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Dioxin-like POPs in national samples from global monitoring plan projects (2017–2019)

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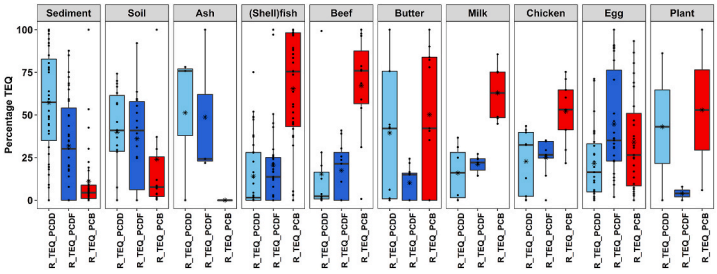
HIGHLIGHTS

- Dioxin-like POPs (dl-POPs, as TEQ) assessed in 185 environmental samples from 27 countries.
- Distribution of TEQs more governed by type of matrix, abiotic or biota, than geography.
- Soil and sediment dominated by PCDD or PCDF; most foods of animal origin by dl-PCB.
- Amounts of dl-POPs found were generally low, although few elevated concentrations encountered.
- Analytical results being highly selective and sensitive are a prerequisite for comparative assessments.

GRAPHICAL ABSTRACT



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ABSTRACT

The global monitoring plan (GMP) established under the Stockholm Convention on Persistent Organic Pollutants (POPs) had defined ambient air, human milk or blood, and water as core matrices to be analyzed and assessed for spatial and temporal distribution. Within projects coordinated by the United Nations Environment Programme (UNEP), developing countries were offered to have other matrices analyzed for dioxin-like POPs (dl-POPs) in experienced laboratories. Subsequently, 185 samples from 27 countries located in Africa, Asia, and Latin America were collected during 2018–2019 and analyzed for polychlorinated dibenzodioxins (PCDD), dibenzofurans (PCDF), and biphenyls (PCB). Using the WHO_{2005} toxic equivalency approach (TEQ), the amounts of dl-POPs found were low (<1 pg TEQ/g); however, singular samples had higher values; *e.g.*, egg from Morocco, fish from Argentina or Tunisia; soil and sediment samples. Results showed that the matrix, abiotic or biota, had more impact on the TEQ pattern than the geographic location. Independent of the location and across all samples, dl-PCB in (shell)fish and beef samples had a contribution of 75% to the total TEQ; milk (63%), chicken (52%), and butter (50.2%) more than 50%. Sediment (57% and 32%) and soil (40% and 36%)) samples were dominated by PCDD and PCDF, respectively; therein, dl-PCB had shares of 11% and 24%. Egg samples (N = 27) did not follow

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the general biota pattern and had 21% of the TEQ from the PCDD, 45% from PCDF, and 34% from dl-PCB; thus, indicating that abiotic matrices such as soil or other material may have an impact.

1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), and polychlorinated biphenyls (PCB) were three of the initial twelve persistent organic pollutants (POPs) listed in the Stockholm Convention on Persistent Organic Pollutants (UNEP, 2001).

The GMP is an instrument of the effectiveness evaluation and provides a harmonized framework to identify changes in concentrations of POPs over time. In addition, aiming to provide representative information on the long-term presence of these compounds in the environment, their time trends and regional and global transport.

The GMP has defined ambient air and water as core matrices for environmental occurrence and transport and human milk or human blood for human exposure. In chapter 2 of the GMP guidance document, recommended congeners within each POP (where a group is listed) are provided. Finally, guidance is also provided as to the reporting of the amounts of POPs in the core matrices and the instrumentation capable for analysis (UNEP, 2019; UNEP, 2021). To maintain focus, methods for sampling and analytical approaches for the measurement of listed POPs were laid down in guidelines and standard operational procedures (SOP) targeted on either the matrix of interest or the POP with the overall goal of generating harmonized and comparative data that can be compared over time and between regions (Fiedler et al., 2019; Fiedler et al., 2020). Within the GMP, most attention is given to the core matrices, *i.e.,* ambient air, human milk/blood and surface water (for perfluorinated POPs only). On the other hand, many countries are interested in determining POP concentrations in foodstuffs, including for regulatory purposes, or sediment and soil. Within the UNEP/GEF GMP2 projects, these additional samples were named 'national samples' (for long: samples of national interest to the participating country). A separate SOP addressing soil, sediment, meat, fish, dairy products or eggs was developed and applied for these projects (UNEP, 2017).

According to text in Annex C, PCDD, PCDF, and PCB should be reported (and assessed) using the toxicity equivalency (TEF) approach and report the data as toxic equivalents (TEQ). The Convention refers to schemes by the World Health Organization (WHO) and refers to the 1998 scheme (van den Berg et al., 1998); however, nowadays researchers and regulatory institutions apply the most recent scheme, *i.e.,* of 2005 (van den Berg et al., 2006). The TEF approach is also recommended in the guidance for the global monitoring plan (GMP) established under the Stockholm Convention (UNEP, 2019; UNEP, 2021).

The occurrences, relative abundances, and distribution of the dioxin-like POPs in samples from abiotic environments and biota collected from 28 developing countries participating in the UNEP/GMP2 projects (UNEP, 2014c; UNEP et al., 2014a; UNEP, 2014b; UNEP, 2014d) are addressed in this study.

2. Materials and methods

2.1. Origin of samples and characterization

Collection of samples followed the SOP developed for the UNEP/GMP2 projects (UNEP, 2017). Accordingly, national samples were collected from 26 developing countries in Africa (n = 10), Asia (n = 4), Group of Latin America and the Caribbean (GRULAC) (n = 8) and Pacific Islands (PAC) (n = 4) through the United Nations Environment Programme/Global Monitoring Plan 2 on Persistent Organic Pollutants (UNEP/GMP2) projects.

The food samples were bought at local markets or supermarkets and represented commonly consumed species or brands. The meat and fish samples were prepared and only muscle meat without skin was analyzed; no offal was included. The butter samples were commercial samples of most consumed brands; they may have been imported but still would characterize consumption behavior in the respective country.

For assessment, samples were grouped using different denominations such as 'type' to differentiate between 'abiotic' and biota' samples, 'Category' or 'matrix' to specify the samples as to sediment, soil, ash, (shell)fish, dairy (includes milk and butter), meat (includes beef, sheep, pork, chicken), egg (includes chicken, duck, and fowl eggs) or plant, which were vegetable oils.

2.2. Chemical analysis

Chemical analysis was performed in three laboratories: CSIC (Barcelona, Spain), Eurofins Ökometric (Bayreuth, Germany) and Eurofins GfA Lab Service (Hamburg, Germany). All laboratories were accredited for PCDD, PCDF, and PCB analysis in the matrices of concern, *i.e.,* soil, sediment, food, biota, and other environmental matrices. All laboratories used very similar approaches, based on EPA 1613, CEN 1948 or EU Santé (European Union, 2017) with Soxhlet or pressurized liquid extraction, multi-step column clean-up and isotope dilution HRGC/HRMS-analysis on 60 m capillary GC columns. All reference substances, reagents and materials were suitable for the intended purpose of determining PCDD, PCDF, and PCB at trace level (*e.g.*, use of solvents of trace analytical grade) and monitored within the QA/QC routines (see below).

Owing to the variety of matrices, different extraction – or, in case of oils, dissolution – procedures were applied depending on the sample nature. All samples were spiked just before the extraction step with known amounts of ^{13}C-labelled PCDD/PCDF and ^{13}C-labelled dl-PCB. Appropriate amounts of solid food samples were extracted using Soxhlet extraction using *e.g.*, toluene/cyclohexane (1:1, v/v), toluene/acetone (9:1, v/v) or toluene. All extracts were evaporated to near dryness and the residue was dissolved in n-hexane. Purification and fractionation of the extracts were carried out by multiple column chromatography. This consisted, *e.g.*, of a multilayer silica column containing acidified silica gel (H_2SO_4, 44%, w/w) for removal of fat and other interfering substances and a basic alumina column (activity Super I) for fractionation of dl-PCB from PCDD/PCDF. The procedure provided two main fractions: Fraction 1, containing the dl-PCB congeners, and fraction 2, where the PCDD/PCDF congeners eluted. Both fractions were concentrated and reduced to near dryness using a gentle stream of nitrogen. The final volume of the extract was adjusted to ca. 10 μL–20 μL after addition of a known amount of $^{13}C_{12}$-isotope labelled injection standards.

The analyses of the target compounds took place by HRGC-HRMS using electron impact ionization (EI). They were performed using either DFS (Thermo Fisher, Bremen, Germany) or Agilent 7890A (Agilent Technologies, Santa Clara, CA, USA) gas chromatographs and DFS (Thermo, Bremen, Germany) or Micromass Premier (Waters, Manchester, UK) high resolution mass spectrometers (sector-field instruments). The separation of PCDD/PCDF and dl-PCB was carried out

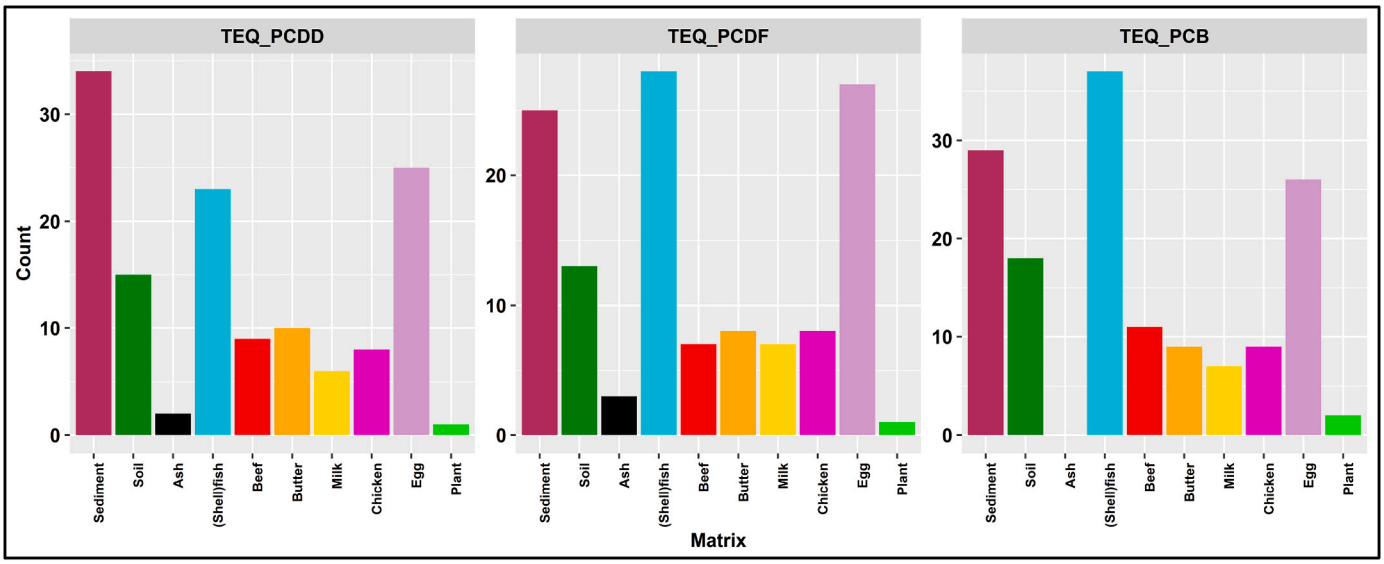


Fig. 1. Graphical sketch displaying the number of samples with amounts above the LOQ for the three TEQs by matrix (n = 185 samples).

on weakly polar fused-silica capillary columns (60 m × 0.25 mm I.D., 0.25-μm d_f DB-5ms UI or VF-X ms; Agilent Technologies, Santa Clara, CA, USA). Injection was performed in splitless mode at 280 °C using helium as carrier gas in constant flow mode. The HRMS system was operated in EI + mode at a resolution of 10,000 (10% valley definition). Data acquisition was carried out in selected ion monitoring (SIM) mode, where the two most abundant ions of the molecular cluster of each homologue group for PCDD/PCDF and dl-PCB were monitored. Calibration and quantification took place using the seventeen 2,3,7,8-chloro-substituted PCDD/PCDF and twelve dl-PCB (four non-ortho PCB: PCB 77, 81, 126, and 169, and eight mono-ortho PCB: PCB 105, 114, 118, 123, 156, 157, 167, and 189) using the corresponding $^{13}C_{12}$-labelled compounds (Wellington Laboratories Inc., Guelph, Ontario, Canada) for isotope dilution quantification.

The results were expressed as toxic equivalents (TEQ) using the WHO-TEFs as established in 2005 (van den Berg et al., 2006). Since PCDD, PCDF, and dl-PCB were listed as three POPs, results are reported as three TEQs (for 7 PCDD, expressed as TEQ_PCDD; for 10 PCDF as TEQ_PCDF and for 12 dl-PCB as TEQ_PCB). Values for dl-POPs were reported in picogram per gram (pg/g), with the values for fish and

Table 1
Descriptive statistics for three TEQ grouped by matrix (n = 185). SD = standard deviation. For median and minimum values < LOQ zero is shown "0". <LOQ indicates that none of the values was above the LOQ for this specific TEQ. All concentrations in pg TEQ/g.

	Sediment (N = 39)	Soil (N = 19)	Ash (N = 3)	(Shell)fish (N = 54)	Beef (N = 12)	Butter (N = 13)	Milk (N = 7)	Chicken (N = 9)	Egg (N = 27)	Plant (N = 2)	Overall (N = 185)
						TEQ_PCDD					
Mean (SD)	1.87 (3.80)	1.92 (3.50)	0.755 (0.826)	0.047 (0.176)	0.044 (0.072)	0.032 (0.044)	0.095 (0.108)	0.188 (0.364)	0.299 (0.650)	0.0009 (0.001)	0.680 (2.22)
Median [Min, Max]	0.0487 [0, 12.8]	0.833 [0, 14.8]	0.628 [0, 1.64]	0 [0, 1.12]	0.006 [0, 0.209]	0.006 [0, 0.101]	0.088 [0, 0.298]	0.067 [0, 1.14]	0.079 [0, 3.32]	0.0009 [0, 0.002]	0.010 [0, 14.8]
						TEQ_PCDF					
Mean (SD)	4.63 (24.0)	3.31 (6.87)	0.363 (0.142)	0.0350 (0.119)	0.089 (0.094)	0.046 (0.074)	0.121 (0.124)	0.136 (0.151)	0.292 (0.474)	0.0009 (0.0001)	1.39 (11.3)
Median [Min, Max]	0.050 [0, 150]	0.791 [0, 29.3]	0.430 [0.200, 0.458]	0.0008 [0, 0.695]	0.059 [0, 0.224]	0.014 [0, 0.261]	0.068 [0.037, 0.385]	0.094 [0, 0.505]	0.066 [0.0002, 1.98]	0.00008 [0, 0.0002]	0.028 [0, 150]
						TEQ_PCB					
Mean (SD)	0.488 (1.56)	0.469 (1.35)	0 (0)	0.306 (1.27)	0.506 (0.725)	0.227 (0.367)	0.347 (0.364)	0.329 (0.583)	0.705 (2.27)	0.0015 (0.0019)	0.421 (1.40)
Median [Min, Max]	0.00166 [0, 8.32]	0.0339 [0, 5.91]	0 [0, 0]	0.00395 [0, 7.85]	0.246 [0, 2.50]	0.0930 [0, 1.28]	0.220 [0.127, 1.16]	0.094 [0.003, 1.86]	0.0573 [0, 11.8]	0.002 [0.0001, 0.003]	0.032 [0, 11.8]

shellfish on fresh weight basis (f.w.), lipid for foods of animal origin and the oils (designated as 'plant'), and dry matter (d.m.) for sediment and soil.

2.3. Quality control and quality assurance

Quality control procedures were applied for ensuring the quality of the results. These procedures included control of isomer-specific GC separation, instrument sensitivity, validity of the instrumental calibration and isotopic mass ratio, and recovery of the target compounds.

Analysis of certified reference materials was also part of the quality control program. Reference materials used were, e.g., the certified reference materials BCR-677 (sewage sludge) and BCR-615 (fly ash) from the Institute for Reference Materials and Measurements (IRMM) of the European Commission-Joint Research (Geel, Belgium). In addition, in-house reference materials (*e.g.*, chicken feed, spiked with PCDD/PCDF and dl-PCB as well as selected matrices from international inter-laboratory studies (*e.g.*, soybean meal, feed oil, and sediment) were used as quality control materials (QCM) for routine internal laboratory control and performance evaluation.

In addition, procedural blanks, covering extraction, purification, and instrumental determination, were periodically analyzed to evaluate the potential contribution of interfering compounds or potential sample carryover.

Recoveries of the target compounds were always in the range of 60%–120% as indicated in the corresponding EU Regulation (European Union, 2017).

The limits of quantification depended on the congener and the matrix. For food samples, the limit for the reported TEQ was at least 1/10 of the legal limit value (European Union, 2011).

2.4. Data handling and assessment

All data were maintained in Microsoft Office 365 Excel®. Statistical evaluations and visualization were made using R packages (versions 4.0.3 and 4.0.5) with R-Studio (version 2022.07.1 + 554).

Following normality test using histogram and density tests, the samples did not show normal distribution. Non-parametric testing was performed using the Kruskal-Wallis H test to determine if there are statistically significant differences between the independent variables and dependent variables. Post-hoc analysis was performed using the pairwise Wilcoxon test. Adjustment of the p-value was made using the Benjamini-Hochberg method (results, see Table S5). Significance level was set to $p = 0.05$. Correlation between variables was determined using Spearman method and hierarchical clustering in the heatmap using Euclidean distances (Ward method).

For statistical operations, concentrations below the limit of quantification (LOQ) were set to zero. All countries are referred to by using their ISO alpha-3 code (ISO, 2020).

3. Results

3.1. Samples, occurrence, and frequency of detection

In total, 185 samples from 27 countries were received and analyzed for dl-POPs. In terms of country participation, it is noted that 15 countries were either not interested in having national samples analyzed or did not manage to provide these samples. The distribution of the samples according to their matrix provided by each country is shown in the supplementary information in Table S1. The eight GRULAC countries provided 37 samples for analysis, four Asian and eleven African countries provided 58 and 65 samples, and four Pacific Islands countries (PAC) only 25 samples. Following the recommendation under the project's objective (UNEP, 2017), fish was the most abundant matrix with 54 samples; all countries but Ethiopia, Brazil, and Jamaica provided fish.

The graphical visualization in Fig. 1 shows for the three TEQs the number of samples with concentrations above the LOQ. There were 21 samples that did not have a single congener (of 28 congeners that contribute to the TEQ) quantified. These samples are shown in Table S2; they constitute 11% of all samples. The summary of the samples, which had quantifiable concentrations are shown in Table S3 and the respective percentages in Table S4. Across the 185 national samples, for 57% of all samples, all three TEQ were determined ($N = 105$). The egg samples had the highest detection frequency (93% or 25 of 27 samples with all three TEQs quantified), followed by milk (86%; but only 7 samples in total). In the 54 (shell)fish samples, 28% had concentrations below the LOQ (corresponding to 15 samples) and 17% of the samples had only one TEQ with measurable concentrations.

The number of results for the three TEQs in either abiotic or biota samples is depicted in Fig. S1. Roughly, it can be seen that the abiotic samples have higher shares – expressed as TEQ - of the combined PCDDD/PCDF than dl-PCB than the biota samples. The latter have high shares of dl-PCB especially in (shell)fish. Composition or pattern of the three TEQ for each sample is shown in the supplementary information in Fig. S2. In most samples, all three TEQ were quantified; exception are the ash samples, which did not have quantifiable dl-PCB. The figure also includes the samples that did not have any dl-POPs above the LOQs.

3.2. Scales of PCDD, PCDF, and PCB

The descriptive statistics for the three TEQ at lower-bound values in the 185 samples are shown in Table 1. The values refer to all samples and therefore, include the 21 samples that did not have any congener (or TEQ) quantified. According to the matrix, all median values were below 1 pg TEQ/g; often below 0.1 pg TEQ/g. Mean values above 1 pg TEQ/g were found for TEQ_PCDD and TEQ_PCDF only in soil and sediment samples. Therefore, it can be concluded that overall, the contamination in the samples from developing countries were low.

The patterns of the individual samples for the three TEQ are displayed with absolute scaling at the left and the contribution of the individual TEQ to the sum of the three TEQs (later referred to as TEQ_tot) at the right (Fig. 2).

Fig. 3 aggregates the individual results as TEQs as box whisker plots. The graphic above groups the samples into abiotic and biota samples (by type) and assigns them to the four project regions. It can be seen that the abiotic samples were dominated by the PCDD, and that dl-PCB do not play a role. Further, it should be noted that the scale for abiotic samples in the Pacific Islands region is much larger than for the other three regions. In contrast, the biota samples have a much smaller range and are dominated by the dl-PCB (lower row of the upper graph). Further details are displayed in the lower graph of Fig. 3 where the different matrices are shown for the three TEQ. The overall picture appeared complex and is further assessed with multivariate statistical methods.

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.

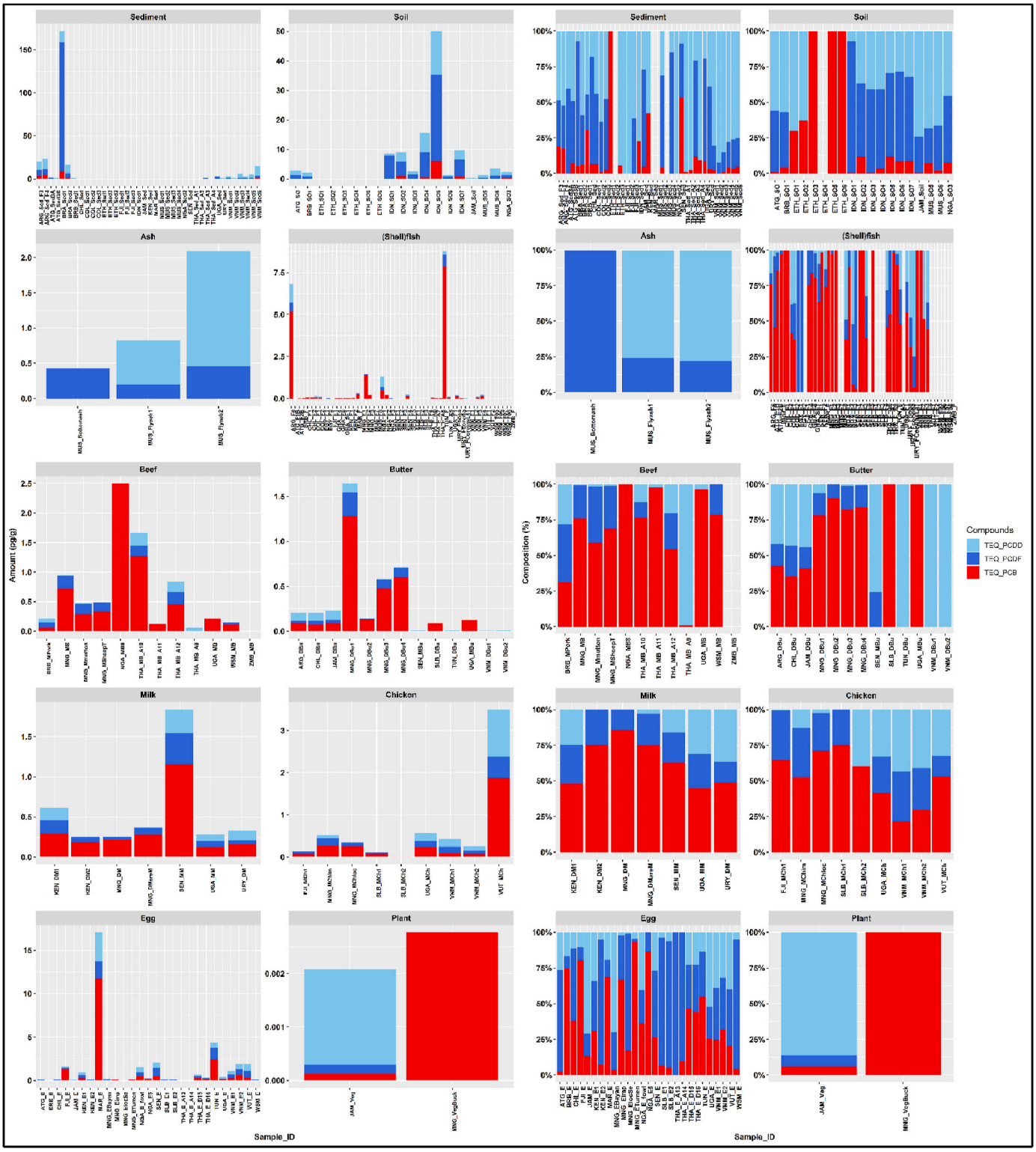
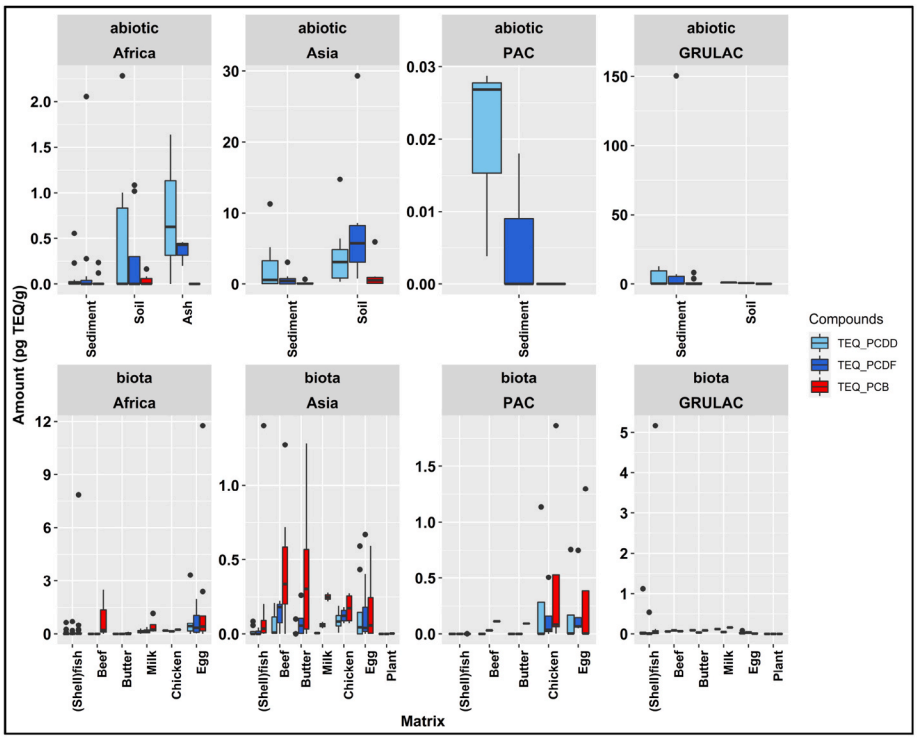


Fig. 2. Stacked bar plots for the three TEQs and each Sample_ID (N = 185) by scale (left) and for the pattern (right, stacked bars at 100%). Samples are grouped according to matrices starting with abiotic samples. Concentration in pg TEQ/g.



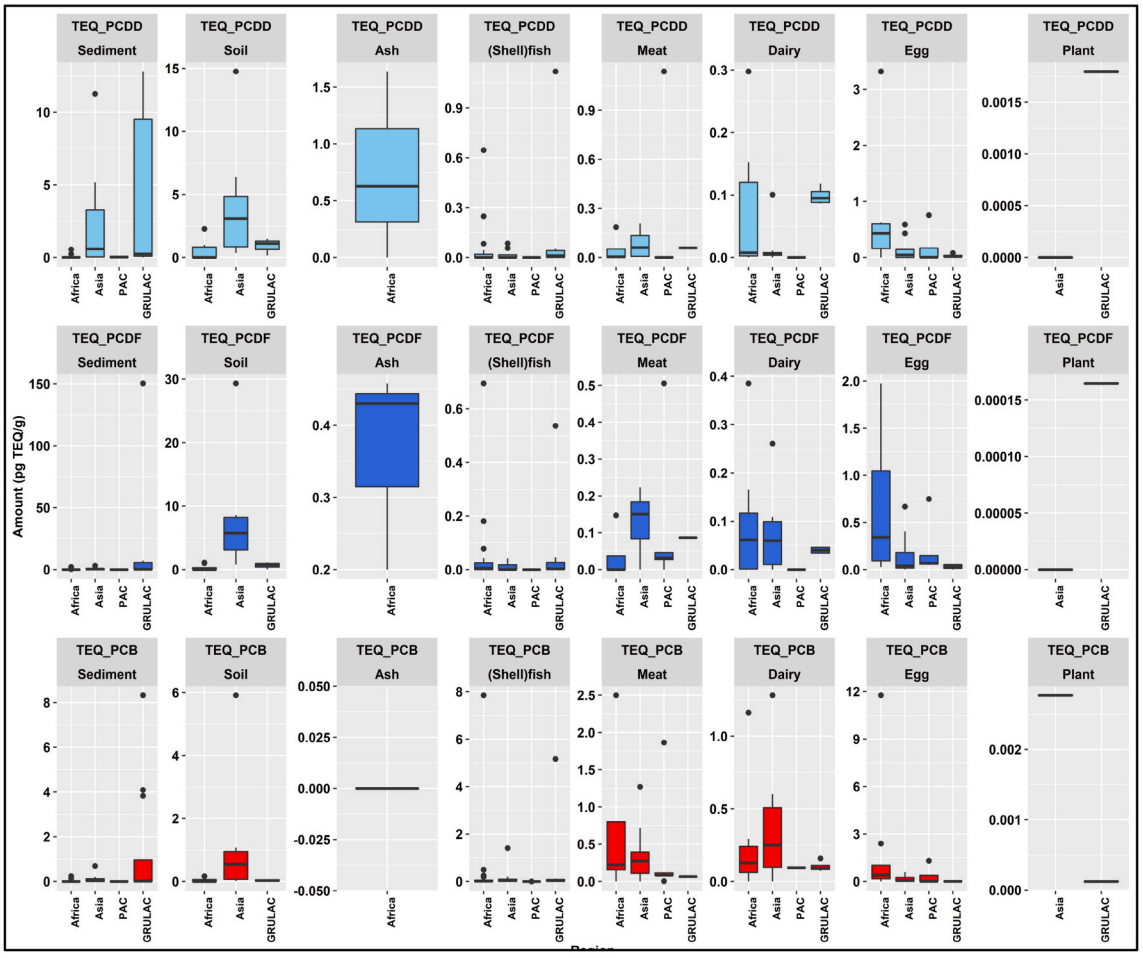


Fig. 3. Scaled box plots for concentrations of three TEQ in the four project regions with facet category, n = 185. Concentrations in pg TEQ/g.

3.3. Multivariate analysis

Principal component analysis (PCA) of the three TEQs explains 86% of the samples (Fig. 4). The first dimension (Dim1) explains 69% of the scale of the samples and the three TEQ contribute almost equally y to Dim1. Dim2 explains 17% of the variation and is characterized by the TEQ_PCB with positive numbers and TEQ_PCDF with negative numbers on the y-axis. The top 30 contributors of the individuals in the PCA are shown in Fig. S3.

There are two extreme samples: The sediment from Brazil (BRA_Sed1, Fig. S3), shown with red color in the regional graph and maroon color in the category and matrix graphs (Fig. 4). The sample had extremely high PCDF values. The second sample is an egg from Morocco (MAR_E) with high TEQ_PCB (see Fig. 4, black dot for Africa and plum colored for egg). Whereas the Morocco egg sample does not change the form of the ellipse for none of the four meta data (region, type, category, matrix), the Brazil sediment sample is unique as to region (other GRULAC samples are located in the 1st quartile) as well as to type and matrix (other sediment samples are located in 1st quartile) whereas the BRA-Sed1 directs the ellipses into the 4th quartile.

Non-parametric testing (Table S5) confirmed the above assumptions since significant differences were found between regions but not for Asia-GRULAC as can be seen that the small ellipse from the Asian samples is wrapped by the GRULAC ellipse. The (shell)fish samples are somewhat unique since they are significantly different from all other terrestrial animal foods (meat, eggs, dairy); no ellipse could be calculated for either category or matrix.

Fig. 5 shows the heatmap for the pattern of 141 samples, which had at least one TEQ above the LOQ. The heatmap shows two distinct dendrograms of almost equal size whereby the lower part is dominated by high shares of dl-PCB and low shares of PCDF and PCDF (green color at left upper part of the lower heatmap) and high shares of PCDF (green color at center bottom of the heatmap). The upper part of the dendrogram is characterized by high shares of PCDD (green color in heatmap at right) and low shares of dl-PCB (mainly) and some with low shares of PCDF. The samples dominated by the PCDD are mainly sediment (maroon color) and ash (black color).

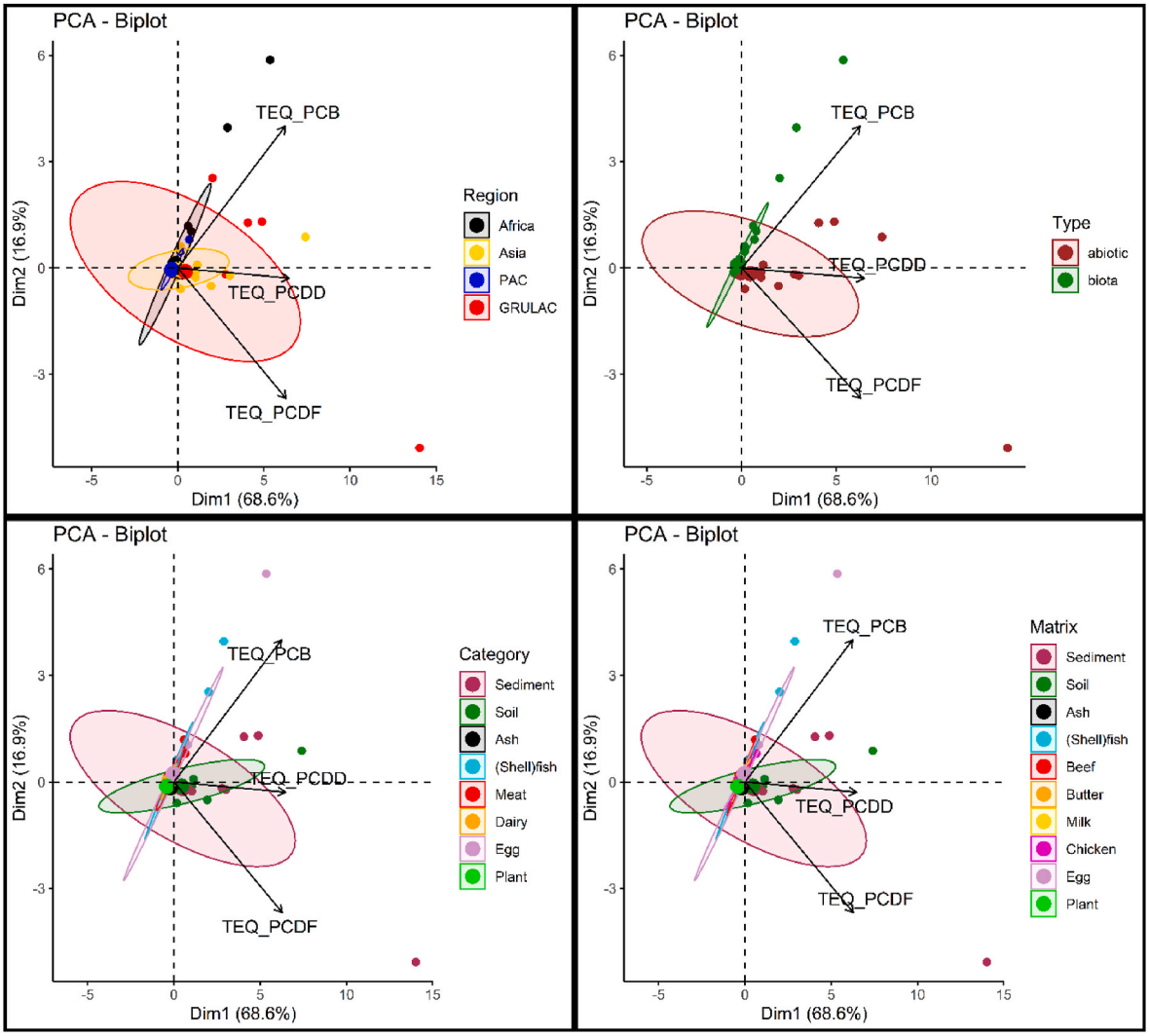


Fig. 4. PCA for three TEQ with ellipses around regions (top left), type (top right), category (bottom left) and matrix (bottom right).

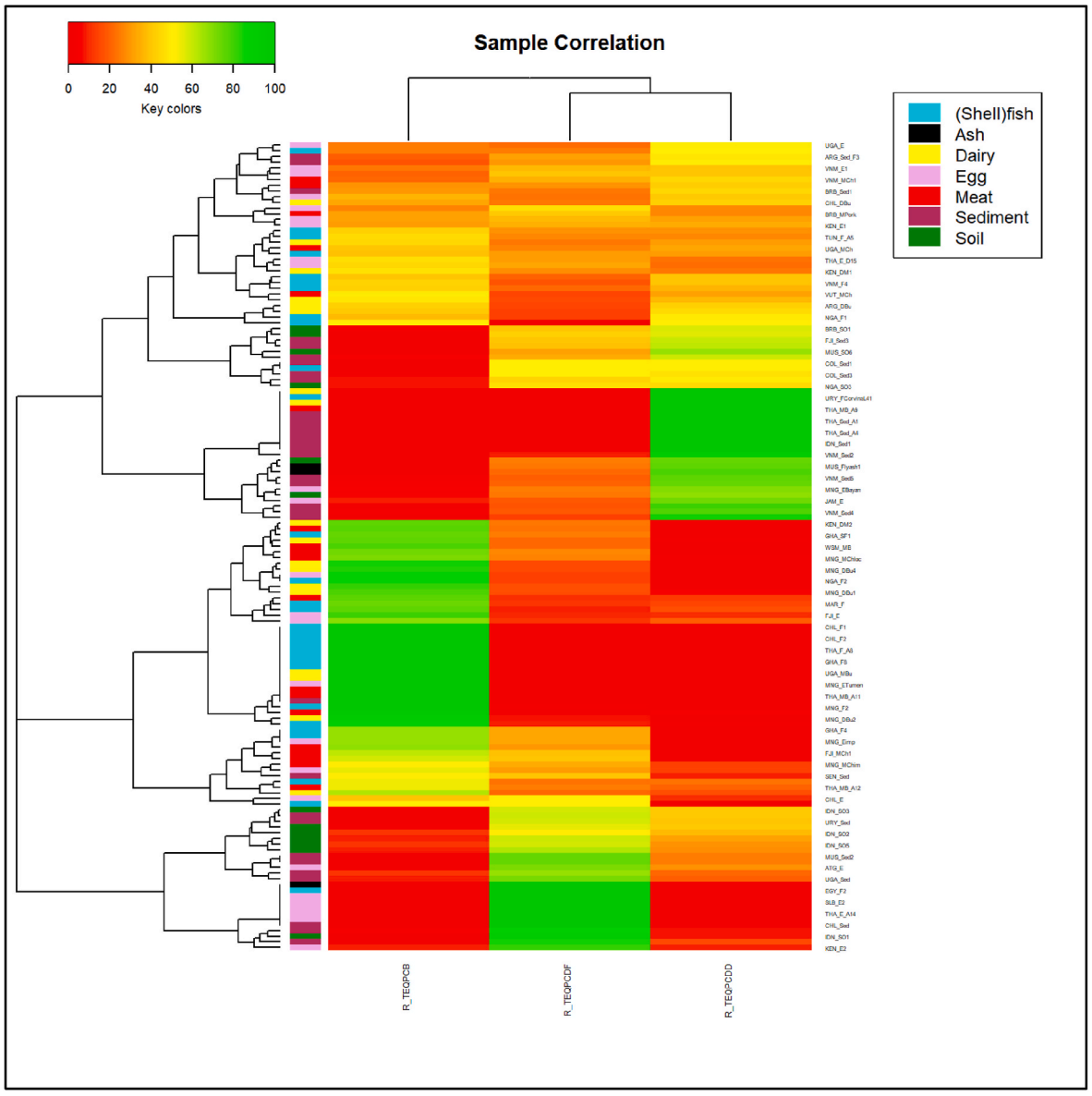


Fig. 5. Heatmap displaying ratios of the three TEQs; N = 141 samples with at least one TEQ > LOQ. The color codes at the dendrogram refer to the categories. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

4. Discussion

Our results indicate relatively low contamination with PCDD, PCDF or dl-PCB in developing countries. For biota, most concentrations were below 1 pg TEQ/g whereby the vegetable oils or plant samples had most congeners below the LOQ. Overall, 21 samples did not have quantified congeners; the lowest TEQs calculated were in the range of 0.001 pg TEQ/g (Table S2).

Our study did not look into transfers between media, *e.g.*, soil → egg or sediment → fish, and colocation of sampling sites was not attempted. Nevertheless, some samples with higher values may be explained by the sampling site. An example would be the set of samples from Argentina targeting potential hotspots, ARG_Sed_F3, ARG_Sed_F4, and ARG_F6, which were collected in the port area (see Fig. S3).

Our sample set of 185 samples had 164 samples with at least one quantified TEQ. No common pattern could be identified, which would imply a regional impact (Fig. S4). On the other hand, it could be seen that the category/matrix had an impact on the TEQ scale and distribution; the descriptive statistics are contained in the supplementary information as Table S 6. Abiotic samples, such as sediment and soil but also ashes from combustion processes, were clearly dominated by PCDD and PCDF, which contributed together with about 80% to the total TEQ (median values). In these samples, dl-PCB played a minor role (Fig. S4, lower row). In beef and (shell)fish, dl-PCB dominated with median contributions of 76% as in most other biota samples. Interestingly, the dairy samples, milk and butter, had similar pattern (as contribution to the total TEQ) whereas the two poultry, chicken meat and chicken egg, exhibited different pattern. The egg samples had the lowest contribution from the dl-PCB (27%) but higher percentages from PCDF (35%) and PCDD (16%) together (median values). It shall be noted that the median values do not add up to 100%.

The sediment and soil samples cannot be well characterized since it is not known if these were for agricultural, forestry or other uses or were sampled with the objective to identify potential hotpots. The concentrations of the soil samples in general were low; however, for those, *e.g.*, exceeding 5 ng TEQ/kg dry matter restrictions as to agricultural uses may apply; if the German regulation would be taken as an orientation (BLAG DEU, 1993). Accordingly, no risk would be identified for the

transfer soil→human, which had a value of 100 ng TEQ/kg soil for the most sensitive use. All values in our dataset were lower.

For comparison with EU food regulation, the amounts presented here have to be converted to upper-bound values; *i.e.*, including the full TEQ into the calculation of the TEQs the maximum values as established for PCDD/PCDF and the total TEQ, which is the sum of PCDD, PCDF, and PCB at upper-bound (European Union, 2011) would be exceeded for the **total TEQ** by one beef sample from Nigeria with a value of 4.38 pg TEQ/g fat (NGA_MB8), one egg sample from Morocco with a value of 17.05 pg TEQ/g fat (MAR_E), and two fish samples, one from Argentina with 6.8 pg TEQ/g f. w. (ARG_F6) and one from Tunisia with 8.8 pg TEQ/g f. w. (TUN_F), and one chicken meat from Vanuatu with 3.69 pg TEQ/g fat (VUT_MCh). The **TEQ_DF** only by the one egg sample from Morocco (see above) with 5.3 pg TEQ/g fat. None of the other samples exceeded the TEQ_DF. One chicken from Vanuatu had 1.71 pg TEQ/g fat and thus, was just below the maximum limit value of 1.75 pg TEQ/g fat.

5. Conclusion

It is an extremely difficult task to (a) generate and (b) interpret the data sets: Although many samples had been collected and analyzed (N = 185), there were only few things in common when breaking down to either geographic location (region or country) or type of sample (abiotic or biota, aquatic or terrestrial) or matrices and their categories. Common to all samples was a high level of quality in sample selection (especially exclusion of hotspots) and with regards to chemical analysis and documentation. On such basis, the quantitative results could be presented with confidence as to scale of contamination with PCDD, PCDF, and dl-PCB. Different levels of information could be assessed given by using metadata and applying refined evaluation techniques, such as multivariate statistical techniques as shown in the principal component analysis (PCA) and in the heatmap.

The presented data are environmental monitoring data and do not replace release/emission inventories and were not directed towards identification of single sources nor specific source regions. A recent report by the United Nations Environment Programme (UNEP) has shown that harmonized national release inventories of PCDD/PCDF are still scarce and that almost half of the Parties to the Stockholm Convention has never submitted a dioxin inventory (UNEP, 2022). The environmental monitoring data generated under the global monitoring plan (GMP) of the Convention are an alternative approach for countries to be aware of the scale of dl-POPs present in their country. For individual countries such monitoring data should be used on a comparative and relative scale. For the core matrices, air (Abad et al., 2022; Fiedler et al., 2022) and human milk, the most recent data have been published and evaluated; here the so-called "other matrices" have been addressed.

The results presented here were the first data for dl-POPs generated in some of the countries and therefore, although possibly only a snapshot, are a valuable starting point for further targeted actions towards better understanding the order of magnitude for the presence of PCDD, PCDF, and dl-PCB. On a comparative basis the presented data are necessary and suitable to highlight the worldwide situation regarding baseline levels of PCDD/PCDF and dl-PCB. It must be concluded that – at generally very low worldwide levels – there is no homogeneous background existing and occasionally quite high concentrations can be found even today, sometimes at regions where such high values have not been expected. This inhomogeneity points to the need of future monitoring activities to close gaps, which have been revealed in this study. Maybe for countries or for certain foods or environmental samples. In a second step, such monitoring may also be targeted towards identification of hotspots of formation or deposition of the PCDD, PCDF and dl-PCB. In order to be successful, sampling approaches must be harmonized, and good quality of the analytical data is mandatory to make the data comparable. Given the low concentrations encountered nowadays, high selectivity and sensitivity of the measurement instruments is required.

From the present research, two important study directions can be derived: First, abiotic matrices have larger ranges of measured values than biota samples; biota of animal origin are the primary matrix of dl-POPs contamination. Nevertheless, often, values level off and the contamination is low. These findings are independently of the geographic location. Second, there is a prevalence of matrix types - and not regions or geography - as the main driving factor for the scale and pattern (TEQ distribution) of dl-POPs. Therefore, it is recommended to differentiate the dl-POPs contamination into the three listed POPs, namely, PCDD, PCDF, and dl-PCB. From such differentiation, the dominance of dl-PCB especially in (shell)fish and beef can be seen. For eggs, pathways of exposure other than feed, may have an impact on the scale and the TEQ distribution. For eggs, not for chicken meat, an impact from soil can be derived.

Credit author statement

Heidelore Fiedler: Funding acquisition Örebro University, Investigation, Data curation, Visualization, Writing – original draft, review and editing, Esteban Abad: Funding acquisition CSIC, supervision chemical analysis, Validation, Writing – review and editing, Manuela Ábalos, Jordi Parera, Nina Lohmann, Frank Neugebauer, Horst Rottler, Michael Horstmann: Chemical analysis, data reporting, 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.

Data availability

Data will be made available on request.

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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.2023.138386.

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