DIOXINS AND DIOXIN-LIKE PCBs IN SAMPLES FROM AFRICAN COUNTRIES PARTICIPATING IN THE UNITED NATIONS ENVIRONMENTAL PROGRAMME

Hagberg, J[1], Li, YM[1], Leslie, H[2], Fiedler, H[3], van Bavel, B[1].

[1]Man-Technology-Environment (MTM) Research Centre, Örebro University, SE-701 82 Örebro, Sweden.
[2]Institute of Environmental Studies (IVM), VU University, Amsterdam, De Boelelaan 1087 1081 HV Amsterdam, The Netherlands.
[3]UNEP Chemicals Branch, chemin de Anémones 11-13, CH-1219 Châtelaine (GE), Switzerland.

Introduction

National samples were collected in collaboration with twelve African countries and from one Caribbean country for analysis of dioxins and dioxin-like PCBs (dl-PCBs). Participating countries were Ghana, Togo, Egypt, Uganda, Kenya, Mauritius, Nigeria, Mali, Zambia, DR Congo, Ethiopia, Senegal and Barbados. Up to date 36 samples of various matrices has been analysed for polychlorinated dibenzo-*p* dioxins and furans (PCDD/Fs) as well as dioxin-like polychlorinated biphenyls (dl-PCBs). The majority of the samples (27 samples) were either sediment or fish samples. Additionally, 3 soil samples and single samples of fish meal, maize grains, cornstarch, baby milk powder, sand and fly ash were analysed. Data for fish and sediment samples from the African countries are presented in this study.

There is only limited data available on levels of dioxins and dl- PCBs in environmental samples from Africa. The results from this study will tentatively give a brief survey of the contamination level of the eastern and western part of the African continent.

Materials and methods

Samples

Twelve fish and thirteen sediment samples from eleven African countries were analysed for PCDD/Fs and dl-PCBs, see table 1. Fish samples were stored in a freezer until extraction. Solid samples were stored at room temperature, shielded from UV light. Sample extracts were stored in amber glass bottles at - 20°C prior to analysis.

Table 1. Countries and samples included in this study.

Country	No. of fish samples	No. of sediment samples
Togo	1	1
Ethiopia	-	2
Kenya	1	1
Mauritius	1	2
DR Congo	1	2
Zambia	1	1
Nigeria	1	1
Senegal	-	1
Uganda	1	2
Ghana	3	-
Mali	2	-

Chemicals

Native and ^{13}C-labelled standards of PCDD/Fs and dl-PCBs were obtained from Wellington Laboratories Inc., Guelph, Canada. Organic solvents used were of pesticide grade and purchased from Fluka (methanol, *n*-hexane, dichloromethane, and toluene). Ethanol was purchased from Sharlau.

Sample preparation

Fish samples were ground with anhydrous sodium sulphate (in the ratio 1 to 5). Open column chromatography was applied for approximately 10 gram of fish tissue.

Extraction and clean up

Sediment samples were extracted by a 24 hours reflux in toluene using a Soxhlet extraction apparatus. Fish homogenates were extracted by a mixture of *n*-hexane: dichloromethane (1:1) using open column chromatography. Prior to extraction all samples were spiked with ^{13}C-labelled internal standards of dioxins and dl-PCBs. After extraction, sample clean-up was done on three open columns (multilayer silica, AlOx and active carbon). The multilayer silica columns contained KOH silica, neutral activated silica, 40% H_2SO_4 silica gel, 20% H_2SO_4 silica gel, neutral activated silica gel and Na_2SO_4 and was eluted with *n*-hexane. This column was followed by an AlOx column eluted with *n*-hexane/ dichloromethane. Additional clean up and fractionation was done on an active carbon column, containing Carbopack C dispersed on Celite 545, which was eluted with 10 ml of *n*-hexane for non-planar compounds and then 80 ml of toluene to extract the planar fraction containing PBDD/Fs. Addition of ^{13}C-labelled recovery standards was done prior to instrumental analysis. Toxic equivalents (TEQs) were calculated using World Health Organization toxic equivalency factors (TEFs) for PCDD/Fs [1].

Instrumental analysis

HRGC/HRMS analysis was performed on a Micromass Autospec Ultima operating at >10 000 resolution using EI ionization at 35 eV. All measurements were performed in the selective ion recording mode (SIR), monitoring the two most abundant ions of the molecular chlorine cluster. Quantification was performed using the internal standard method. PCDD/Fs and dioxin-like PCBs were analysed by injecting 1 µl of extract using splitless injection on a 30 m BPX 5 (0.25 mm id, 25 µm) column (SGE; Ringwood, Australia).

QA/QC

Recoveries of the labelled compounds ranged from 55 – 115% for PCDD/Fs and 50-130% for the dl- PCBs. As a reference material, a fish sample from the UNEP intercalibration study was used. With every batch of samples, an extraction blank was also prepared and analysed, as well as monitoring of instrumental blanks of toluene was performed routinely. Detection levels were calculated at a S/N ratio of 3, corrected for recovery of the internal standard. The criteria for positive peak identification were isotope ratio within ±15% of the theoretical value and retention time match within 10 seconds of the corresponding labelled compound.

Results and discussion

Levels of PCDD/Fs and PCBs

All fish samples showed overall low levels for both PCDD/Fs and dl-PCBs except for three fish samples from Ghana which showed a significantly higher contribution of dl-PCBs compared to the other African countries. The levels for PCDD/Fs ranged from 0.006 to 5.3 pg WHO_{1998}-TEQ g^{-1} lipids in all samples while the PCB levels in fish samples from all countries except Ghana ranged from 0.08 to 3.1 pg WHO_{1998}-TEQ g^{-1} lipids. The three fish samples from Ghana had levels ranging between 19.5 and 34.9 pg WHO_{1998}-TEQ g^{-1} lipids. Based on fresh weight concentrations all fish samples were well below the EU maximum limit for PCDD/Fs (i.e. 4 pg WHO_{1998}-TEQ g^{-1} w. w.) and all samples were below the EU maximum limit for PCDD/Fs and dl-PCBs (i.e. 8 pg WHO_{1998}-TEQ g^{-1} w. w.) [2].

Levels of PCDD/Fs and PCBs were also low in the sediment samples from all countries except from Togo. Levels were ranging between 0.02 to 2.5 and 0.006 to 0.64 pg WHO_{1998}-TEQ g^{-1} for PCDD/Fs and PCBs, respectively. These levels are comparable to low background concentrations found in Europe [3]. However, the PCB concentration in Togo sample was significantly higher (i.e. 77 pg WHO_{1998}-TEQ g^{-1}) but the fish sample from the same site did not show any elevated PCB concentrations.

Congener profiles

Overall the PCB congener pattern was similar in samples from the same country except for the Togo samples (see Figure 1). All fish samples except one from Ghana showed very similar PCB patterns dominated by the following congeners: PCB-118 > PCB-105 > PCB-156 > PCB-167 > PCB-123. The same pattern was found in the sediment samples but with some variations. This pattern was also found in samples from South Africa as well as in sediment samples from European countries and reflects the use of different PCB formulation in industrial applications [3-4]. One of the fish sample from Ghana showed however a different PCB profile (PCB-118 > PCB-105 > PCB-123 > PCB-114 > PCB-156) and possibly it was taken from another site than the other two samples. Interestingly the Togo sediment sample showed a totally different PCB pattern, where the non-*ortho* PCBs (PCB-77 and PCB-126) were the dominating congeners. According to Chi et al. (2007), non-*ortho* PCBs do not solely originate from commercial PCB mixtures; they are also characteristic from industrial waste incineration and coal combustion [5].

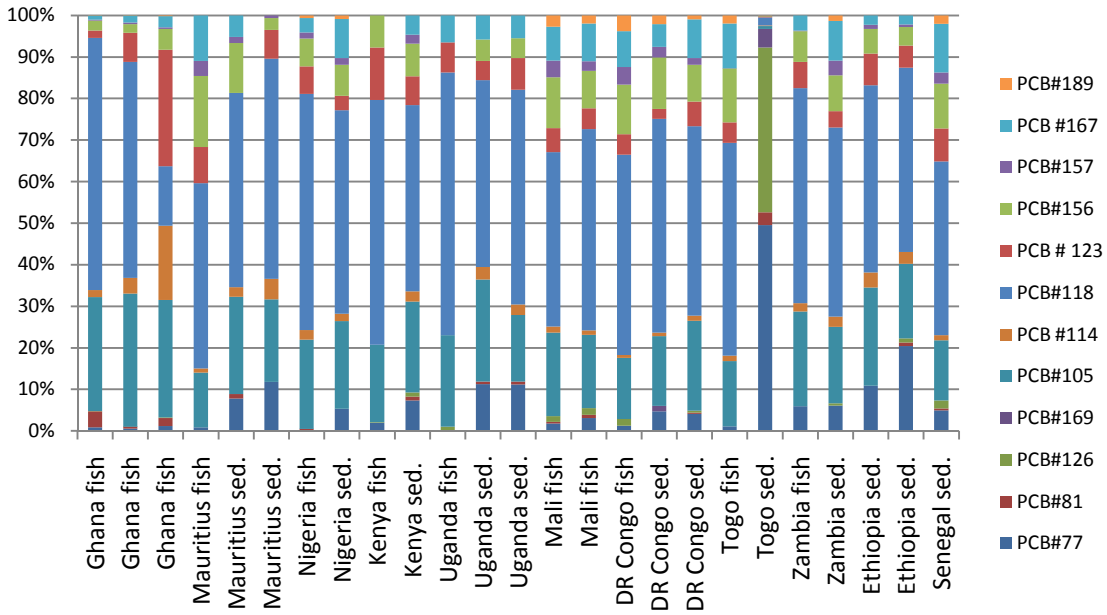

Figure 1. PCB congener profiles for both fish and sediment samples.

The PCDD/Fs pattern showed more differences between different sample types from the same country as well as between different countries, see figure 2. The difference between fish and sediment samples from the same country can possibly be explained by the very low concentrations of PCDD/Fs in most of the fish samples (i.e. most of the PCDD/F congeners were below the detection limit). For most countries the PCDD/F pattern was similar when comparing the same sample type. All sediment samples were strongly dominated by foremost octachlorodibenzo-*p*-dioxin and 1, 2, 3, 4, 6,7, 8-heptachlorodibenzo-dioxin. Those were also the dominating congeners in the fish samples from Zambia, DR Congo and Uganda and are often, in a global perspective, encountered as some of the predominant congeners in different kind of samples (i.e. biological and environmental samples) [6]. The predominance of the OCDD and the HpCDD can possibly be resulting from a former use of pentachlorophenols (PCPs) [7]. The fish samples from Kenya and Mauritius contained extremely low levels and had only one or two furan congeners over the detection limit. The Nigerian fish sample had equal amount of dioxins and furans and had a different congener pattern than the sediment sample. Both samples were from the capital Abuja, the sediment sample from the centre of the city while the fish sample was from a satellite settlement. The difference in pattern could possibly be due to that these congeners are more accumulative and persistent in biological samples or that there are regional differences between the city centre and the outskirts of the city. The fish samples from Ghana and Mali were overrepresented by low chlorinated furans suggesting that incineration sources are more common close to the sampling points or in these countries. There were no sediment samples available to compare fish data against.

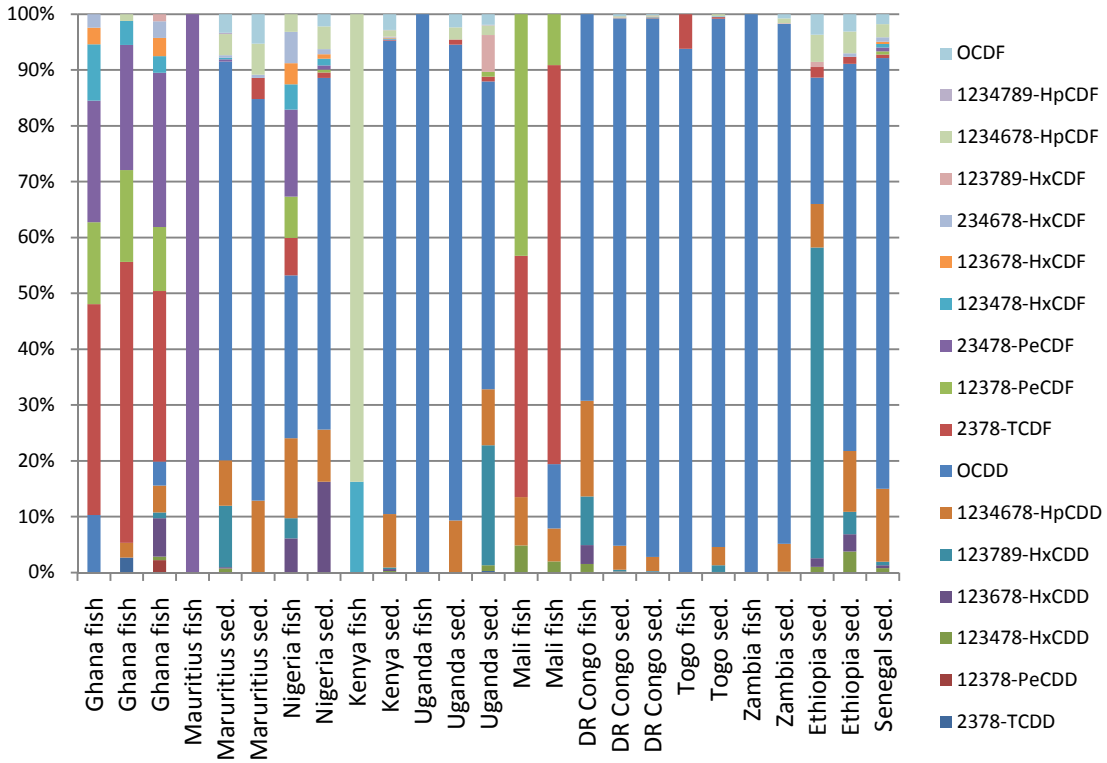

Figure 2. PCDD/F congener profiles for both fish and sediment samples.

Conclusions

Overall the PCDD/F concentrations in all samples from the African region were low. A few samples showed significantly higher levels of dl-PCBs but all fish samples contained still concentrations below the EU maximum limit for both PCDD/Fs and dl-PCBs and the levels found in the sediment samples were in the range that are considered background levels in European countries.

Acknowledgement

UNEP as the financing organization of the study, all participating countries and Wellington Laboratories are greatly acknowledged.

References

1. Van den Berg M, Birnbaum L, Bosveld ATC, Brunstrom B, Cook P, Feeley M, Giesy JP, Hanberg A, Hasegawa R, Kennedy SW, Kubiak T, Larsen JC, van Leeuwen FXR, Liem AKD, Nolt C, Peterson RE, Poellinger L, Safe S, Schrenk D, Tillitt D, Tysklind M, Younes M, Waern F, Zacharewski T. (1998); *Environ Health Persp*. 106(12): 775-792.
2. European Commission (2006). Commission Regulation (EC) No 1883/2006.
3. Nieuwoudt C, Quinn LP, Pieters R, Jordaan I, Visser M, Kylin H, Borgen AR, Giesy JP, Bouwman H. (2009); *Chemosphere* 76: 774-783.
4. Nunes M, Marchand P, Vernisseau A, Le Bizec B, Ramos F, Pardal MA. (2011); *Chemosphere* 83: 1345-1352.
5. Chi KH, Chang MB, Kao SJ. (2007); *Chemosphere* 68: 1733-1740.
6. Marin S, Villalba P, Diaz-Ferrero J, Font G, Yusà V. (2011); *Chemosphere* 82: 1253-1261.
7. Masunga S, Yao Y, Ogura I, Sakurai T, Nakanishi J. (2003); *Chemosphere* 53: 315-324.