IPCP Webinar Series: POPs in plastic and monitoring approaches
Part III: Extraction, clean-up, and analysis of POPs in plastics; 22/23 May 2023

Experience of capacity building on extracting and analysing brominated POPs in plastic in Africa with a South-North Cooperation

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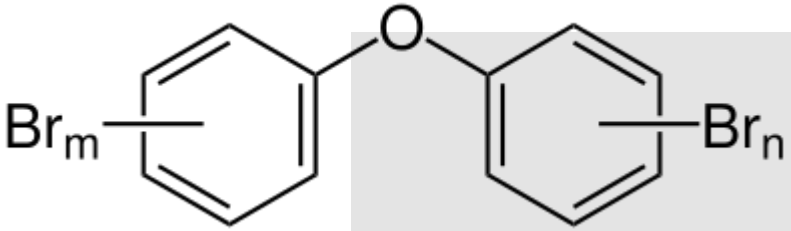
STOCKHOLM CONVENTION

Overview of the Presentation

- Introduction
- Part 1: Capacity Building in Sweden and Germany
  - Monitoring of PBDEs in e-waste
- Part 2: How PBDEs analysis was established in Nigeria
  - Monitoring of PBDEs in dumpsites
- Conclusion
- References
- Acknowledgements



Introduction

- Polybrominated diphenyl ethers (PBDEs) were one of the most widely used BFRs and have emerged as contaminants of concern due to their widespread use, ubiquitous environmental distribution, great bioaccumulation and biomagnification potentials, long-range transport, and toxicity (Meunhor, 2011; Xiao et al., 2012; Eguchi et al., 2009) and tetraBDE, pentaBDE, hexaBDE and heptaBDE were listed in the Convention 2009 while decaBDE was listed 2017.

- PBDEs are found in plastics in electronic equipment, vehicles, buildings and textiles, and are released into the environment from products and in particular through the indiscriminate disposal of end-of-life products.

- Plastic in waste electrical and electronic equipment (WEEE or e-waste) is considered to contain the largest share of PBDEs in the waste stream (Petreas and Oros 2009; Schlummer et al. 2007; Wäger et al. 2010, 2012; Stockholm Convention 2012b).

Introduction

- Developing countries have imported and are still importing PBDE-containing products like vehicles, electrical equipment (EEE) and e-waste (Breivik et al., 2011; Sindiku et al., 2015a, 2015b; Babayemi et al., 2014, 2018).

- A concern is whether levels of PBDEs & other BFRs increase in humans and the environment and cause toxic effects.

- In Nigeria, a major source of PBDEs are polymers from e-waste. In the past especially from cathode ray tubes (CRTs) of TV sets and computer monitors from these consumer electronic and ICT products that were imported from Europe, North America and Asia. There is no production of BFRs in Nigeria or other African countries.

BASEL CONVENTION
Controlling transboundary movements of hazardous wastes and their disposal

Known and Suspected Routes of e-waste Dumping

There is currently no system for tracking legal or illegal (under international law) shipments of electronic waste, and therefore, there is no quantitative data on volumes or even all of the true destinations. Some electronic waste is shipped as "working equipment" only to end-up as waste upon arrival. This map indicates information collected through investigations by organizations such as the Basel Action Network, Silicon Valley Toxics Coalition, Toxics Link India, SCOPE (in Pakistan), Greenpeace and others.

Nigeria has been a hub for e-waste imports from industrial countries since the early 2000 and especially after 2008 when China restricted e-waste imports.

WEEE in Africa: Reuse, Refurbishment and ”Recovery” of Materials

Stockholm Convention Project with capacity building and monitoring of PBDEs in Nigeria

- In 2010 a monitoring project for PBDEs in e-waste plastic was initiated by the Secretariat of the Stockholm Convention Secretariat and the Basel Convention Regional Center Nigeria (Professor Osibanjo) financed by a small grant project from the Norwegian government.
- Two Nigerian PhD students (Omotayo Sindiku & Joshua Babayemi) were selected under supervision of Prof. Osibanjo and Dr. Weber to conduct the research.
- My PhD was on monitoring and analysis of PBDEs and other brominated flame retardants in plastic.
- A second PhD (Joshua Babayemi) was on material and substance flow analysis conducted with the free STAN tool from Vienna University.

Stockholm Convention Project with capacity building and monitoring of PBDEs in Nigeria

- For the capacity building for analysis of PBDEs I did a 3 month training at the Fraunhofer Fraunhofer Institute Freising/Germany (Dr. Schlummer; Dr. Gruber)
- In a second phase I went 6 month to Umea University/Sweden (Prof. Tysklind) for the analysis of polybrominated dioxins and furans (PBDD/F) in WEEE plastic.
- One lesson learned: The visa application to Europe can take long time and need to be considered in the overall planning.
- The second PhD student could not get a PhD grant to visit Vienna University due to age restriction. Lessons learned: There are age restrictions for funding PhD students.

Monitoring of PBDEs in E-waste

- We samples 382 WEEE plastic from 158 TV CRT casings and 224 computer CRT casings taken from eight locations in Ogun State and Lagos State in southwest Nigeria.
- We noted the importation regions and the year of production for assessing if a time trend and regional use of BFRs can be found.

SINDIKU 2023

Sindiku et al. (2015) Environ Sci Pollut Res Int. 22, 14489-14501. DOI: 10.1007/s11356-014-3266-0

Materials and Methods: Sample preparation and Screening by ED-XRF (cooperation Fraunhofer Institute)

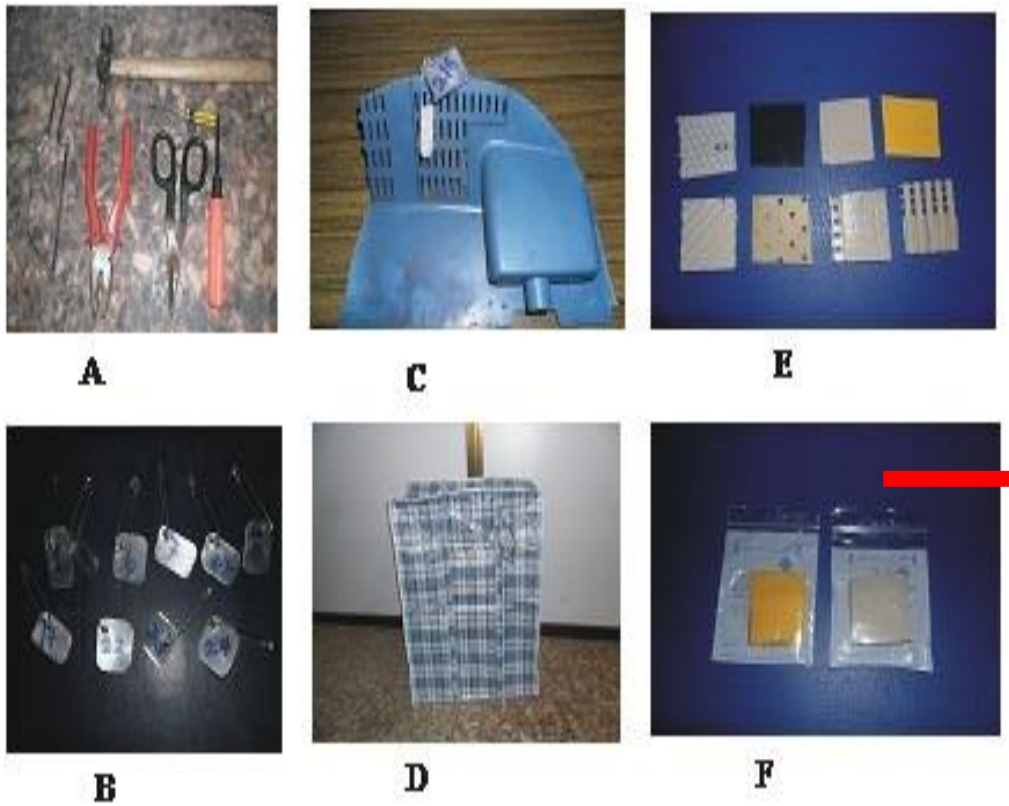


Figure 1: Sample preparation steps

XRF screening we conducted in Fraunhofer Institute in Freising during my 3 month research and capacity building stay there.

Figure 2: EDXRF (SPECTRO X-LAB 2000)

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Materials and Methods: Analysis of BFRs by GC-ECD in cooperation with Fraunhofer Institute

Within the 3 months stay at Fraunhofer Institute (Freising, Germany) I got also educated in extraction and clean-up of PBDEs/BFRs from e-waste plastic and analysis with GC/ECD and also GC/MS analysis.

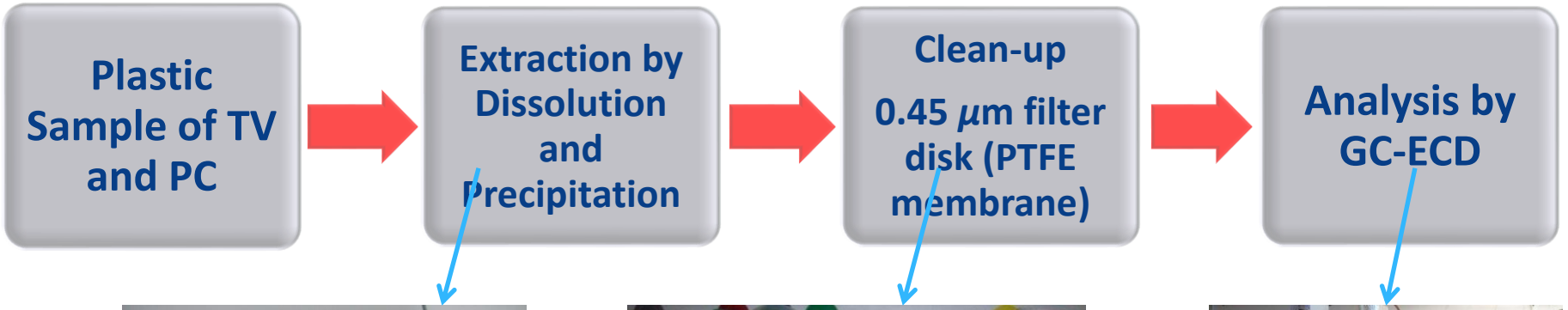


Fig. 3: Extraction process

Figure 4: Clean-up steps

Fig 5:Thermoscientific GC-ECD

Extraction procedure of the plastic for BFR analysis

- Extraction was done by Dissolution and Precipitation method according to an established method by Schlummer et al., 2005; 2007.
- 0.5 grams of the polymer samples was weighed into a well-labelled extraction glass vial covered with alumina foil paper. Dark-brown glass vial can also be used.
- 5 mL of Tetrahydrofuran was added.
- The glass vial was tightly capped and placed on the mechanical shaker for two hours.
- After complete dissolution of the polymer sample, 6 – 12 mL of n-Hexane was added stepwisely with rigorous shaking until a very good precipitate is formed.
- The glass vial was capped and placed on the mechanical shaker for 15 minutes until a clear solution was obtained.
- The glass vial was then allowed to stand for another 15 minutes.

Extraction procedure of the plastic for BFR analysis

- The extract/supernant was then decanted into a cleaned, well-labelled and pre-weighed collection glass vial covered with alumina foil paper.
- The precipitate was re-dissolved in 5 mL Tetrahydrofuran and placed on the shaker for 15 minutes.
- Another 6 – 12 mL of n-Hexane was added stepwise with rigorous shaking and it was placed on the shaker for 15 minutes.
- The extract was decanted into the glass vial.
- The entire procedure was repeated thrice.
- Some plastic did not dissolve in Tetrahydrofuran, Xylene was used in dissolution and the polymer was precipitated with Acetone

Fig. 3: Extraction process

Clean-up of the extracts

- An aliquot of the supernatant separated from the precipitated polymer was passed through a 20 mL syringe filter equipped with a 0.45 µm filter disk (PTFE membrane).
- Filtered extracts of the samples were then diluted with the 100-fold amount of toluene and placed in GC vials prior to chromatographic analysis.

Figure 4: Clean-up steps

Results and Discussion: Sampling of e-waste plastic

- **Number of samples from each region of production/assembly/year of manufacture.**
- **In 2010 only tetraBDE to heptaBDE were listed which are PBDE homologues of commercial PentaBDE and commercial OctaBDE where production stopped in 2004. There in this study only CRTs produced between 1981 and 2006 were sampled.**

Region	Computer	Television	Year of manufacture
Europe	50	100	1981 - 2003
Asia	100	58	1983 - 2005
America	74	0	1990 - 2006
Total	224	158	

Sindiku et al. (2015)Environ Sci Pollut Res Int. 22, 14489-14501. DOI: 10.1007/s11356-014-3266-0

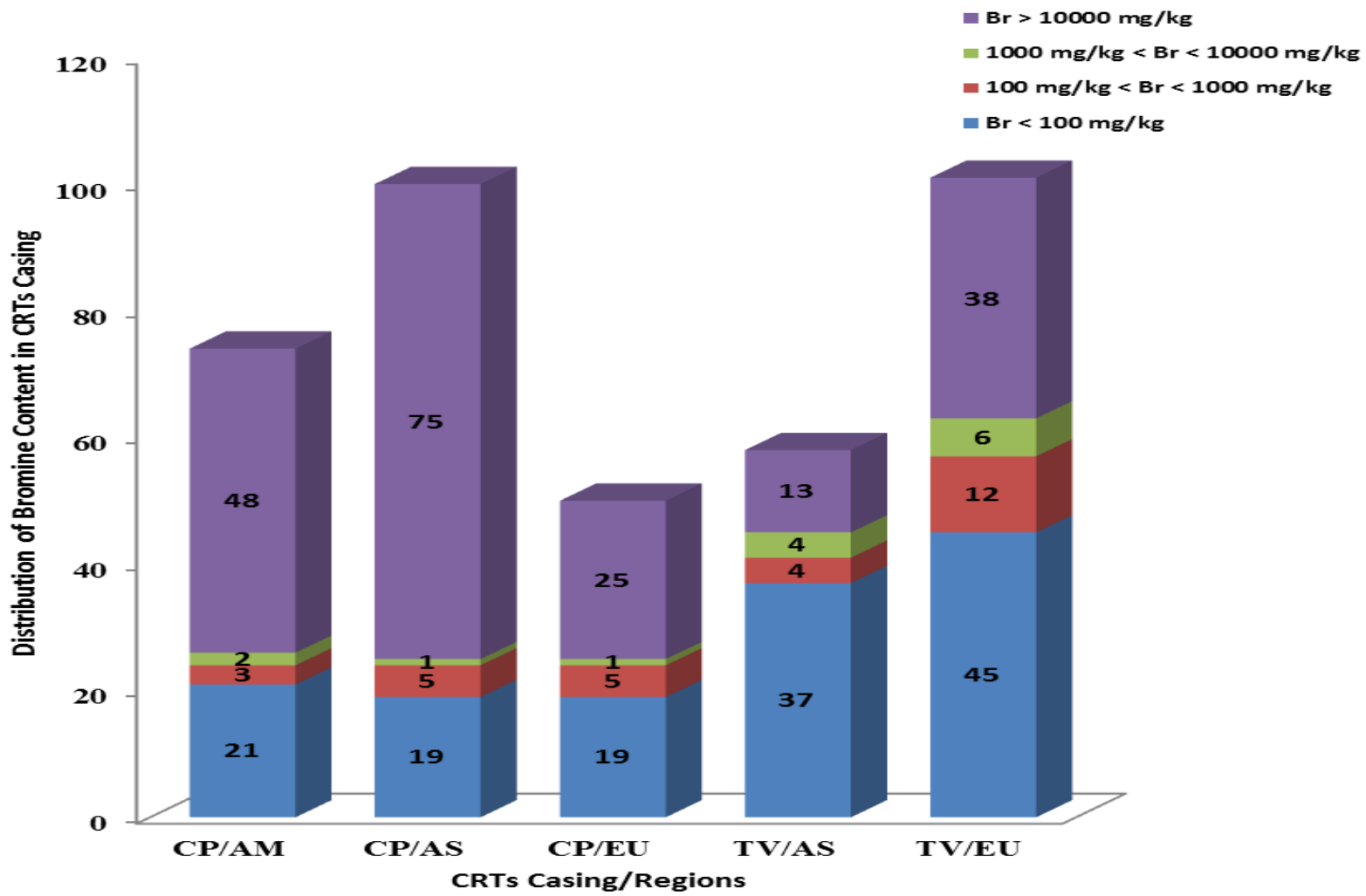
Results and Discussion: Screening of Plastic of TV and Computer by EDXRF

Concentration ranges (mg/kg) of selected elements determined by XRF

		Concentration range (mg/kg)			
Material type/Region	No screened	Bromine (Br)	Chlorine (Cl)	Phosphor (P)	Antimony (Sb)
CP/ America	74	<5 -102000	<50-16700	58-20400	<5 – 12600
CP/Asia	100	<5 - 99400	<50-24400	59-17400	<5 – 41700
CP/Europe	50	<5 – 94000	<50-22300	94-14800	<5 – 10600
TV/Asia	58	<5 -106000	<50-19000	50-8700	<5 – 10700
TV/Europe	100	<5 -105000	<50-20600	46-10100	<5 – 11200

Sindiku et al. (2015)Environ Sci Pollut Res Int. 22, 14489-14501. DOI: 10.1007/s11356-014-3266-0

Results and Discussion: Contents of Bromine



Distribution of bromine content in CRT plastic of TVs and computers from different world regions (America, Asia and Europe) sampled in Nigeria

Results and Discussion: BFRs analysis by GC-ECD

- **Sample containing c-OctaBDE**
  - **These impacted samples resulted in an average concentration of 1280 mg/kg for all the 382 samples which is above the maximum permissible level of 1000 mg/kg as stipulated by the RoHS Directive 2011/65/EU Annex II**
  - **Therefore these polymers can only be used for recycling into electronics after removing the bromine containing casings.**

Plastic casings of TV and Computer where OctaBDE have been detected

Sample Type	Conc. Of OctaBDE (mg/kg)	Country of production	Year of manufacture
TV CRT	290000	U.K	1986
TVC CRT	64100	Germany	1986
TV CRT	994	China	1989
TV CRT	6610	Germany	1983
TV CRT	59300	Germany	1988
CP CRT	50900	U.S.A	2003
CP CRT	9470	U.S.A	2005
CP CRT	8690	China	2003

Results and Discussion: Analysis of BFRs in plastic of TV and PC

- **Sample containing Deca-BDE**
  - 34 samples out of the 382 samples screened/analysed for BFRs contained c-DecaBDE with concentrations ranging from 675 to 230000 mg/kg which corresponds to an average concentration of 3850 mg/kg for all the 382 polymers TV and Computer screened and therefore more than 3 times above the RoHS limit in average.

Results and Discussion: Inventory of total brominated flame retardants in Nigerian CRT plastics

Total amount of PBDEs (in kg) in plastic fraction of TV and Computer CRT in Nigeria.

Calculation base	Category	OctaBDE	HexaBDE	HeptaBDE	DecaBDE
Impact factors SC Inventory Guidance (2012)	TV	188	21	81	
	PC	154	6	23	
	Total	**242**	**27**	**104**	
Measured impact factors from this study	TV	583	64	251	1860
	PC	11	1	20	20
	Total	**594**	**65**	**256**	**1880**

Establishing PBDEs analysis in Nigeria

- Back in Nigeria I transferred knowledge on PBDE analysis to Basel Convention centre and University of Ibadan and we established the first analytical capacity of PBDE in Nigeria.
- In establishing PBDEs in Nigeria, we took the opportunity of the GRC laboratory established by UNIDO at the Basel Centre and GC-ECD Nigerian government bought for federal institute for industrial research,
- Some of the challenges faced were lack of fund to purchase chemicals and other equipment needed, Power problem, lack of support from the government and lack of equipment required for extraction and clean up.
- We raised money by ourselves and bought all the PBDEs standards, chemicals and every other things needed. Its took us almost two years to put all our resources together to get everything needed for the analysis. I trained some of my colleagues on PBDEs analysis and we test run for few months before we started the real work.
- After we established the analysis we selected as research topic the monitoring of PBDE pollution around dump sites and e-waste sites which are sites where plastic from WEEE and end-of-life vehicles are openly burnt in Nigeria with associated envirobnmental pollution and human exposure and therefore pressing issues.

Establishing PBDEs analysis in Nigeria and conduct research

- We conducted and published several research on the monitoring of PBDE pollution in eggs, milk, vegetables and soils around dump sites and e-waste site in Nigeria.

Contents lists available at ScienceDirect

Emerging Contaminants

journal homepage: www.keaipublishing.com/cn/journals/emerging-contaminants

Polybrominated diphenyl ethers (PBDEs) concentrations in soil, sediment and water samples around electronic wastes dumpsites in Lagos, Nigeria

Oloruntoba Kike[a, b], Omotayo Sindiku [a, d, *], Oladele Osibanjo [a], Roland Weber [c]

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Polybrominated diphenyl ethers (PBDEs) concentrations in soil and plants around municipal dumpsites in Abuja, Nigeria☆

Kike Oloruntoba [a, b], Omotayo Sindiku [a], Oladele Osibanjo [a], Christine Herold [c], Roland Weber [c, *]

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Polybrominated diphenyl ethers (PBDEs) in chicken eggs and cow milk around municipal dumpsites in Abuja, Nigeria

Kike Oloruntoba[a,b], Omotayo Sindiku[a], Oladele Osibanjo[a], Simona Balan[c], Roland Weber[d,*]

However there was no project opportunity to further analyse POPs in plastic in Nigeria. Now a GEF project on plastic management is currently developed (PPG-phase).

Contribution to knowledge

- The plastic in e-waste study has contributed for the first time the much needed data on the types and levels of new listed brominate POPs in e-waste plastic. And in the follow-up studies also for soil, vegetables, eggs and cow milk around dumps in Nigeria.
- Data from this study:
  - Has/is being used by the Secretariat of Stockholm Convention to develop a methodological guidance document on monitoring of new POPs in products and articles.
  - Can also be used by Policy Makers for decision making vis-à-vis Nigeria's obligation as a Party to the Stockholm's Convention on Persistent Organic Pollutants.
- Similar capacity building projects should be conducted for other POPs and would be beneficial for the continent.

Conclusion

- Monitoring capacity of PBDEs and other BFRs in WEEE plastic has been established by a North-South co-operations already 2011-2013 (Nigeria-Germany-Sweden).
- The screening, extraction and clean-up methodology of Fraunhofer Institute can also be applied in developing countries. However often equipment, analytical standards and in particular research funding and projects is missing.
- Strategic development of research and monitoring capacity in developing countries is needed which can guide the improvement of plastic management and recycling
- There is a need for better monitoring and proper management of electronic waste and other waste containing PBDEs and other POPs in Nigeria (and other African countries) to protect the environment and humans from the adverse effect of these pollutants.
- More research co-operations are needed and projects which facilitates such research co-operations. This should include long term considerations on how to use the acquired skils of students when they return to the country.

Thank you for your attention and co-operation!

Part II: Monitoring of PBDEs in eggs, milk, soil and plants around dump sites in Nigeria

- In recent years, open dumpsites of municipal wastes have received particular attention with regard to environmental contamination. Especially in developing countries the large amount of products containing PBDE compounds are disposed with other waste plastic and garbage in landfills or open municipal waste dumpsites, and uncontrolled burning of solid waste largely fuelled by plastics is the common practice (Babayemi et al., 2018, Babayemi et al., 2015, 2019).

- It has been established that PBDEs may be released into the environment during improper handling and disposal of e-waste and other products containing PBDEs that is prevalent in developing (Weber et al. (2011) Waste Manag. Res. 29, 107-121)

- Therefore we initiated PBDE monitoring studies of PBDE around dump sites in Nigeria including soil, plants, eggs and milk.

Monitoring of PBDEs in soil from Nigeria dumpsites

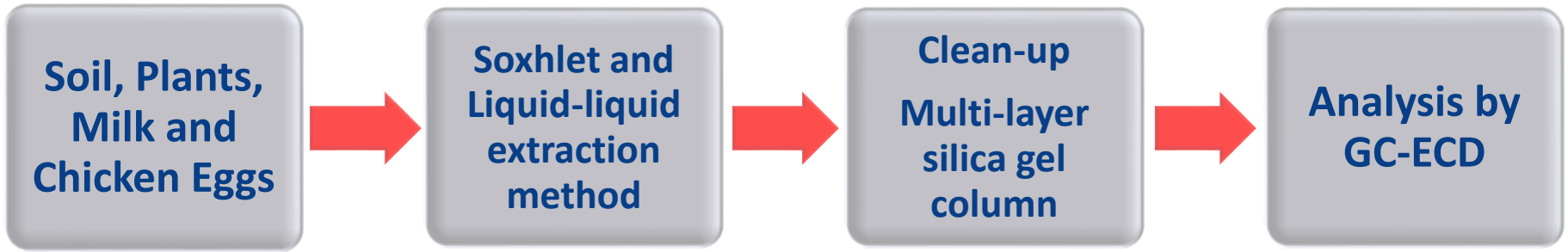
- Sample collection and preparation:
  - **Soil, chicken eggs, cow milk and Plant samples collected from two main dumpsites in Abuja**
    - The study covered the two largest municipal waste dumpsites (i.e. Karmo and Anjanta Landfill Facilities) operated since 1995 and 2003, respectively
    - A total of 96 soil was collected over a period of two years in two municipal waste dumpsites in Abuja.
    - Fifty-six samples each of free-range chicken eggs and cow milk were collected. Control samples were collected approximately 5 km away from the dumpsites.

Monitoring of PBDEs in plants from Nigeria Dumpsites

- Forty (40) fresh samples of 5 different edible plant species which include: pumpkin (Cucurbita pepo), spinach (Amaranthus spp.), tomato (Lycopersicon esculentum), sweet potatoes (Ipomoea batatas) and forage crops such as bentgrasses (Agrostis capillaris) were collected from the 2 sampling locations during the wet seasons in the 1st and 2nd year.

- All the samples were air dried at room temperature and stored in the freezer until further analysis.

Materials and Methods: Analysis of PBDE established in Nigerian laboratory from SC project



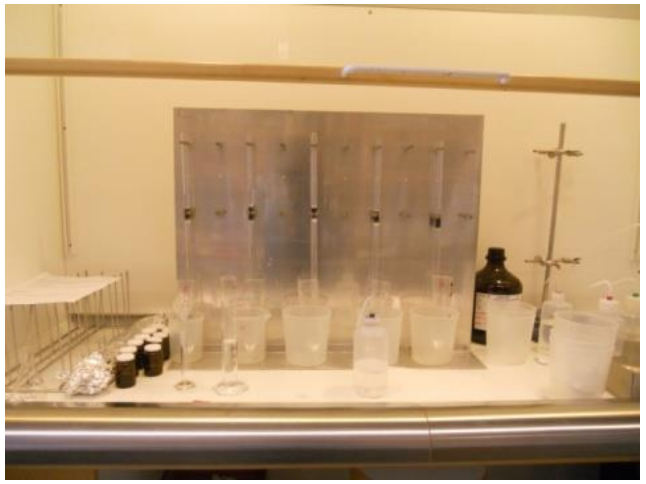


Fig. 7: Clean-up process

Fig. 8: Agilent GC-ECD

Fig. 14: Schematic diagram of the Chemical Analysis for PBDEs

PBDESs in soil depth in Nigeria Dumpsites

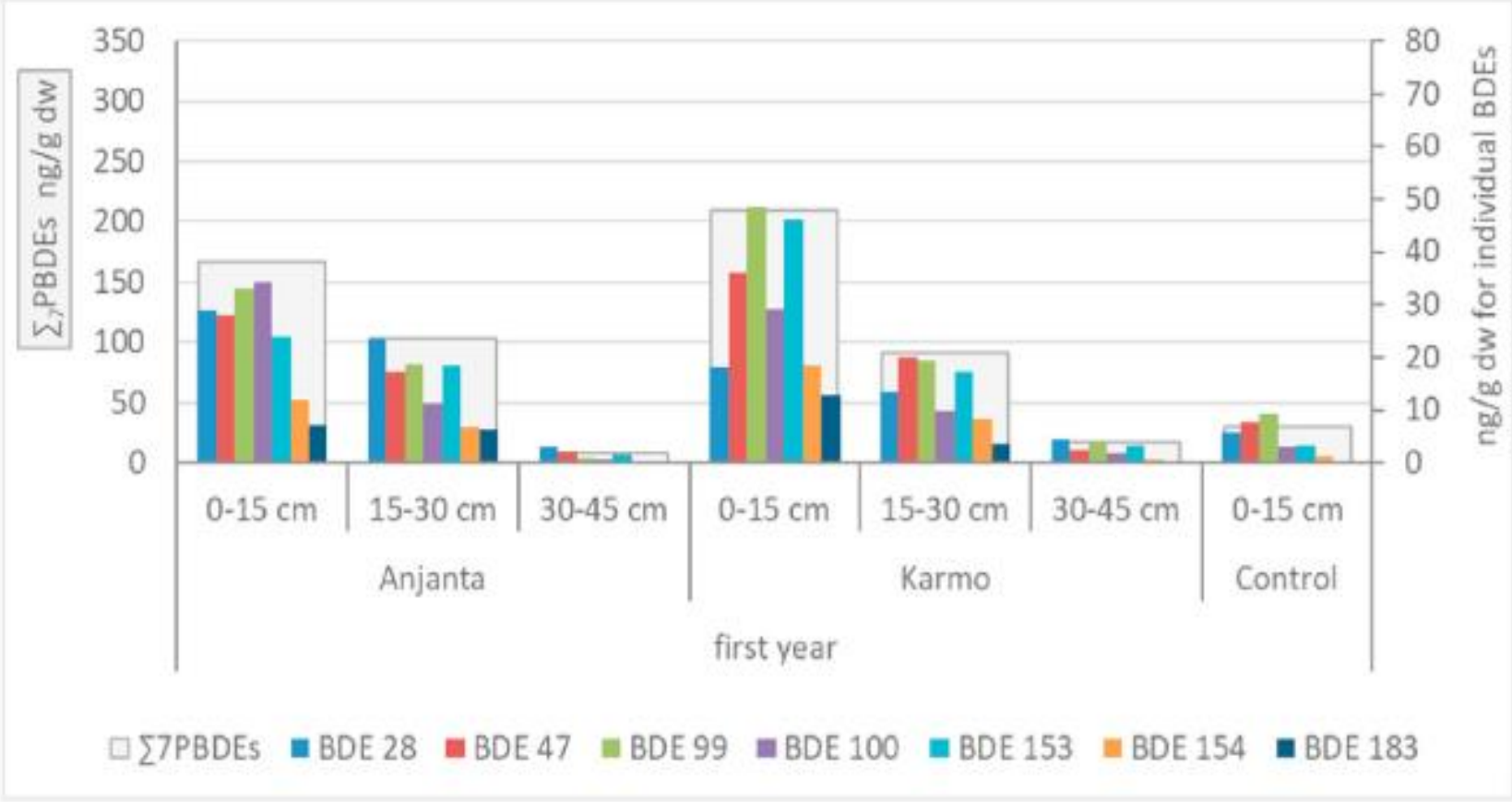


Fig. 1. PBDE movement pattern across soil depths at Anjanta and Karmo dumpsites in the first year.

PBDEs in soil at different depth around Nigeria Dumpsites

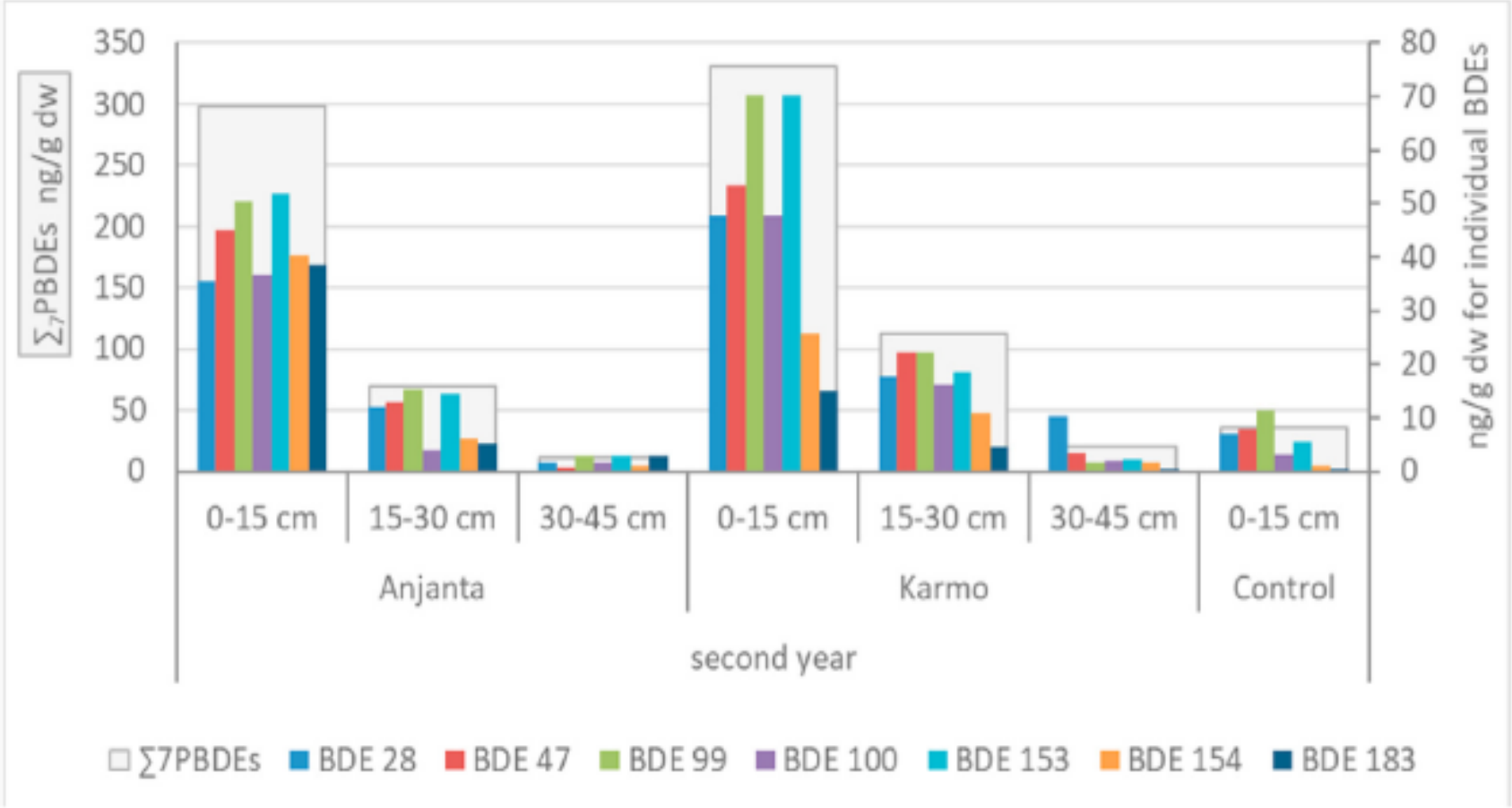


Fig. 2. PBDE movement pattern across soil depths at Anjanta and Karmo dumpsites in the second year.

Comparison of PBDEs in Soil, root and shoot of plants in Nigeria Dumpsites

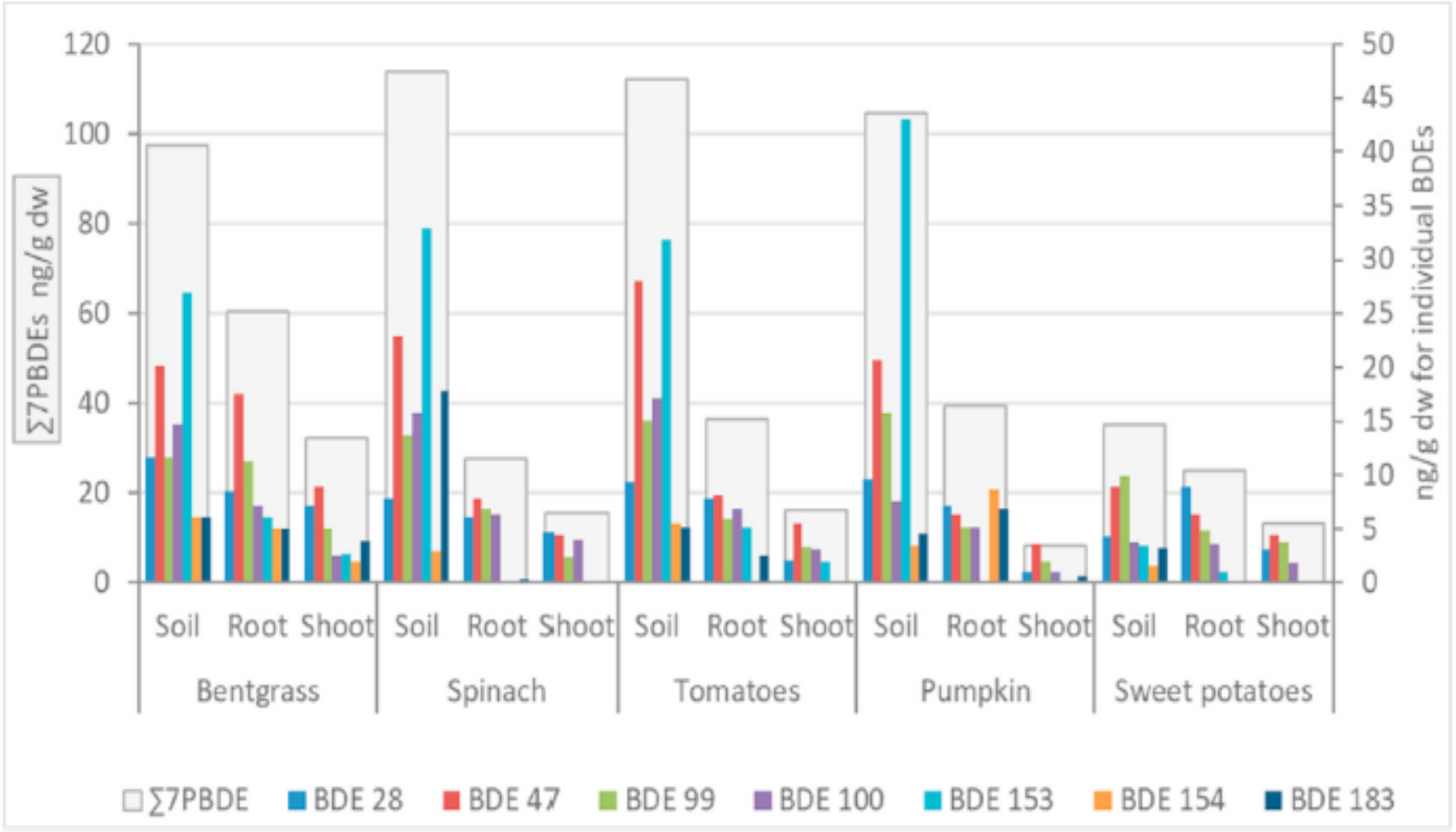


Fig. 3. PBDE levels in soils, roots and shoots of plants from the municipal dumpsites.

PBDE congener profiles in chicken eggs

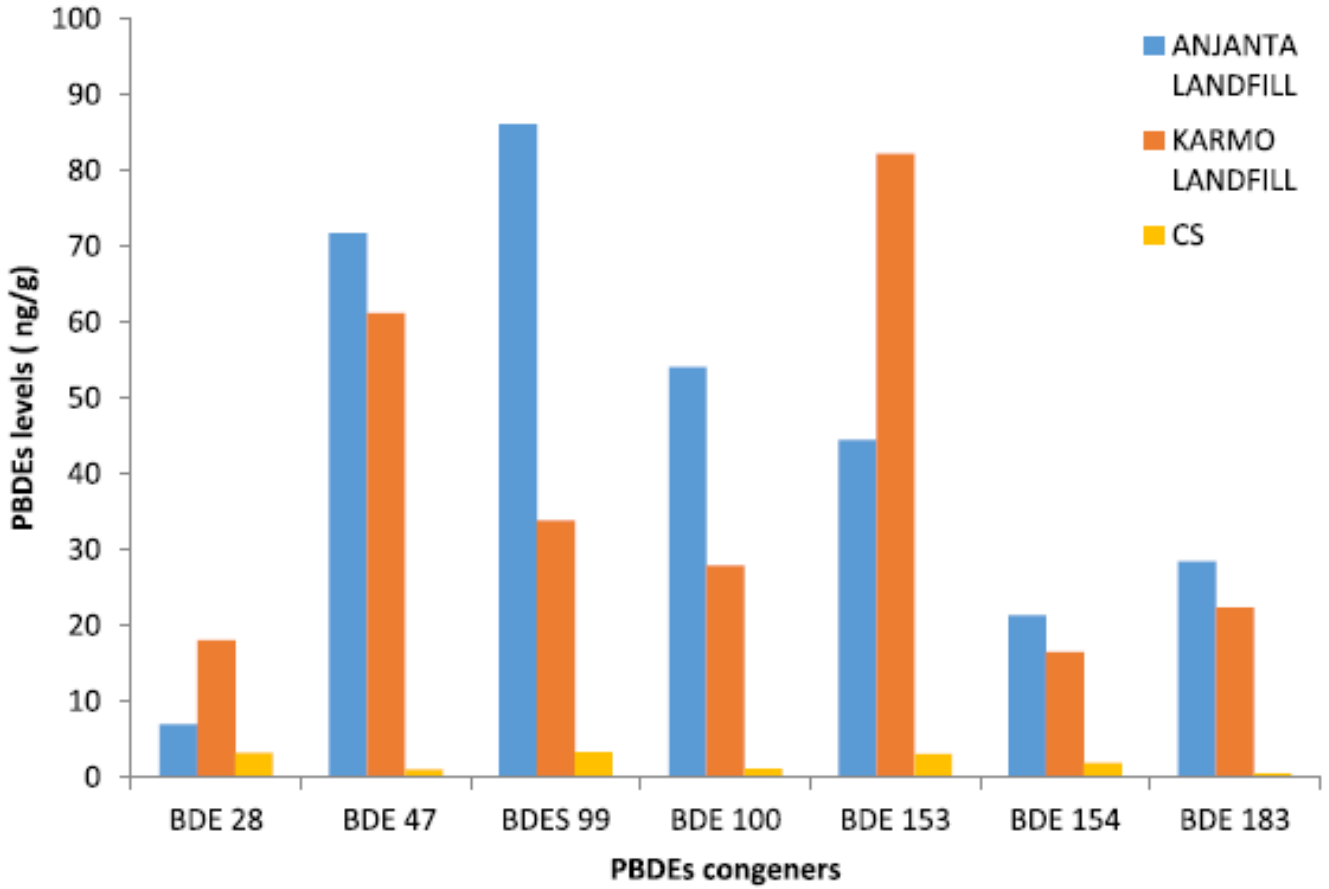


Fig. 2. PBDE congeners profile in the free-range chicken eggs collected at the two municipal dumpsites and control site in Abuja, Nigeria.

PBDEs in Cow milk

Table 5: Lipid percentage and concentration (median and min-max range) of lower PBDE congeners (ng/g lw) in cow milk collected from municipal dumpsites in Abuja, Nigeria

	Anjanta Dumpsite		Karmo Dumpsite		
PBDE congener	Year 1	Year 2	year 1	year 2	Control
Lipid %	5.72±0.77	6.35±1.21	8.04±1.22	10.1±1.72	6.72±0.98
28	6.83±0.12	3.19±0.06	6.9 ±0.34	9.38±2.52	0.48±0.17
47	22.1±1.23	12.0±2.77	45.6±3.87	59.9±6.02	11.2±4.23
99	6.93±0.17	16.4±1.98	17.0±1.53	7.31±0.05	3.38±0.24
100	4.07±0.09	10.6±2.71	2.25±0.07	0.02±0.01	0.25±0.07
153	2.84±0.07	9.05±0.97	0.66±0.02	0.45±0.12	2.8±0.12
154	2.95±0.11	ND	0.91±0.08	5.48±1.32	0.05±0.02
183	1.19±0.03	ND	2.79±0.07	4.29±1.17	ND
$\sum_{7}$PBDEs	46.9±13.8	51.2±9.70	76.1±7.20	86.8±12.9	18.2±5.83

HELP KEEP ELECTRONIC WASTE FROM GROWING!!!