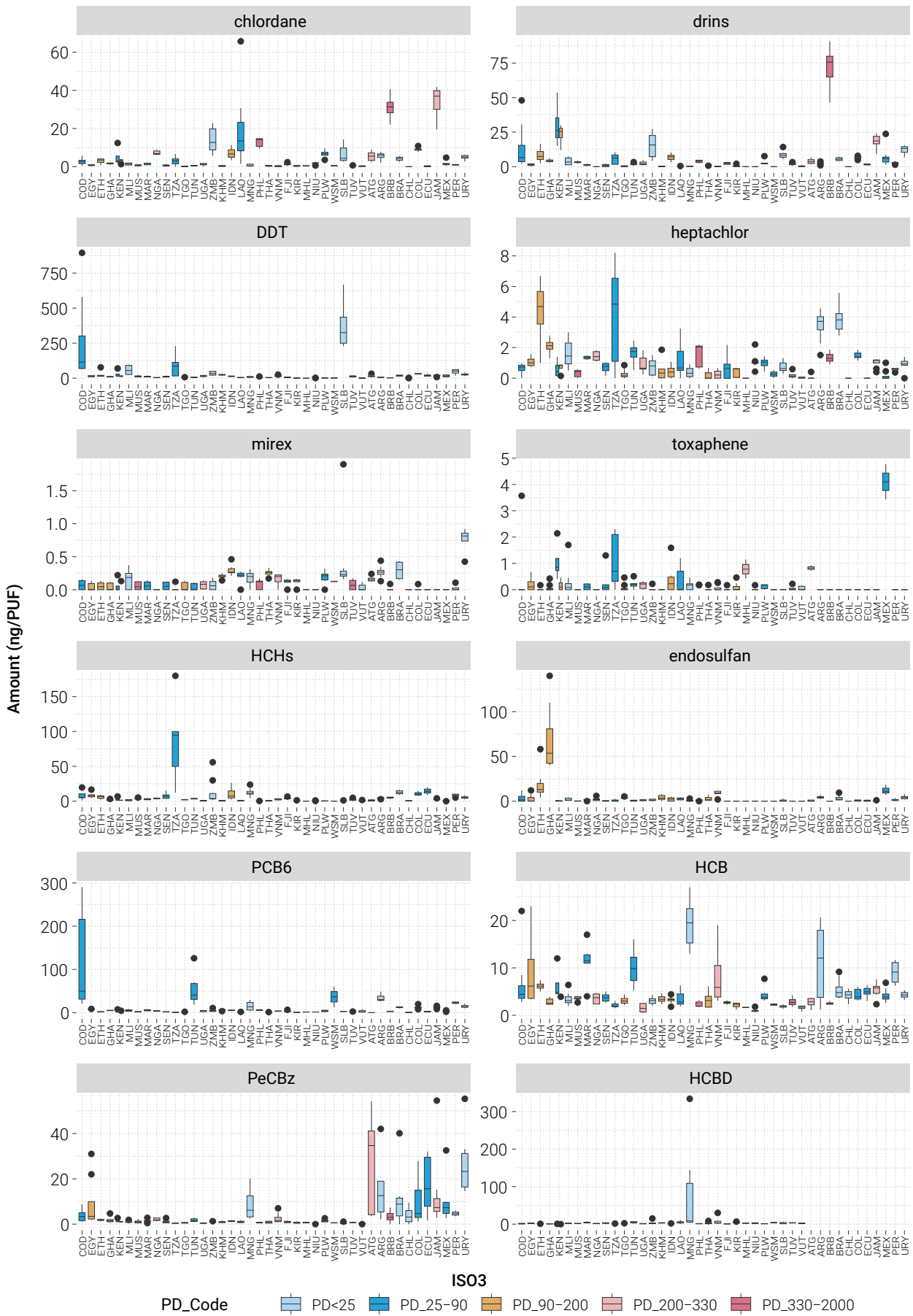
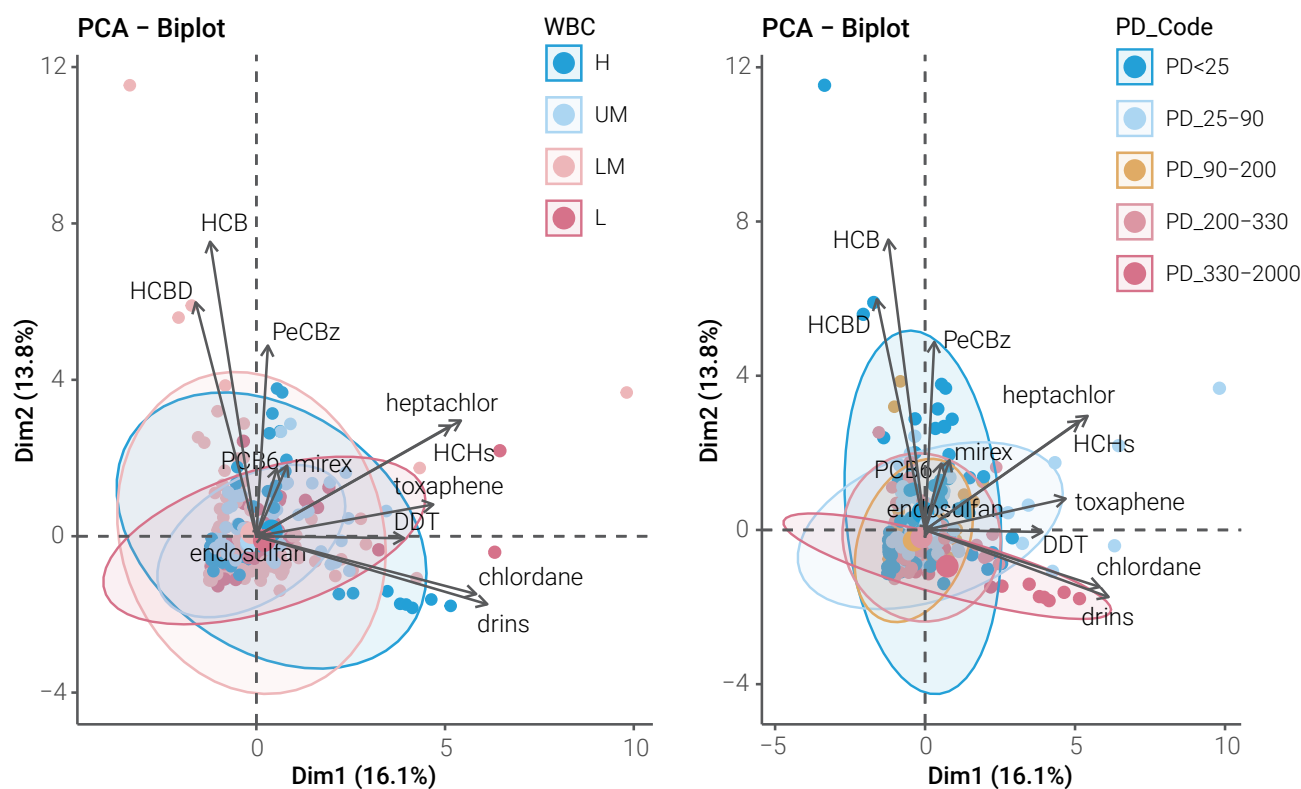


Figure 37: PAS/PUFs: Scaled boxplots for chlorinated POPs colored according to PD\_Code (N=294; N=211 for HCBd, N=232 for toxaphene)





**Figure 38:** PAS/PUFs: Scaled boxplots for chlorinated POPs at global level and colored according to PD\_Code (N=294; N=211 for HCBd, N=232 for toxaphene)



**Figure 39:** PAS/PUFs: PCA for OCPs+industrial POPs according to income (as WBC, left) and population density (PD\_Code, right). All values were normalized to 1 PUF and 3-months exposure (N=294; N=211 for HCBd, N=232 for toxaphene)

## 4.2. Dioxin-like POPs

With respect to income, the median TEQ for PCDD was highest in the high-income countries whereas the mean values did not have too much difference. For dl-PCB, the values were more evenly distributed (Table 13).

Figure 40 and Figure 41 show the WBC classification codes for the two TEQs. Outliers were mainly found for the lower income groups (LM and L). The income distribution showed significant differences for dl-POPs ( $p=0.00017$ ); and pairwise significant differences always between neighboring WBC classifications: H to UM ( $p=0.025$ ), UM to LM ( $p=0.00015$ ), and LM to L ( $p=0.025$ ).

**Table 13:** Descriptive statistics for dl POPs according to income (WBC) (Amounts in pg TEQ/PUF)

	Central tendencies	H (N=30)	UM (N=51)	LM (N=81)	L (N=33)	Overall (N=195)
<b>TEQ_DF</b>	Mean (SD)	10.1 (6.22)	6.39 (8.13)	14.8 (16.7)	12.8 (18.0)	11.5 (14.2)
	Median [Min, Max]	13.1 [0.0433, 17.7]	3.51 [0.0005, 33.5]	8.45 [0.0929, 69.2]	4.29 [0.0552, 77.7]	6.41 [0.0005, 77.7]
<b>TEQ_PCB</b>	Mean (SD)	2.43 (2.37)	2.12 (2.06)	4.13 (3.60)	2.42 (2.80)	3.05 (3.07)
	Median [Min, Max]	1.07 [0.253, 7.01]	2.10 [0.00234, 11.0]	3.20 [0.00326, 16.4]	0.825 [0.00037, 8.67]	2.34 [0.00037, 16.4]



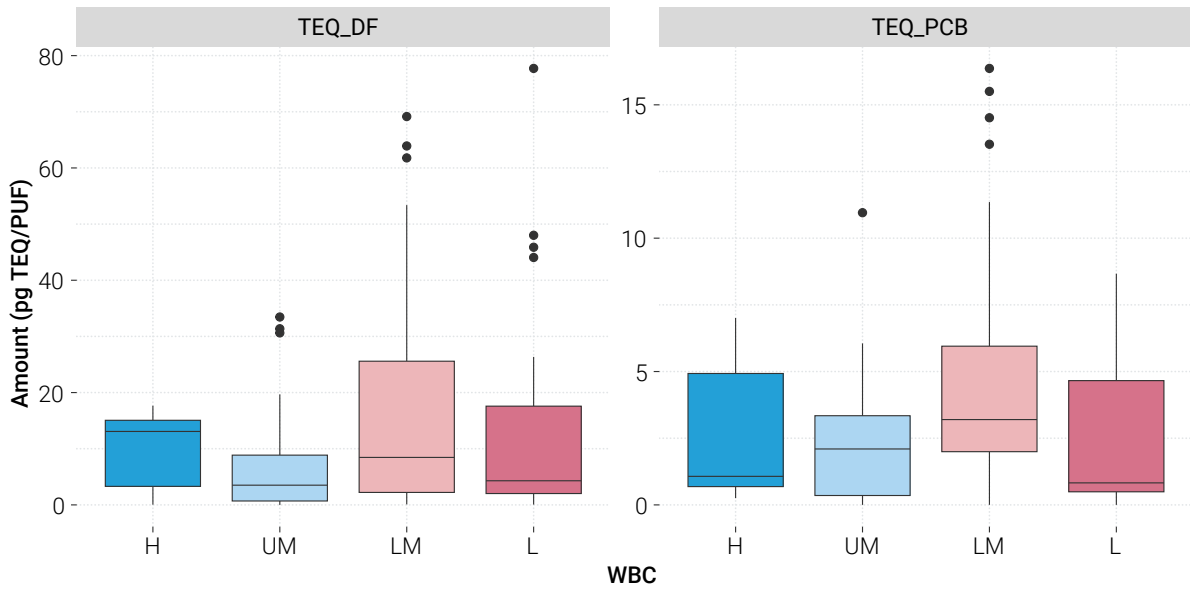


Figure 40: PAS/PUFs: Scaled boxplots for dl-POPs as TEQ colored according to WBC (n=195)

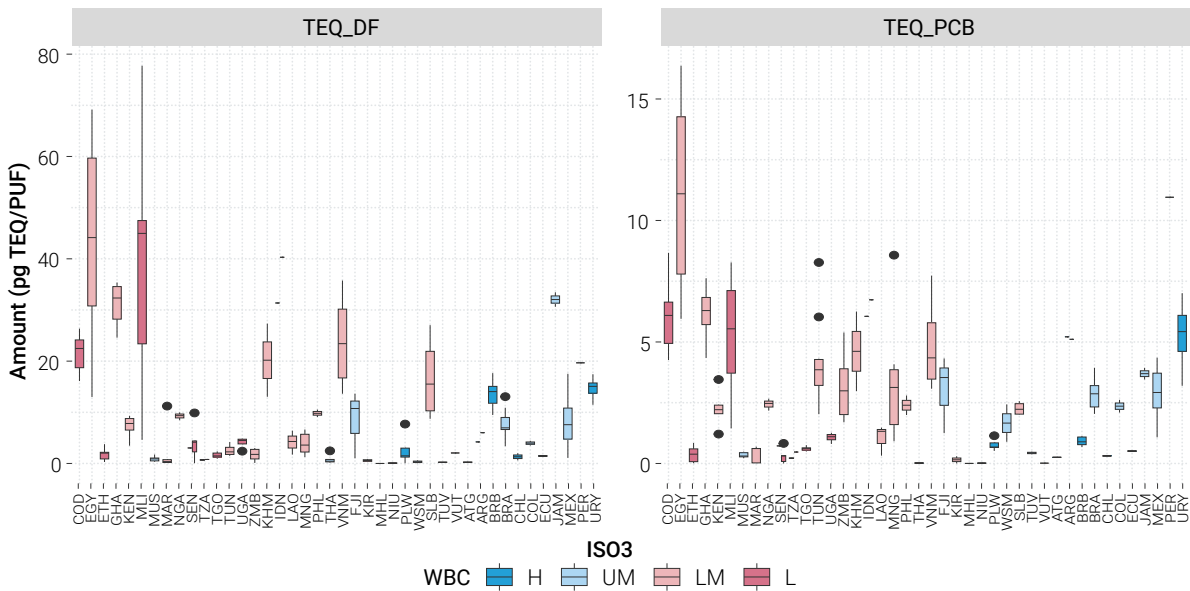


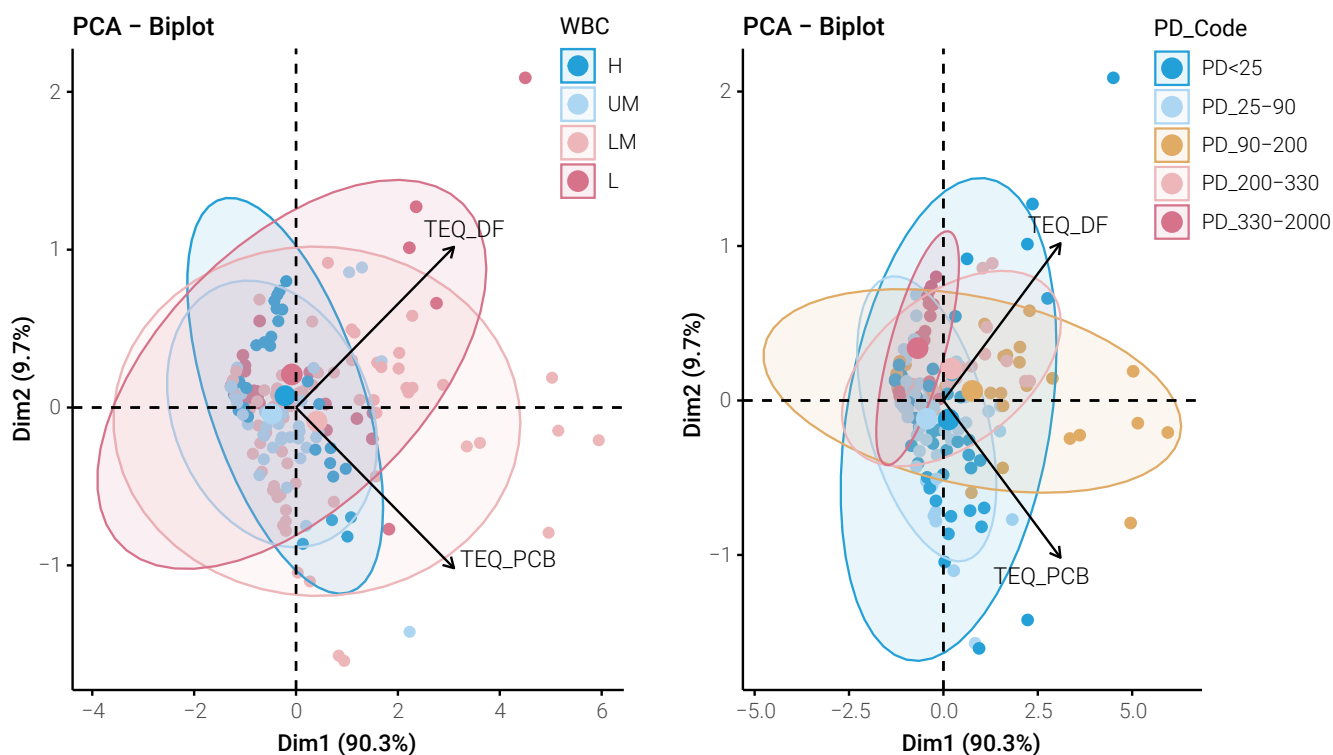
Figure 41: PAS/PUFs: Scaled boxplots for dl-POPs as TEQ by country according to WBC (n=195)

Table 14: Descriptive statistics for dl POPs according to population density (PD\_Code) (Amounts in pg TEQ/PUF)

	Central tendencies	PD<25 (N=51)	PD_25-90 (N=63)	PD_90-200 (N=39)	PD_200-330 (N=22)	PD_330 -2000 (N=20)	Overall (N=195)
TEQ_DF	Mean (SD)	11.7 (14.5)	5.91 (6.55)	19.8 (21.1)	15.7 (12.4)	8.08 (6.52)	11.5 (14.2)
	Median [Min, Max]	6.87 [0.0005, 77.7]	3.47 [0.0396, 26.4]	13.0 [0.162, 69.2]	13.8 [0.0005, 35.8]	9.92 [0.205, 17.7]	6.41 [0.0005, 77.7]
TEQ_PCB	Mean (SD)	3.62 (2.42)	2.36 (2.08)	4.57 (4.92)	3.07 (2.19)	0.843 (0.623)	3.05 (3.07)
	Median [Min, Max]	3.20 [0.0124, 11.0]	2.03 [0.000374, 8.67]	2.98 [0.00305, 16.4]	3.10 [0.0023, 7.73]	0.738 [0.216, 2.80]	2.34 [0.0004, 16.4]







**Figure 44:** PAS/PUFs: PCA for di-POPs as TEQ according to income (as WBC, left) and population density (PD\_Code, right). All values were normalized to 1 PUF and 3-months exposure

### 4.3. Brominated POPs

The results of the 293 BFR measurements grouped by the WBC are shown in Table 15. Most BFR peak in the LM group for the mean values. For the median values, the highest values are associated with the higher incomes. Interestingly, the maximum values were found in the lower income groups; e.g., PBDE and PBB153 with a measure-

ment in a low income country (L), PBDE 209 and HBCD in lower-middle (LM).

Figure 35 and Figure 36 show the WBC classification codes for each BFR as scaled box plots for the overall samples and by country. Although there were many outliers found and often, a POP peaked in one or a few countries, the median values are very similar (Figure 36). Subsequently, with respect to income, no significant differences were found ( $p=0.74$ ).

**Table 15:** Descriptive statistics for BFR according to income (WBC) (Amounts in ng/PUF)

	Central tendencies	H (N=41)	UM (N=89)	LM (N=120)	L (N=43)	Overall (N=293)
<b>PBDE8</b>	Mean (SD)	2.06 (2.14)	3.24 (3.88)	1.35 (1.79)	1.61 (3.34)	2.06 (2.96)
	Median [Min, Max]	1.38 [0, 9.13]	1.25 [0, 14.9]	0.790 [0, 9.84]	0.210 [0, 16.3]	0.980 [0, 16.3]
<b>PBDE 209</b>	Mean (SD)	4.48 (4.28)	0.860 (1.72)	9.04 (20.4)	5.74 (11.1)	6.64 (16.5)
	Median [Min, Max]	3.55 [0, 12.0]	0 [0, 7.20]	2.25 [0, 130]	2.40 [0, 58.0]	1.50 [0, 130]
	Missing	35 (85.4%)	49 (55.1%)	2 (1.7%)	0 (0%)	86 (29.4%)
<b>PBB153</b>	Mean (SD)	0 (0)	0.0034 (0.0165)	0.0069 (0.034)	0.0491 (0.163)	0.0111 (0.0680)
	Median [Min, Max]	0 [0, 0]	0 [0, 0.100]	0 [0, 0.230]	0 [0, 0.870]	0 [0, 0.870]
<b>Sum of HBCD</b>	Mean (SD)	1.27 (1.56)	2.34 (5.14)	3.89 (10.7)	2.79 (6.70)	2.90 (7.94)
	Median [Min, Max]	0.770 [0, 6.40]	0.580 [0, 35.7]	0.370 [0, 75.6]	0.400 [0, 39.4]	0.490 [0, 75.6]
	Missing	0 (0%)	3 (3.4%)	0 (0%)	0 (0%)	3 (1.0%)

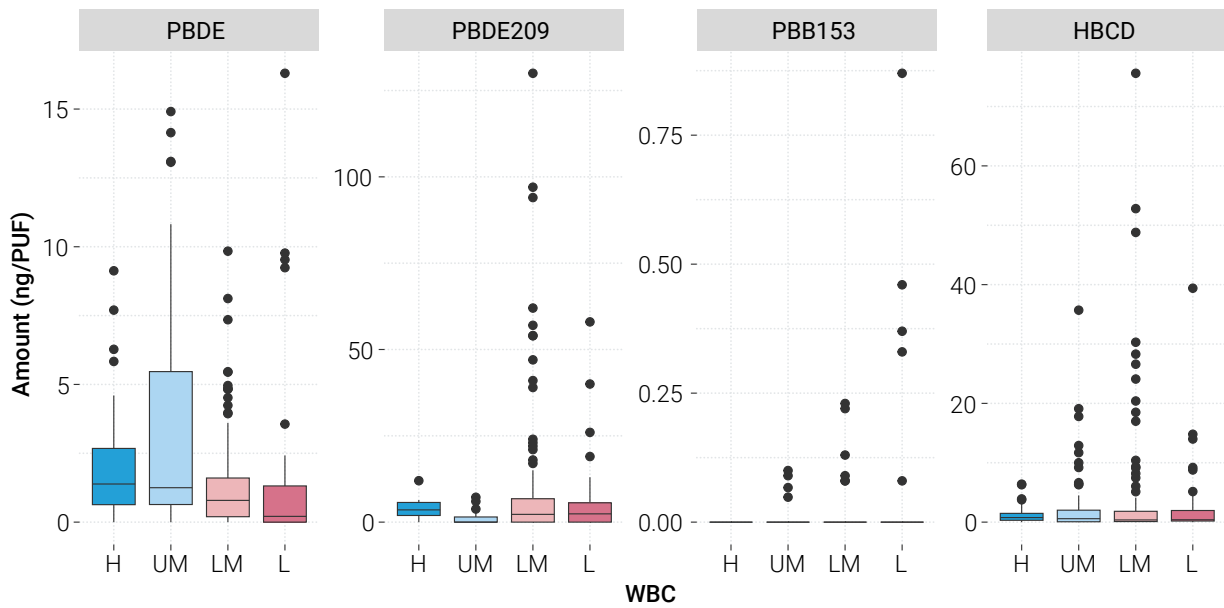


Figure 45: PAS/PUFs: Scaled boxplots for brominated POPs colored according to WBC

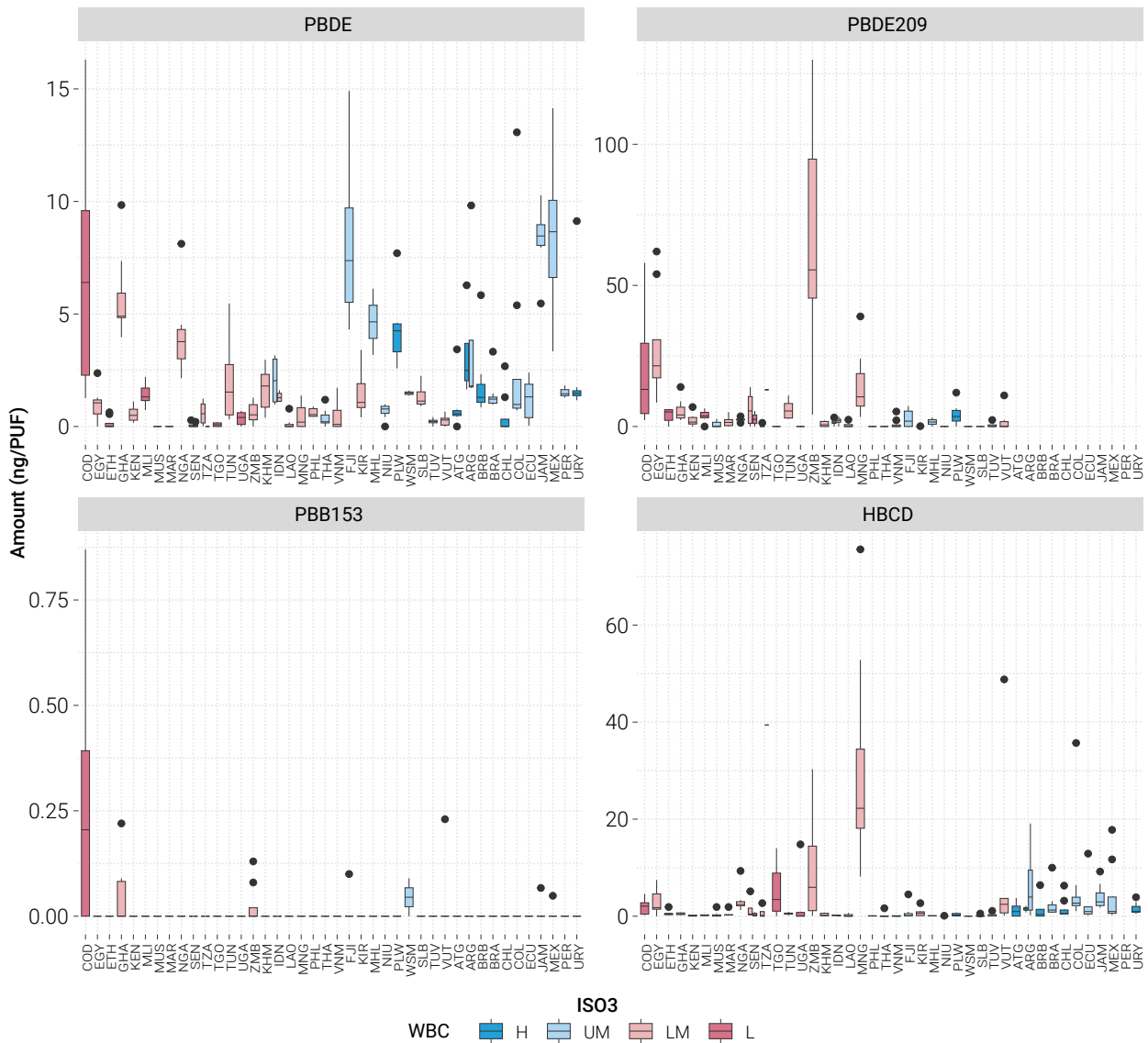


Figure 46: PAS/PUFs: Scaled boxplots for brominated POPs by country and colored according to WBC (n=293)

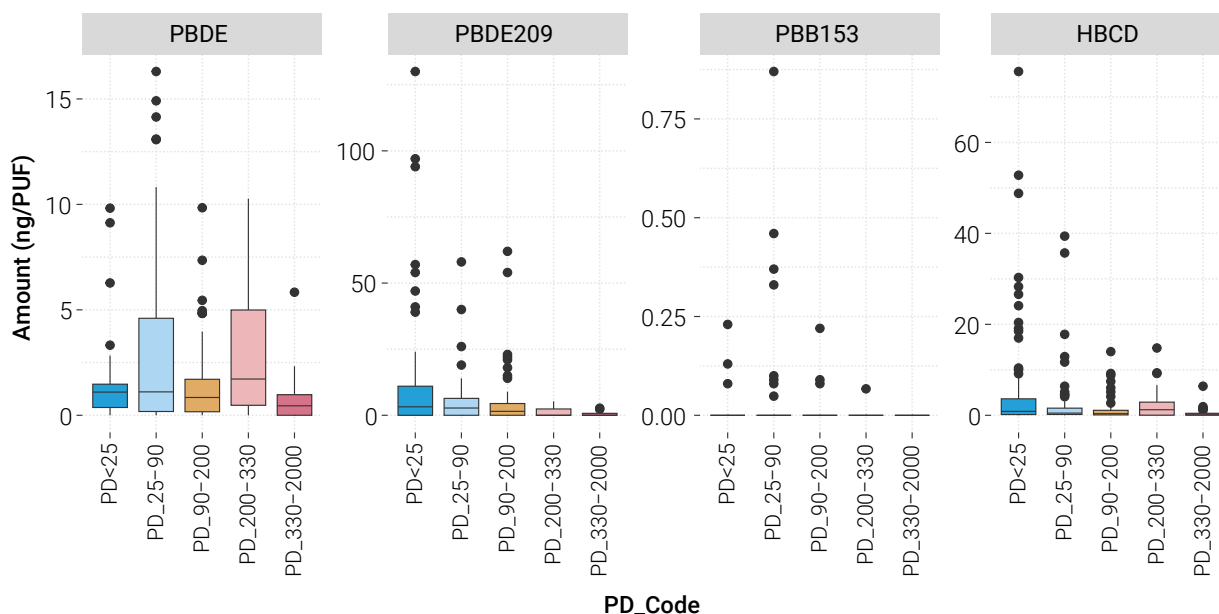
The assessment for population density is shown in Table 16, whereby densely populated countries had the highest values for all four BFRs. Figure 47 and Figure 48 show the graphical representation as box whiskers plots. It must be noted that the differences of the concentrations with respect to PD\_Codes were significant; p-value = 0.0022. Interestingly, the pairwise assessment showed that significant

differences were found only for the PD\_330-2000 to all other PD\_Codes (p-values ranged from p=0.009 to p=0.001).

These similarities can also be seen in the PCAs for chlorinated POPs where ellipses largely overlap; however, the ellipse for PD\_330-2000 is very narrow and located around the origin (Figure 49).

**Table 16:** Descriptive statistics for BFR according to population density (PD\_Code) (Amounts in ng/PUF)

	Central tendencies	PD<25 (N=80)	PD_25-90 (N=85)	PD_90-200 (N=64)	PD_200-330 (N=39)	PD_330-2000 (N=25)	Overall (N=293)
<b>PBDE</b>	Mean (SD)	1.29 (1.62)	3.12 (4.08)	1.48 (1.95)	3.09 (3.33)	0.775 (1.23)	2.06 (2.96)
	Median [Min, Max]	1.10 [0, 9.82]	1.11 [0, 16.3]	0.845 [0, 9.84]	1.72 [0, 10.3]	0.450 [0, 5.84]	0.980 [0, 16.3]
<b>PBDE209</b>	Mean (SD)	15.2 (29.3)	5.54 (9.72)	5.06 (11.2)	1.27 (1.57)	0.533 (0.957)	6.64 (16.5)
	Median [Min, Max]	3.20 [0, 130]	2.75 [0, 58.0]	1.50 [0, 62.0]	0 [0, 5.30]	0 [0, 2.70]	1.50 [0, 130]
	Missing	35 (43.8%)	PBB153		15 (38.5%)	10 (40.0%)	86 (29.4%)
<b>PBB153</b>	Mean (SD)	0.006 (0.031)	0.0276 (0.118)	0.00609 (0.0310)	0.002 (0.011)	0 (0)	0.011 (0.068)
	Median [Min, Max]	0 [0, 0.230]	0 [0, 0.870]	0 [0, 0.220]	0 [0, 0.0670]	0 [0, 0]	0 [0, 0.870]
<b>HBCD</b>	Mean (SD)	6.04 (13.1)	2.27 (6.19)	1.31 (2.58)	2.13 (3.13)	0.575 (1.33)	2.90 (7.94)
	Median [Min, Max]	0.860 [0, 75.6]	0.480 [0, 39.4]	0.360 [0, 14.0]	1.22 [0, 14.8]	0.0700 [0, 6.40]	0.490 [0, 75.6]
	Missing	3 (3.8%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)	3 (1.0%)



**Figure 47:** PAS/PUFs: Scaled boxplots for brominated colored according to PD\_Code (n=293)

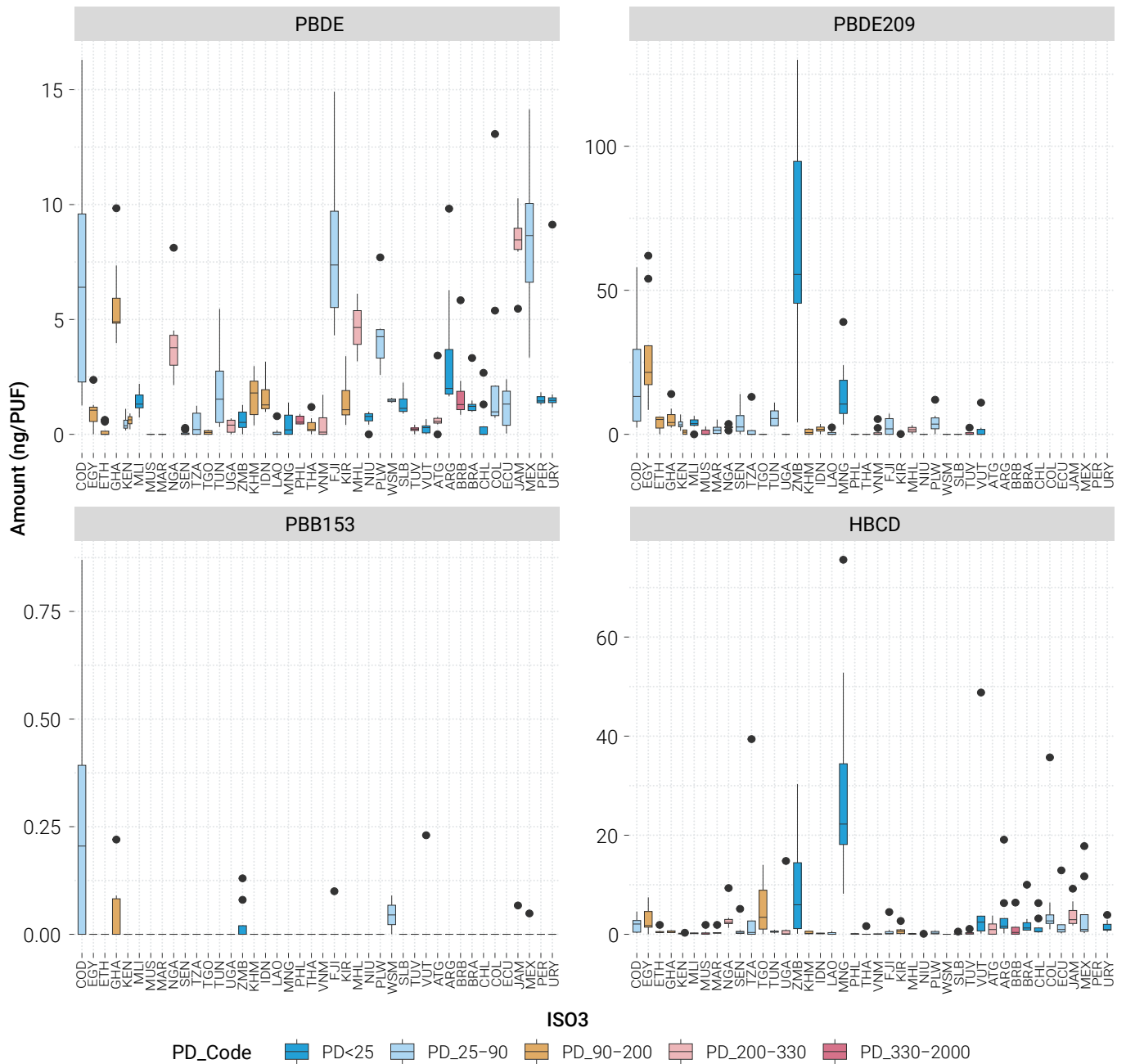
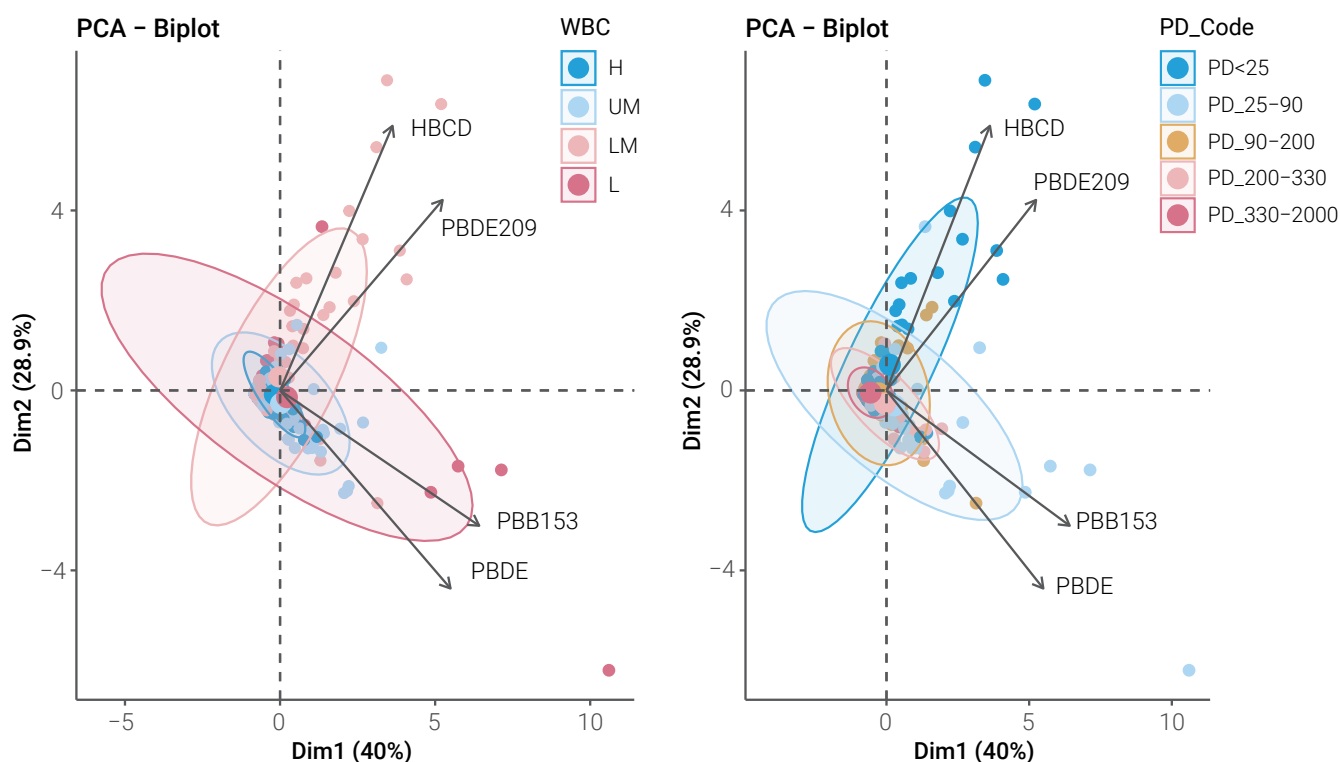


Figure 48: PAS/PUFs: Scaled boxplots for brominated POPs by country and colored for PD\_Code at global level (amount in ng/PUF) (n=293)



**Figure 49:** PAS/PUFs: PCA for BFR according to income (as WBC, left) and population density (PD\_Code, right). All values were normalized to 1 PUF and 3-months exposure

## 4.4. Fluorinated POPs

As was found for the regions, the scale of POPs in PAS/PUF was very different for the four POPs (Table 17). With respect to income, all maxima were due to the Zambia measurements, and therefore, associated with LM income group.

Figure 50 and Figure 51 show the WBC classification codes for the four PFAS as scaled box plots for the overall samples and by country. The Kruskal Wallis test finds no significant differences with a  $p=0.048$  between the different groups according to the income (WBC). The pairwise assessment showed that none of the combinations was significantly different; however, the  $p$ -values for all combinations with L were 0.053, whereas the others were  $p=0.966$ .

**Table 17:** Descriptive statistics for PFAS according to income (WBC) (Amounts in pg/PUF)

	Central tendencies	H (N=51)	UM (N=92)	LM (N=122)	L (N=52)	Overall (N=317)
<b>PFOS</b>	Mean (SD)	211 (186)	405 (516)	1710 (6020)	146 (127)	847 (3860)
	Median [Min, Max]	177 [0, 1010]	205 [0, 2260]	124 [0, 36000]	95.5 [37.8, 726]	136 [0, 36000]
<b>PFOA</b>	Mean (SD)	227 (132)	224 (119)	361 (469)	174 (125)	268 (313)
	Median [Min, Max]	192 [58.9, 655]	215 [0, 649]	202 [59.6, 3180]	139 [63.0, 833]	192 [0, 3180]
<b>PFHxS</b>	Mean (SD)	9.60 (15.2)	18.8 (37.8)	241 (998)	5.52 (9.95)	101 (628)
	Median [Min, Max]	0 [0, 54.4]	0 [0, 206]	0 [0, 7880]	0 [0, 43.6]	0 [0, 7880]
<b>FOSA</b>	Mean (SD)	166 (279)	98.5 (217)	142 (427)	18.7 (31.7)	112 (315)
	Median [Min, Max]	37.0 [0, 894]	0 [0, 964]	0 [0, 1890]	0 [0, 113]	0 [0, 1890]



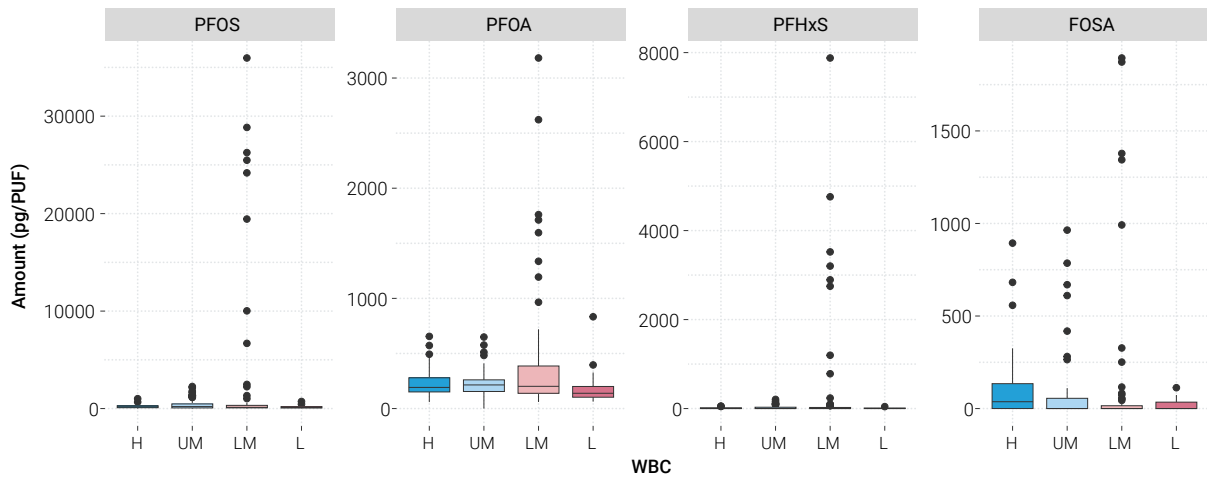


Figure 50: PAS/PUFs: Scaled boxplots for PFAS colored according to WBC (n=317)

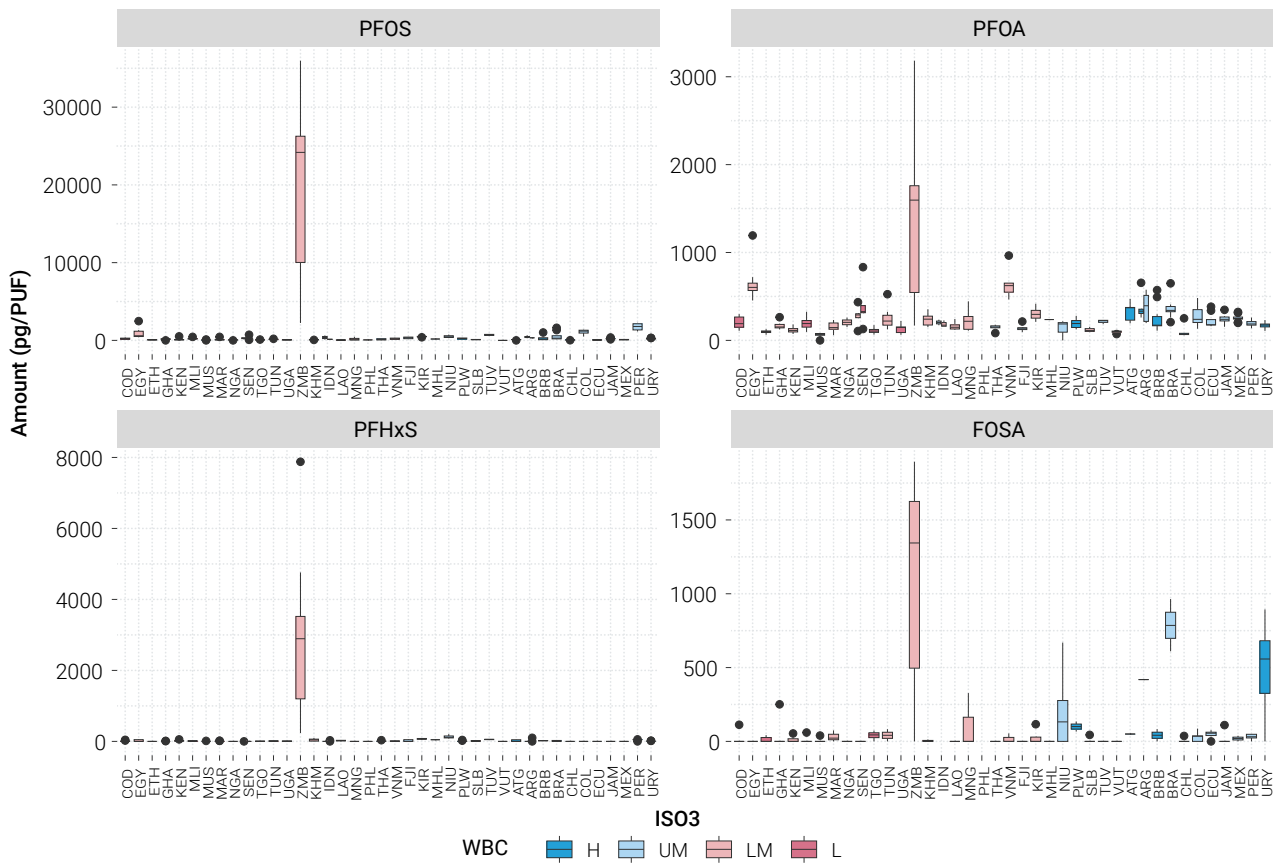


Figure 51: PAS/PUFs: Scaled boxplots for 4 PFAS by country and colored according to WBC (n=317)

The descriptive statistics for the four PFAS grouped according to population density is shown in Table 18. It can be seen that for PFOS, the highest values are associated with least densely populated countries (PD<25), which includes Zambia. The impact of the Zambian data on the population density can be seen in the graphical representation in Figure 52 and Figure 53. It is important to notice that the countries in the study are not producers of PFAS, and the values reflect the use of them and are highly influenced by the location of the sampling sites and its surroundings.

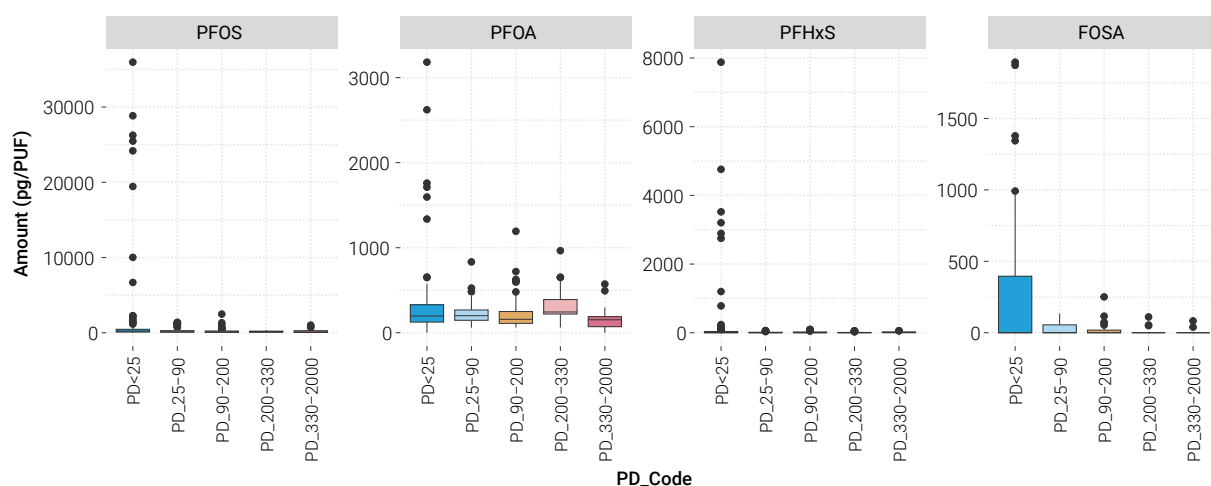
The differences as to the PD\_Codes were significant,  $p = 0.0027$ . Pairwise significant differences were found for all countries of PD<25 with the other four PopDen groups; p-values were either  $p=0.019$  or  $p=0.23$  or  $p=0.35$ . All others had p-values from 0.26 to 0.74.

These similarities can also be seen in the PCAs for chlorinated POPs where ellipses largely overlap

Figure 54 shows the unique location of the values assigned to LM (for WBC) and PD<25 (for PopDen) as indicated by the ellipses in light pink and dark blue respectively.

**Table 18:** Descriptive statistics for PFAS according to population density (PD\_Code) (Amounts in pg/PUF)

	Central tendencies	PD<25 (N=90)	PD_25-90 (N=91)	PD_90-200 (N=70)	PD_200-330 (N=42)	PD_330-2000 (N=24)	Overall (N=317)
PFOS	Mean (SD)	2520 (7150)	246 (309)	243 (366)	144 (93.3)	222 (282)	847 (3860)
	Median [Min, Max]	214 [0, 36000]	125 [0, 1370]	107 [0, 2480]	114 [0, 372]	87.2 [0, 1010]	136 [0, 36000]
PFOA	Mean (SD)	353 (521)	225 (112)	225 (193)	323 (197)	164 (137)	268 (313)
	Median [Min, Max]	197 [0, 3180]	201 [59.6, 833]	158 [63.5, 1190]	244 [63.0, 965]	153 [0, 572]	192 [0, 3180]
PFHxS	Mean (SD)	323 (1150)	7.66 (14.1)	17.9 (27.5)	8.24 (16.2)	15.6 (17.8)	101 (628)
	Median [Min, Max]	0 [0, 7880]	0 [0, 65.6]	0 [0, 96.1]	0 [0, 54.4]	14.0 [0, 59.8]	0 [0, 7880]
FOSA	Mean (SD)	291 (496)	29.1 (37.6)	20.7 (50.5)	11.3 (29.0)	11.1 (26.6)	112 (315)
	Median [Min, Max]	0 [0, 1890]	0 [0, 135]	0 [0, 251]	0 [0, 110]	0 [0, 83.0]	0 [0, 1890]



**Figure 52:** PAS/PUFs: Scaled boxplots for 4 PFAS colored according to PD\_Code (n=317)

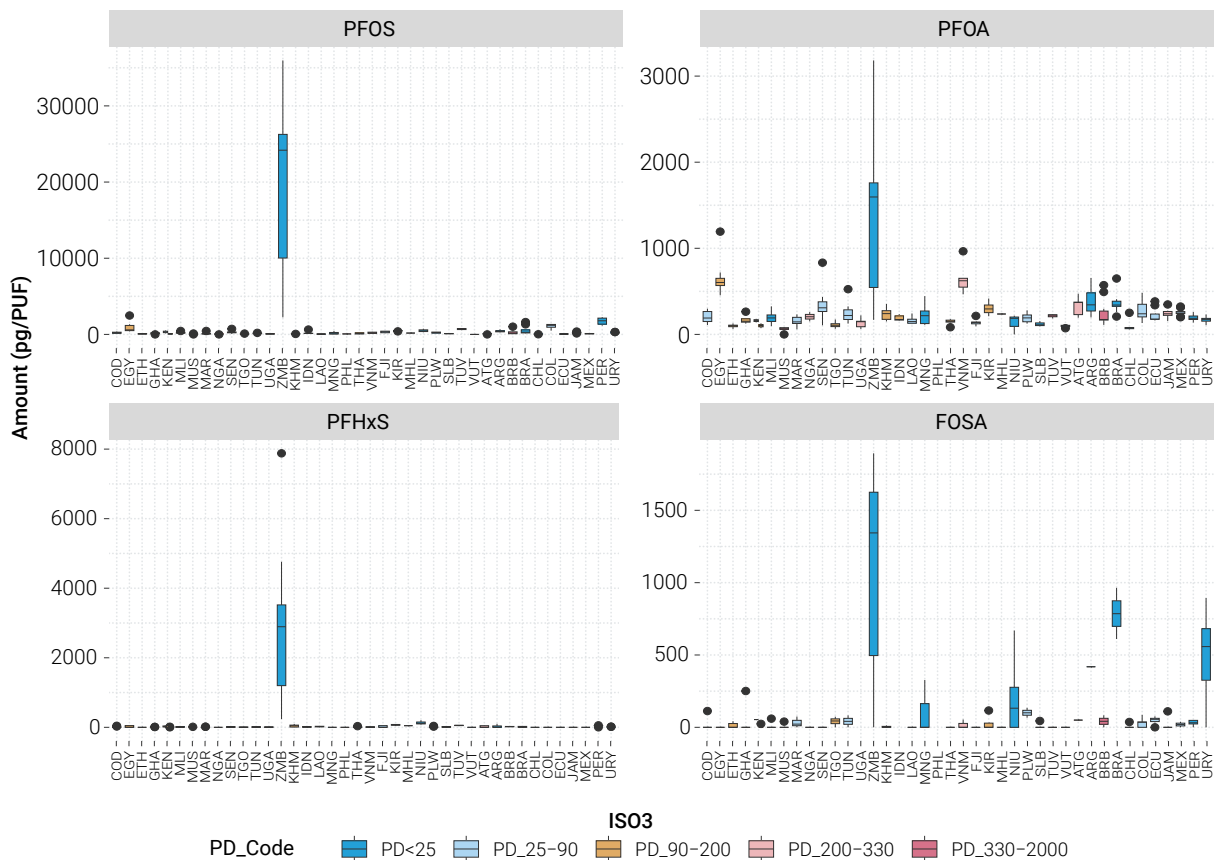


Figure 53: PAS/PUFs: Scaled boxplots for 4 PFAS by country and colored according to PD\_Code (n=317)

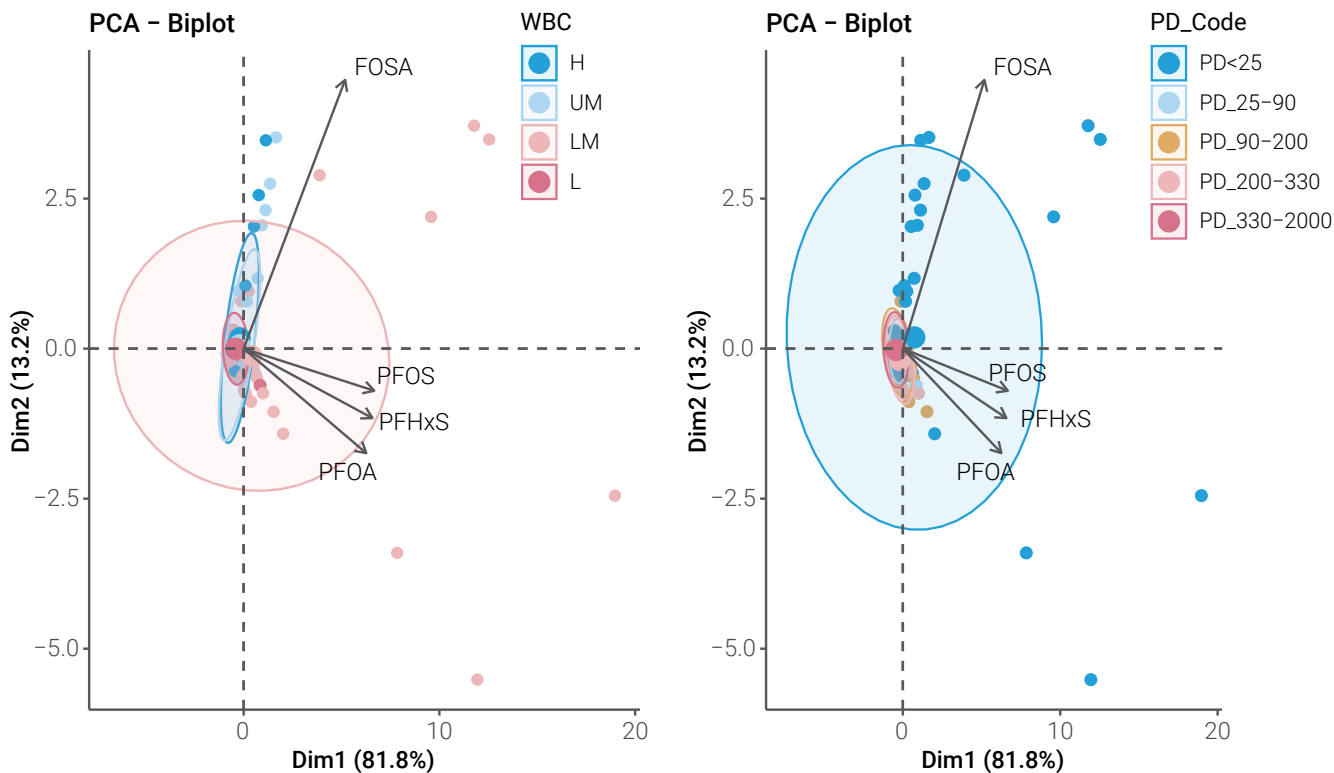


Figure 54: PAS/PUFs: PCA for PFAS according to income (as WBC, left) and population density (PD\_Code, right). All values were normalized to 1 PUF and 3-months exposure (n=317)



# SECTION 5

## Discussion





## 5. DISCUSSION

### 5.1. General observations as to prevailing POP in certain countries

In the present GMP2 projects, more than 290 samples from PAS/PUFs have been analyzed for OCPs, industrial chlorinated POPs, and brominated flame retardants and almost 200 samples have been analyzed for dl-POPs. Chemical analysis was performed in three laboratories: thus, minimizing interlaboratory differences. Such approach allows reduces bias in the interpretation of data. Nevertheless, some observations could be derived from principal component analysis for the different POPs groups:

- The most striking findings were the extreme values obtained for PFAS in Zambia (Figure S 5, top). All the ZMB samples are located in either the 1<sup>st</sup> or 4<sup>th</sup> quartile at the right site of Dim1. Since Dim1 explains 81% of all the values; the scale is extraordinary and includes the highest measured amounts.
- For the BFR (Figure S 5, bottom), 40% of the data are explained by Dim1 and 30% by Dim2. It can be seen that by scale, African samples are high with respect to Dim1; however, these dots are associated with the Democratic Republic of the Congo and not with Zambia. Along Dim2, representing HBCD and PBDE 209, the highest values for Africa are due to Zambia but overall, the samples from Mongolia dominated (especially for HBCD).
- A similar picture, but without the extreme values, as for PFAS is obtained for the dl-POPs (Figure S 6, top). The data from Egypt have the highest values and are found at right of Dim1, representing 90% of the datapoints.
- For OCPs including PCB<sub>6</sub> and dl-POPs, the results from Zambia did not constitute any outliers (Figure S 6, bottom). The extreme values were associated with United Republic of Tanzania for Dim1 associated with drins and heptachlor and Mongolia for Dim2, associated with HCBd.

The contributions of the variables to the first two dimensions (Dim1, Dim2 and combined) to the PCAs and the contributions of the variables (OCPs+industrial Cl-POPs, dl-POPs, BFR, and PFAS) to the PCAs are shown in the Supplementary information as Figure S 5, and Figure S 6.

### 5.2. Lessons learned from active air sampling

The active air sampling and analysis component of the UNEP/GEF projects had difficulties in implementation due to late commitments or changed commitments by the countries. Further, only very few filters (GFF+PUF+XAD) were exposed; transport and chemical analysis posed additional problems. Finally, the few samples had been analyzed by four different laboratories so that interlaboratory differences cannot be excluded in cases where one group of POPs was analyzed by two different laboratories. The scattered datapoints from the AAS samples differed from the PAS/PUF largely as could be seen in the composition of the individual POPs within the POPs group. The best match was obtained for dl-POPs.

### 5.3. Comparison with GMP1 data

Countries in Africa, PAC, and GRULAC had participated in the two rounds of projects of POPs monitoring coordinated by UNEP Chemicals and Health Branch (formerly "UNEP Chemicals"), referred to later as GMP1 and GMP2, respectively. GMP1 was implemented about ten years ago and had PAS/PUFs exposed during the years 2010 and 2011; typically, four measurements samplings. GMP1 had 32 countries (UNEP n.d. a) and GMP2 (UNEP n.d. b) had 42 countries participating. The results from the GMP1 project were published as (UNEP 2012; Bogdal *et al.* 2013; Fiedler *et al.* 2013) and the GMP2 results in the present report and additionally in the regional reports (UNEP 2024a; UNEP 2024b; UNEP 2024c; UNEP 2024e).

Since, GMP1 included only the initial POPs and the three HCHs ( $\alpha$ -HCH,  $\beta$ -HCH, and lindane), other newly listed POPs cannot be included into the comparison. Toxaphene was not analyzed in GMP2 and therefore, is excluded. In addition, Asian countries did not participate in GMP1 and therefore, have to be excluded as well. Finally, not all countries submitted PUFs for analysis in either GMP1 or GMP2, only countries and POPs could be assessed where at least one datapoint for one POP in both GMPs were present.

Finally, there were 194 PUFs available for OCPs (GMP1=67 and GMP2=127) from Africa and the Pacific Islands, 297 for PCB (GMP1=103, GMP2=194) from Africa, the Pacific Islands, and GRULAC, 158 for polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD, PCDF) (GMP1=39, GMP2=119) from Africa, the Pacific Islands, and GRULAC, and 153 for dl-PCB (GMP1=34, GMP2=119) from Africa, the Pacific Islands, and GRULAC.



The following figures depict the concentrations measured in either GMP1 or GMP2 for each country (Figure 55 for OCPs and HCB, Figure 56 for PCB<sub>6</sub>, and Figure 57 for dl-POPs as TEQ). If a decline would have occurred, the values, shown as box whisker plots, for the second measurement campaign (pink boxes) would be lower than for the boxes representing GMP1 (blue color). In general, declines were observed throughout the POPs and countries. Strong declines were determined for DDT (Figure 55), such as in Ethiopia, Mali, Kiribati, Tuvalu and Samoa. The highest DDT values were found in the Democratic Republic of the Congo; however, no decline was found; on much lower level, the median value for DDT in Mauritius was higher during GMP2 than GMP1. For HCB, increases were detected.

For PCB<sub>6</sub>, data from GRULAC were available in addition to the data from Africa and PAC (Figure 56). Both, increasing and declining values were obtained. It should also be noted that very often, for one of the GMPs, the data stretches across larger ranges as can be seen from the boxes and the whiskers. The ranges for measured data differed by two orders of magnitudes with many values close to the limit of detection (*i.e.*, median values close to zero) as shown in

many African countries in GMP1 but also some few countries in PAC during GMP2. Constantly quite high values were found in Democratic Republic of the Congo and Jamaica. In Samoa, much higher PCB<sub>6</sub> amounts were found in GMP2 as well as in many African countries, in Mexico, and Solomon Islands but on much lower level.

For dl-POPs, as TEQ for PCDD/PCDF and dl-PCB, there was only one data point during GMP1 for many countries. Most countries showed an increase of the values during GMP2 implementation (Figure 57). Marked decreases for PCDD/PCDF could be determined in Democratic Republic of the Congo, Peru, and Brazil, whereas values in Mali, Jamaica and in Fiji increased. For dl-PCB, there values were lower in general than for PCDD/PCDF and values were often close to limit of quantification.

In summary, indicator PCB and dioxin-like POP were quantified in all countries at all times; decreases of about 30% based on median values were determined. A 50% increase was found for HCB. By scale, DDT remained with the highest values, although more than 60% decrease was found, mainly due to smaller values in the Pacific Islands. PCB<sub>6</sub> showed an overall decline of 29% (Fiedler, Abad and de Boer 2023).

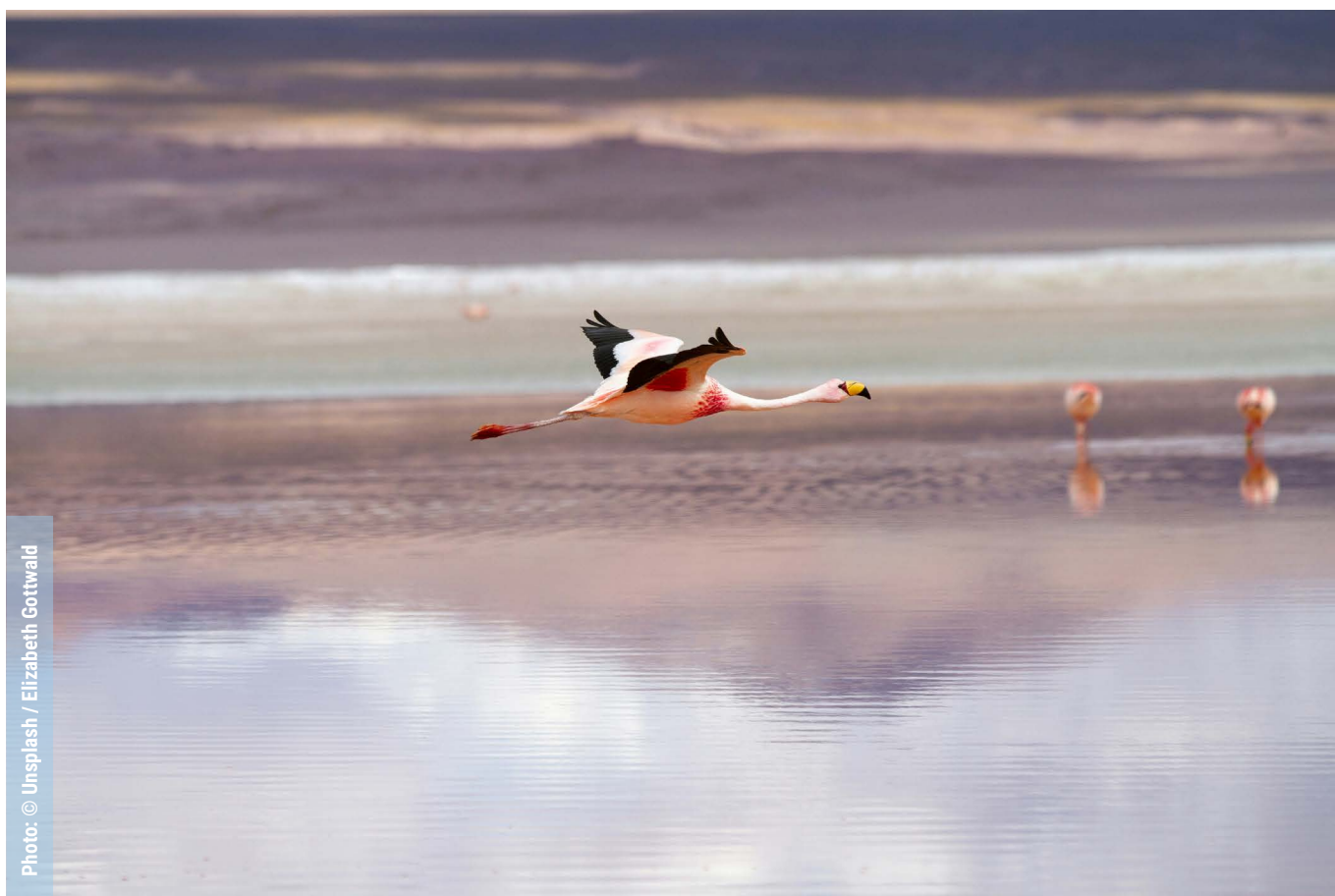


Photo: © Unsplash / Elizabeth Gottwald

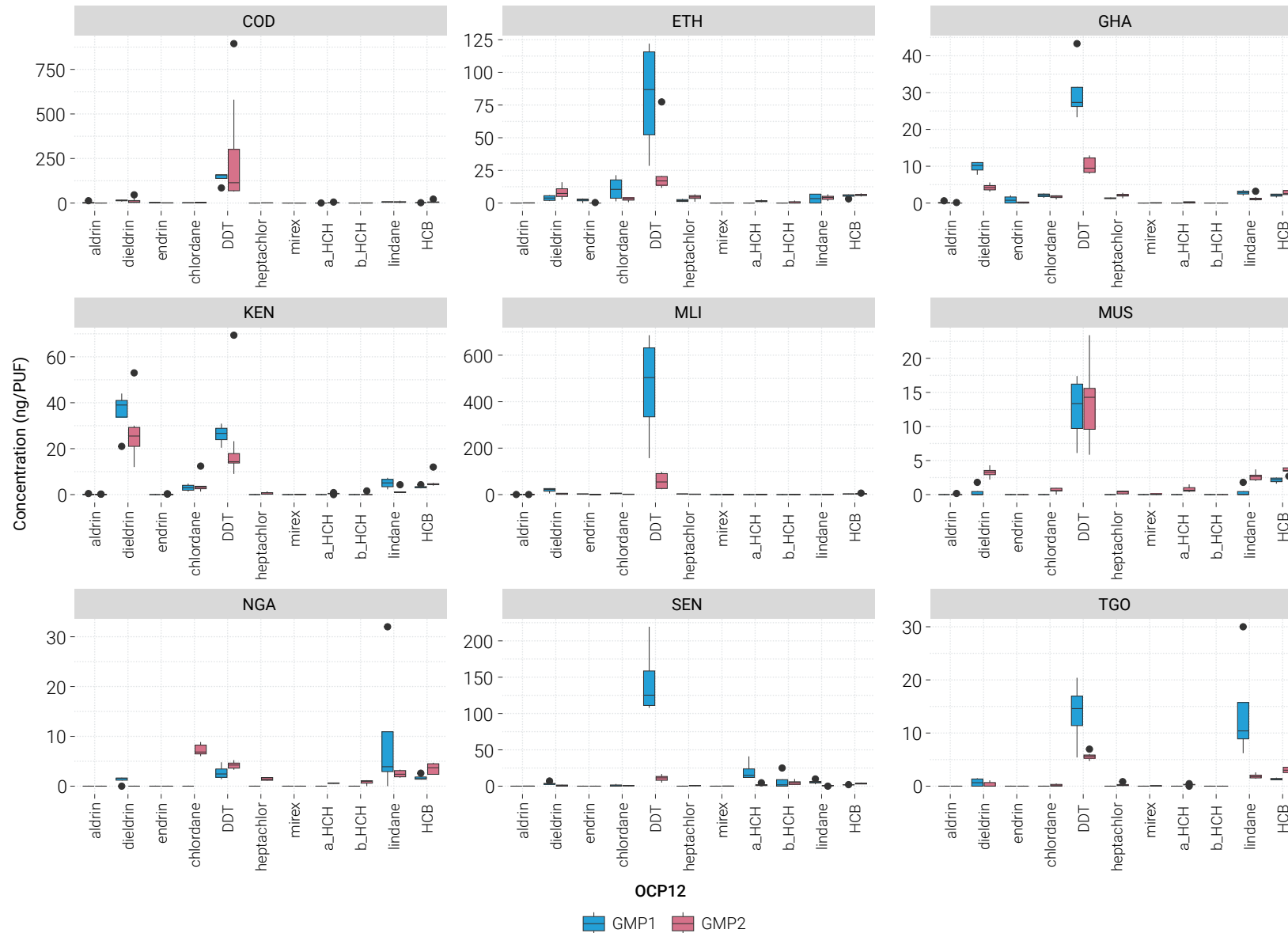


Figure 55: PAS/PUFs GMP1 vs. GMP2: Box whisker plots for OCPs and HCB by country colored by GMP

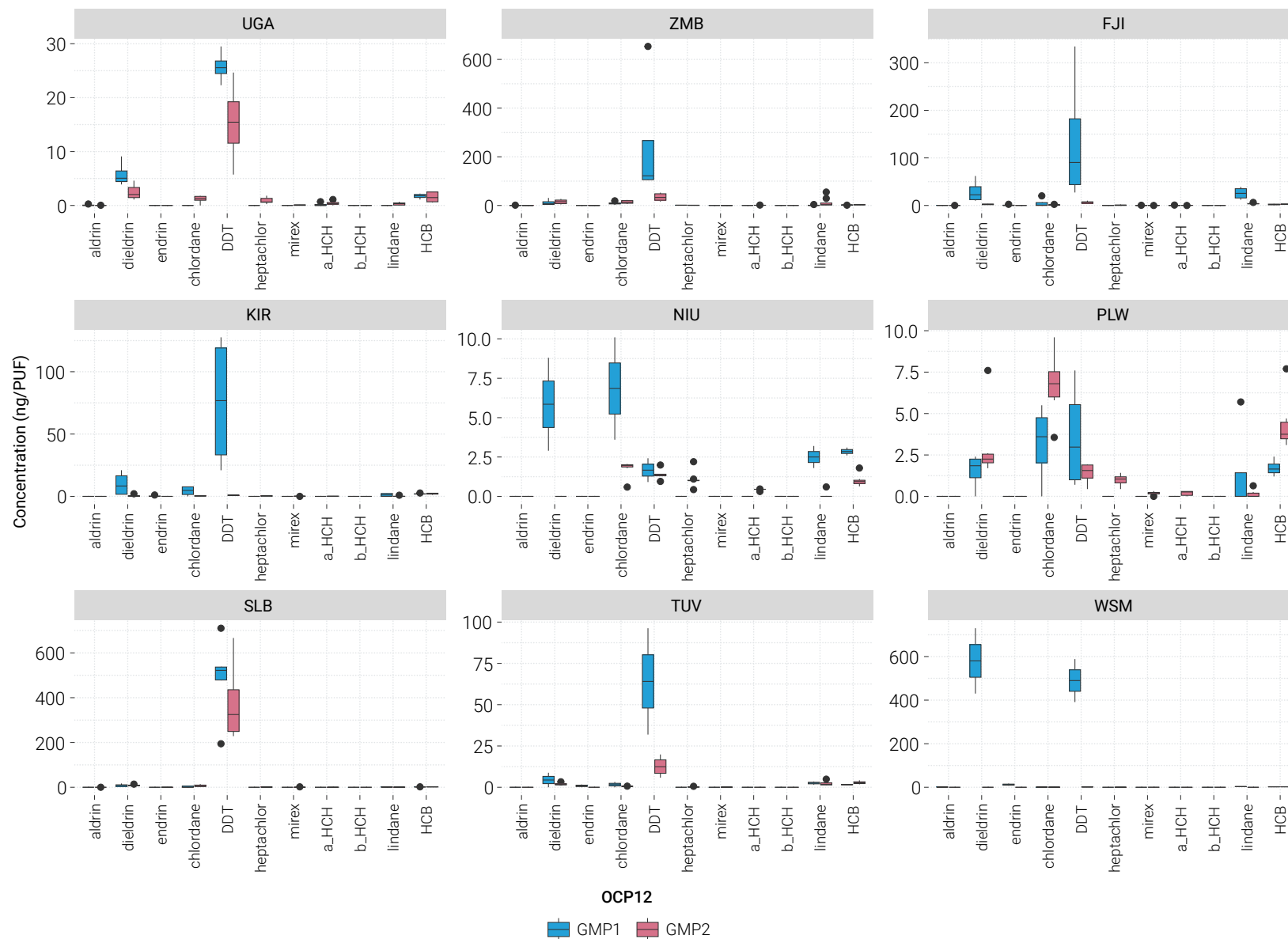


Figure 55: Continued

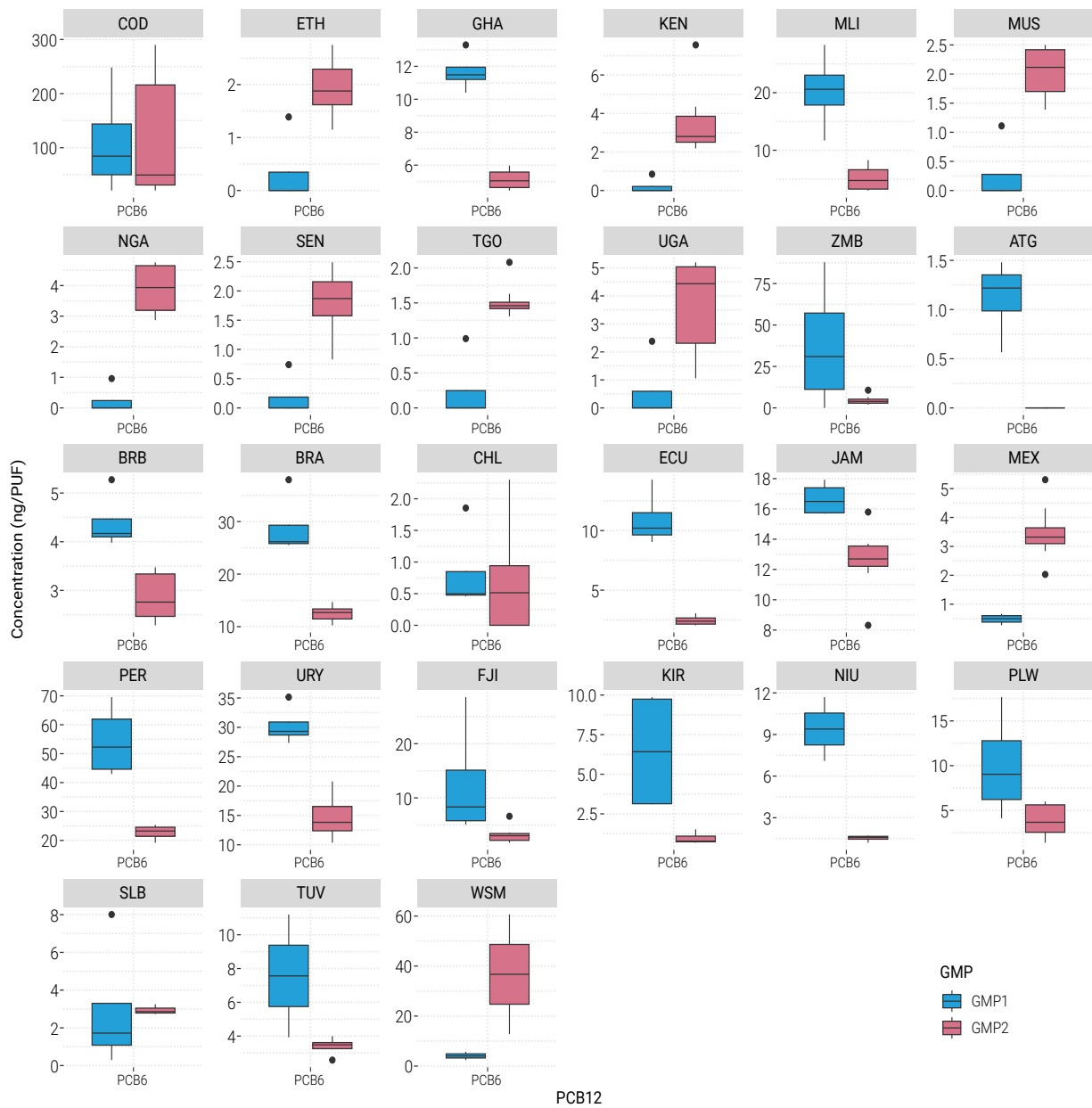


Figure 56: PAS/PUFs GMP1 vs. GMP2: Box whisker plots for PCB<sub>6</sub> by country colored by GMP

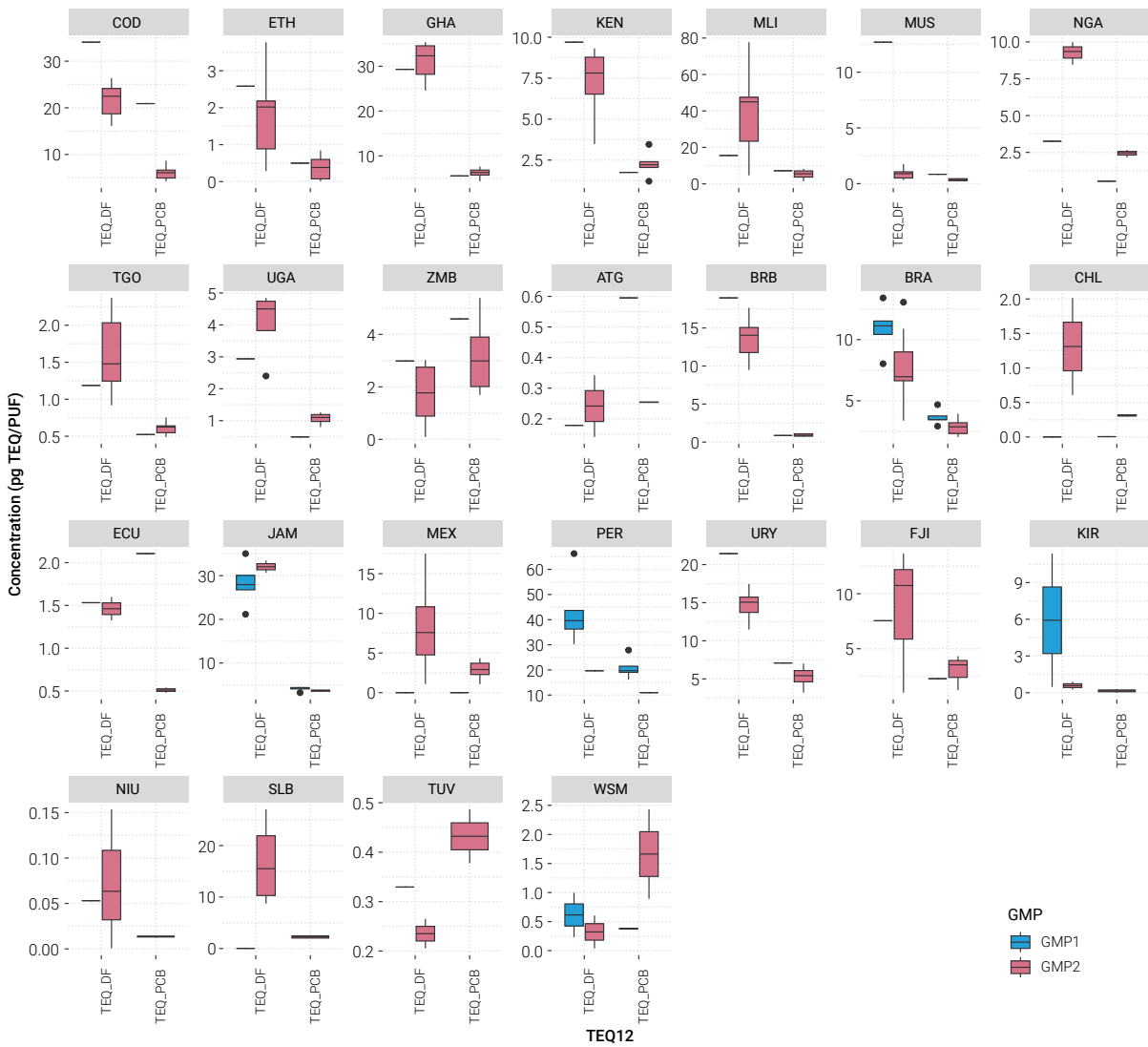


Figure 57: PAS/PUFs GMP1 vs. GMP2: Box whisker plots for dl-POPs by country colored by GMP





# SECTION 6

## Recommendations / Conclusions

Photo: © Unsplash / Rainhard Wiesinger

Our assessment showed that on relative scale – per PUF – trend analysis was achieved and that such approach should be undertaken at regular intervals, not necessarily on an annual basis

Some POPs posed analytical challenges, especially PFAS causing deterioration in the exposed PUFs. Some POPs had median values of zero throughout the projects; these included aldrin, endrin, mirex, and b-HCH. It is recommended to continue including them in the scheme of recommended analytes but instead of analyzing them quarterly the temporal resolution can be each two years or each five years. However any laboratory should be aware that high sensitivity (low LODs) is required for meaningful results.

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.

Care should be taken when selecting samples for interpretation. As was shown in the tables and graphics of the present report for the CI POPs in air, the samples from the year 2019 for example (only few samples few countries sampled this year) were significantly different from all other years (see Table 3).

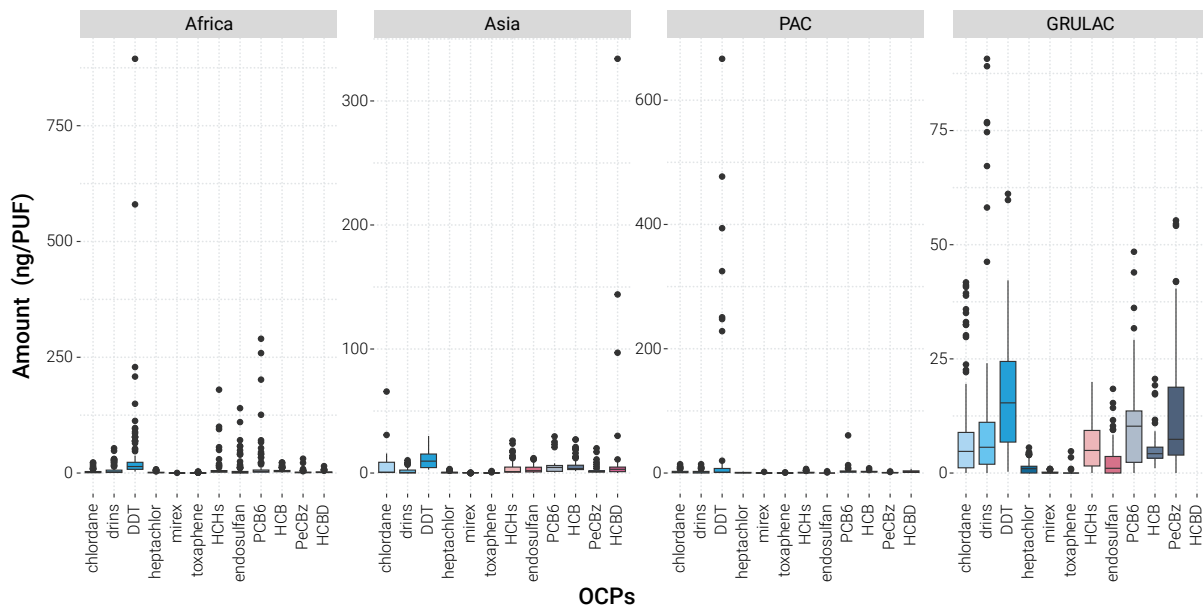
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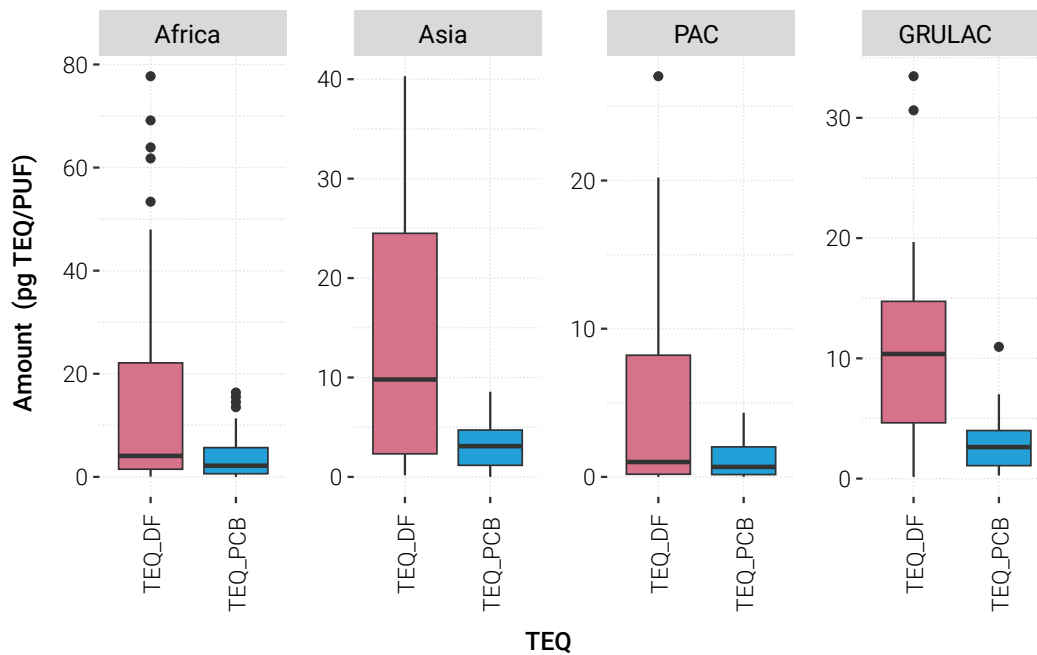
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# 8. ANNEX: SUPPLEMENTARY INFORMATION



**Figure S 1:** PAS/PUFs: Scaled box plots for OCPs shown in each region; values normalized to 1 PUF and 3 months exposure (N=294 for most OCPs, N=323 for toxaphene, N=211 for HCBD)



**Figure S 2:** PAS/PUFs: Scaled boxplots for two TEQ by region; values normalized to 1 PUF and 3 months exposure (n=195)



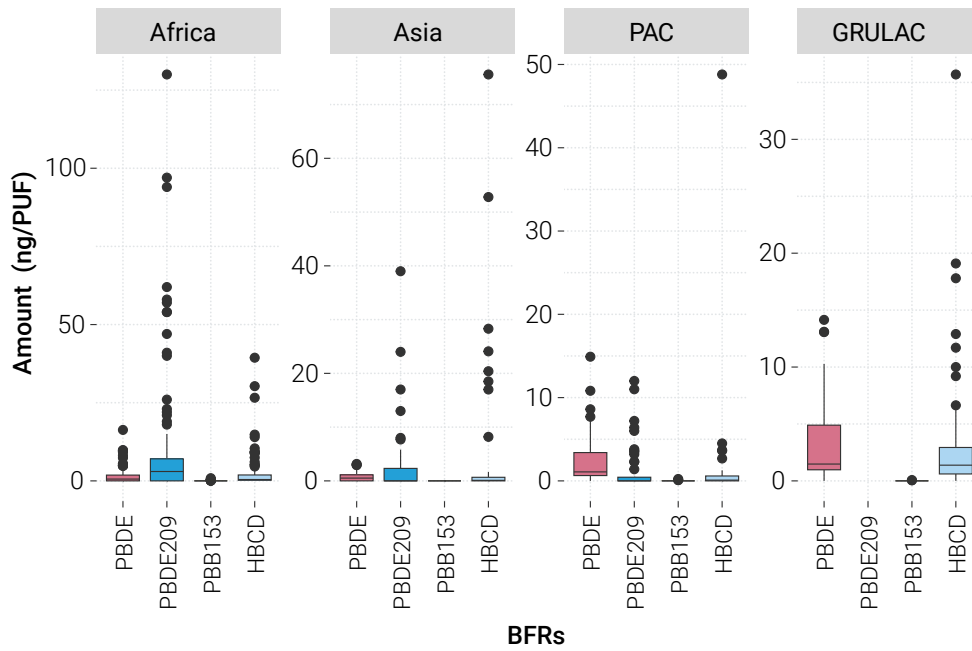


Figure S 3: PAS/PUFs: Scaled boxplots for brominated POPs by region; values normalized to 1 PUF and 3 months exposure (n=293)

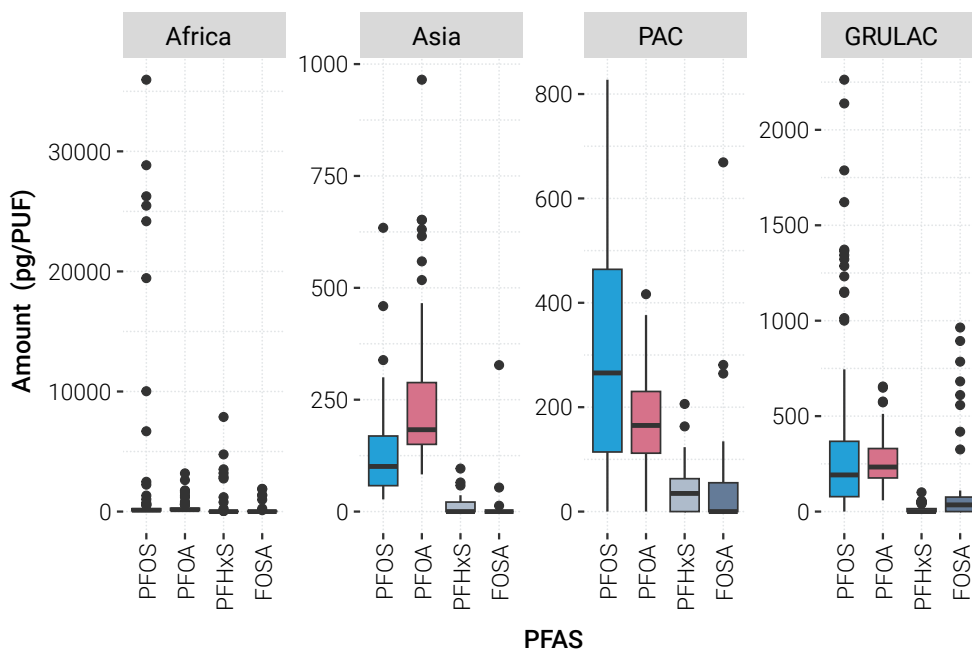


Figure S 4: PAS/PUFs: Scaled boxplots for 4 PFAS colored by region; values normalized to 1 PUF and 3 months exposure (n=317)

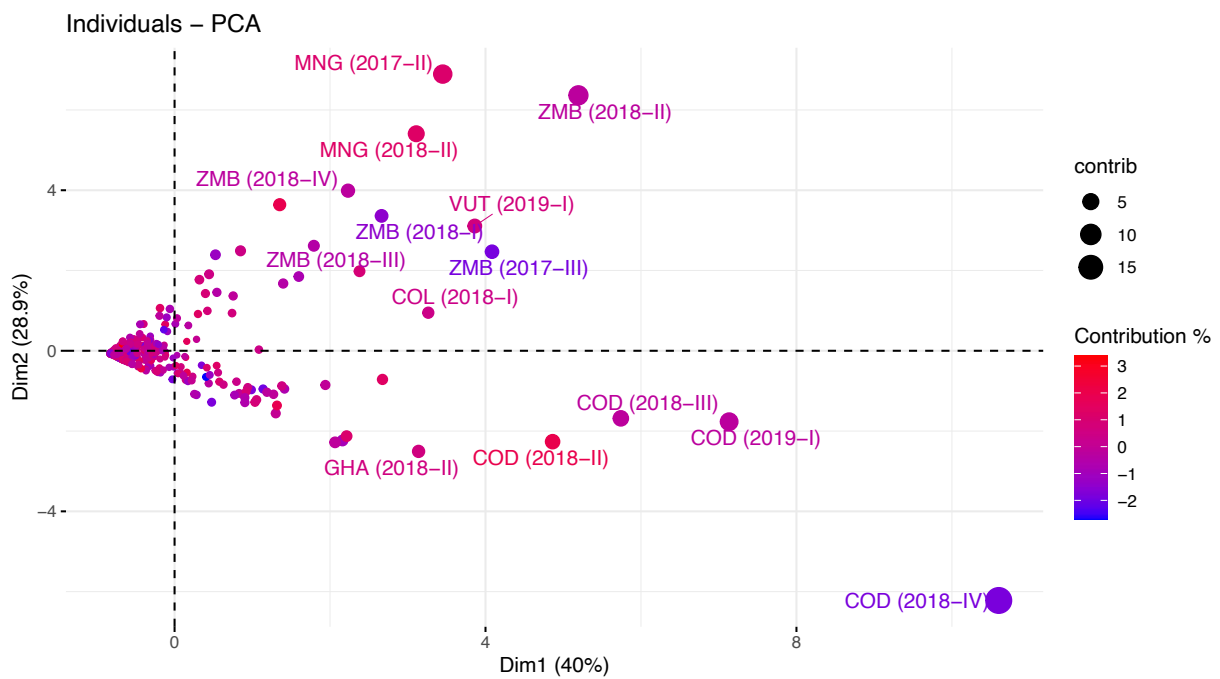
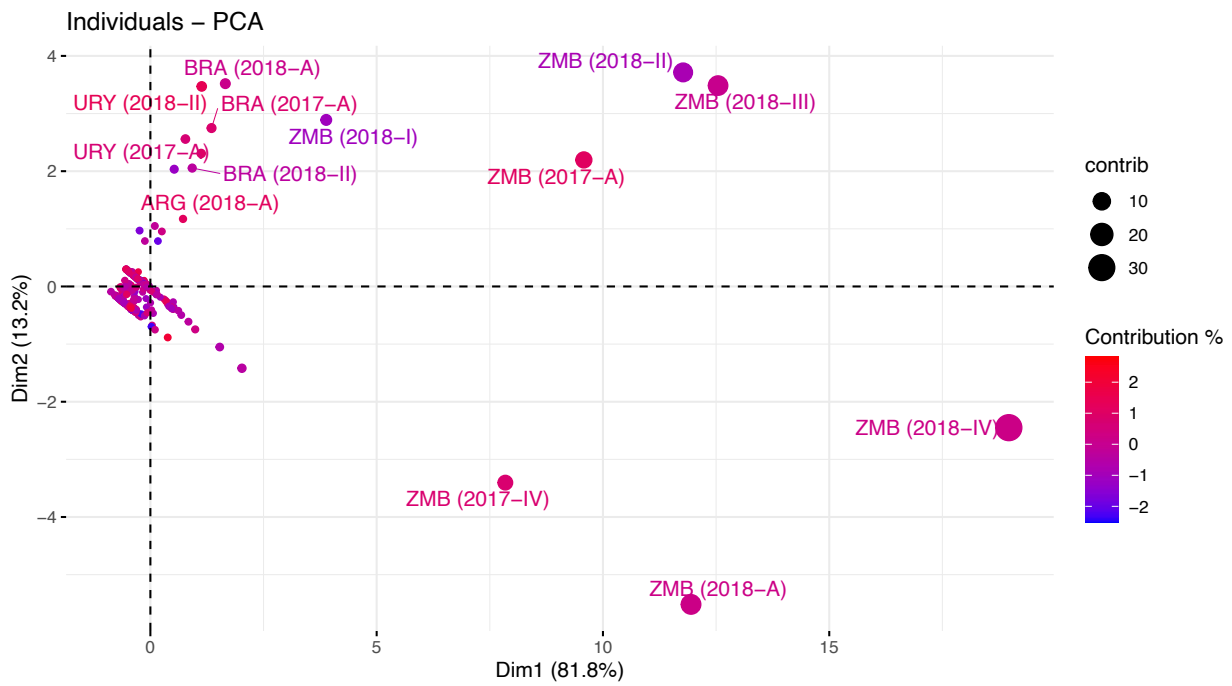


Figure S 5: PAS/PUFs: Location of the individuals in the PCAs Top: PFAS; bottom: BFR

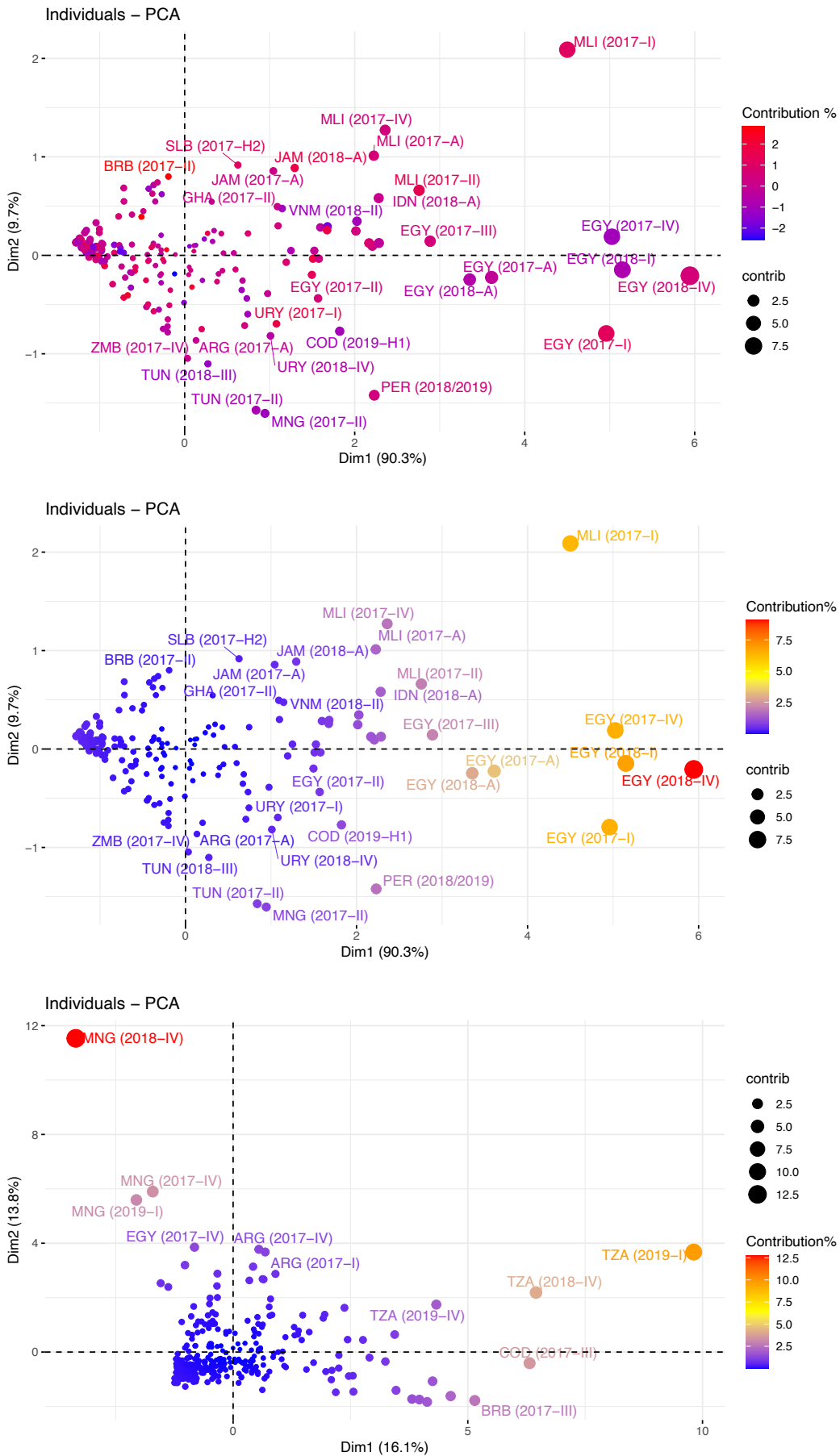


Figure S 6: PAS/PUFs: Location of the individuals in the PCAs top: dl-POPs; bottom: OCPs and industrial POPs

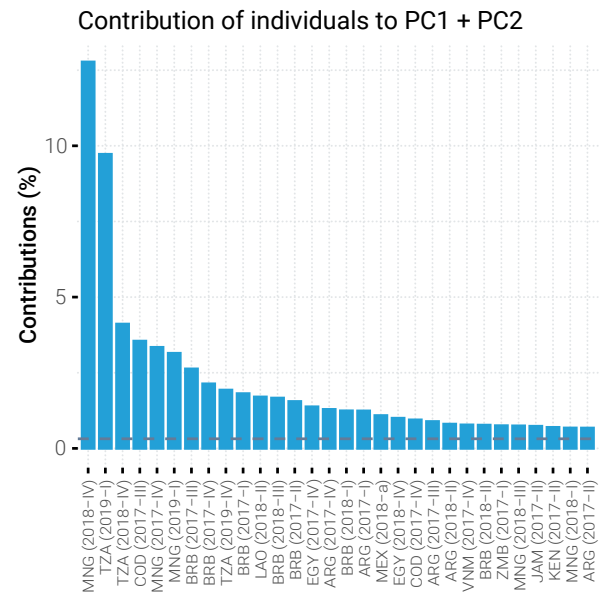
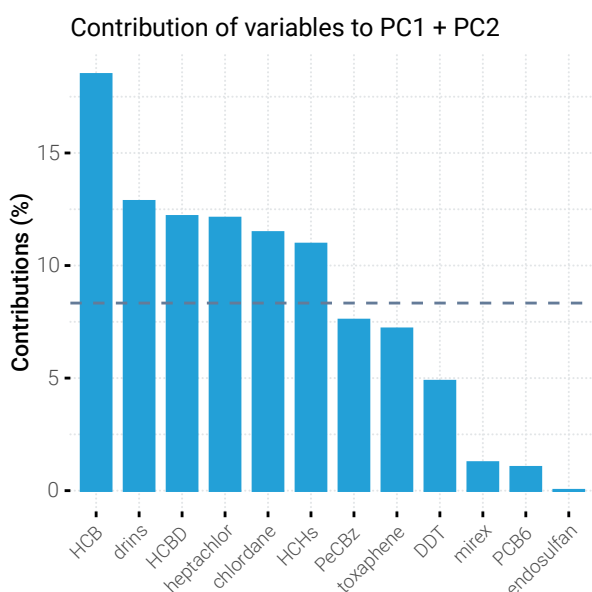
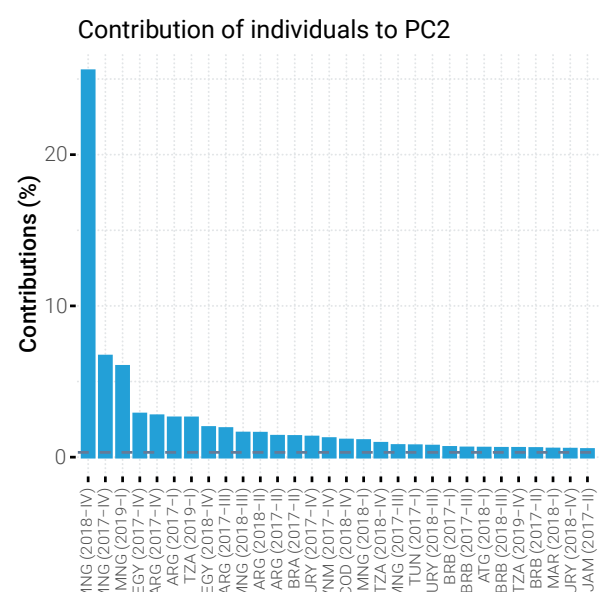
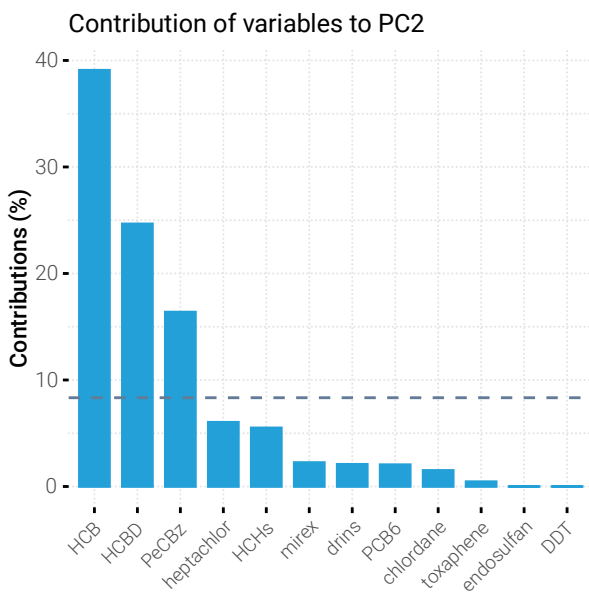
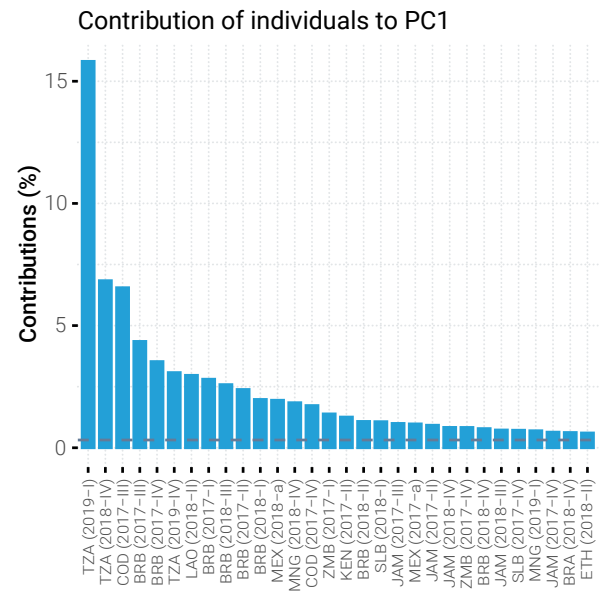
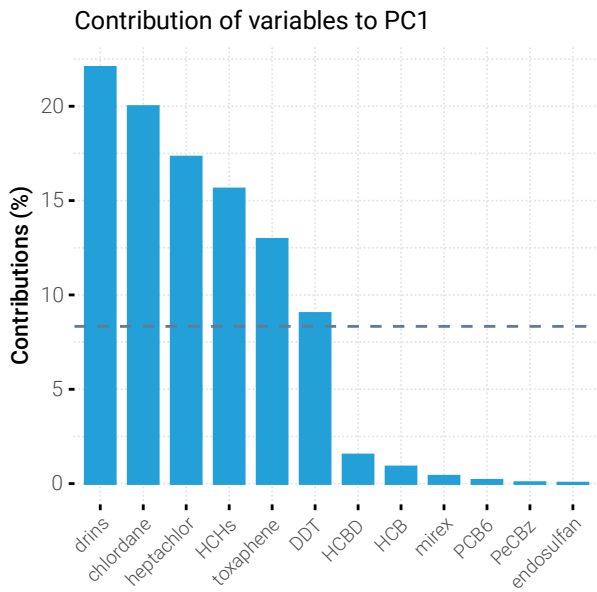


Figure S 7: PCA: Contribution of variables (OCPs and industrial CI-POPs) and individuals to PC1 and PC2

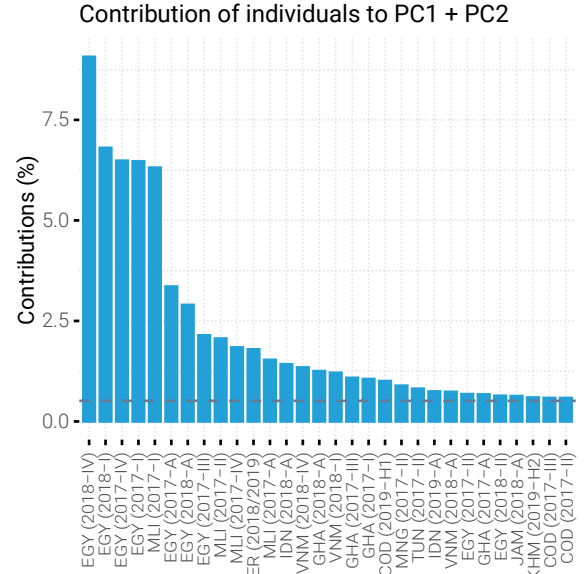
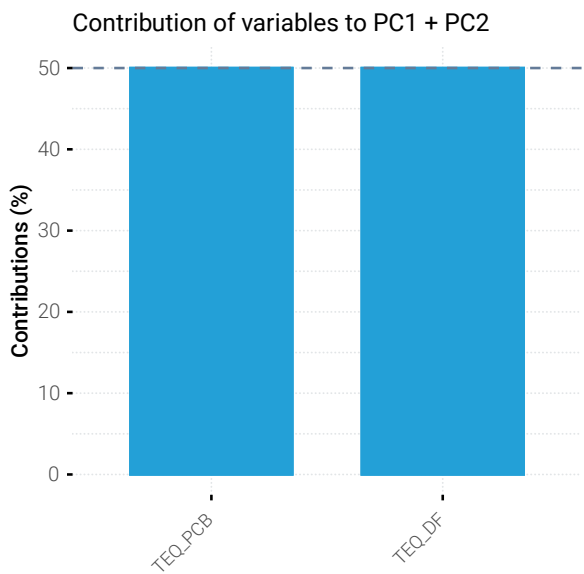
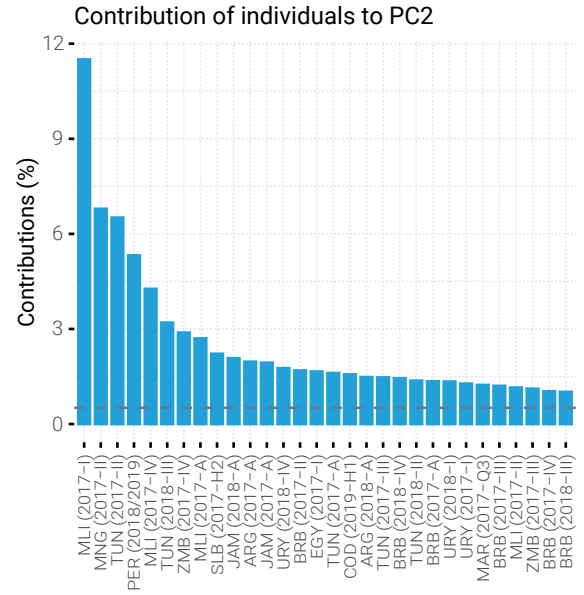
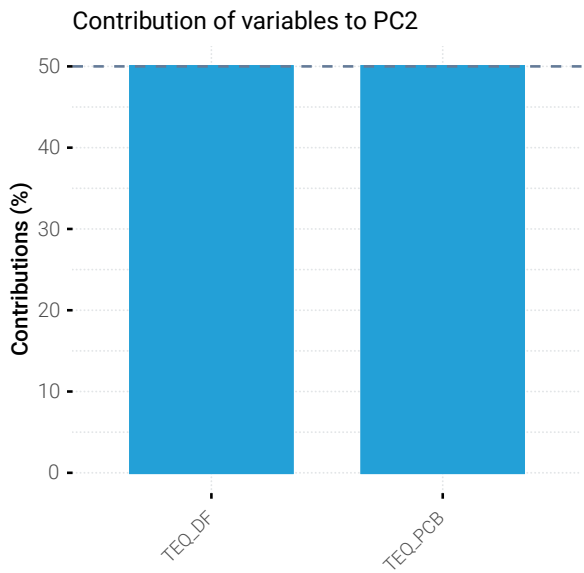
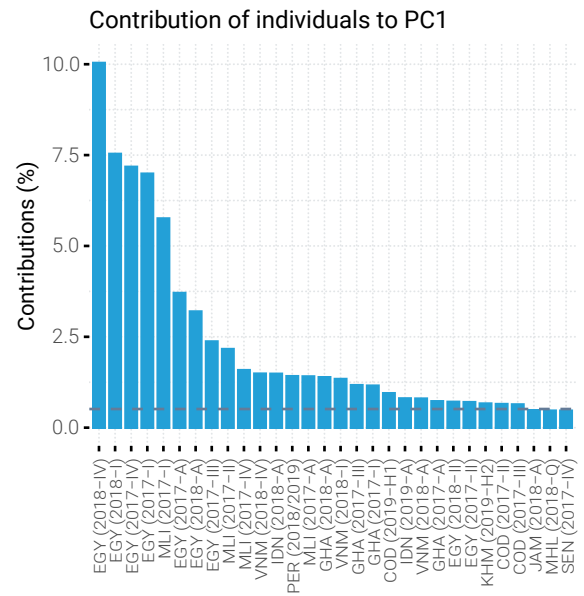
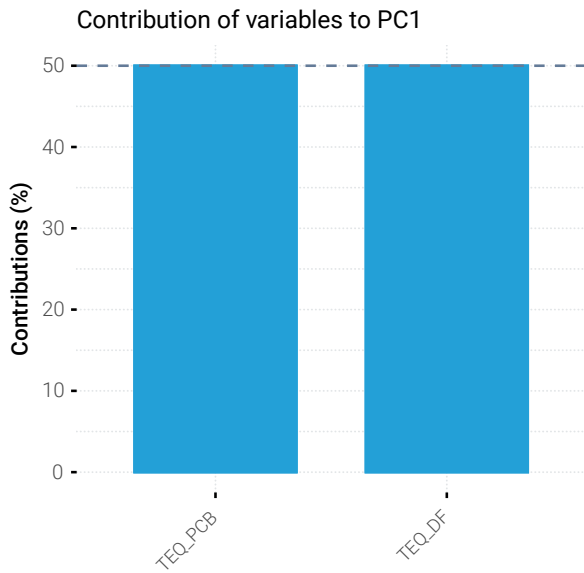


Figure S 8: PCA: Contribution of variables (dl-POPs) and individuals to PC1 and PC2



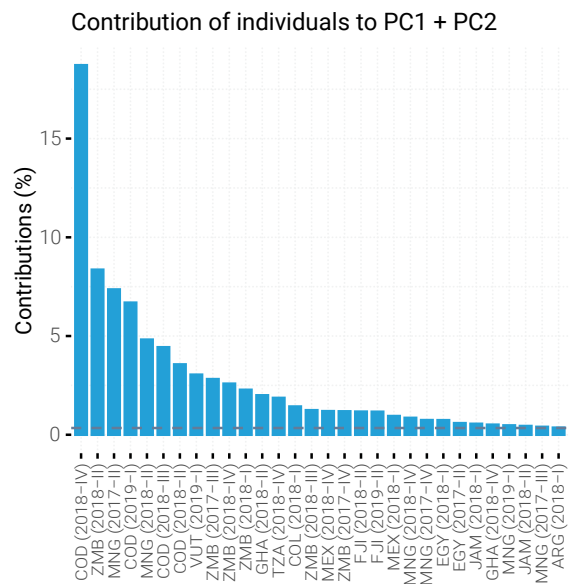
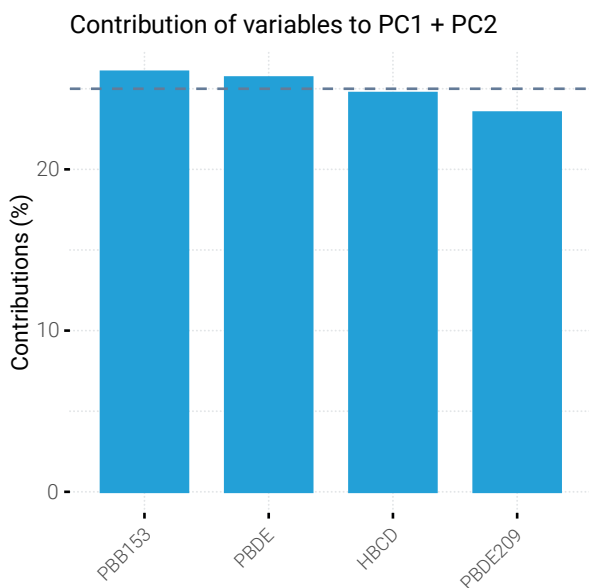
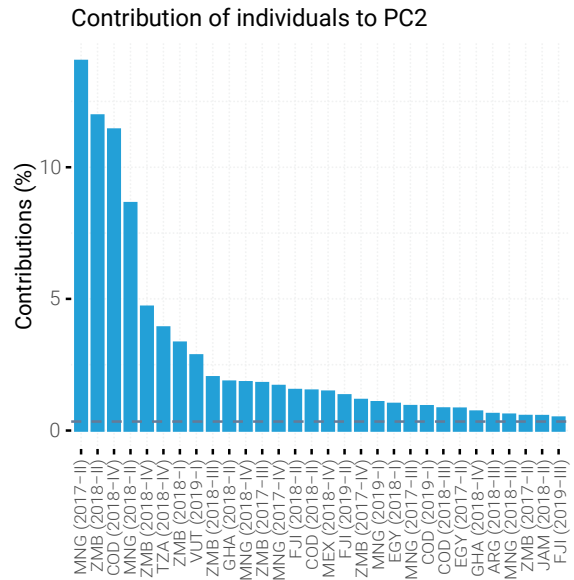
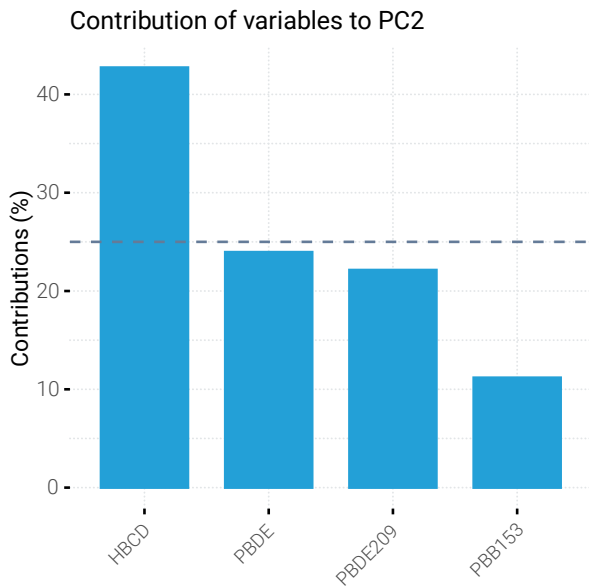
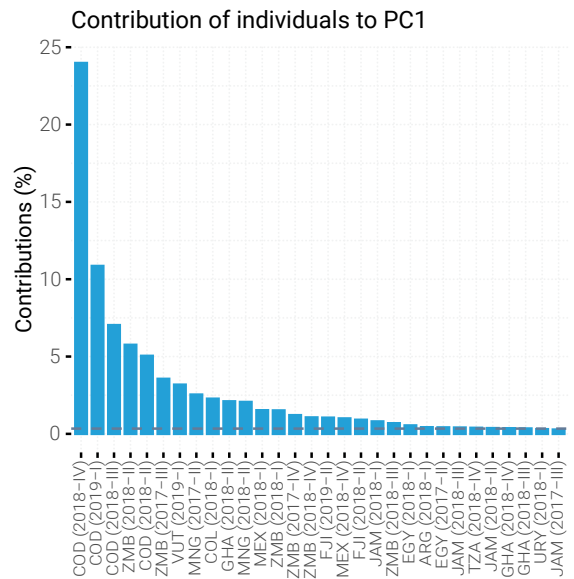
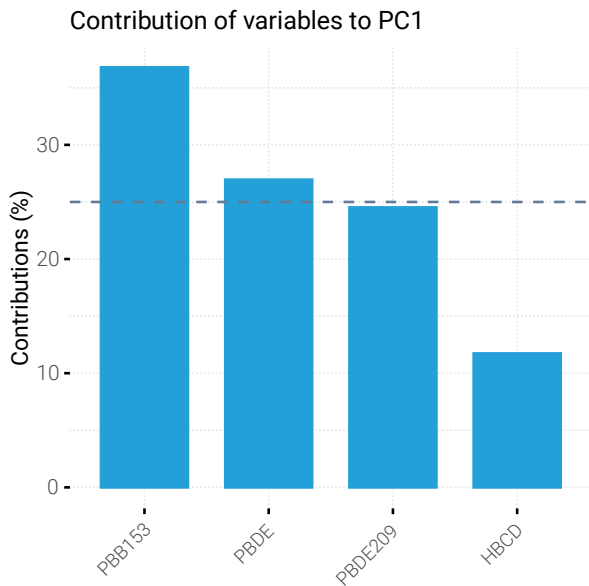


Figure S 9: PCA: Contribution of variables (BFR) and individuals to PC1 and PC2





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