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REVIEW ARTICLE

Monitoring polychlorinated dibenzo-p-dioxins/dibenzofurans and dioxin-like polychlorinated biphenyls in Africa since the implementation of the Stockholm Convention—an overview

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Abstract
Polychlorinated dibenzo-p-dioxin (PCDDs), polychlorinated dibenzofurans (PCDF), and dioxin-like polychlorinated biphenyl (dl-PCB) are groups of toxic compounds released into the environment as unintentional by-products of combustion. They persist, bioaccumulate through the food chain, and cause adverse health effects. This review attempts to collate available information on the release of PCDD/Fs and dl-PCBs and other critical data relevant to their monitoring in Africa during the existence of the Stockholm Convention (SC). Much as the implementation of the SC may be lagging, literature showed that there has been encouraging efforts that have been made with respect to PCDDs/Fs and dl-PCBs monitoring in Africa. Results from a global monitoring study showed that PCDD/Fs released to air in Africa stood at 18–532 fg WHO_{98} TEQ/M^3 while dl-PCBs were 7–278 fg WHO_{98} TEQ/m^3. In human milk, the total concentration of PCDD/Fs, i.e., WHO 2005 TEQ LB has been reported to range from 0.5 ng/g fat to 12 ng/g fat. Fourteen laboratories in Africa participated in inter-laboratory assessments of persistent organic pollutants (POPs) with two specifically for PCDD/Fs analysis. This shows that some efforts are being made to boost capacity in Africa. Levels of PCDDs/Fs and dl-PCBs in clay consumed by pregnant women have been reported in Cameroon, Democratic Republic of Congo (DRC), Nigeria, Zimbabwe, Côte d'Ivoire, and Uganda with a maximum concentration of 103 pg TEQ/g. This finding was very significant since women are the most impacted through exposure to POPs, a fact that is acknowledged by the SC.

Keywords PCDD/Fs · dl-PCBs · Stockholm Convention · POPs · Africa · Stockholm

Introduction

Environmental management of persistent organic pollutants (POPs) is a global issue whose mandate has been vested into the Stockholm Convention (SC). The SC is a global agreement between countries referred to as Parties. The agreement was adopted in 2001 and entered into force in 2004. The objective of the SC is to protect human health and the environment from adverse effects resulting from exposure to POPs (Stockholm Convention. 2001). These pollutants circulate globally through the atmosphere, the hydrosphere, and the food chain, so they can be found in places where they have never been produced (Jones and De Voogt 1999). Originally, the SC aimed at dealing with twelve (12) POPs which were termed the "dirty dozen" and were further classified into pesticides, industrial chemicals, and by-products. Parties have been adding new compounds to the original list of 12, with 16 new listed POPs added up until 2017 (UNEP 2017). With respect to 16 new listed POPs, there is very little data published within the African context and this could create gaps when considering measures for their sound management.

Africa is the second largest and second most populous continent with an estimated population of 1.2 billion in 2015 living in 54 sovereign states (UN 2016). It is divided into

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Northern Africa, Southern Africa, Eastern Africa, Western Africa, Central Africa, and the Island states with six different climatic zones which can influence the movements of POPs. Most African countries depend on agriculture which contributes largely to their GDPs. The industrial sector is gaining momentum although it contributes marginally to the GDP in many African countries. The main manufacturing products are textiles, foodstuff, beverages, and leather. Mining is also growing significantly with power generation, storage, and transport sectors which are key to social economic development. All these manufacturing activities are potential sources of unintentionally produced POPs (UPOPs) such as PCDD/Fs. Twenty-eight (28) countries from Africa were among the first signatories to the SC since its adoption on 25th March 2001. When it entered into force in 2004, twenty-three (23) parties were from Africa. All African countries except South Sudan and Western Sahara are Parties to the SC (Stockholm Convention 2018).

As part of the SC requirement spelled out in Article 3 on "measures to reduce or eliminate releases from intentional production and use," several Parties have undertaken initiatives to reduce the production and release of pesticides and industrial chemicals to the environment. However, several challenges evolved in addressing Article 5 on "measures to reduce or eliminate releases from unintentional production" because the pollutants in this category are unintentionally released and can sequester themselves in different media, i.e., air, water land, products, and residue.

The current list of unintentionally produced POPs includes polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), polychlorinated biphenyls (PCB), hexachlorobenzene (HCB), and pentachlorobenzene (PeCBz), polychlorinated naphthalenes (PCNs), and hexachlorobutadiene (HCBD). This review focused on polychlorinated dibenzo-p-dioxin (PCDDs), polychlorinated dibenzo furans (PCDF), and dioxin-like polychlorinated biphenyl (dl-PCB). These are indicators of other UPOPs for most sources as stressed by the UNEP 2013 toolkit. Even before the creation of the SC, there were global initiatives to analyze and monitor PCDD/Fs and dl-PCBs, but big data gaps were identified in developing countries. This could be due to a lack of technical, financial infrastructure, and institutional capability to conduct research on PCDD/Fs and dl-PCBs. Although these technical aspects come with huge financial obligations, through support from institutions such as Non-Government Organizations (NGOs) and individual efforts, there have been a few studies reported on PCDD/Fs and dl-PCBs from different countries in Africa since the establishment of the SC (Booth et al. 2013; van den Berg et al. 2017).

These reports are scattered in different global reports, global reviews, and publications, and due to this, it is difficult to discern the trends in the analysis of PCDD/Fs and dl-PCBs. This naturally creates a need to collect this information, study the trends, and explore the gaps. Assessment in this regard will highlight the shortcomings that different African countries which are Parties to the SC face with regard to scientific research on PCDD/Fs and dl-PCBs. It is important to note that Article 11 of the SC on "research, development, and monitoring" emphasizes the need for Parties to undertake appropriate research, development, and monitoring of POPs within their means. PCDD, PCDF, and dl-PCB are among POPs that are predominantly produced as a result of anthropogenic activity. PCDD/Fs are produced naturally in forest fires and volcanic eruptions, but their main sources are from unintentional by-products of combustion such as burning of wastes, incinerators, and industrial processes such as iron and smelting, textiles, and cement kilns (Jones and De Voogt 1999; Pan et al. 2010; Vallack et al. 1998). Even though PCDD/Fs and dl-PCBs are released to the environment at very low concentrations, they are persistent and bioaccumulate through the food chain. The health effects on humans are adverse and they can alter the development of different cells to cause cancer and destruction of the endocrine system thereby inducing reproductive problems (Ahlborg et al. 1994; USEPA 1985; WHO 2010). Despite their known human health effects, there is little information about their sources, concentrations, transformation, and human impacts in Africa. This review is an attempt to compile as much information from as many available reports on PCDD/Fs and dl-PCBs, their trends, sources, and human exposure in Africa since the SC came into force. The review also examines available methods of analysis for PCDD/Fs and dl-PCBs. Finally, an analysis of existing gaps is also undertaken.

Measures taken by African countries on PCDD/Fs and dl-PCBs after the SC entered into force

The SC is a binding global agreement designed to protect human health and the environment from the hazardous effects of POPs (Templeton 2014; UNEP 2001). Cognitive of this information about POPs, many countries limited their production and release as early as 1990 before the SC came into force (Sow et al. 2014). As part of the SC implementation strategies, it was agreed that Parties should undertake appropriate research, pertaining to persistent organic pollutants. This is the basis of Article 11 of the SC where research on the presence, sources, levels, and trends in humans and the environment were emphasized. Parties were also required to develop analytical techniques for measurement of POPs (Resource Futures International 2001). As the negotiations for the creation of the SC came to a close, African countries realized that they had accumulated stockpiles of pesticides which were classified as such. They thus requested for help in dealing with the stockpiles of POPs pesticides which were in thousands of tons. As a result, the Africa Stockpiles Program (ASP) was launched in September 2005 for a period of 12–15 years and worked to clean up the pesticides, dispose of them safely, and prevent the problem from recurring (CropLife International 2012). At the same time, the inventories for all POPs were being created in many African State Parties. These included unintentionally produced POPs such as PCDD/Fs and dl-PCBs using the standardized UNEP Toolkit. Until recently, many countries have not reported analytical data on PCDD/Fs to correlate with the inventories that were created using the Toolkit in Africa. This is a hurdle in as far as the monitoring of release to the environment is concerned.

After the SC entered into force, each Party was required to develop action plans, i.e., national implementation plans (NIPs) for the sound management of POPs. Each State Party through the NIPs was required to establish an inventory on PCDD/Fs every five (5) years. The first inventories were made in Canada, Germany, and the USA (Fiedler 2007). Since many countries did not have the technical and financial capacity to analyze PCDD/Fs from all potential sources, the United Nations Environment Program (UNEP) Chemicals developed a standardized toolkit for the identification and quantification of PCDD/Fs (UNEP 2005). This toolkit was updated in 2013 and includes three parts (Stockholm Convention 2013). Part I is a general guidance on setting up an inventory, updating and revising it. It also includes guidance on data quality and quality control and how to determine activity rates, and others aspects. Part II contains information on emission factors and source categories. Part III contains emission factors for other unintentional POPs and annexes. This methodology makes it possible for developing countries to estimate annual releases of PCDD/Fs without collecting environmental samples to carry out chemical analysis. A major shortcoming of the toolkit method is that it only highlights sources and provides approximations of emissions for each environmental medium, product, and residue but it cannot provide the relative impacts of these to humans or the ecosystem (UNEP 2005). Most African countries produced their first inventories of PCDD/Fs releases to air, water, land, products, and residue using the toolkit as seen in Table 1. However, scientific research data on the concentrations of PCDD/Fs and dl-PCBs in matrices such as soils, sediments, water, and food products such as fish, eggs, and milk critical in establishing exposure assessment are still scanty (Fiedler 2007). From Table 1, it is apparent that not all African Parties submitted the NIP reports where an estimate of PCDD/Fs releases using the toolkit methodology was reported.

Some countries such as Guinea, Mozambique, Niger, Somalia, and Uganda submitted the NIP reports but the data on estimation of PCDD/Fs was not clear; some were in graphs so it was hard to present them in Table 1. As such, discrepancies and inconsistencies in the outcomes are thus expected and this is expected to complicate comparative analyses. The Global Environmental Facility (GEF) and UN agencies such the United Nations Development Organization (UNIDO) or United Nations Environment Program (UNEP) as well as the International POPs Elimination Network (IPEN) are assisting developing countries and countries with economies in transition to implement the Stockholm Convention. IPEN supports the analysis of PCDD/Fs and dl-PCBs in areas which were thought to be highly contaminated such as dumpsites and absolute pesticide stockpiles. The first studies on PCDD/Fs and dl-PCBs in chicken eggs from African countries 2004–2006 were conducted by IPEN (DiGangi 2006; Sow et al. 2014). Results for these studies are shown in Table 2. Levels of PCDD/Fs and dl-PCBs in chicken eggs from Senegal, Tanzania, Kenya, and Egypt exceeded the European Union (EU) limit. The highest concentrations of PCDD/Fs and dl-PCBs were detected in chicken eggs from Egypt. These were the first studies of PCDD/Fs to be conducted in those countries.

As mentioned above, Parties need to update inventories to see the change over time in the concentrations of PCDD/Fs and dl-PCBs from major sources. Such inventory data are the bases to address and reduce emission sources to reduce or prevent human exposure from food contaminated with these toxins. Despite the progress made so far, efforts are still needed to continuously and consistently monitor these unintentionally produced POPs in Africa.

The African response to the global monitoring plan under the SC

To assess the effectiveness of the SC in minimizing human and environmental exposure to POPs, the global monitoring program was established to collate monitoring data from all regions of the world. The MONET-Africa project was implemented in 2008 with fifteen (15) countries participating in the ambient air monitoring program within the region. At all sites, PCDD/PCDF were detected in the passive samples with some sites with elevated PCDD/Fs and dl-PCBs levels with the major source reported to be industry activities and open burning as seen in Table 3. In this study, the concentration of PCDD/Fs in Egypt was found to be higher than in other countries in Africa while the lowest levels were in Kenya. The high concentration in Egypt correlated well with the industrial activities' frequency of combustion and open burning in the areas (Klanova et al. 2009; Lammel et al. 2009). The seven indicator PCBs were also included in the analysis (PCB 28, PCB 52, PCB 101, PCB118, PCB 138, PCB 153, PCB 180).

The second round of analysis under the same program was performed 2010–2012, and in addition to the air samples, human milk was included. The highest levels of PCDD/Fs WHO TEQ $_{2005}$ in air samples were reported in Khartoum, Sudan, Brazzaville, Congo, and Reduit, Mauritius. Their

Table 1 Annual releases of PCDD/Fs (g TEQ/a) in different matrixes estimated using the UNEP toolkit method

Country	Annual release (g/TEQ/a)					
	Air	Water	Land	Products	Residue	Total
Algeria	14,796.25	0.35	0.92		4914.72	22,642.32
Botswana	256.83	0.047	2.599	0.092	32.315	291.883
Burkina Faso	300.329	12.551	59.689	10.7	401.5	784.769
Burundi	190.364	0		0.1	4.895	195.359
Cameroon	396.56	0.02	186.20	0.027	13.74	596.54
Central Africa	190.223	NA	NA	NA	NA	190.223
Chad	60,694.3	372.5	3.2	18.1	120.2	61,208.3
Republic of Congo	246,097	102	29,670	32	24,511	300,412
Côte d'Ivoire	417		6		0.7	432.7
Egypt	1870		100	250	650	2870
Ethiopia	153.70	3.843	5.954	29.553	21.5	214.70
Gabon	134.94	5.27	NA	NA	32.84	173.05
Gambia	107	3.96			65.4	176.36
Ghana	386	0.12	279		3.04	668.16
Guinea Bissau						2512
Kenya	2173.8	0.1	6.6	12.0	679.8	2872
Lesotho	292.3	149.1	0	2.1	1264.6	1708.1
Liberia	259.1	547.5	10	0.0	450.7	1267.3
Madagascar	119		29.6	4.7	180	334.3
Malawi	15,507.97	ND	38.8	ND	0.3958	15,547.168
Mali	34.94	0.0	0.525	2.17	1.788	39.42
Mauritania	1882.84				0.45	1883.29
Mauritius	19.59	5.41	0.32	0.50	4.58	30.4
Morocco	166.971	3.295	0.224	19.108	45.950	235.548
Namibia						176.449
Nigeria	2783.984	0.034	2521.427	0.00	34.417	5339.862
Rwanda	64.798	1.004	1.845	0.087	54.3	122.034
Senegal	147.38				267.71	417.09
Seychelles	4.1	0.0	0.0	0.1	1.2	5.4
Sierra Leone	646.16	0.09	8.00		588.01	1242.26
South Africa	708.94	2.79	64.16	30.87	1956.46	2763.44
Sudan	375	0.000	52.400	24.00	539.600	991.600
Swaziland	47.32	0.012	69.52	0.13	0.22	117.20
Tanzania	516.6892	0	181.442	0	248.4689	946.600
Tunisia	139.469	0.500	0.660	0.969	67.170	208.768
Zambia	289.7	0.0	48.4	0.0	144.9	483
Zimbabwe	186	0.27	155		1	342

Source (Stockholm Convention 2008)

sources were attributed to uncontrolled combustion processes mostly incineration at low temperature and open burning of wastes. The highest level of dl-PCBs was reported in Khartoum and Brazzaville. In human milk, all participating countries reported quantifiable levels of PCDDs ranging from 15.30 pg. g/fat to 465.16 pg/g fat. For dl-PCBs in human milk, Nigeria and Senegal reported the highest contamination while the lowest were reported in samples from Ethiopia and Kenya. In comparison with other regions worldwide, Africa's contribution of PCDD/Fs to air was reported to be the second highest, with a concentration of 51 median and 18–532 fg WHO_{98} TEQ/m^3. The first in this study was Latin America with a concentration median of 74 and a range of 9–678 fg WHO_{98} TEQ/m^3. dl-PCBs were highest in Africa at 11: 7–278 fg WHO_{98} TEQ/m^3 (Bogdal et al. 2013). Overall, the monitoring program recommended that passive air sampling is good for general monitoring of pollution. In this vein, African countries were advised to make use of passive air

Table 2 PCDD/Fs and dl-PCBs in chicken eggs from hot spot contaminated areas in Africa

Country	Concentration (WHO 1998 TEQ (pg/g fat))		Sources	References
	PCDD/Fs	dl-PCBs		
Tanzania	3.03	0.7	Absolute pesticide stockpiles	IPEN 2005d
Egypt	125.78	11.74	Metallurgical industry, uncontrolled burning of wastes and cement kilns	IPEN 2005a
Senegal	35.10	3.44	Burning of wastes in dumpsites	IPEN 2005c
Kenya	22.92	8.10	Burning of wastes in dump sites	IPEN 2005b
EU limits	3	2	Hen eggs and egg products	European Commision 2002

sampling stations for routine POPs monitoring. As a general guideline, the study also recommended that each African country should erect at least one passive air sampling station for PCDD/F monitoring in air.

Sources of dioxins, furans, and dl-PCBs

The major historic contamination source for PCDD/F were organochlorine industries and their products such as pentachlorophenol, 2,4,5-T, 2,4-D or PCBs (Weber et al. 2008). At that time, data suggested that they had exceeded releases from present-day sources. PCDD/Fs are currently classified as unintentionally produced by-products in industrial processes or through anthropogenic thermal activities except for scientific research (Breivik et al. 2004; Schecter et al. 2006). PCBs were produced as industrial chemicals from 1929 to the 1980s and used in transformers, hydraulic lubricant, plastics, and paints but can also be unintentionally produced in chemical combustion processes (Alcock and Jones 1996; Brown et al. 1995; Quaß and Fermann 1997). The major source of PCDD/Fs in Africa is open burning as highlighted in Table 1. PCDD/Fs and dl-PCBs are found in air, water, soil, products, and residues which are natural sinks of environmental toxins. It is believed globally that the main contributors of PCDD/Fs and dl-PCBs to the environment are industrial processes. Research statistics have shown that countries with high industrial and high economic activities release more PCDD/Fs and dl-PCBs to the environment (Booth et al. 2013; Dopico and Gómez 2015). After the industrial processes, residential heating and combustion of wastes are also important point sources of PCDD/Fs and dl-PCBs released to the environment. There is a relationship between economic status and release of PCDD/Fs and dl-PCBs. From literature, countries or regions with similar economic status have been observed to have similar release patterns of dioxins (Cao et al. 2013). Since most of the African countries are classified as least developed, the expectation is that the release of PCDD/Fs and dl-PCBs should be very low. PCDD/Fs and dl-PCBs in some areas though are not only contributed by effluents from nearby point sources, but tend to emanate from far-flung places. This is due to the dispersion and transportation mechanisms of PCDD/Fs and dl-PCBs which are very volatile or semi-volatile and very mobile. Africa has been observed as one of the continents that receive PCDD/Fs and dl-PCBs from as far as Europe with countries from Northern Africa such as Egypt being the most impacted (Booth et al. 2013; Dopico and Gómez 2015).

Table 3 Levels of PCDD/Fs and PCBs in Africa in passive air samples, the first regional report of the Global Monitoring Plan of the SC (January–July 2008)

Country	PCDD/Fs (pg I-TEQ/filter)		PCBs (pg I-TEQ/filter	
	Min	Max	Min	Max
Congo	6.2	9.8	6.8	16.2
Egypt	505.5	616.7	25.3	46.4
Ethiopia	1.4	4.0	1.2	2.5
Ghana	11.9	33.8	6.9	20.3
Kenya	–	0.7	0.7	71.3
Mali	1.8	1.8	0.7	26.1
Mauritius	1.0	1.2	1.1	3.5
Nigeria	2.0	9.3	1.4	12.9
South Africa	0.1	1.5	0.8	6.1
Senegal	59.2	79.4	54.3	132.9
Sudan	28.5	29.	13.8	39.2
Togo -	1.3	2.72	0.7	5.3
Tunisia	6.7	19.0	8.1	19.1
Zambia	–	1.7	1.5	7.9

Source: UNEP/GEF 2009

Studies have indicated the presence of PCDD/Fs and dl-PCBs in different sample matrices in Africa, which were attributed to industrial activities, biomass burning, transportation, household heating, discharges from cities, sewage processing, e-waste burning, hospital waste incineration, and transformer oil as shown in Table 4. The levels of PCDD/Fs and dl-PCBs in most African countries have been determined to be below the standards set by most other countries in the world such as Germany and the USA where the action level is

Table 4 Sources and concentrations of PCDD/Fs and dl-PCBs reported from different countries in Africa

Country	Concentrations	Sample matrix	Attributes (Sources)	References
Ghana	0.002–2.1 pg/g WHO TEQ PCDD/Fs d.w.	Soil	e-waste burning	(Tue et al. 2016)
Kenya	0.09–3.1 pg/g WHO 2005 TEQ PCDD/Fs d.w. 0.001–0.43 WHO 2005 TEQ	Sediments	Thermal and fossil fuel combustion	(Omwoma et al. 2015)
Algeria	16.1–152 fg TEQ/m^3	Air	Cement plant	(Khedidji et al. 2015)
Algeria	249–923 fg TEQ/m^3	Air	Industries	(Moussaoui et al. 2012)
Ethiopia	23.78 pg TEQ/g d.w.	Sediments	Sewage treatment, textile industries, household wastes	(Urbaniak and Zalewski 2011)
South Africa	0.12–32 ng WHO_{2005}- TEQ kg^{-1}, d.w. 0.34 and 20 ng WHO_{2005}-TEQ kg^{-1}, d.w.	Soil and sediments	Industrial and peoples settlements	(Nieuwoudt et al. 2009)
Egypt	1.8–38.1 pg/g fresh weight WHO 1998 TEQ	Sediments	Industries	(El-Kady et al. 2007)

d.w. dry weight

1000 ng WHO_{2005} TEQ/kg. It is worth mentioning that soil levels of PCDD/Fs have been observed to have an impact on their levels in products. For instance, in beef and chicken, if soil levels are 5 ng PCB-TEQ/kg, rearing chickens and exposing them highly to this soil could lead to even 2 ng PCB-TEQ/kg which can lead to exceedance of EU limits in meat and eggs (Weber et al. 2018).

Exposure of humans to PCDD/Fs and dl-PCBs

Although human exposure to PCDD/Fs and dl-PCBs can occur through inhalation and dermal contact, the main route is through ingestion of contaminated foods (Domingo and Bocio 2007). Since PCDD/Fs and dl-PCBs are lipophilic, the major food sources of these chemicals are fat-containing animal products (Bilau et al. 2008; Kim et al. 2013). Fish and seafood contribute the highest dietary exposure to foods followed by dairy and milk products with the third being fats and oils derived from meats although this depends on the country and food consumption habit of the people. It can also be age dependent. Fruits and vegetables contain very low amounts of these toxins (Irene et al. 2009; Loutfy et al. 2006; Perelló et al. 2015; Perelló et al. 2012; Tard et al. 2007). It is imperative therefore to monitor the concentration of PCDD/Fs and dl-PCBs in foods especially of animal origin such as eggs and fish in order to evaluate the status of these foods with respect to these toxic chemicals to humans. It has been reported that eggs can be critical indicators of PCDD/F and PCB contamination in soils and are a conduit from soil pollution to humans (Weber et al. 2015). Exposure levels can be established by determining daily intakes of PCDD/Fs and dl-PCBs through specific food substances. The dietary intake is calculated by multiplying the respective concentration of PCDD/Fs and dl-PCBs detected in food by the amount of the same food consumed by an 18-year-old adult with an average weight of 70 kg or children 6–10 years, with an average weight of 30.4 kg (Maira et al. 2012) as given by Eq. 1.

$$\text{Daily intake (pg WHO-TEQ kg-b.w.d)} = \text{Occurrence (pg WHO-TEQ w.w.) x Consumption (g/kg b.w.d)} \quad (1)$$

In Africa, few studies have reported the exposure of humans to PCDD/Fs and dl-PCBs through different foods. Most studies on the levels of PCDD/Fs and dl-PCBs in foods such as fish, eggs, and milk from Africa, were designed to determine their concentrations. Speculatively, the low number of studies that relate concentrations to human exposure could be due to lack of information on the quantity of particular food stuffs consumed by adults and children in different geographical dispositions. A few studies have reported the exposure levels and the results were below established standards such as the European Commission (EC), the Scientific Committee on Food (SCF) recommended tolerable weekly intake of 14 pg WHO-TEQ kg/b.w. and WHO tolerable daily intake of 1–4 pg TEQ kg/b.w./day (European Commission 2000; Van Leeuwen and Younes 1998). One interesting study reported results of PCDD/Fs and dl-PCBs levels in a clay soil which is consumed by pregnant women in Africa. Clay soils from more than 20 countries in Africa were screened and analyzed for PCDD/Fs and dl-PCBs. Clays from Cameroon, the Democratic Republic of Congo (DRC), Nigeria, Zimbabwe, Côte d'Ivoire, and Uganda showed positive results with a maximum concentration of 103 pg TEQ/g as seen in Table 5. With an estimated daily clay intake of 30–80 g per day of an adult of 65 kg, the exposure was found to be 33–887 pg/b.w./week. This was very high compared to the established exposure limit of 14 pg/ kg/b.w. (Reeuwijk et al.

Table 5 Human exposure to PCDD/Fs and dl-PCBs through consumption reported in Africa

Country	Concentration	Exposure level	Route of exposure	Reference
Tanzania	LOQ-20 pg bio-TEQ/g lw	6 TEQ pg/b.w./week	Chicken eggs	(Polder et al. 2016)
African Countries	103 pg TEQ/g	333–887 Pg TEQ kg/b.w./wk.	Clay soil	(Reeuwijk et al. 2013)
Uganda	0.01–0.16 TEQ/g PCDD/Fs 0.001–0.74 pg TEQ/g dl-PCBs	N.E	Fish	(Ssebugere et al. 2013)
Egypt	PCDD/Fs 240–775 pg/g f.w PCBs695–853 pg/g f.w	N.E	Fish	(El-Kady et al. 2007)
Ghana	3.4 pg WHO-TEQ/g lipid wt	N.E	Fish	(Adu-Kumi et al. 2010)
Kenya	PCDD/Fs3.35 pg TEQ/g	0.08–2.15 pg TEQ/kg-day	Dietary	(Shih et al., 2016)

N.E not established

2013). This study was very successful since it was able to link the congener patterns of PCDD/Fs in the clay soil and the patterns observed in human milk analyzed from similar countries. This study was unique in the literature available from Africa.

Accumulation of PCDD/Fs and dl-PCBs in humans

Once ingested, PCDD/Fs and dl-PCBs sequester themselves into the adipose tissue of the human body and accumulate to amounts that will be high enough to cause adverse health problems. The body burden of PCDD/Fs and dl-PCBs is transmitted through human milk, blood, and adipose tissues. The concentration of PCDD/Fs and dl-PCBs in these matrices are usually if not all the time closely similar. Human milk has been used as a matrix for biomonitoring of POPs due to its ease of availability and its high lipid content which makes the extraction of POPs easier (Djien Liem et al. 2000; Needham et al. 2010; Todaka et al. 2010; Todaka et al. 2011). WHO/UNEP have reported a series of studies on the analysis of PCDD/Fs and dl-PCBs in human milk globally from 1987 to 2010. In a study conducted between 2000 and 2003, it was reported that high levels of PCDD/Fs in human milk are found in highly industrialized countries. In the same study, Egypt was found to have a very high concentration of PCDD/Fs (14.9–51.50 TEQ pg/g fat) compared to other countries from Asia, Europe, and America (van Leeuwen and Malisch 2002). In another series of studies by WHO/UNEP which were done between 2005 and 2010, it was reported that Cote de'Ivoire and DRC had the highest levels of PCDD/Fs in human milk while Uganda and Kenya had the lowest compared to the rest of the African countries which participated (van den Berg et al. 2017). Mindful of the fact that POPs in air and human milk are used for effectiveness evaluation of the

Table 6 2005 WHO TEQ LB of dl-PCBs, PCDDs, and PCDFs in human milk

Country	Year	Concentration of dl-PCBs pg/g fat	Concentration of PCDDs pg/g fat	Concentration of PCDFs pg/g fat
Uganda	2009	0.7	1	0.5
Togo	2010	3.3	1.9	1
Sudan	2006	1.7	2.3	2.1
Senegal	2009	3.8	4.4	1.8
Nigeria	2008	2.8	1.9	1
Niger	2011	1.6	1.8	0.7
Mauritius	2009	1.1	1.9	0.6
Mali	2009	1.8	2.1	1
Kenya	2009	0.7	1.1	0.4
Cote d'Ivoire	2010	2.7	9.5	1.1
Ghana	2009	2.2	1.9	1
Ethiopia	2012	0.6	0.6	0.2
Egypt	2001	4.6	6	9.1
Djibouti	2011	1.9	3	1
DRC		1.9	11.1	0.8

Source: GMP (2015)

DRC Democratic Republic of Congo

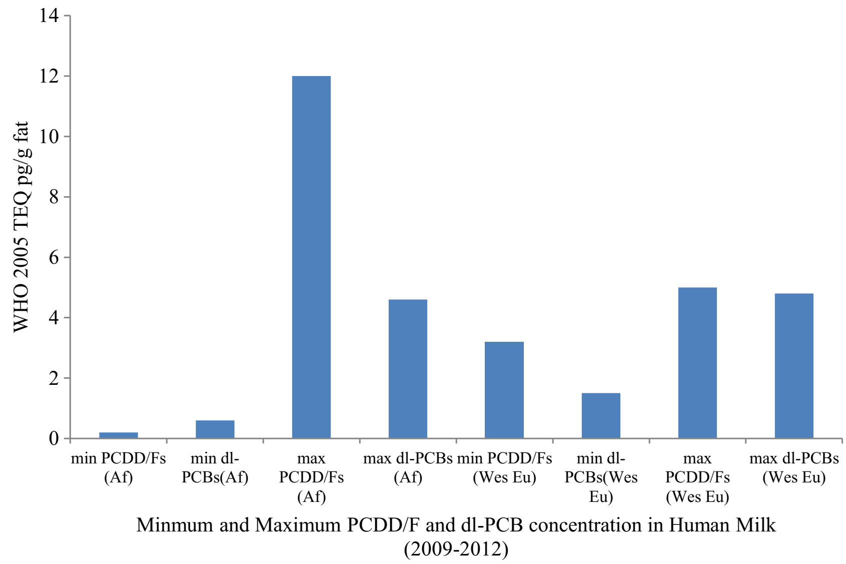

Fig. 1 Minimum and maximum levels of PCDD/Fs and dl-PCBs in human milk in 15 selected African and 5 Western European Countries between 2009 and 2012 (Af, Africa; Wes Eu, Western Europe)

SC, there was a UNEP POPs Global Monitoring Plan study that was carried out between 2008 and 2012 for PCDD/Fs and dl-PCBs in human milk for 15 African countries (UNEP – GEF-GMP 2015). The results of this study are shown in Table 6 and were presented using the 2005 WHO re-evaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds (2005 WHO TEQ LB) values for dl-PCBs, PCDDs, PCDFs, and the sum of concentrations of seven isomers of PCDDs in human milk.

From Table 6, Togo, Senegal, Nigeria, and Cote d' Ivoire had very high levels of dl-PCBs with the highest recorded in Egypt in 2002. The value for Egypt was recorded in 2002 making it lie outside the bracket years of 2008 and 2012. Uganda, Kenya, and Ethiopia had the lowest values. Overall, values for di-PCBs ranged between 0.6 and 4.6 WHO TEQ LB pg/g fat. For PCDDs, the highest levels were found in the Democratic Republic of Congo (DRC) followed by Côte d'Ivoire and then Egypt. Values ranged between 0.5 and 12 pg/g fat WHO TEQ LB. The highest PCDF values were recorded in Egypt, followed by Sudan and then Senegal, and overall, the levels ranged between 0.2 and 9.1 pg/g fat. The sum of the concentrations for seven isomers of PCDDs was highest in the DRC, followed by Djibouti and then Cote d' Ivoire and overall ranged between 15 and 465 pg/g fat (GMP 2015). It is important to note that these 15 countries represent only about 27% of the total number of countries in Africa. This is in contrast to a similar survey that was carried out between 2009 and 2012 in the most recent survey where Australia, New Zealand, Ireland, Israel, and Switzerland participated with one pooled sample per country (GMP 2015). In this same survey (GMP 2015) which was carried out in human milk, the levels of dioxin-like PCBs ranged from 1.5 to 4.8 WHO-TEQ 2005 pg/g lipid and the levels of indicator PCBs ranged from 12.0 to 78.9 ng/g lipid. The levels of PCDD/Fs ranged from 3.2 to 5.0 pg WHO-TEQ/g lipid which was ten times less than the PCDD levels. A comparison of the minimum and maximum levels of PCDD/Fs and dl-PCBs in human milk between 15 African countries and 5 Western European countries between 2009 and 2012, i.e., as discussed above is given in Fig. 1.

A direct comparison was not possible, and therefore, Fig. 1 gives a rough guide that calls for systematic studies in future where statistical considerations would level the scientific approach to the surveys. Even before the 2009–2012 study, five studies had already been carried out in Western European countries whereas this was the first GMP survey carried out in human milk in Africa. Perhaps, this underscores the need for Africa to strengthen its capabilities to monitor these toxins in human tissue, i.e., milk or blood regularly. This would compel policy makers to put in place appropriate preventive and remediation measures to prevent human exposure to the toxins. It is also clear that there is a need to investigate the public health implications of human exposure to these contaminants especially in people who live around contaminated areas. Other recent studies on the levels of PCDD/Fs and dl-PCBs blood in Africa have been reported to date albeit on a scanty level as seen in Table 7.

Table 7 Studies on the concentration of PCDD/Fs and dl-PCBs in human blood

Country	Concentration	Matrix	References
South Africa	6.9 ± 3.3 pg/g lipid	Blood	(Pieters and Focant 2014)
Ghana	2.1–42.7 pg/g lipid	Blood	(Wittsiepe et al. 2015)

Table 8 Analysis of PCDD/Fs and dl-PCBs using different methods

Sampling place	Extraction method	Analysis technique	Analysis carried out in	Reference
South Africa	SPE with disposable cartilages	GC-HRMS	Belgium	(Pieters and Focant 2014)
Uganda	Accelerated solvent extraction (ASE)	GC-HRMS	German	(Ssebugere et al. 2013)
Kenya	Accelerated solvent extraction (ASE)	HRGC-MS	German	(Omwoma et al. 2015)
Tanzania	ASE	CALUX analysis	Belgium	(Mihale et al. 2013)
South Africa	ASE	GCXGC-TOFMS & CALUX	South Africa	(De Vos et al. 2013)
South Africa	ASE	CALUX & GCxGC-μECD	South Africa	(Rimayi et al., 2016)
South Africa		CALUX &GC-MS	South Africa	(Roos et al., 2011)
Ghana	Soxhlet extraction	GC-HRMS	Japan	(Tue et al. 2016)
Egypt	ASE	GC-HRMS	German	(El-Kady et al. 2007)

Analytical methods available in Africa for the analysis of PCDD/Fs and dl-PCBs

Analytical chemistry plays an important role in the monitoring of PCDD/Fs and dl-PCBs in different environmental matrixes. Efforts have been made to develop and validate cheap and robust sensitive analytical techniques especially in developing countries for the same purpose. This is because expensive techniques such as high-resolution gas chromatography-mass spectrometry (HRGC-MS) and related hyphenated techniques are out of reach for many resource-poor laboratories (De Vos et al. 2011b). Although HRGC-MS has been recommended as the best technique for the analysis of PCDD/Fs and dl-PCBs (U.S. Environmental Protection Agency 1994; U.S. EPA 2001), it is not readily available in developing countries. As a necessity, bioanalytical techniques such as immunoassays or reporter gene bioassays have been used. Some bioassays which are relatively cheap and easy to set up such as the Chemical-Activated LUciferase gene eXpression (CALUX) (Hiyoshi Corporation 2009) and the Dioxin Responsive Chemical-Activated LUciferase gene eXpression (DR-CALUX®) cell-based assay (quantitative approach) (Scippo et al. 2004; Dorneles et al. 2014) have given results in food monitoring that were comparable to GC-MS for the detection of each congener of the 17 toxic 2,3,7,8-polychlorodibenzo-p-dioxins/furans (PCDD/Fs) and 12 dioxin-like polychlorobiphenyls (DL-PCBs). These techniques have been acknowledged in European countries and could be used as alternatives for food monitoring in Africa. Previously, bioassay methods were used in conjunction with HRGC-MS for confirmation. Confirmation was usually done where collaborative efforts were made with laboratories where HRGC-MS was available. GCXGC-TOFMS, GC-MS/MS, and GCXGC-ECD are a promising technique which is cheaper and easy to run especially in developing countries (De Vos et al. 2011a, b). GC-MS/MS has been recommended by the USEPA as a confirmatory instrument for PCDD/Fs in food matrices. However, in Africa, very few countries have used this technique for analysis of PCDD/Fs. With the effort made regionally and at national levels, the capacity for analysis of PCDD/Fs and dl-PCBs in both academic and non-academic institutions is slowly growing in Africa. The first round of the bi-annual inter-laboratory assessment of POPs was conducted from 2009 to 2011, between forty-seven (47) laboratories which reported on PCDD/Fs and dl-PCBs. Out of these 47 laboratories, only two were from Africa and among them, only one located in Egypt had access to GC-HRMS (Abalos et al. 2013). According to the bi-annual inter-laboratory assessment of POPs third round 2016/2017, a total of 175 laboratories from 66 countries participated. Among 59 laboratories which reported for analysis of PCDD/Fs, 2 laboratories were from Africa and among 56 laboratories which reported for analysis of dl-PCBs, 3 laboratories were from Africa (Fiedler et al. 2017). This shows that laboratory capacity for analysis of PCDD/Fs and dl-PCBs in Africa is increasing but at a snail's pace. Since the SC came into force in 2004, individual studies on POPs have been carried out in Africa using different analytical techniques available in and outside the continent. Table 8 summarizes studies from the literature on PCDD/Fs that have been carried out in some African countries and the analytical sample preparation and detection techniques used.

Sample preparation methods in Africa for analysis of PCDD/Fs and dl-PCBs

Dioxins, furans, and dl-PCBs are found in extremely low levels in environmental samples, so they require multiple-sample preparation steps before analysis. This process is complicated by the presence of matrix interferences which usually are found in higher abundances than the analytes of interest. PCDD/Fs and dl-PCBs are usually complex mixtures of congeners from as many as 135 dioxins, 75 furans, and 209 PCBs (Barcelo 2013). Many studies have reported the use of classical techniques such as Soxhlet extraction methods but this is laborious and time consuming and consumes a lot of solvents (Perelló et al. 2015; Tang 2013; Tue et al. 2016; Zhang et al. 2009). This is because new techniques such as ultrasonic-assisted extraction (UAE), pressurized liquid extraction, microwave-assisted extraction (MAE), and supercritical fluid extraction (SFE) are not easily accessed especially by poorly resourced laboratories (Wang et al. 2010). The modern techniques are fast and use less solvent compared to old classical extraction methods. However, African researchers collaborating with laboratories from the developed world have had access to modern sample extraction techniques as seen in Table 8.

Existing gaps

This review has shown that few studies exist on PCDD/Fs and dl-PCBs in Africa. There still is no data on PCDD/Fs and dl-PCBs in a few African countries. After the creation of SC, the emphasis was placed on intentionally produced POPs with limited studies on unintentionally produced POPs. It is speculated here that this could have been due to limited capacity both technical and human to carry out such a complex undertaking.

There has been a general lack of follow-up studies in many African countries even when a cleanup has for the contaminants has been carried out. An example to demonstrate this aspect is the study that was conducted by IPEN on the levels of PCDD/Fs in some African countries in point sources such as dump sites and absolute pesticides stockpiles. No follow-up data has been made available in the literature to date.

Studies on exposure to PCDD/Fs and dl-PCBs are scanty and in many countries not available in Africa. Analytical data for PCDD/Fs and dl-PCBs has been reported mainly on matrices such as air, soil, and sediments. Very few research groups have reported their presence in food and in humans that dwell around potentially contaminated areas. The latter data is important in order to establish public health implications of PCDD/Fs and dl-PCBs around those point sources.

Analysis of PCDD/Fs and dl-PCBs is still expensive. The instruments are out of reach for many African countries and sample preparation is laborious. There is still a lot to be done to develop the analytical capacity to achieve the desired SC goals of reduction or elimination of POPs.

Conclusion and recommendations

The detailed literature review has shown that some Parties to the SC do not have any information on PCDD/Fs and dl-PCBs in the environment. PCDD/Fs and dl-PCBs are formed as unintentional by-products of combustion so the likelihood that these toxins are present in these countries is extremely high. Thus, the SC should as a matter of urgency should be implemented in its entirety in all countries in Africa that are Parties. Since the SC became effective in 2004, impressive efforts have been made in the quest to establish the levels of PCDDs/Fs and dl-PCBs.

Literature did bring to the surface the established thresholds for PCDDs/Fs and dl-PCBs in Africa as is obtaining in other continents and more so in individual countries. It is proposed that these standards must be established either at the continental level or at country level for African countries. An encouraging outcome of this review is that levels of PCDDs/Fs and dl-PCBs are well below the recommended levels as established by other countries. As already demonstrated, most African countries had on average lower PCDD/F and dl-PCB levels in human milk compared to European countries. This is encouraging but continuous monitoring is still recommended.

Literature also did not indicate continuous and consistent monitoring of PCDD/Fs and dl-PCBs in Africa. This could be due to a lack of technical and institutional capacity. Constraints to do with equipment and infrastructure were notable in the literature. Few countries in Africa have passive air sampling stations for PCDD/Fs and dl-PCBs. However, it was not clear if these stations are accessible by different institutions and researchers to afford to monitor PCDD/Fs and dl-PCBs. There is a need to have sampling stations in every country or at least each region for joint monitoring processes. This will boost initiatives aimed at reducing emissions of PCDD/Fs in Africa.

Few studies were able to relate the concentration of PCDD/Fs and dl-PCBs in the matrix of exposure and the concentrations in the human body. These studies need to be broadened in order to establish public health implications of PCDD/Fs and dl-PCBs especially to people who live around contaminated areas.

Institutional capacities for the analysis of PCDD/Fs and dl-PCBs need to be established in Africa since literature indicated that dependency on external capacity is still rampant which makes the process expensive and difficult.

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Electronic supplementary material

Compliance with ethical standards

Conflict of Interest The authors declare that they have no conflict of interest.

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