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Preliminary trends over ten years of persistent organic pollutants in air - Comparison of two sets of data in the same countries

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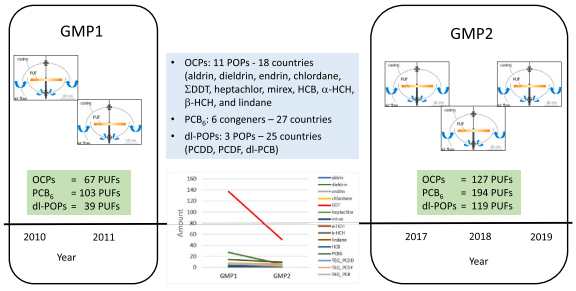
HIGHLIGHTS

- Persistent organic pollutant data in 27 countries assessed during two time series.
- Comparison on relative scale found declining trends for most POPs.
- Increasing trends found for hexachlorobenzene and chlordane.
- Regional trends often driven by a few countries.
- DDT remain with highest values; others had non-detectable levels at onset.

GRAPHICAL ABSTRACT

Summary overview on PAS/PUFs exposed and analytes captured



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ABSTRACT

In two series of ambient air measurement campaigns to support the implementation of the global monitoring plan (GMP) component of the Stockholm Convention on Persistent Organic Pollutants (POPs), passive air samplers (PAS) using polyurethane foams were implemented by the United Nations Environment Programme (UNEP). With the same laboratories responsible for the chemical analyses of the different groups of POPs, a total of 423 PUFs were analyzed for organochlorine pesticides (OCPs) including hexachlorobenzene (HCB) and polychlorinated biphenyls (PCB); 242 for dioxin-like POPs. For trend analysis, to compare amounts of POPs in the PUFs during the first phase in 2010/2011 and the second phase from 2017 to 2019, only results were assessed that were generated in the same country and for the same POP in both campaigns. Finally, there were 194 PUFs available for OCPs (GMP1 = 67 and GMP2 = 127), 297 for PCB (GMP1 = 103, GMP2 = 194), 158 for polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD, PCDF) (GMP1 = 39, GMP2 = 119), and 153 for dl-PCB (GMP1 = 34, GMP2 = 119). Indicator PCB and dioxin-like POPs 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 region. 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.

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1. Introduction

Article 16 of the Stockholm Convention on Persistent Organic Pollutants (POPs) requests Parties to measure POPs in humans and the environment and evaluate the effectiveness of reduction/elimination measures taken under the Convention (Fiedler et al., 2019, 2020; UNEP, 2001). A global monitoring plan (GMP) for persistent organic pollutants (POPs) was established through decision SC-3/19 at the third meeting of the Conference of the Parties (COP-3) of the Stockholm Convention in 2007 (UNEP, 2007). The COP decided on ambient air, human milk, or blood as core matrices to assess temporal and spatial trends for the initial twelve POPs at global or regional basis. Since that national and international institutions have undertaken environmental monitoring and biomonitoring for POPs to support the implementation of the Stockholm Convention.

The United Nation Environment Programme (UNEP) through its Chemicals (today: Environment and Health) Branch in Geneva had coordinated two series of environmental monitoring projects to support the implementation of the Stockholm Convention's global monitoring plan. They are later referred to as UNEP/GEF projects since most of the financial support was obtained by the Global Environment Facility (GEF), the interim financial mechanism of the Convention. The first series of projects had ambient air sampling implemented in 2010 and 2011 with 32 countries (named GMP1 projects) and the second series of projects was from 2017 to 2019 with 42 countries (named GMP2 projects). Project implementation is documented at Global monitoring plan implementation phase 1 (GMP1) | UNEP - UN Environment Programme for GMP1 projects and https://www.unep.org/explore-topics/chemicals-waste/what-we-do/persistent-organic-pollutants/global-monitoring-plan-2?_ga=2.232754711.902486169.1658929370-828395074.1642324017 for GMP2 projects.

To facilitate collaboration and comparability of approaches and results between countries in a region and at global level, harmonized protocols and standard operational procedures were developed and applied in each country. In addition, one expert laboratory was assigned to analyze a specific group of POPs across all projects. Sampling of ambient air using passive air sampling as a simple and cost-effective tool to investigate environmental occurrence and transport (UNEP, 2019) is a common approach to assess changes with time and location.

In the UNEP/GEF GMP projects, passive air samplers (PAS) consisting of two bowls as protective chamber and equipped with pre-cleaned polyurethane foam (PUF) disks were exposed at a designated location in each country. The sampling sites should not be located near point sources of POPs. Exposure was for three months so that at the end of each quarter of the year, the PUFs were exchanged (UNEP, 2019; UNEP, 2017). In the GMP projects, up to 12 PAS were set up per location to capture the different groups of POPs whereby half of the PUFs were shipped to experienced expert laboratories and the other half should be analyzed in the national laboratory when capacity was available. Here we have used only the data that were generated in the central expert laboratories.

This paper summarizes the results for those POPs that were analyzed in both UNEP cycles of GMP projects, namely exposures in 2010/2011 and from 2017 to 2019 and the countries that participated in both series of UNEP/GEF GMP projects. The recommendations contained in the guidance to the GMP were closely followed in both project cycles (UNEP, 2019, 2021).

2. Materials and methods

2.1. Origin of samples and characterization

Results from ambient air samples were available from 27 countries for analysis of the initial intentional POPs, comprising organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCB) and in 25 countries for analysis of dioxin-like POPs (dl-POPs). The geographic location of the sites are detailed in the Supplementary information in Table S 1 and the number of samples and countries of origin in Table S 2 and Table S 3. In most cases the stations were identical; in a few cases the station was different but still very close (within 3 km) to the one used before.

The sampling equipment consisted of PAS equipped with preconditioned PUFs following the general aspects established in the guidance document for the global monitoring plan for POPs (latest version (UNEP, 2021)). Specific protocols had been developed for the sampling during the first phase of the project (GMP1, 2010–2012, adapted from (Kohoutek et al., 2006)) and the second phase of the project (GMP2, 2017–2019 (UNEP, 2017)).

Briefly, PUFs designated for analysis of OCPs were pre-cleaned with dichloromethane, and PUFs for analysis of dioxin-like POPs (dl-POPs) with toluene. PAS with PUFs at about 2 m above ground level were set-up, and exposed for three months, equivalent to one season. PUF exchanges were made four times per year. Pre-cleaned PUF disks were received from RECETOX, Masaryk University, Brno, Czech Republic for African and Pacific Islands countries and from CSIC for GRULAC countries for GMP1 and GMP2. During GMP1, the Pacific Islands used commercially available PUFs (Tish Environmental, USA). For details of the PUFs, see Table S 4 in the supplementary information and the standard operational procedure (UNEP, 2017) or relevant publication (Abad et al., 2022). The sampling sites were designated by each country, most of them were located at the meteorological stations of the capitals or sites where other data, temperature, precipitation or wind measurements, were available but not requested to record; thus, locations that were supervised or otherwise protected. Temperatures were assigned and are available from the authors. It shall be noted that correction factors proposed as by Harner (2016) were generated at loctions outside of our study area and at different times. Thus, applying universal factors would not add accuracy to our original data. For the purpose of this paper, we have refrained from making any temperature corrections. We also did not make any corrections for atmospheric pressure, precipitation or wind speed.

Further information on the sampling locations are detailed in the regional reports of the UNEP/GEF GMP2 projects (Fiedler and UNEP, 2022).

The results were published for GMP1 (Bogdal et al., 2013; Fiedler et al., 2013; UNEP, 2012) and GMP2 (Abad et al., 2022; de Boer et al., 2023). Here we assess only results for a specific POP from countries where data were available for at least one sample in GMP1 and one sample in GMP2 for trend analysis and compare these findings with literature data.

2.2. Chemical analysis

Organochlorine pesticides and industrial chemicals: The POPs listed in the annexes of the Stockholm Convention include initial organochlorine pesticides (OCPs) listed in the Stockholm Convention, including their transformation products as detailed in the guidance documents for the global monitoring plan (chapter 2, latest version (UNEP, 2021). Thus, ΣDDT includes *o,p'* and *p,p'* isomers of DDT, DDD, and DDE, indicator PCB (designated as PCB_6), include the congeners PCB 28, PCB 52, PCB 101, PCB 138, PCB 153 and PCB 180; chlordane includes *cis*- and *trans*-chlordane, *cis*- and *trans*-nonachlor, and oxychlordane; heptachlor includes heptachlor itself and *cis* and *trans*-heptachlor epoxide. Aldrin, endrin, dieldrin, hexachlorobenzene (HCB) are single compounds; toxaphene was not monitored in GMP1. On the other hand, although not among the initial 12 POPs, three isomers of hexachlorocyclohexane (HCH) were included and referred to as three separate POPs according to the listing in Annex A of the Stockholm Convention, namely α-HCH, β-HCH, and lindane (γ-HCH) (UNEP, 2007, UNEP, 2009a, UNEP, 2009b, UNEP, 2009c). This group of chemicals is further referred to as OCPs/PCB.

For chemical analysis, general guidance is contained in a standard

operating procedure (SOP) developed for the UNEP GMP projects (UNEP, 2014). All ambient air samples were analyzed by the Vrije Universiteit Amsterdam, the Netherlands and CSIC, Barcelona, Spain (de Boer et al., 2023 accepted). Chemical analysis used gas chromatography with capillary columns coupled to mass selective detectors (GC/MS or GC/MSMS) or – in rare cases – to electron capture detector (ECD).

Dioxin-like POPs (dl-POPs): dl-POPs comprise 7 congeners of PCDD, 10 PCDF, and 12 dioxin-like PCB (dl-PCB). The amounts are reported for these three groups of POPs as toxic equivalents using the toxicity equivalency factors established by an expert group of the WHO (van den Berg et al., 2006) Extraction, clean-up, separation, identification and quantification of dl-POPs followed established and validated methods using high resolution gas chromatographic columns (HRGC) coupled to sector-field high-resolution mass spectrometers (HRMS). The samples were analyzed by MTM Örebro University (GMP1) and CSIC, Barcelona, Spain, for Latin America and the Caribbean (GRULAC) during GMP1 and GMP2 and in addition, for African and Pacific Islands (PAC) countries in GMP2. The analytical procedures follow general principles (DIN/CEN, 2006; US-EPA, 1994; US-EPA, 2007) and specifically (Abad et al., 2022).

The data assessed comprised the analytical results as quantified in each PUF and three months of exposure. No further data manipulation was done since at the onset of the GMP1 projects, it was agreed to report results per PUF on a comparative basis. Models to recalculate results from PAS into volumes using the equations as developed by Harner (2016) were not used.

The POPs laboratories at MTM Örebro University, Vrije Universiteit Amsterdam, and CSIC had successfully participated in the rounds of the UNEP-coordinated interlaboratory assessments for POPs with the majority of z-scores $<|2|$ or within $\pm 25\%$ from assigned value (the individual reports are available at the UNEP WebPage ((van Bavel et al., 2012; van Bavel et al., 2012; Nilsson et al., 2014; Fiedler et al., 2017, 2021), in the literature (Abalos et al., 2013; de Boer et al., 2022; van Leeuwen et al., 2013; Fiedler et al., 2022b). An assessment of laboratories participating in the GMP projects was recently published (Fiedler et al., 2022a).

2.3. Data handling and assessment

All data were maintained in Microsoft Office 365 Excel®; statistical evaluations and visualization were made using R version 4.0.3 and R packages with R-Studio version March 1, 1056. Significance level was set to $p = 0.05$.

In order to assess the individuals/observations of our multidimensional quantitative variables, we investigated chemical variance amongst our samples by using principal component analysis (PCA) using the R-packages FactoMineR and factoextra; graphs were produced with ggplot2. In PCA, the original data are linearly transformed into new directions (or principal components) along which the variation in the data is maximal. By reducing the dimensionality of multivariate data into two PCAs, the data are visualized with a minimal loss of information (STHDA, 2017). To show if values decreased or increased over time, trendlines were computed using R and the ggplot2 package. For the trendlines, a linear model (lm) approach is used with the formula = y ~ x. For each year, the following values were calculated and used in the model: median, 10^{th} percentile, and 90^{th} percentile. In the model, missing values were removed (na.rm = TRUE; nānot available, rm~remove). For the global trends, the confidence interval around the trendline is shaded in grey color.

All countries are referred to by using their ISO alpha-3 code (ISO, 2020); also shown in Table S 1.

For initial statistical operations, values below the limit of quantification (LOQ) or detection (LOD) were set zero. There is quite some literature about the use of non-detects/left-censored values. Although some authors, *e.g.* (Jaspers et al., 2013), claim to obtain more information from a dataset when applying specific models for non-detects such as the Kaplan-Meier method, there are also warnings to be very careful in doing this (Shoari et al., 2016). The main reason is that the distribution of the data is important, and that distribution is not always known. Our paper deals with multidimensional data including geography, orography, potential POPs sources, weather events, sampling equipment (although standardized) and others. We attempted to remove uncertainty in analysis by not taking into consideration the OCP measurements in GRULAC from 2010/2011 to increase confidence in our data and establish preliminary time trends. The trends in space and time we try to observe are based on a large number of observations and variables, although at relatively coarse level. The trends will not be impacted by addition of values for LOQs/LODs or half of these instead of using zero. Amounts of OCPs and PCB_6 are reported in nanogram per PUF (ng/PUF); amounts of dl-POPs are reported in pg TEQ/PUF. All values refer to one PUF and an exposure period of three months.

3. Results

The amounts found in the PUFs from the UNEP GMP1 project, which was implemented in 2010/2011 in 32 countries, were published (Bogdal et al., 2013; Fiedler et al., 2013; UNEP, 2012) and summarized in a report by UNEP (Fiedler, 2020). The data from the GMP2 projects are summarized in the four regional reports and complemented by a global assessment containing the air monitoring data from passive and active samplers (Fiedler and UNEP, 2022; Fiedler, 2023). From the initial 12 POPs, toxaphene was not analyzed in the GMP1 project and therefore, could not be included into this assessment.

3.1. Descriptive statistics

The descriptive statistics for OCPs and PCB_6 are displayed in Table 1a and Table 1b and for dl-POPs in Table 2. Unfortunately, DDT and other OCP data analyzed in GMP1 from GRULAC could not be included in this assessment, because they did not meet the QA/QC criteria. Further, from GMP1, there were no samples from Egypt (African project) for all POPs under consideration and no samples from Senegal analyzed for dl-POPs. Therefore, the OCPs set includes 11 countries from Africa and nine from the Pacific Islands, total of 18 countries, and 11 POPs, namely aldrin, dieldrin, endrin, chlordane, ΣDDT, heptachlor, mirex, and HCB and in addition the newly listed POPs, α-HCH, β-HCH, and lindane. The PCB_6 set includes an additional nine countries from Latin America; thus, 27 countries in three regions. The dl-POPs comprised 10 countries from Africa, six from the Pacific Islands, and nine from Latin America; thus, a total of 25 countries with the initial three POPs analyzed, PCDD, PCDF, and PCB (as TEQs).

For OCPs, there were 194 samples available with 67 from GMP1 and 127 from GMP2. For PCB_6, there were 297 samples available with 103 from GMP1 and 194 from GMP2. For dl-POPs, there were 158 samples available with 39 from GMP1 and 119 from GMP2. From Table 2, it can be seen that in the Pacific Islands, there were five samples from GMP1 in the PAC region, where no results for dl-PCB could be generated due to interferences in the analytical procedure (Fiedler et al., 2013). The mean and median values for each country in either GMP1 or GMP2 for OCPs and PCB_6 are included in the Supplementary information as Table S 5 and Table S 6, and for the dl-POPs as Table S 7 and Table S 8.

Within the OCPs (Table 1a), the highest values overall were measured for ΣDDT with an overall mean value of 137 ng/PUF and 3 months in GMP1 and 50.2 ng/PUF in GMP2. The corresponding median values were 37.4 ng/PUF and 11.6 ng/PUF, respectively. The absolute maximum value was found in Asia in GMP2 (895 ng/PUF). Second highest values were found for dieldrin with mean values of 27.1 ng/PUF in GMP1 and 5.71 ng/PUF in GMP2. All other OCPs had mean values below 5 ng/PUF but above 1 ng/PUF; *e.g.*, lindane, chlordane or HCB. All mean and median values and subsequent interpretation must be taken with caution since for all POPs, the standard deviations were large and, in most cases, larger than the mean value. Further, some POPs

Table 1a
OCPs in PAS/PUFs: Descriptive statistics for each region and GMP project cycle. Amounts in ng/PUF and 3-months exposure.

	Africa		PAC		Overall	
	GMP1 (N = 44)	GMP2 (N = 86)	GMP1 (N = 23)	GMP2 (N = 41)	GMP1 (N = 67	GMP2 (N = 127)
			aldrin			
Mean	0.366	0.053	0.116	0.006	0.280	0.038
(SD)	(1.96)	(0.099)	(0.332)	(0.029)	(1.60)	(0.0855)
Median	0	0	0	0	0	0
[Min, Max]	[0, 13.0]	[0, 0.480]	[0, 1.50]	[0, 0.150]	[0, 13.0]	[0, 0.480]
			dieldrin			
Mean	9.68	7.19	60.3	2.59	27.1	5.71
(SD)	(11.5)	(10.3)	(171)	(3.28)	(102)	(8.93)
Median	5.20	3.40	8.80	1.70	5.50	2.60
[Min, Max]	[0, 44.0]	[0, 53.0]	[0, 730]	[0, 14.0]	[0, 730]	[0, 53.0]
			endrin			
Mean	0.652	0.118	1.28	0.022	0.869	0.0872
(SD)	(1.20)	(0.309)	(3.77)	(0.080)	(2.40)	(0.262)
Median	0	0	0	0	0	0
[Min, Max]	[0, 3.60]	[0, 1.70]	[0, 17.0]	[0, 0.350]	[0, 17.0]	[0, 1.70]
			chlordane			
Mean	2.97	3.37	3.57	2.85	3.18	3.21
(SD)	(4.92)	(4.55)	(4.77)	(3.33)	(4.84)	(4.19)
Median	1.30	1.78	2.00	1.79	1.40	1.78
[Min, Max]	[0, 21.3]	[0, 22.8]	[0, 20.2]	[0, 14.2]	[0, 21.3]	[0, 22.8]
			DDT			
Mean	108	42.6	192	66.2	137	50.2
(SD)	(167)	(115)	(230)	(153)	(193)	(128)
Median	29.0	14.1	96.3	1.92	37.4	11.6
[Min, Max]	[1.40, 686]	[3.29, 895]	[0.700, 710]	[0.320, 667]	[0.700, 710]	[0.320, 895]
			heptachlor			
Mean	0.618	1.26	0.050	0.694	0.423	1.08
(SD)	(0.989)	(1.34)	(0.198)	(0.541)	(0.850)	(1.17)
Median	0	0.900	0	0.630	0	0.850
[Min, Max]	[0, 3.30]	[0, 6.68]	[0, 0.930]	[0, 2.20]	[0, 3.30]	[0, 6.68]
			mirex			
Mean	0	0.064	0.017	0.160	0.006	0.0948
(SD)	(0)	(0.079)	(0.083)	(0.294)	(0.049)	(0.183)
Median	0	0	0	0.130	0	0.100
[Min, Max]	[0, 0]	[0, 0.370]	[0, 0.400]	[0, 1.90]	[0, 0.400]	[0, 1.90]
			α-HCH			
Mean	1.91	0.808	0.037	0.188	1.27	0.608
(SD)	(7.04)	((0.852)	(0.175)	(0.174)	(5.76)	(0.764)
Median	0	0.550	0	0.240	0	0.440
[Min, Max]	[0, 41.0]	[0, 5.40]	[0, 0.840]	[0, 0.470]	[0, 41.0]	[0, 5.40]
			β-HCH			
Mean	0.650	0.680	0	0	0.427	0.460
(SD)	(3.80)	(1.63)	(0)	(0)	(3.08)	(1.37)
Median	0	0	0	0	0	0
[Min, Max]	[0, 25.0]	[0, 9.90]	[0, 0]	[0, 0]	[0, 25.0]	[0, 9.90]
			lindane			
Mean	4.39	3.09	5.84	1.06	4.89	2.44
(SD)	(6.69)	(6.68)	((10.5)	(1.61)	(8.16)	(5.65)
Median[Min, Max]	2.85 [0, 32.0]	1.65 [0, 55.0]	2.30 [0, 39.0]	0.440 [0, 6.40]	2.60 [0, 39.0]	1.20 [0, 55.0]
			HCB			
Mean	2.40	3.99	1.93	2.36	2.24	3.46
(SD)	((((1.25)	(2.58)	(0.665)	(1.28)	(1.11)	(2.37))
Median	2.05	3.50	1.80	2.30	2.00	3.00
[Min, Max]	[1.10, 6.60]	[0.550, 22.0]	[0.620, 3.50]	[0.640, 7.70]	[0.620, 6.60]	[0.550, 22.0]

including initial POPs, such as aldrin, endrin, mirex, heptachlor, but also the newly listed POP β-HCH had at least half of the values < LOD.

Although in general, smaller mean and median values were found in GMP2, maximum values for several POPs were measured in GMP2, such as chlordane, DDT, heptachlor, mirex, lindane, and HCB.

The 297 results for PCB_6 include values from GRULAC; thus, from three regions, and are shown in Table 1b. The mean and median values for PCB_6 were 14.4 ng/PUF and 4.14 ng/PUF in GMP1 and 9.50 ng/PUF and 2.96 ng/PUF in GMP2. These values were in the same order of magnitude as dieldrin; thus, at levels of the higher values among the initial POPs.

The descriptive statistics for the three dl-POPs is contained as Table 2. It shall be noted that for GMP1, five PUFs from the Pacific could not be analyzed for dl-PCB due to analytical reasons. In addition, the overall results are biased towards the more recent data since the GMP2 data constitute 75% of all data due to higher frequency in the GMP2 design. In GMP1, mean values for PCDD were almost the same as for PCDF, and dl-PCB were only slightly lower. A different picture was seen

Table 1b
PCB_6 in PAS/PUFs: Descriptive statistics for each region and GMP project cycle. Amounts in ng/PUF and 3-months exposure.

	Africa		GRULAC		PAC		Overall	
	GMP1 (N = 44)	GMP2 (N = 86)	GMP1 (N = 36)	GMP2 (N = 67)	GMP1 (N = 23)	GMP2 (N = 41)	GMP1 (N = 103)	GMP2 (N = 194)
				PCB_6				
Mean	16.5	13.8	16.4	7.23	7.50	4.20	14.4	9.50
(SD)	(42.6)	(46.5)	(18.0)	(6.93)	(6.24)	(9.28)	(30.0)	(31.7)
Median	0.370	2.98	10.2	3.37	6.03	2.58	4.14	2.96
[Min, Max]	[0, 248]	[0.830, 290]	[0.269, 69.6]	[0, 25.4]	[0.290, 28.6]	[0.680, 60.6]	[0, 248]	[0, 290]

Table 2
PCDD, PCDF and dl-PCB in PAS/PUFs: Descriptive statistics for each region and GMP project cycle. Amounts in pg TEQ/PUF and 3-months exposure.

	Africa		GRULAC		PAC		Overall	
	GMP1 (N = 10)	GMP2 (N = 54)	GMP1 (N = 21)	GMP2 (N = 49)	GMP1 (N = 8)	GMP2 (N = 16)	GMP1 (N = 39)	GMP2 (N = 119)
				TEQ_PCDD				
Mean	4.18	4.09	11.2	6.06	1.26	3.78	7.39	4.86
(SD)	(4.67)	((5.25)	(8.69)	(4.97)	((2.09)	(5.89)	(8.03)	(5.28)
Median	2.39	1.79	14.5	6.11	0.107	0.204	4.44	2.95
[Min, Max]	[0.0822, 14.3]	[0.00174, 21.7]	[0, 28.8]	[0.0610, 22.8]	[0.00384, 4.90]	[0.000538, 19.3]	[0, 28.8]	[0.000538, 22.8]
				TEQ_PCDF				
Mean	7.25	8.42	10.4	4.78	1.36	2.13	7.71	6.07
(SD)	(7.19)	(11.0)	(9.39)	(2.92)	(2.32)	(2.72)	(8.49)	(8.03)
Median	4.54	3.16	7.94	4.45	0.303	0.356	6.22	3.91
[Min, Max]	[0.751, 19.8]	[0.0895, 56.1]	[0, 37.5]	[0.0560, 11.9]	[0, 6.47]	[0, 7.69]	[0, 37.5]	[0, 56.1]
				TEQ_PCB				
Mean	4.29	2.90	7.32	2.87	1.01	1.42	5.87	2.69
(SD)	(6.34)	(2.55)	(8.17)	(2.20)	(1.10)	(1.38)	(7.46)	(2.32)
Median	1.30	2.13	4.07	2.58	0.388	1.07	3.46	2.25
[Min, Max]	[0.490, 20.9]	[0.0105, 8.67]	[0.00369, 27.9]	[0.253, 11.0]	[0.372, 2.28]	[0.00326, 4.32]	[0.00369, 27.9]	[0.00326, 11.0]
Missing					5 (62.5%)		5 (12.8%)	

in GMP2, where PCDF > PCDD > dl-PCB with similar intervals. The median values always had PCDF > PCDD > dl-PCB (all values as TEQ) and pg/PUF and three months).

3.2. Individual samples

The results for each sample analyzed under the UNEP GMP1 projects and the UNEP GMP2 are detailed in Fig. 1 for OCPs (includes HCB), in Fig. 2 for PCB_6, and in Fig. 3 for dl-POPs. All sample names refer to the country, the year and the season of sample collection. The sequence of countries in both figures is alphabetical according to the ISO-3 alpha code and starting with Africa, followed by GRULAC, where available), and the Pacific Islands (PAC). The sequence of the samples starts with the oldest samples from the second season in 2010 and ends with the latest season in either 2018 or 2019, depending on the exposure periods in the country. For OCPs and PCB, no annual samples were analyzed; therefore, there are no bars referring to the whole year as is done for dl-POPs in Fig. 3.

In the Supplementary Information, Table S2 summarizes the number of PUFs with results for OCPs (including HCB) and PCB by monitoring cycle (GMP1, GMP2), year, and country. Table S 3 provides the information for the dl-POPs.

3.2.1. OCPs and indicator PCB

For the 18 countries with OCP data, the graphical presentation of the results as stacked bars from each PUF is shown in Fig. 1. It is noted that the axes have different scales to enable visualization of comparatively high values as were found in the Democratic Republic of Congo (COD), Mali (MLI), Zambia (ZMB), Fiji (FJI), Solomon Islands (SLB), and Samoa (WSM). From optical inspection, it can be seen that in most countries ΣDDT is dominating. Kenya (KEN) and Samoa (WSM) had high shares of dieldrin (light green color). In Niue (NIU) and Palau (PLW), HCB were relatively more present. Overall, highest amounts were found for ΣDDT and dieldrin in Africa in both GMPs. The abundance of lindane in Nigeria and Togo (GMP1) is noticeable. Chlordane was found mainly in Nigeria (NGA), in GMP2 as well as in Niue and Palau in both GMPs.

The bar graphs for 27 countries with PCB_6 results are shown in Fig. 2. By far, the highest values were found in the Democratic Republic of the Congo (COD) in both GMPs. The values vary widely between seasons. Otherwise, in the Latin American countries (GRULAC) like Brazil (BTA), Peru (PER), and Uruguay (URY) dominated the PCB measurements. Individual elevated samples were also found in Zambia (ZMB) and Fiji (FJI).

3.2.2. Dioxin-like POPs (as TEQs)

For dl-POPs, there were a total of 158 results available; it shall be noted that in the PAC for five PUFs in GMP1 (four countries), the laboratory was not able to quantify dl-PCB; therefore related samples from Kiribati (KIR), Niue (NIU), Solomon Islands (SLB), and Tuvalu (TUV) had to be excluded when analyzing correlations (see section 3.5.2). The number of samples with results are detailed in Table S 3 and the descriptive statistics in Table 2. The graphical sketch displaying the TEQs from PCDD, PCDF and dl-PCB as stacked bars for each PUF are shown in Fig. 3. In most samples, the combined PCDD/PCDF were dominating (blue colors) over the dl-PCB (red color). An exemption are the samples from Zambia (ZMB) and Antigua and Barbuda (ATG) in both

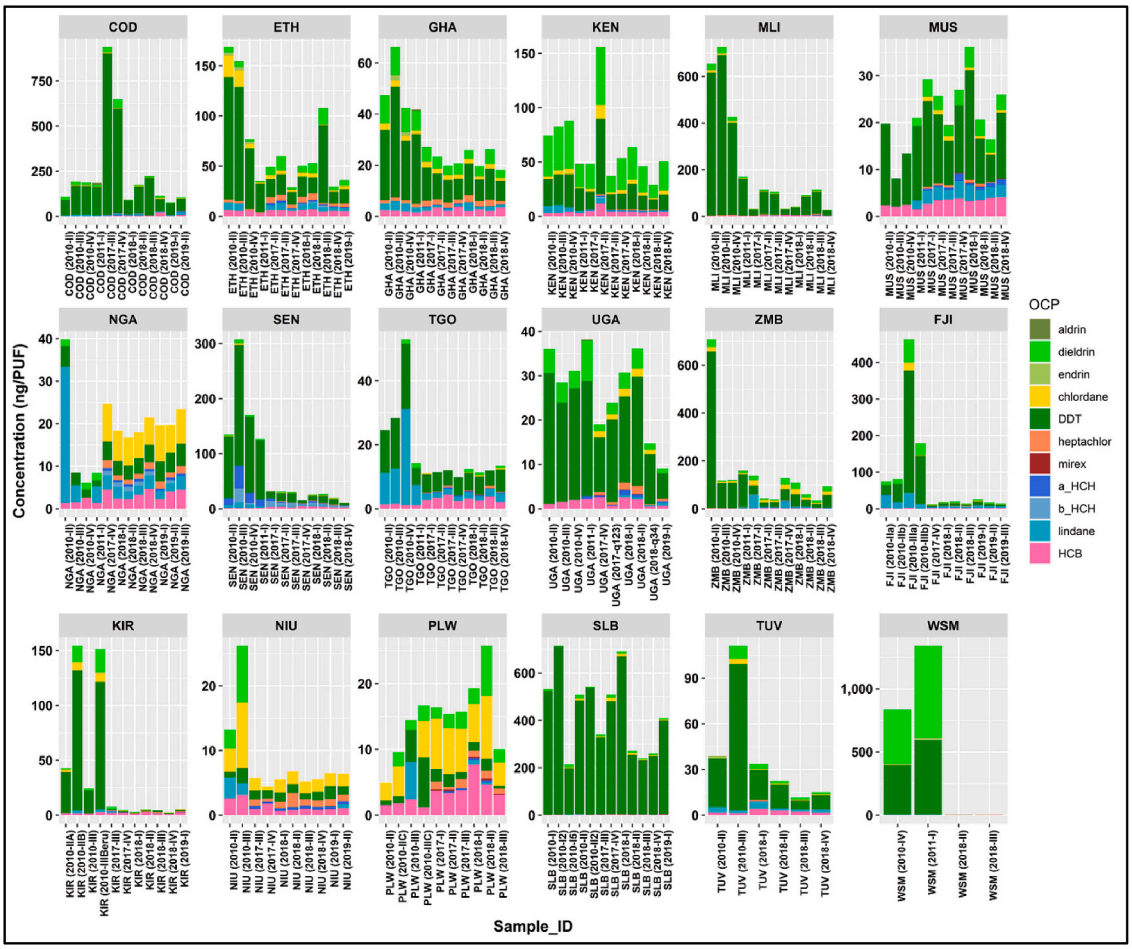

Fig. 1. Stacked bar graphs for OCPs by Sample_ID. Amounts in ng/PUF and 3 months exposure (N = 194).

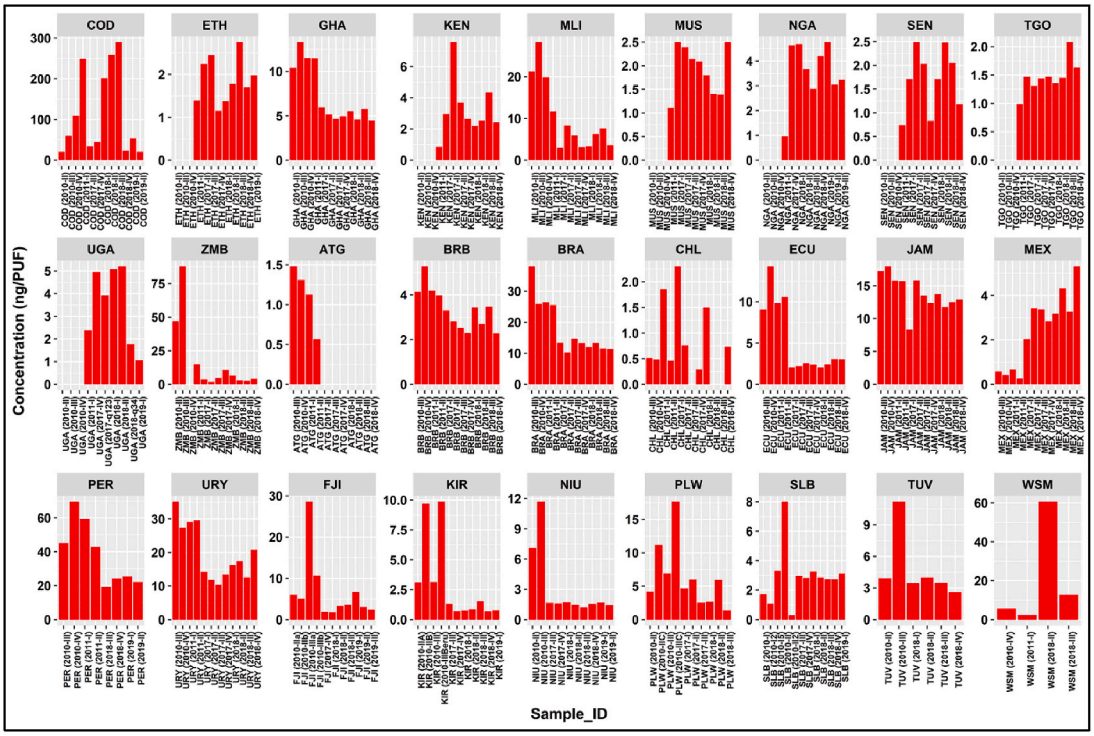

Fig. 2. Stacked bar graphs for PCB_6 by Sample_ID. Amounts in ng/PUF and 3 months exposure (N = 297).

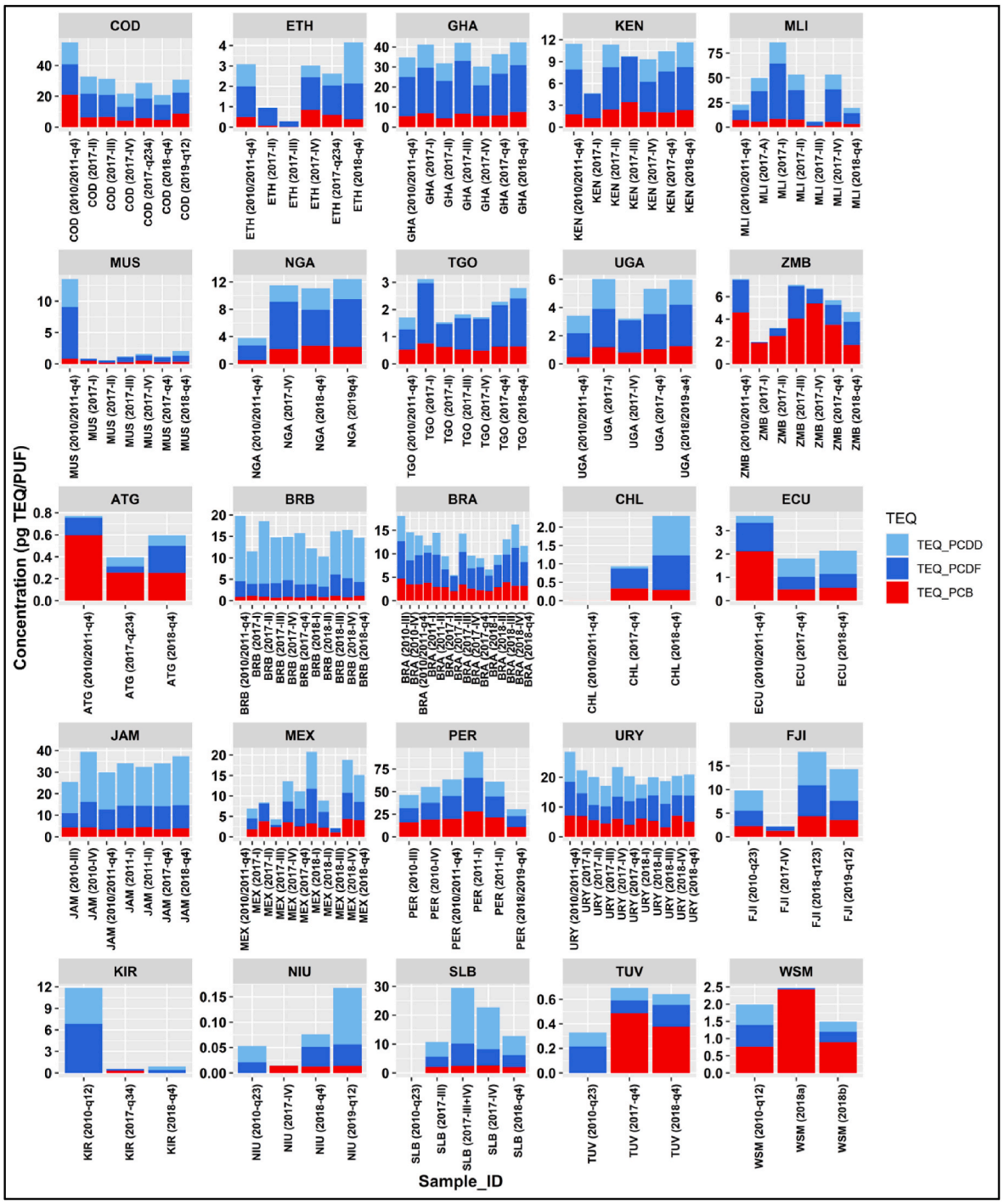

Fig. 3. Stacked bars for dl-POPs (as three TEQ) in PAS/PUFs by sample and for each country. Amounts in pg TEQ/PUF and 3 months exposure (N = 158).

GMPs as well as Tuvalu (TUV) and Samoa (WSM) in GMP2.

3.3. Grouped analysis

3.3.1. OCPs and indicator PCB

A regional analysis of the presence of OCPs and PCB_6 is given in Figure S 1 and Figure S 2. For OCPs, the scale on the y-axis is similar for Africa and the Pacific Islands; thus, the higher values for DDT in PAC in GMP1 is evident. For PCB_6, the scale in Africa is much larger than for GRULAC and PAC. Fig. 4 compares the median values and quartiles of the OCPs and PCB_6 for each chemical. The median values are always quite low in comparison to outliers, which occurred for different POPs in certain regions or GMPs. Within the OCPs, chlordane, heptachlor, and HCB had higher values in GMP2 than in GMP1. With respect to PCB_6, consistently high values were seen in Africa.

3.3.2. Dioxin-like POPs

A detailed analysis of the contribution to the total TEQ, consisting of TEQ_PCDD, TEQ_PCDF and TEQ_PCB, shows that in GRULAC TEQ_PCDD > TEQ_PCDF > TEQ_PCB in both GMPs. In Africa, the median values are in the following order TEQ_PCDF > TEQ_PCDD > TEQ_PCB (Fig. S 3). In general, median values for TEQs were lower in GMP2 than in GMP1. The opposite is found only for TEQ_PCB where GMP2 > GMP1 in Africa and PAC (Fig. 5).

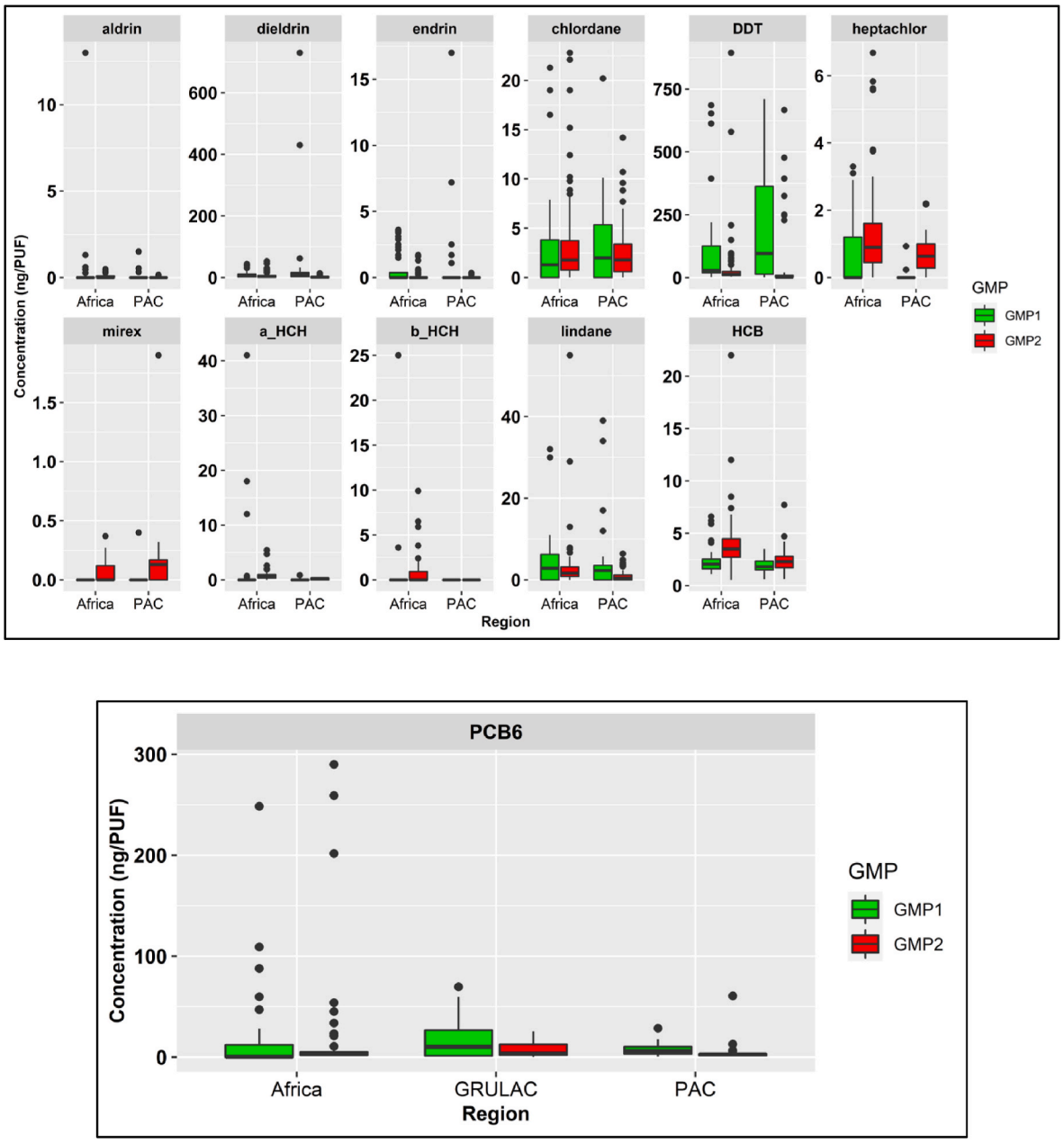

Fig. 4. Box plots for OCPs and PCB_6. Amounts in ng/PUF and 3 months exposure.
The whiskers represent the minimum and maximum concentrations without the outliers. The lower border of the box represents the first quartile (25%), the line inside the box the median and the upper border is the third quartile (75%). The dots outside the whiskers are outliers, which were defined as all concentrations greater or smaller the interquartile range multiplied by 1.5.

3.4. Multivariate analysis of POPs in PAS/PUFs

Multivariate assessment using PCA and visualization was done for the PAS/PUF and the results are highlighted according to project region and GMP (Fig. 6). The location of the samples and their contribution to the individuals is shown in Figure S 4. The PCA of the 194 PAS/PUF samples analyzed for OCPs shows that the composition of the samples is quite scattered since the first two dimensions of the graph (Fig. 6, top) represent only 37% of the distribution. The second dimension (Dim2) is dominated by samples with higher values of α-HCH and β-HCH in the 2nd quartile; all the samples therein are from Africa. The drins – especially dieldrin and endrin - are more found in the Pacific samples. There are quite distinct ellipses for the two regions, grouping their samples together. This finding is also supported by significance tests, which give highly significant differences between the two regions (p-value = 2.3×10^{-7}). The difference between the two GMPs were also significantly different (p-value = 8.5×10^{-5}).

The PCA for the 158 dl-POPs results is shown in Fig. 6, bottom left for regions and right for the GMPs, which explains 92% of the variation. The location of the samples and their contribution to the individuals is shown in Figure S 5. Samples with a high contribution from TEQ_PCB are located in the first quartile and samples with high contribution from TEQ_PCDD are in the fourth quartile. In both quartiles, the highest values were found in GMP1. The vector representing TEQ_PCDF is between those for PCB and PCDD. It can also be seen that the x-axis, Dim1, represents the scale of the TEQ_PCDD, TEQ_PCDF, and TEQ_PCB. The ellipse around the results from GMP1 (green colour) is much wider than for GMP2, although fewer samples, to include the relatively high values for TEQ_PCB (1st quartile) based on the GRULAC samples.

Significance tests showed highly significant differences between the

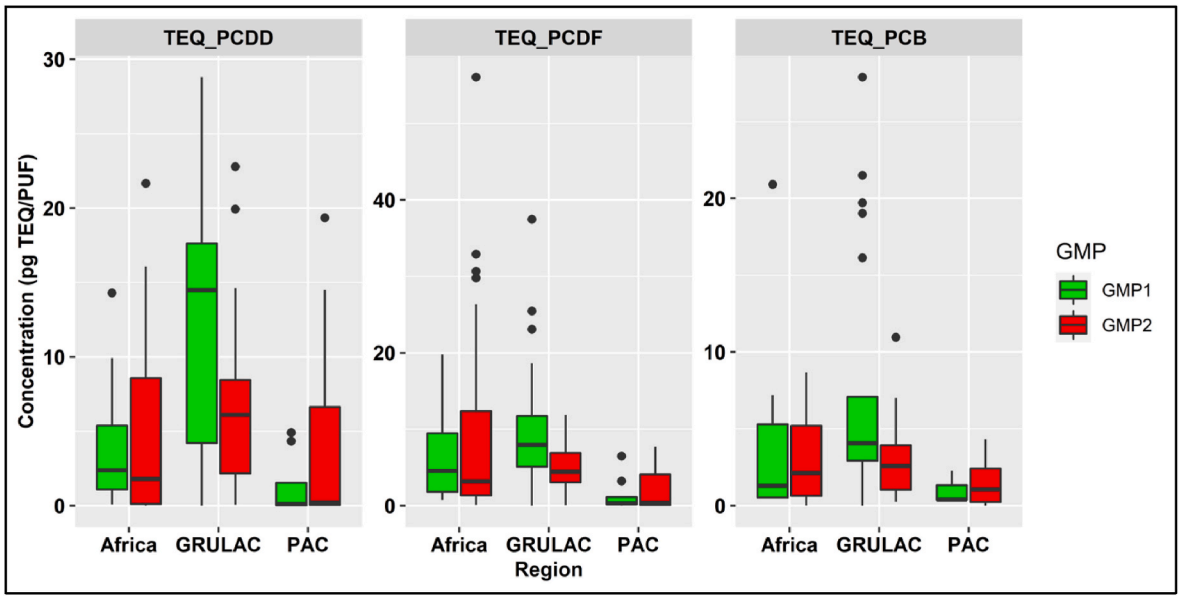

Fig. 5. Box plot for three TEQs according to TEQ. Amounts in pg/PUF and 3 months exposure.
The whiskers represent the minimum and maximum concentrations without the outliers. The lower border of the box represents the first quartile (25%), the line inside the box the median and the upper border is the third quartile (75%). The dots outside the whiskers are outliers, which were defined as all concentrations greater or smaller the interquartile range multiplied by 1.5.

three regions (p-value = 1.1×10^{-11}) but also for pairwise comparison (p-value≪0.001). The difference between the two GMPs was also significant; however, the p-value was just 0.049).

3.5. Time trends

3.5.1. Global trends

Marked time trends at global level could not be identified from our datasets. It shall be noted that for OCPs and PCB_6 all but DDT and HCB, the 10th percentiles were below LOD and that even for heptachlor, α-HCH, aldrin, endrin, and mirex, the 25th percentiles were below LOD. Median values for aldrin, endrin, mirex, and β-HCH were also below the LOD (Supplementary information, Table S 9). These very low values hamper trend analysis. However, they clearly show that the amounts of these compounds have decreased to a minimum. Therefore, the trendlines for aldrin, endrin, heptachlor, mirex, α-HCH, and β-HCH as shown in Figure S 6 are for completeness only. An increasing trend could be determined for chlordane and HCB as shown in Fig. 7. For ΣDDT, although the highest level was found, no global trend could be determined. For dieldrin, a downward trend could be seen; however, in all measurements, wide variation of measured data was found. For PCB_6, a slight downward trend was found. Although the confidence intervals were relatively narrow, the high bars/lines indicate many extreme values in all years.

For the dl-POPs, downward trends were calculated (Fig. 7, bottom) with the strongest slope for PCDD and the least for dl-PCB. Especially the PCDD trendline is accompanied by a large confidence interval.

3.5.2. Trends by region

Fig. 8 details the global trend into the regions, which provides further insight into the comparison of the two data series and individual POPs. Whereas the global trendline for DDT did show neither increase nor decrease, it can be seen from Fig. 8 that a decrease in DDT and dieldrin amounts was found for the Pacific Islands whereas Africa remained at initial values. For HCB, increase of values was seen in Africa but not for the Pacific. Lindane values decreased slightly in both regions. PCB_6 remain on the same level for Africa and PAC whereas for GRULAC, a U-shape curve was obtained with slightly decreasing values in from 2010 to 2011 measurements and increasing values from 2017 to 2019.

For the dl-POPs, GRULAC showed decreasing trends for PCDD, PCDF, and dl-PCB, although with extreme values in 2010/2011, which disappeared in GMP2. African values indicate small increases (most marked for PCDF) and PAC measurements remain on the same low level.

3.5.3. Trends by country

Some examples for country-specific trends are displayed in Fig. 9 to illustrate the regional trends by country; some graphics show decreasing and some show increasing trends.

Strong decreasing trends were seen for ΣDDT: In the Pacific, the very high values in WSM in GMP1 (580 ng/PUF for mean and median values) were no longer found in GMP2 (mean and median < LOD); however, it shall be noted that in both GMPs, there were only two measurements. For the Solomon Islands (SLB), a similar downward trendline was generated, however, the decrease was much lower since in GMP2, the mean and median values were 370 ng/PUF and 325 ng/PUF. In Africa, the same phenomenon was seen in MLI with four measurements in GMP1 and eight in GMP2: GMP1 values (mean = 464 ng/PUF, median = 504 ng/PUF) decreased in GMP2 (mean = 58.1 ng/PUF, median = 54.5 ng/PUF). For PCDD (as TEQ), strong decreases were seen for the Democratic Republic Congo in Africa, and Peru in GRULAC.

On the other hand, at national level, the overall regional increase for chlordane shows that in Africa and the Pacific Islands, these regional trends seem to be driven by two countries in each region: Ethiopia and Nigeria in Africa and Palau and Solomon Islands in the Pacific Islands. In GRULAC, almost parallel trends were seen for PCB_6 and dl-PCB; strong declines were seen in Peru (PER).

4. Discussion

Our data analysis showed the following strengths. All data were presented on the basis of mass concentration per PUF and three months exposure time. This approach is robust and allows for direct comparisons since the same thermodynamic and kinetic rules apply to all measurements. A further strength of our projects is that not more than two laboratories analyzed the same group of POPs. The timespan was nine years with a 5-year gap between the two series of measurements, which can be separated timewise.

Despite the fact that the same countries and locations were analyzed

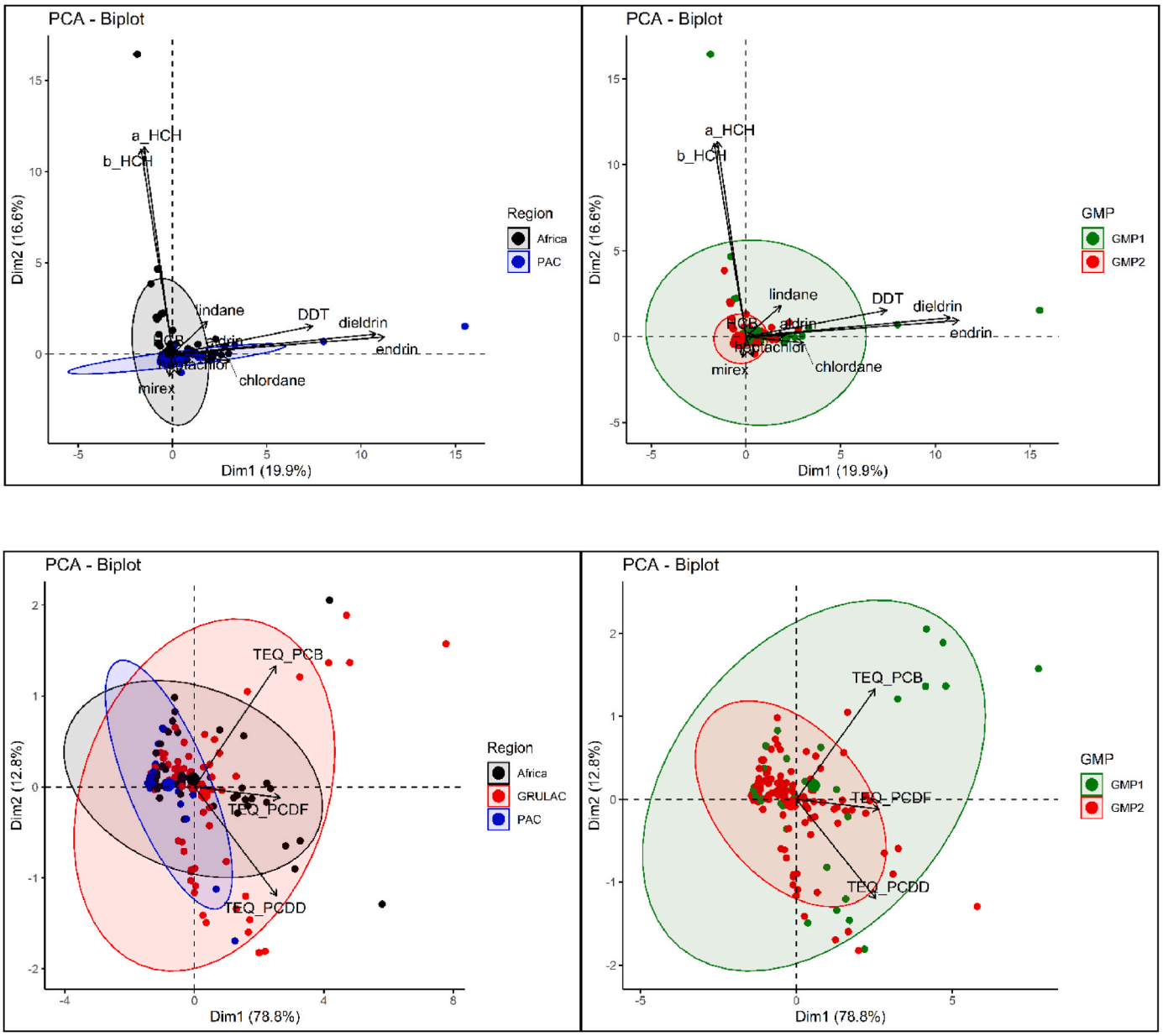

Fig. 6. PCA for OCPs (n = 194) and dl-POPs (as TEQ, n = 158) with ellipses around the GMPs and the project region. All values are normalized to 1 PUF and 3-month exposure.

by the same laboratories, only a few global observations could be made; these include.

- All 12 POPs analyzed in both series could be quantified but it must be noted that often, the amounts in the PUFs were very low and posed analytical challenges. Throughout the projects, the median values for aldrin, endrin, mirex, and β-HCH were zero. With often very low concentrations and leveling off, it cannot be expected that concentrations will further decrease
- Overall, the concentrations found in the first series (2010/2011) were higher than in the second series of measurements. Using median values, declines were between 29% (for PCB_6) and 69% (for ΣDDT). However, the global mean and median value in GMP2 was higher for HCB (54% and 50%). An increase in both values was also found for chlordane (1% and 27%) but on lower scale. Mean values increased for heptachlor, mirex, and β-HCH but on so low level that the median values were zero (see Table S 10).
- A common pattern per continent/region could not be identified.
- General **global trends** as to increase or decrease were hard to be concluded. A relatively clear declining trend from the first series (in 2010/2011) and the second series of measurements (2017–2019) could be seen for PCDD (as TEQ) but not for other POPs. Some increasing trends were observed, for chlordane, heptachlor, and HCB.
- For some POPs, it was observed that one region had a different trend than the other regions, thus, differentiating the global trend analysis. Examples included: ΣDDT decreased only in the Pacific but not in Africa; PCDD (TEQ) only in GRULAC but not in Africa or the Pacific Islands (PCDF to a lesser extent).
- A country-by-country comparison showed that detailed monitoring would be needed to assess data on a national scale or even for a location. The data indicate that local sources or activities may be more important than long-range transport considerations or empiric thermodynamic or kinetic considerations.

Our data and analysis to some extent confirm but also contradict the

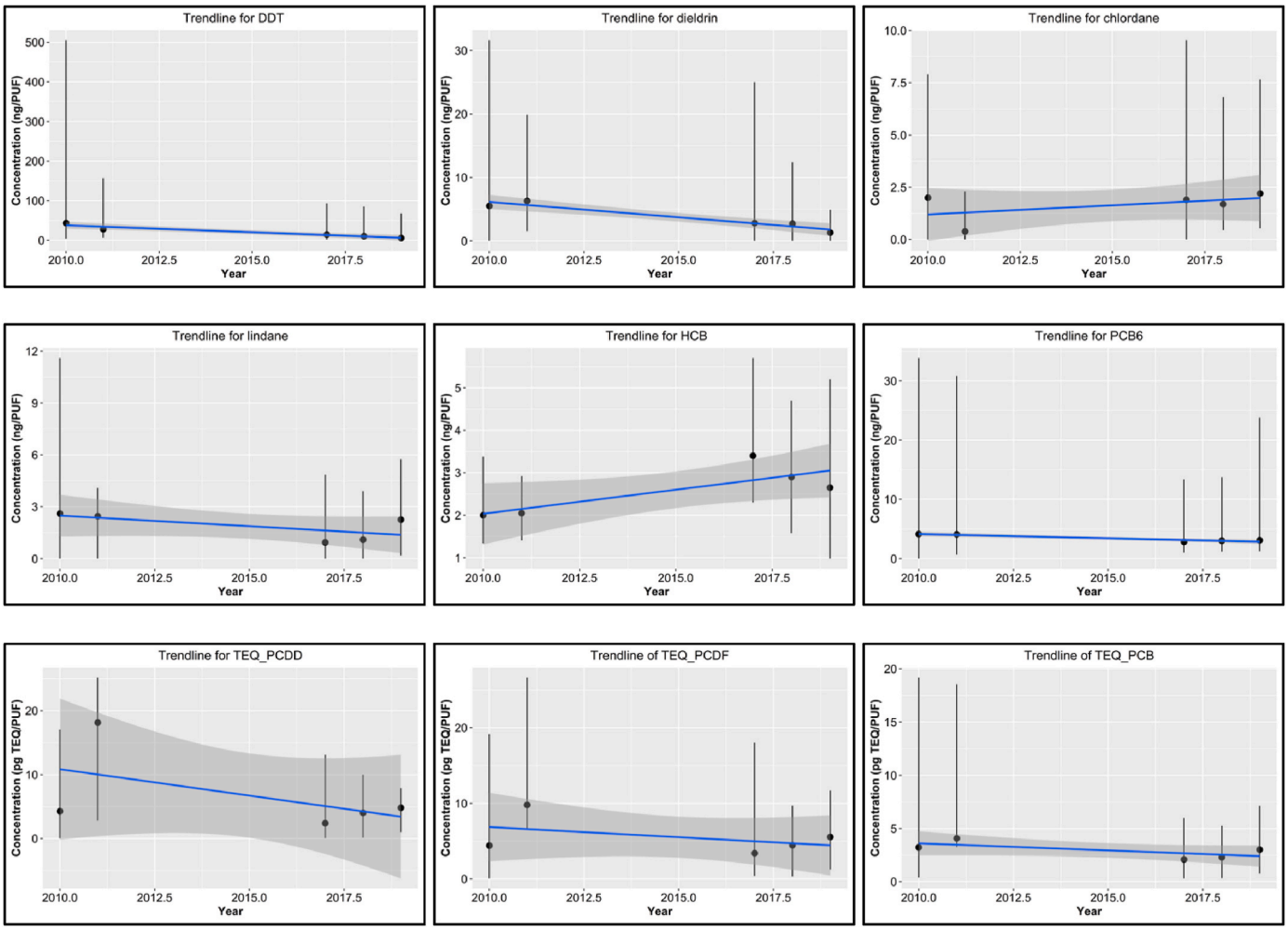

Fig. 7. Global trendlines for selected OCPs, PCB_6, and dl-POPs (bottom) with confidence intervals. Dots represent the median value in a given year; the whiskers the 90 th percentile on top and the 10th percentile on bottom.

preliminary conclusions as stated in the draft report from the global monitoring plan that was prepared by the government representatives for the effectiveness evaluation of the Stockholm Convention (UNEP, 2022). It should be noted that the effectiveness evaluation report contains orders of magnitude more data but has aggregated these in a different way such as that annual averages are being put as input and not during assessment only as we did for the trendlines. Further, the report largely relies on model assumptions and conversion to volume-based concentrations using a refined Harner model (Harner, 2016). We confirm the findings of increasing trends for HCB in the draft UNEP report. The slight increases of heptachlor and lindane were not found in the global report. The global report highlights a decrease for the legacy POPs, which we found for PCDD, and to much lesser extent for PCDF and dl-PCB, which were not included in detail in the global report.

There are not many datasets for comparison available since publications either address different geographies and are targeting the temperate climate or even Artic regions or are report on levels prior to our sampling year (Choi et al., 2008; Harner et al., 2004; Pozo et al., 2006) or cover several stations in one country, such as reported for Mexico (Wong et al., 2009) or Brazil (Tominaga et al., 2016). The values reported in these studies cannot be directly compared since they are reported on volume basis. The Mexican data were from 2002 to 2004 samplings and showed local differences for ΣDDT with relatively high concentrations in malaria areas. We found relatively high ΣDDT concentrations in GMP2. For OCPs (and PCB, HCB) our GMP1 data confirm the earlier findings that there is not much seasonal variation between measurements (Fig. 2). The UNEP GMP1 project in Brazil was continued beyond 2011 until 2015 and included OCP, PCB and dl-POPs (Tominaga et al., 2016). The results presented in this paper contain our data but report on volume basis using an earlier version of the Harner model (Harner, 2016). The authors found that the highest TEQs were found in the 2010 samplings, which is also seen in Fig. 3 of this paper. However, variations were not significant within our series of measurements or the literature data. Both sources have the PCDF (as TEQs) dominating over the PCDD and the dl-PCB. The decreasing trend 2010–2015 reported in Brazil for PCB_6 was confirmed by our set and including the more recent years (Fig. 9).

Most data from passive air sampling are reported on volume basis although the networks, such as MONET use passive sampling equipment, and state that the data are generated as 'primary data in ng per PUF per sampling period' (Kalina et al., 2019). In these data for each sampling day beyond 84 days, an increment value in ng per PUF per day is added. This correction assumes linear uptake of the POPs. Our results have not been corrected for additional or missing days but had been unified to a more general 3-months period. In an assessment of 15 years of sampling in Europe, values below LOD were computed at ½ LOD whereas we attributed zero. For PCB, Kalina et al. found decreasing trends in the order of 12%–20% for the lighter PCB and 9%–11% per year for the heavier PCB. For OCPs, Kalina et al. found consistently decreases of 6%–16% per year for α-HCH and 7%–23% per year for γ-HCH. Less consistent data were found for HCB, which even showed increases during several years. The inconsistency is attributed to local

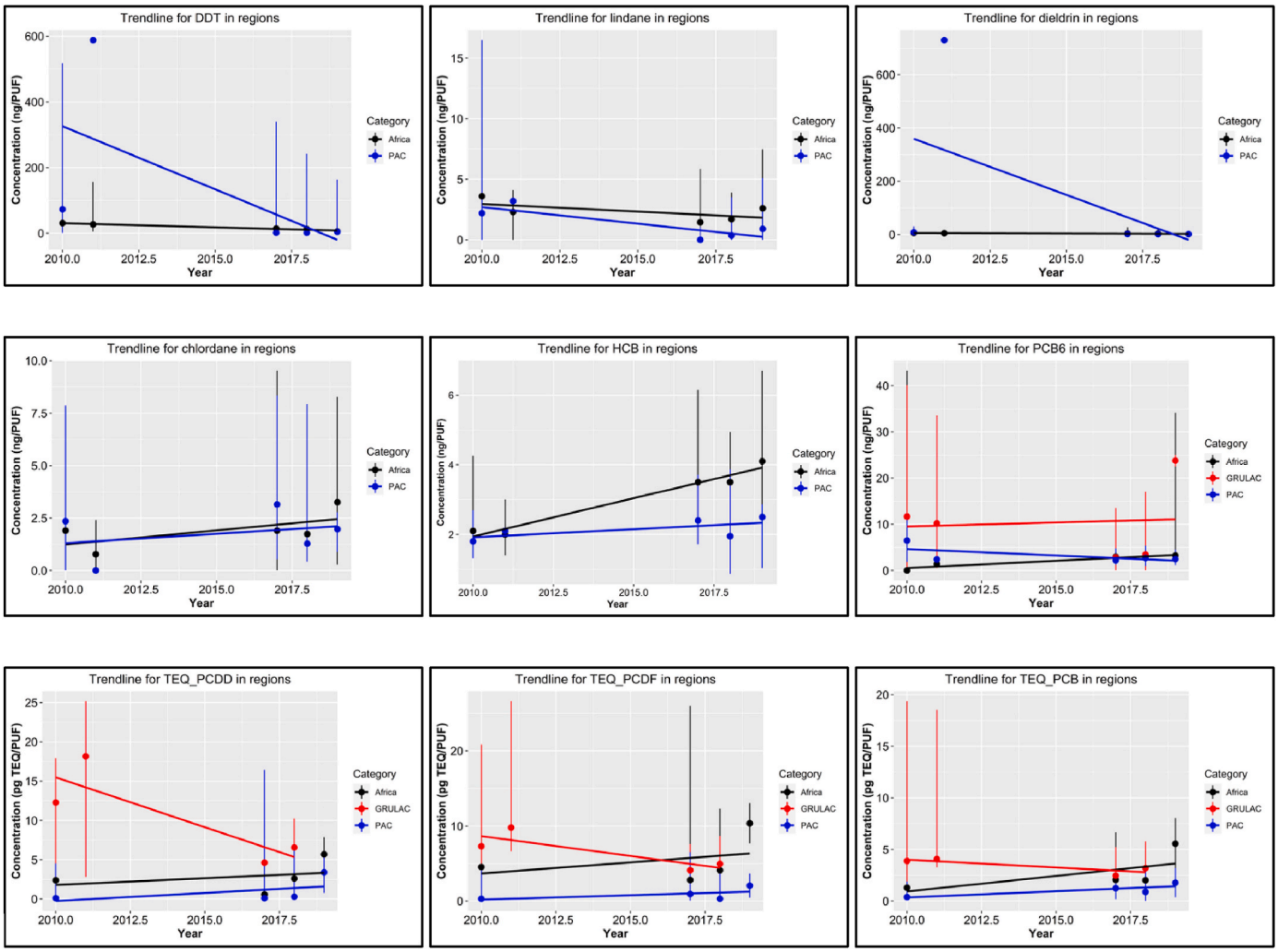

Fig. 8. Time trends in regions for selected OCPs, PCB_6, and dl-POPs. Dots represent the median value in a given year; the whiskers the 90 th percentile on top and the 10^{th} percentile on bottom.

sources. The authors concluded that the passive air sampling provides steeper decreasing trends than active sampling. Data for ΣDDT were not provided and only *p,p'*-DDE analyzed.

5. Conclusion

We conclude that monitoring programs do not have to be implemented every year and that a preferred approach would be defined intervals between measurement series. However, the series should be as complete as possible, *e.g.*, four samples, equally distributed over one calendar year.

Overall data assessment is limited through variation in countries that may represent a certain group. In our case, there was an abundance of sampling sites located in the tropical regions whereas other reports and publications, including the reports for the effectiveness evaluation of the Stockholm Convention are centered around northern hemisphere countries located in the temperate or even polar regions. We have included dioxin-like POPs as initial POPs from the onset of our projects. Notwithstanding, analysis of the POPs poses challenges, but these are not limited to newly listed POPs since the interlaboratory assessments, such as coordinated by UNEP to support the global monitoring plan, have shown that best results were observed for analytically challenging POPs, such as PCDD, PCDF, PFAS, PBDE and most unsatisfactory results were obtained for the "simple" POPs, such as DDT (de Boer et al., 2022; Fiedler et al., 2022a, Fiedler et al., 2022b).

It was observed that it takes long time until POPs measurements, such as from the air monitoring, are available for assessment at a global level. Therefore, we advocate that the air monitoring with PAS/PUFs should be implemented at determined intervals and with an *ad hoc* selection of chemical analytical laboratories that are qualified through interlaboratory assessments. Such approach would allow timely generation of results at high quality.

Credit author statement

Heidelore Fiedler: Investigation, Data curation, Visualization, Funding acquisition Örebro University, Writing – original draft, review and editing Esteban Abad: Funding acquisition CSIC, supervision chemical analysis (dl-POPs, OCPs and PCB6 in GRULAC), Validation, Writing – review and editing Jacob de Boer: Funding acquisition Vrije Universiteit Amsterdam, supervision chemical analysis (OCPs and indicator PCB), Validation, Writing – review and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

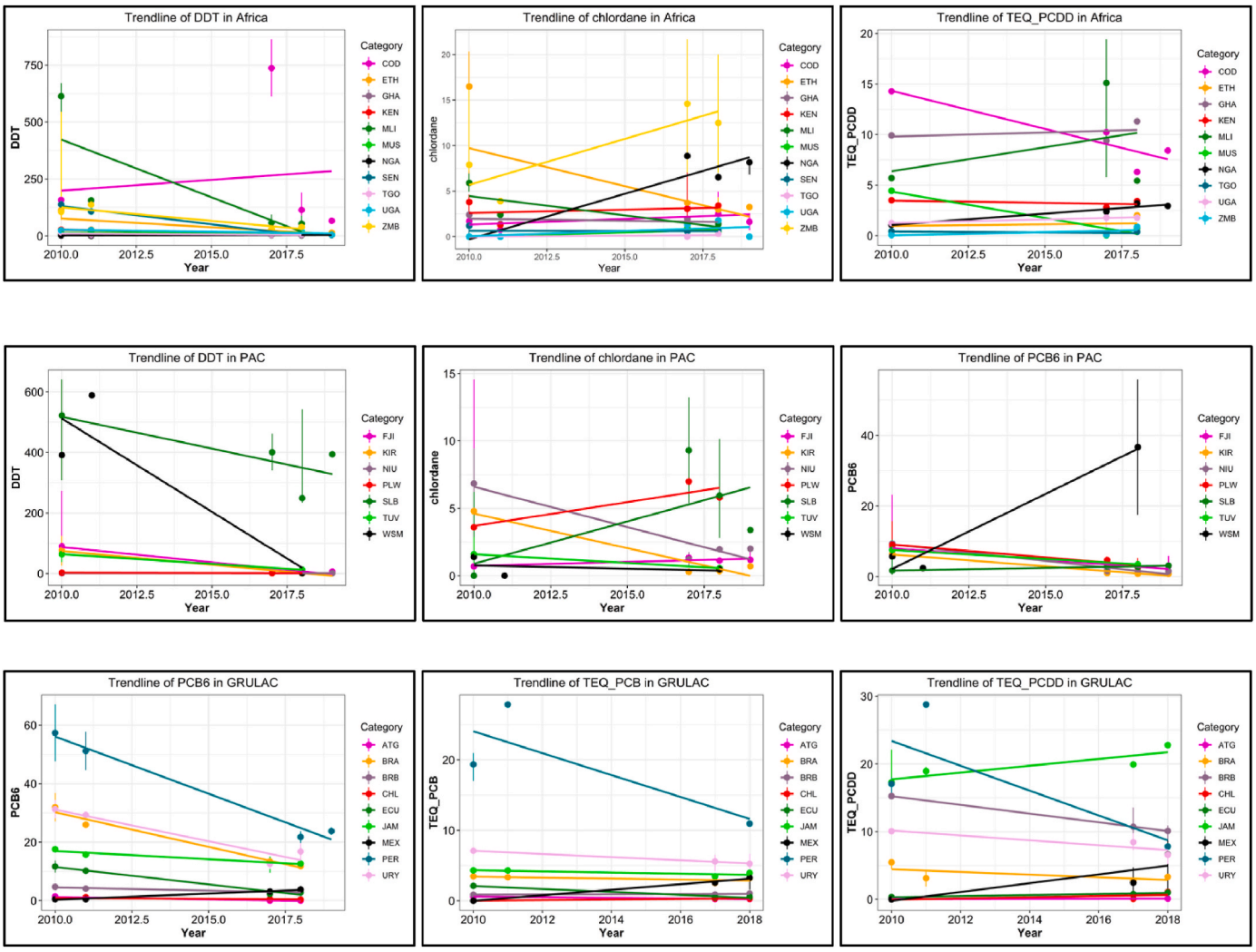

Fig. 9. Time trends by country in regions for selected POPs. Amounts in ng/PUF for OCPs and PCB_6, pg TEQ/PUF for dl-POPs.

Data availability

All data are available from UNEP or sources referenced in the paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2023.138299.

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