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## MATERIAL FLOW AND SUBSTANCE FLOW ANALYSIS OF POP-PBDEs IN NIGERIA AND THE RISK OF DIOXIN FORMATION AND RELEASE

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### Introduction

In 2009 the first brominated flame retardants - commercial pentabromodiphenyl ether (c-PentaBDE) and certain congeners of commercial octabromodiphenyl ether (c-OctaBDE), hexabromobiphenyl (HBB) - were included in the Stockholm Convention and, are therefore officially recognised as persistent organic pollutants (POPs). The production and use of c-PentaBDE and c-OctaBDE has stopped approximately in 2004<sup>1</sup>. Despite the stop of the production and use, large amounts of articles containing POPs-PBDEs are still in use and in the recycling and end of life flow.

A large share of PBDE/BFR containing articles have been shipped or are still being shipped to developing and economy in transition countries, either as new or second hand goods (e.g. as electrical and electronic equipment (EEE) or vehicles), as plastic/polymers for recycling or illegally as waste (e.g. waste electrical and electronic equipment (WEEE))<sup>2-6</sup>. In addition polybrominated dioxins and furans (PBDD/F) have been found in WEEE plastic of television and computer in Nigeria, frequently in the ppm range<sup>7</sup>.

The end of life management and treatment of POPs pesticide stockpiles and PCBs has revealed large challenges when developing countries are requested to manage POPs or POPs containing materials and, only small progresses have been made in the 10 years Stockholm Convention implementation<sup>8,9</sup>. Since PBDEs have been listed as POPs, it became obvious that another large POPs stockpile need to be managed<sup>1,5,6</sup>. Currently, there is no appropriate end of life treatment of WEEE plastic or car shredder residues in Nigeria. All current end of life practice – recycling, open burning or landfilling/dumping – can lead to the release of PBDE and to formation and release of PBDD/F. Therefore, in this study we wanted to assess the scale of potential PBDEs release in the end of life phases and the likeliness of formation of PBDD/F and brominated-chlorinated PXDD/F from current end of life management of PBDE/BFR containing WEEE plastic and to explore research needs in this respect.

### Materials and methods

#### *Time period and inventory year considered*

The time period considered for the MFA/SFA study was 2000 to 2010. For this period import data were available and compiled in the Nigerian EEE/WEEE inventory<sup>10</sup>. Within these years most of overall EEE/WEEE imports including EEE in current use and end of life for the considered target inventory year 2010 took place.

#### *Data acquisition*

WEEE import statistics (2000-2010) for Nigeria according to UN Comtrade database and statistics of installed data base of EEE in Nigeria has been taken from the Nigerian inventory report<sup>10</sup>, along with information from other available data and finding from the Nigerian PBDE inventory project.

#### *System definition for MFA/SFA*

The system boundary consists of the country Nigeria. The goods included in this study are the WEEE/EEE category 3 (cat 3) (IT and telecommunications equipment) and category 4 (cat 4) (consumer equipment), in particular the impacted polymer fraction. The substances addressed in the substance flow analysis were POP-

PBDEs listed under the Stockholm Convention. The stocks and flows considered are import, use and end-of-life management (reuse, recycling, thermal treatment and landfilling/dumping). The system comprises the EEE/WEEE materials of TVs/PCs cathode ray tubes (CRTs) and non-CRT devices of WEEE category 3 and 4 and focus on the listed POP-PBDE (hexaBDE and heptaBDEs), which were major homologues of c-OctaBDE.

#### ***Tool for graphical modeling***

The STAN tool was used for the graphical modeling. STAN is the short name for subSTance flow Analysis and the STANdard for Material Flow Analysis) and is a freeware developed and hosted at the Vienna University of Technology that helps to perform material flow analysis according to the Austrian standard ÖNorm S 2096.

#### **Results and discussion**

Based on the Nigerian WEEE inventory and the Stockholm Convention guidance for establishing POP-PBDE inventories<sup>1</sup>, the polymer content of WEEE plastic from CRTs of TVs and PCs were calculated for the different life cycle stages relevant for Nigeria (import, use/stock and end of life with the share of the different scenarios). The PBDE data in the CRT plastic were taken from the PBDE monitoring study<sup>11</sup>. The data from the calculations of the polymer flow (the material) and the associated POP-PBDEs (hexaBDE and heptaBDE) (the substance) were fed into the STAN software for visualizing the substance flow of POP-PBDEs in WEEE/EEE in cat 3 and 4 in Nigeria (Fig. 1). From the 1,270 t of imported POP-PBDEs (1,011 t heptaBDE and 259 t hexaBDE) about 370 t were in stock in 2010, while 900 t have entered the EoL between 2000 and 2010 (Fig. 1).

#### ***Open burning of WEEE plastic***

Approximately 259,000 tonnes of polymers containing approx 140 t of POP-PBDE and a considerable higher amount of DecaBDE have been subjected to open burning largely as backyard burning, partly for recycling purpose of metals and, partly as inappropriate waste management practice. By this approach, a large amount of PBDE have been released into the environment with likely long-term pollution of these areas as has been found at e-waste recycling sites<sup>2a, 7-9</sup>. A recent assessment of a city in China has shown that the PBDE contamination at a major E-waste recycling area has penetrated the food chain at high levels (e.g. in eggs and fish). High-end estimates of exposure for young children exceeded the U.S. Environmental Protection Agency reference doses for BDE-47 and BDE-99 by factors of approximately 2.5 and 1.5, respectively<sup>12</sup>.

Since PBDEs are partly degraded during the open burning process it is a challenge to estimate how much of the 140 t POP-PBDEs are finally released into the environment. A Japanese research group has derived an emission factor of  $9 \times 10^{-2}$  based on open burning simulation in laboratory<sup>13</sup>. This would mean that about 13,000 kg POP-PBDEs have been released from this practice into the environment in Nigeria. Furthermore, ones of the degradation products from open burning of PBDE/BFR containing plastic are the more toxic brominated and mixed halogenated dioxins and furans (PBDD/F and PXDD/F)<sup>14</sup>. PBDD/F and PXDD/F from open burning of PBDE/BFR containing WEEE plastic have contaminated soils and atmosphere<sup>2a, 14</sup>. As pre-furans, the conversion rates from PBDE to PBDD/F (and in the presence of chlorine source PXDD/F) are high and were up to 10% in a laboratory pyrolysis experiment of PBDEs<sup>15</sup>. In areas with long term WEEE recycling applying open burning, the total PXDD/F contamination and dioxin-like toxicity in soil far exceeded international PCDD/F limit values for soils<sup>14</sup> and can be considered Dioxin/POPs contaminated sites<sup>16</sup>. For Nigeria this practice has/is also taking place and the associated contaminated areas need urgently an assessment for contamination levels and related human exposures in particular via cattle and chicken/egg frequently found in such areas. Our initial measurements of PBDD/F and PCDD/F in soils from Nigeria impacted by open WEEE burning have confirmed PBDD/F in soils. Concentration of total PBDD/F in the soil samples analysed ranged from 12 to 4180 ng/g (0.06 to 156 ng TEQ/g) dry weight. The contamination of highly impacted soil of 29.8 ng (max. 156 ng) TEQ/g dry weight from PBDD/F in the Nigerian soils by far exceeded international soil limits set for PCDD/F and even exceeded the provisional Basel low POPs limit for PCDD/F (15 ng TEQ/g). Due to the similar toxicity of PCDD/F and PBDD/F<sup>17</sup> such soil could be considered POPs waste.

#### ***Disposal to landfills/dumpsites***

The approx. 640 t of POP-PBDE (and a considerable higher amount of DecaBDE) in the WEEE plastic disposed/dumped (Figure 2) are partly released over time<sup>18,19</sup> and serve as future source of PBDE release into the environment. Furthermore, these largely unmanaged dumpsites frequently catch fire and can continuously smolder. Studies showed that landfill fires releases brominated and chlorinated dioxins at similar levels<sup>20</sup>, revealing that PBDE/BFR containing materials is an important Dioxin source from landfills/dumps. These releases add to the releases from open burning and can have a similar order of magnitude, considering the estimated 4.5 time amount of POP-PBDE in landfills and that only a fraction of this is burned in landfill fires.

Furthermore, considering the increased interest in landfill mining, future exposure to PBDE and other POPs disposed in landfills/dumpsites need to be taken into account. A major exposure from landfill mining and use as feed additive has taken place from POPs/Dioxin containing waste from an organohalogen production resulting in contamination of the feed and food chain in Europe from import of contaminated animal feed from Brazil<sup>21</sup>

#### ***Recycling of PBDE containing plastic***

It is estimated that approx. 120 t of POP-PBDE (and a considerable higher amount of DecaBDE) have been recycled back into plastic products in Nigeria. However, no survey has been made in Nigeria to identify to what products these plastic is recycled. Considering that the flows of plastics from WEEE containing PBDEs/BFRs, by recycling ends up in sensitive uses such as children toys, household goods and even coffee cups<sup>22-24</sup>, there is an urgent need to assess and control the uses of WEEE plastic in Nigeria and other developing countries. Furthermore, the recycling of WEEE leads also to releases and in particular, human exposure from the recycling process itself<sup>2a, 12, 24</sup>. Considering that PBDD/PBDF are present at ppm level in the Nigerian WEEE plastic from CRT casings<sup>7</sup> also exposure to PBDD/F needs to be considered. Furthermore the moulding of plastic can result in further formation in PBDF from PBDEs, in particular when considering that the temperatures in recycling of plastic in Nigeria might not be as controlled as in industrial countries. Further assessment in this respect is needed considering the establishment of plastic recycling facilities in Nigeria<sup>11</sup>.

#### ***Future assessment need***

This preliminary assessment highlights that the flow and releases of the approx. 1,260 t of POP-PBDE need to be better assessed. In addition a considerable higher amount of DecaBDE (probably more than 5,000 t) in Nigerian WEEE plastic need to be considered in the assessment of the formation, releases and exposure to PBDD/F and related compounds.

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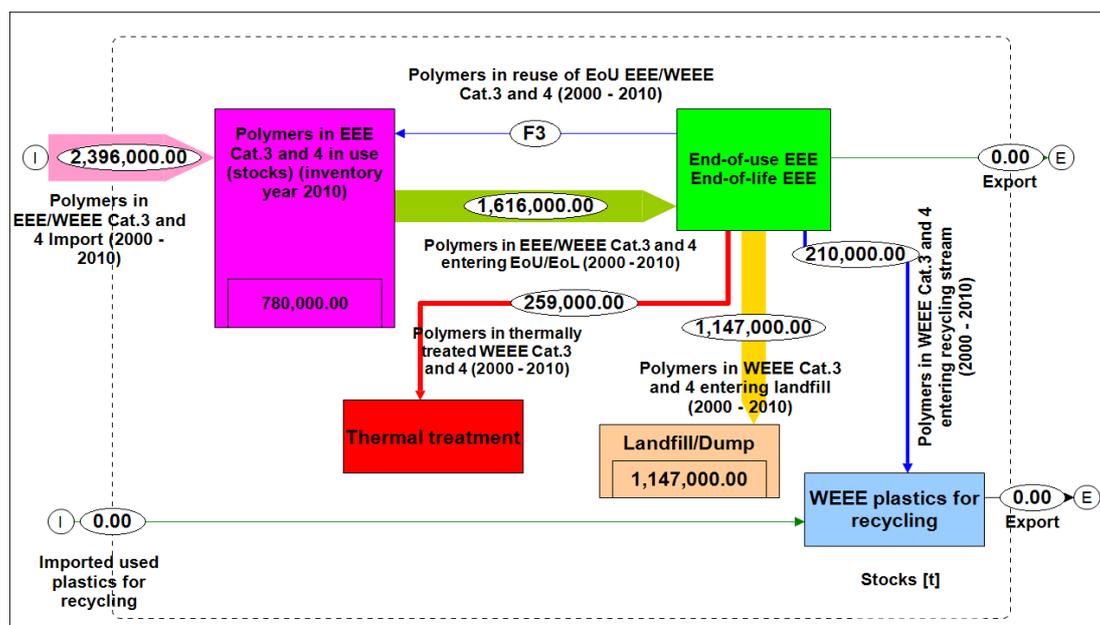
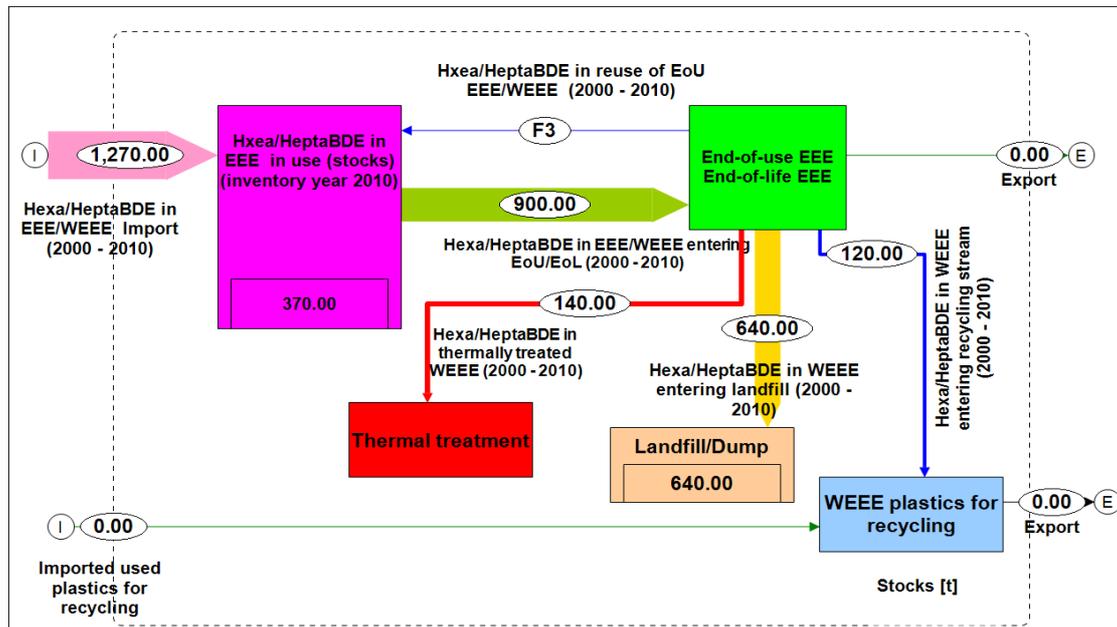


Figure 1: Material flow of WEEE/EEE polymers (tonnes) of cat 3 and 4 in Nigeria (considering the years 2000-2010 for flows; stocks for inventory year 2010)



**Figure 2:** Substance Flow of POP-PBDEs (tonnes) in cat 3 and 4 WEEE/EEE polymers in Nigeria considering the years 2000-2010 in flows; stocks for inventory year 2010.