FROM RELEASE INVENTORIES TO BODY BURDEN – SOME EXAMPLES FROM POPs MONITORING PROJECTS

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Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs)[1] entered into force on 17 May 2004 and presently has 179 parties (status: June 2015). It aims to eliminate the production, use, and trade of POPs listed in either annex A, B or C, to protect human health and the environment. After more than ten years after entry-into-force, an abundance of data has been generated by countries and research groups; many of these are administered or made available by the secretariat of the Basel, Rotterdam and Stockholm Conventions. At the seventh meeting of the Conference of the Parties to the Stockholm Convention in May 2015, information has been presented, among others, on national reporting, national implementation plans, and progress in the implementation of the Stockholm Convention.
This paper presents information in relation to production or generation of POPs compiled in inventories at national or global level, concentrations in the environment using ambient air data and information on body burden using human milk data. The pathway source inventory-environmental concentration-body burden is evaluated for "typical classes of POPs".

Materials and methods

Information is being assessed from submission by Parties for the 1st, 2nd and 3rd national reports[2], initial and updated national implementation plans (NIPs)[3],
Information on the production, use, and disposal of DDT[4] and PCB[5] has been compiled by the Chemicals Branch of the United Nations Environment Programme and was made available on the WebPage of the Conference of the Parties.
Results generated for the second regional reports under the Global Monitoring Plan (GMP) in relation to article 16 of the Stockholm Convention (for reports, see [6]) are made available through the data warehouse, a visualization and data tool developed and hosted by the Stockholm Convention Regional Centre in the Czech Republic[7].

Results

Figure 1 shows a graphical sketch of the pre-dominant sources and pathway for certain groups of POPs. It should be noted that the "typical" POPs are lipophilic, undergo long-range transport mainly through atmospheric transport and are bioaccumlating in fatty tissues. They are either unintentionally generated or intentionally produced. The best studied unintentionally generated POPs are polychlorinated dibenzo-*para*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF). UNEP has developed a Toolkit for the quantification of PCDD/PCDF releases at the source where they are formed and released. Most of the PCDD/PCDF sources have relatively high release heights (thermal sources); they undergo long-range transport in the air. PCDD/PCDF releases can be reported on annual basis. Production amounts of intentionally produced POPs were much higher than for the unintentional PCDD/PCDF; however, they vary widely in application: PCB were used predominantly in closed systems such as in transformers and capacitors; they mainly enter the environment through leaks and leaching; they are typical legacy chemicals and reporting on an annual basis cannot be done. POPs pesticides largely are legacy POPs with no new production (drins, mirex, toxaphene, chlordane) and past uses in agriculture; today, DDT is a public health pesticide with restricted use in indoor residual spraying. For all of these chlorinated POPs, dietary intake has been identified as the major pathway of exposure. Newly listed POPs, such as the polybrominated diphenyl ethers, are predominantly occurring in indoor applications;

therefore, inhalation of indoor air seems to be more important than outdoor exposures. Finally, perfluorooctane sulfonic acid (PFOS) is dissociated into free PFOS anions and counter-cations; the main transport medium is water.

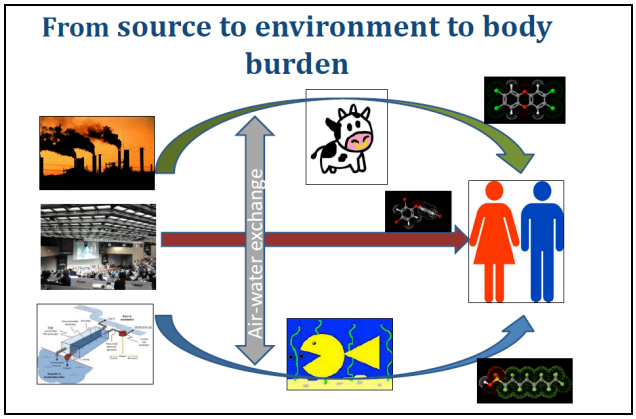


Figure 1: Pathway 'source-fate in the environment-human body burden' for POPs groups such as PCDD/PCDF, PBDE, and PFOS

Inventories:
The most comprehensive information is available for releases of sources of **PCDD/PCDF**. The most recent inventories have been compiled by Fiedler[8]. The eleven countries with the highest total and air releases are shown in Table 1.

Table 1: Countries exhibiting the highest PCDD/PCDF releases – totals to 5 vectors and air (only)

Country	Air (g TEQ/yr)	Total (g TEQ/yr)	Country	Air (g TEQ/yr)	Total (g TEQ/yr)
China	5,043	10,238	Brazil	1,168	2,235
India	2,827	8,658	Turkey	1,249	2,163
Indonesia	1,847	7,352	Argentina	874	2,111
Nigeria	2,784	5,340	Russian Federation	1,785	1,785
Kenya	3,103	4,738	Australia	498	1,780
South Africa	709	2,763			

DDT: The UNEP report identified nine countries that produced DDT and where quantitative data were available. These countries were Azerbaijan, Bangladesh, Brazil, the Democratic People's Republic of Korea (DPRK), India, Indonesia, the People's Republic of China (PRC), Serbia, and the United States of America (U.S.A.). Production started in the 1940s and is ongoing until today; however, at much lower volumes and presently only in India for export. The accumulated amounts of DDT reach 2,793 tonnes[4].
PCB: The preliminary assessment by UNEP showed that globally between 1 and 1.5 million tonnes of PCB have been produced. It is not possible to estimate how many tonnes of PCB products have been used in various applications. Typically PCB above the 50 mg/kg threshold are contained in inventories. In general, the quality of the PCB inventories is poor. From data available, the UNEP report concluded that between 1.6 and 3.1 million tonnes of PCB containing oils and materials have been destroyed to date. Accordingly, ca. 9.3 million tonnes of PCB and PCB-containing equipment still to be eliminated. It can be assumed that large amounts of PCB will be "mobilized" for destruction to meet the 2025/2028 goals of the Stockholm Convention.
For other POPs, no estimates have been undertaken under the Stockholm Convention.

Concentrations of POPs in the core matrices of the Global Monitoring Plan (GMP) for POPs:
The GMP has identified ambient air and human milk or human blood as the core matrices for POPs monitoring to contribute to the effectiveness evaluation (article 16 of the Convention). With the listing of PFOS into annex B of the convention, surface water has become a recommended core matrix. The UNEP Chemicals Branch has implemented several monitoring projects and in total has contributed 13,080 data points. The regional distribution is shown in Table 2; from Table 3 it can be concluded that for the new POPs, information is still scarce.

Table 2: Datapoints to UN region (by UNEP)

Region	No of data points
Africa	2,522
Asia-Pacific	2,644
CEE	1,843
GRULAC	3,299
WEOG	2,772
Total	**13,080**

Table 3: Data points for new POPs

New POPs	No of data points
HBCD	126
PBB 153	126
PBDE	62
PFOS	56
HCHs	477
Endosulfans	240
PeCBz	46

Ambient air concentrations using passive air samplers and polyurethane foam disks (PUF) for a three months exposure period. The following Figures have been generated from the interactive POPs GMP datawarehouse (hosted by Recetox, Brno, Czech Republic).
The sites exhibiting the ten highest PCDD/PCDF concentrations in ambient air are Jamaica, Peru, Senegal, Brazil, Sudan, and Mauritius and are shown in Figure 2. Figure 3 shows the PBDE data provided by UNEP.

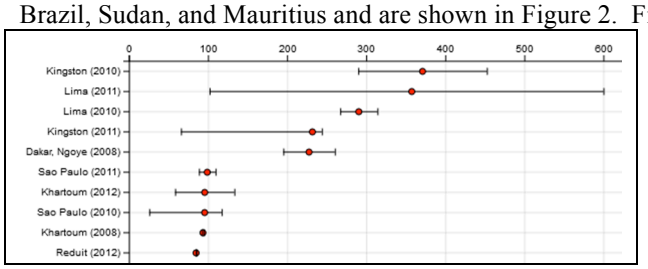


Figure 2: PCDD/PCDF concentrations in ambient air (in fg TEQ/m³), recalculated from PUF disks; representing an annual average. Figure generated from www.pops-gmp.org

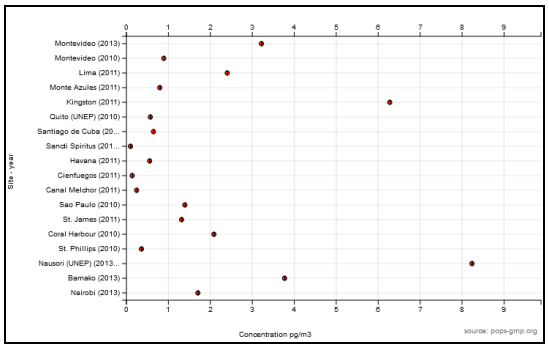


Figure 3: PBDE 99 in ambient air (pg/m³); recalculated from PUF disks. Figure generated from www.pops-gmp.org

Information for PFOS in air and **water** is still scares. The data available for air and water are shown in Figure 4.

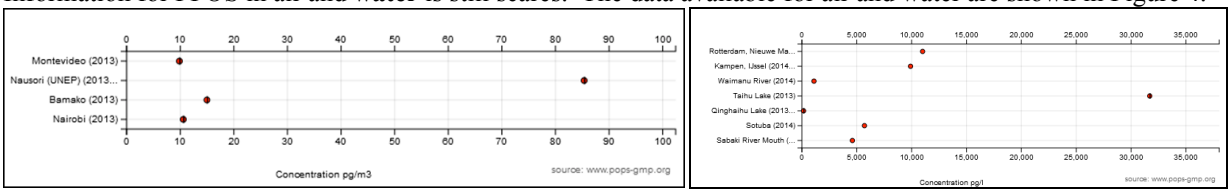
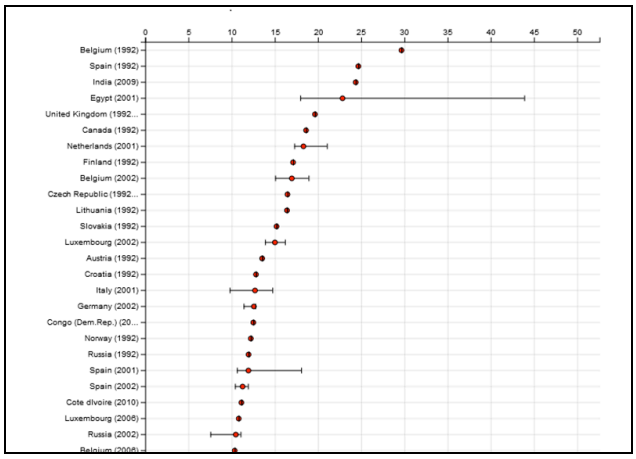


Figure 4: PFOS in ambient air (left) and in surface waters (right)

Human milk: UNEP and the World Health Organization jointly implement a survey on concentrations of POPs in human milk. The sampling protocol and the data reporting assess baseline concentrations (*i.e.*, mothers not exposed to known sources of POPs) of *primiparae* reporting one sample *per* country. PCDD/PCDF data are available since the 1980s; for some PCB results as well. For other POPs, data have been generated since from 2001. So far, for the GMP, the samples presented in the dataware house since 2001 have been analysed by the UNEP/WHO reference laboratories at the State and Veterinary Institute in Freiburg, Germany (for chlorinated and brominated POPs) and MTM Research Centre, Örebro University, Sweden, for PFOS. All data can be retrieved at the GMP data warehouse www.pops-gmp.org.



So far, more than 9200 data points have been generated under the UNEP-WHO agreement. The results are from pooled samples whereby one country is represented by one data point per sampling round. Figure 5 shows the concentrations of PCDD/PCDF (in pg WHO_{1998}-TEQ/g fat) according to declining concentrations. It can be seen that the highest concentrations were found in relatively old samples such as from 1992 (Belgium, Spain, UK, Canada). Among the developing countries, the sample from India (collected in 2009) had the highest median concentration.

Figure 5: PCDD/PCDF in pools of human milk

Discussion

At present, the global data base is not sufficient to establish a clear relationship along the pathway release from source – environmental concentration (*e.g.*, in air or water) – human body burden. It also has to be taken into account that the POPs presently listed in the annexes of the Stockholm Convention have have different chemical-physical properties, different sources and pathways in the environment. Although largely, food intake is the most import source of human exposure, for PBDE and other brominated flame retardants inhalation may contribute significantly to the body burden. For PFOS, water is the major transport medium and pathway for human exposure. Therefore, assessments source-environment-humans have to be done on compound/POPs-specific basis and often on congener-specific basis.

Despite many efforts, the quality and coverage of source inventories vary highly; the most satisfactory are for PCDD/PCDF; they are also available in quite large numbers (presently close to 90 national inventories). A further complication is that due to long-range transport and transformation in the environment, patterns of POPs at source can be different from patterns at receptor. Finally, only for very few POPs, human risk assessments have been undertaken.

Acknowledgements:

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References:

1 Stockholm Convention on Persistent Organic Pollutants (2001 and updates): www.pops.int

2 National reports are accessible from the following webpage http://chm.pops.int/Countries/Reporting/NationalReports/tabid/3668/Default.aspx

3 National implementation plans are accessible from the following webpage http://chm.pops.int/Implementation/NIPs/NIPTransmission/tabid/253/Default.aspx

4 UNEP (2015): Initial Situation Analysis on DDT – Status 2015; accessible for download as document UNEP/POPS/COP.7/INF/7 from http://synergies.pops.int/2015COPs/MeetingDocuments/tabid/4243/language/en-US/Default.aspx

5 UNEP (2015): Preliminary assessment of efforts made toward elimination of PCB; accessible at http://www.unep.org/chemicalsandwaste/Portals/9/POPs/PCB/Preliminary%20Assessment%20of%20Efforts%20Made%20Toward%20the%20Elimination%20of%20PCB_UNEP%20Chemicals%20Branch_2015_Final.pdf

6 Second regional reports (2015), accessible as UNEP/POPs/COP.7/INF.38 from http://synergies.pops.int/2015COPs/MeetingDocuments/tabid/4243/language/en-US/Default.aspx.

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