ASSESSMENT OF PATTERNS OF TOXIC EQUIVALENTS IN NATIONAL SAMPLES FROM MONITORING IN DEVELOPING COUNTRIES

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Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs) ((1, 2) has adopted a global monitoring plan (GMP) of POPs to provide comparable monitoring information on the presence of POPs listed in Annexes A, B or C of the Convention and to follow changes over time and assess the effectiveness of the measures taken under the Convention (3). The United Nations Environment Programme (UNEP) is assisting developing countries with capacity building and sampling in developing countries and analysis in expert laboratories to contribute with national data. Whereas the global monitoring plan places an emphasis on the core matrices such as ambient air, water (for perfluoroalkane substances), and human milk or human blood, many countries have an interest to know the POPs concentrations in samples such as soil or sediments, in foods or residues. Within the regional projects coordinated by the United Nations Environment Programme (UNEP), so-called 'national samples' were collected and analyzed for POPs. Here, the results from three regions, namely Africa, Asia, and the Pacific Islands countries, hereafter abbreviated as PAC) were assessed as to the pattern of dioxin-like POPs (dl-POPs) expressed as toxic equivalents (TEQ) to investigate if the TEQ-pattern were different for the various matrices or regions.

Materials and methods

Samples of interest to the countries were collected at national level following sampling and sample preparation criteria as established in the guidelines for national samples (4). Samples were shipped to Örebro University and all chemical analyses were performed by accredited dioxin laboratories using capillary gas chromatographs coupled to high resolution sector-field mass spectrometers.

In total, 147 samples were analyzed for dl-POPs and results expressed as toxic equivalents (TEQ) using the World Health Organization's toxicity equivalency factors (TEFs) as established in 2005 (5). TEQs values were calculated as lower-bound, i.e., values below the limit of quantification (LOQ) were set to be equal to 0. The following partial TEQs were determined as shown at left and the contributions of each partial TEQ to the total TEQ was determined as shown at right:

Congeners contained in partial TEQs	Contribution to total TEQ
(a) TEQ_PCDD: includes 7 PCDD congeners (b) TEQ_PCDF: includes 10 PCDD congeners (c) TEQ_noPCB: includes 4 non-ortho PCB (d) TEQ_moPCB: includes 8 mono-ortho PCB (e) TEQ_DF: sum of (a)+(b) (f) TEQ_PCB: sum of (c)+(d)	2 TEQ: TEQ_DF + TEQ_PCB 4 TEQ: TEQ_PCDD + TEQ_PCDF + TEQ_noPCB + TEQ_moPCB

Samples included soil, sediment, ash, fish, meat, dairy, and vegetables. From the 147 samples analyzed, 39 had three partial TEQs below the limit of quantification. These were excluded from the assessment.

For statistical assessment, samples were grouped into 'matrices' by differentiating between abiotic and biotic samples and aquatic or terrestrial samples. Further differentiation as to meat or eggs, different gazing animals or poultry was made as well.

All data were maintained in Microsoft Office 365 Excel®; statistical evaluations were made using R packages 4.0.3 with R-Studio Version 1.3.1056. Significance level was set to 0.05.

Results and discussion

A total of 108 samples had at a minimum two groups of TEQ values above zero and were used for pattern analysis. Of these, six did not have a TEQ for PCDD/PCDF and six did not have a value for dl-PCB. In more detail, 18 samples had no TEQ_PCDD, 20 no TEQ_PCDF, 14 no TEQ_noPCB and 17 no TEQ_moTEQ. Graphical sketches displaying the percentages or contributions (as ratio) to the total TEQ from either two TEQs (DF and PCB) or four TEQs (PCDD, PCDF, noPCB and moPCB) are shown and discussed in the following figures.

The ratios of the six TEQs for each matrix as aquatic and terrestrial abiotic samples (corresponding to sediment and soil), aquatic, terrestrial or soil-impacted biota samples (fish and shellfish; meat or dairy from grazing animals, and poultry meat or eggs) is shown in Figure 1. Quite distinct pattern can be seen such as that the TEQ from PCDD/PCDF (TEQ_DF) dominated largely over the TEQ from dl-PCB (TEQ_PCB) in both abiotic samples, aquatic and terrestrial. For the biota_soil samples, the dominance of the TEQ_DF is still seen for the eggs but the poultry meat (mainly chicken) the contribution from PCDD/PCDF and dl-PCB to the total TEQ is almost equal. On the other hand, the TEQ_PCB is higher than the TEQ_DF in aquatic biota (fish, shellfish) and terrestrial biota (dairy, and beef, lamb or mutton meat). Overall, the similarity of the pattern between meat and dairy products in the biota_terr is obvious and more expressed than between chicken/duck eggs and meat in biota_soil. Despite the optical differentiation, none of the pattern showed statistical differences; p-values always were around 0.5 or greater.

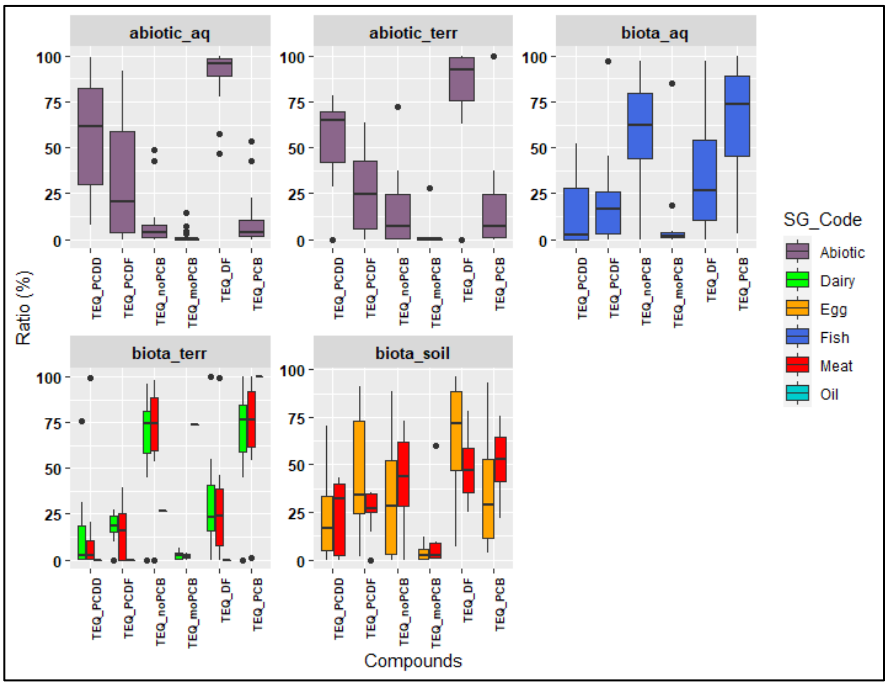

Figure 1**.** Box plots for six partial TEQs as contribution to the total TEQ grouped and scaled for matrices. The whiskers represent minimum and maximum concentrations without outliers. The lower border of the box represents the first quartile (25%), the line inside the box the median and the upper 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

The graphical sketch as box whisker plots in the three project regions is shown in Figure 2 with samples aggregated according to matrix. Whereas differences between the matrices can be seen, there are no obvious differences between the regions. However, it is noted that from the Pacific Islands, there were no abiotic_terr and no biota_aq from the Pacific Islands for comparison.

The principal component analysis in Figure 3 explains 44% of the samples along the x-axis (Dim1) and 33.3% of the pattern along the y-axis (Dim2); thus, 77% of the total. Although it can be seen that certain clusters are formed as indicated by the different colors assigned to the matrices, in summary the ellipses overlap largely. Some differences, but not statistically significant as shown in xx, the abiotic aquatic samples (abiotic_aq) are dominated by the PCDD and PCDF as well as the abiotic terrestrial samples (abiotic_terr). Especially the TEQs for abiotic_aq have almost no contribution from the PCB. On the other hand, the TEQs for the biotic terrestrial samples (biota_terr) have stronger impacts from TEQ_noPCB.

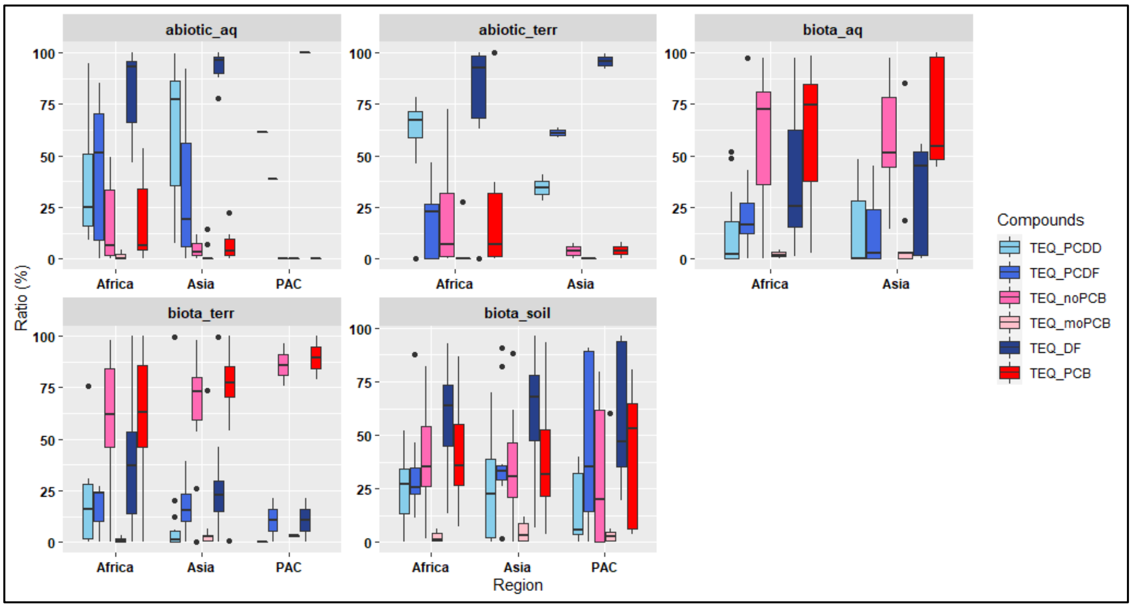

Figure 2. Box plots for six partial TEQs aggregated for regions and scaled for matrix (n=108).

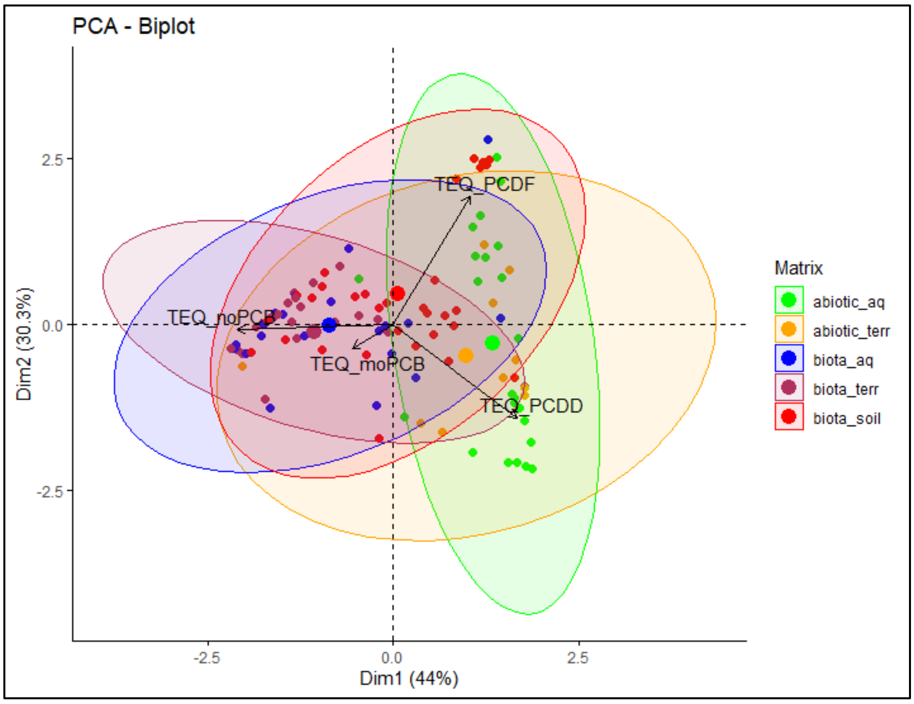

Figure 3. PCA for TEQ pattern using four partial TEQs (for PCDD, PCDF, noPCB and moPCB) of 108 national samples with ellipses around the matrices

Figure 4 shows the correlation of the partial TEQs to the respective totals. The TEQ_PCB completely negatively correlated to the TEQ_DF (r=-1). For the four partial TEQs, the TEQ_no_PCB is very strongly correlated to the total TEQ_PCB (r=0.92), which means that the TEQ from the non-ortho PCB dominated the TEQ for all dl-PCB and the mono-ortho PCB did not play any role (r=0.31). In addition, the correlation between TEQ_noPCB and TEQ_moPCB is weak (r=0.31). For the PCDD/PCDF and across all samples, there is no overall correlation between the TEQ_PCDD and TEQ_PCDF (r=-0.03) but a stronger correlation of the TEQ_PCDD to the TEQ_DF (r=0.75) than for the TEQ_PCDF to the TEQ_DF (r=0.48). As expected, there are weaker negative correlations between the PCDF and PCB (r=-0.48; and noPCB, r=-0.43) than for the PCDD with the PCB (r=-75; and noPCB, r=-65).

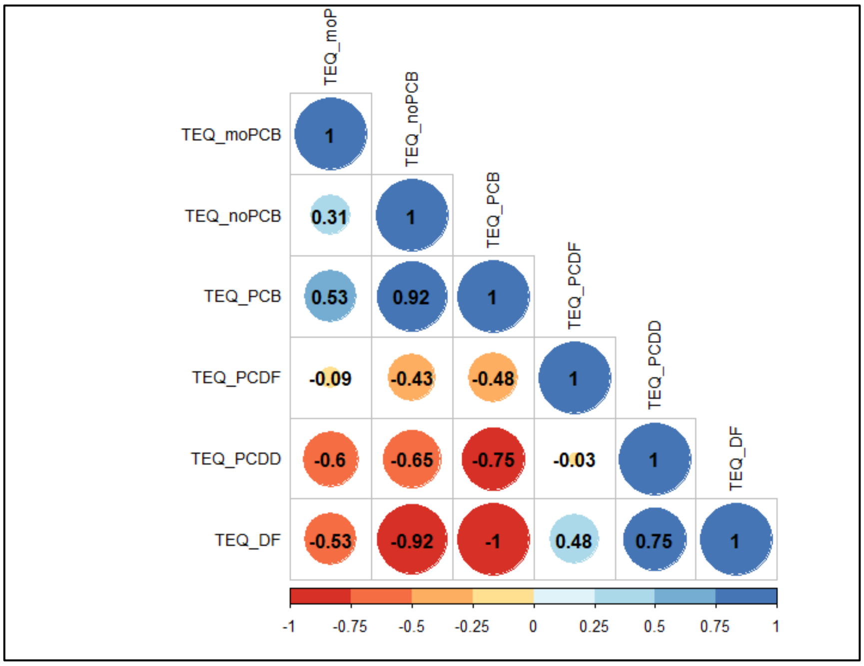

Figure 4. Correlation plot for the share of the six TEQs to their respective totals

To conclude:

- The contribution of the partial toxic equivalents as TEQs from PCDD, PCDF, non-ortho substituted OCB or mono—ortho substituted PCB or from PCDD/PCDF and dl-PCB to the total TEQ showed some distinct pattern within 108 national samples of different origin or types.
- A regional differentiation as to the patterns between samples from either Africa, continental Asia or the Pacific Islands countries could not be seen.
- Abiotic samples such as soil and sediment tend to have higher contributions from PCDD and PCDF than from dl-PCB. The potential influence from soil contamination is indicated in the egg samples.
- Biota samples often showed a dominance of the TEQs from PCB (mainly non-ortho substituted PCB) over the contribution from PCDD/PCDF.
- Quite strong either positive or negative correlations were found for the partial TEQs. The TEQs from mono-ortho PCB did not play any role.

Acknowledgements
This work was developed under agreement with the United Nations Environment Programme (UNEP), Nairobi, Kenya (UNEP grant to ¨Orebro University ‘GEF GMP2 GF4030’). The funds to UNEP were provided by the Global Environment Facility (GEF), Washington, D.C., USA, through four regional projects ’(Continuing) Support for the implementation of the Global Monitoring Plan under the Stockholm Convention in the African/Asian/Pacific Islands Region’. Further thanks are expressed to the national project teams in the project countries for collection and provision of samples for analysis.

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