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PCB MIXTURES IN A COMPLEX WORLD

Polychlorinated biphenyls (PCBs) in Africa: a review of environmental levels

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Abstract Several studies have shown an increase in PCB sources in Africa due to leakage and wrongly disposed transformers, continuing import of e-waste from countries of the North, shipwreck, and biomass burning. Techniques used in the recycling of waste such as melting and open burning to recover precious metals make PCBs contained in waste and other semivolatile organic substances prone to volatilization, which has resulted in an increase of PCB levels in air, blood, breast milk, and fish in several regions of Africa. Consequences for workers performing these activities without adequate measures of protection could result in adverse human health effects. Recent biodegradation studies in Africa have revealed the existence of exotic bacterial strains exhibiting unique and unusual PCB metabolic capability in terms of array of congeners that can serve as carbon source and diversity of congeners attacked, marking considerable progress in the development of effective bioremediation strategies for PCB-contaminated matrices such as sediments and soils in tropical regions. Action must be taken to find and deal with the major African sources of these pollutants. The precise sources of the PCB plume should be pinned down and used to complete the pollutant inventories of African countries. These nations must then be helped to safely dispose of the potentially dangerous chemicals.

Keywords PCBs in Africa · PCBs in e-waste · Bioremediation · PCBs waste management

Overview of sources of PCBs in Africa

Polychlorinated biphenyls (PCBs) are persistent organic pollutants (POPs) that are subject to international restrictions on usage and emissions. PCBs were manufactured and applied as flame retardants from the late 1920s until the mid-1980s, although they were also used in a multitude of other applications, particularly in electrical equipment

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(Bergman et al. 2012). They were extensively used between the 1950s and 70s for a broad range of applications such as coolants and lubricants in transformers, generators, and capacitors contained in electrical and electronic products, as well as hydraulic and heat exchange fluids because of their general chemical inertness; insulating capacity, heat stability, and low burning capacity (ATSDR 2000). They have also been used as plasticizers and sealing agents in products such as rubber and especially in polyvinyl chloride plastics used to coat electrical wiring, adhesives, paints, and inks. Although the usage of PCBs was generally banned over 30 years ago, they still exist in old electrical equipment and environmental media to which humans can be exposed. PCBs are also expected to be present in electronic waste (e-waste) streams (Menad et al. 1998).

The general population is exposed mainly via food, mostly from contaminated animal fats; two major episodes of food poisoning took place in Japan (1968), Taiwan (1979), where cooking oil was accidentally contaminated with PCBs. Indoor air can also contribute to human exposure. Worldwide monitoring programs have shown that PCBs are present in most samples of human milk. In February 2013, 26 experts from 12 countries met at the International Agency for Research on Cancer, Lyon, France, to reassess the carcinogenicity of PCBs (Lauby-Secretan et al. 2013). The working group concluded that all PCBs can induce formation of reactive oxygen species, genotoxic effects, immune suppression, an inflammatory response, and endocrine effects to various extents and through different pathways. On the basis of sufficient evidence of carcinogenicity in humans and experimental animals, the working group classified PCBs as carcinogenic to humans (group 1) (Lauby-Secretan et al. 2013).

Global production of PCBs mainly occurred in the US, Europe, and Russia, and approximately 97 % of this was used in the Northern Hemisphere, mostly between 30 and 60°N. In those areas, significant efforts have been focused to reduce sources, while monitoring campaigns have also been conducted to help identify hot spot regions. Consequently, significant reductions in atmospheric concentrations are now typically observed in the Northern Hemisphere. In parallel to the reductions in emissions of PCBs in former use regions, recent studies have recorded surprisingly high levels of PCBs far from source regions (Jaward et al. 2004; Gioia et al. 2008, 2011). High PCB levels were recorded off the West African coast on cruises on board the research vessels R/V Pelagia and R/V Polarstern in 2001, 2005, and 2008. The highest values of the seven indicator PCB congeners, namely CB-28, CB-52, CB-101, CB-118, CB-138, CB-153, and CB-180 (Σ_7PCBs), were 200 pg/m^3 in 2005 and 190 pg/m^3 in 2008, in samples collected about 400 km off the West African coast, in agreement with PCB concentrations in major US and European cities. Africa has not been a producer and major user of PCBs, and these concentrations were simply too high to be rationalized by historical usage of PCBs in Africa (Gioia et al. 2011). Emission due to fires was investigated to be a source based on satellite and polycyclic aromatic hydrocarbons data which are by-products of incomplete combustion, but fires alone could not explain these high levels (Eckhardt et al. 2007). The study clearly indicated that there are important sources of PCBs that are not accounted for in the emission inventories for West Africa. Only recently, PCB data from passive air samplers deployed on the African continent have become available. Klanova et al. (2009) reported a monthly average concentration of 100 pg/m^3 or more in urban/industrial sites in several African countries such as South Africa, Senegal, Kenya, Egypt, Democratic Republic of Congo, Ghana, Mali, and Sudan; these levels are comparable to those in US and European cities. Similar air concentrations in excess of 100 Σ_7PCBs pg/m^3 were also found in Ivory Coast and the Gambia in 2008 (Gioia et al. 2011).

Africa is second to Asia in terms of size and population. Increasing industrialization, population, urbanization, and globalization, as basis for legal and illegal imports of new and fairly used goods and wastes, has given rise to increasing concern on pollution and related issues. Emerging sources of PCBs includes (1) increasing demand for electronic equipment, increasing generation of e-waste, and subsequent illegal recycling and treatment of electrical equipment and waste incineration (Sepulveda et al. 2010; Gioia et al. 2011; Breivik et al. 2011); (2) disassembling of transformers with leaching of oil into the environment and disposal of unsalvageable parts to landfill and local vicinity (Greenpeace China, 2003); (3) open burning for recovery of valuable metals, plastic peeling and melting, melting of circuit boards over open fires, and metal extraction in acid baths (Lau et al. 2012); and (4) ship wreckage (Gioia et al. 2011).

The illegal transboundary movements of e-waste banned under the Basel Convention have also contributed significantly to the presence of POPs on the African continent. According to Pucket et al. (2002), approximately 7 million tons of e-waste was generated in the US in 1998, of which 50–80 % was exported. With relatively strict adherence to international restrictions on usage and emissions in the countries of the North and less local concern on environmental monitoring, control, and pursuance of alternatives in the countries of the South, the levels of PCBs in Africa is rising. The Stockholm convention requires all nations to establish an inventory of all POPs, including PCBs and PCB-contaminated equipment and materials. Some of the poorest nations, including a number of African countries face even more serious problems because they are a repository for hazardous waste or they engage in labor-intensive activities, such as ship dismantling. This leads to hazardous waste streams containing asbestos, PCBs, and waste oil.

Human exposure and environmental levels of PCBs

Due to the ubiquitous presence of PCBs in the environment, general routes of human exposure include contaminated outdoor or indoor air, drinking water, direct dermal contact, and food. Dismantling PCB-containing wastes could release PCBs into the atmosphere, and dioxin-like PCBs could be formed during combustion processes (Tiernan et al. 1983; Ballschmiter and Zell 1980). Therefore, inhalation is a relatively important exposure pathway, especially for e-waste workers conducting open burning activities, who may have higher possibility to be exposed to high levels of PCBs through inhalation of vapors, in addition to dermal contact (Freels et al. 2007). PCBs can bioaccumulate and biomagnify at higher trophic levels; therefore, levels in fish can be much higher than the levels in the plankton, which is at the base of the food chain. A positive relationship between PCB concentrations in human samples and dietary intake of fish and shellfish have been reported (Fitzgerald et al. 1998; Kostyniak et al. 1999; Stewart et al. 1999). Furthermore, monitoring of PCBs in food has been used to assess human exposure in a number of countries (Schecter et al. 1997; Nakata et al. 2002; Moon and Ok 2006).

Although several monitoring studies on PCBs in abiotic and biotic matrices have been conducted in the developed world, less information is available in developing countries, particularly in Africa. Rollin et al. (2009) investigated the concentrations of selected POPs in blood from delivering women in South Africa (SA). The study took place in seven geographical regions of SA, and 96 pregnant women admitted for delivery participated. Fifteen PCB congeners were analyzed in maternal placenta. Findings revealed that rural sites had the lowest levels of POPs. Levels of PCBs were found to be low in all samples and across all sites. Linderholm et al. (2010) investigated the levels and temporal trends of POPs in adults from Guinea-Bissau. Serum samples were obtained from an open cohort of police officers, and repeated samples were obtained from 33 individuals at 5 time points between 1990 and 2007, giving a total of 147 samples. Total PCB levels (CB-138, CB-153, CB-170, CB-180, and CB-187) measured between 1990 and 2007 in the study significantly decreased over time; 1990–1991 (140–310 ng/g fat), 1993–1995 (110–240 ng/g fat), 1997–1999 (110–210 ng/g fat), 2001–2003 (95–170 ng/g fat), and 2005–2007 (63–130 ng/g fat).

Bodin et al. (2011) analyzed mangrove molluscs exposed to POP contamination in Senegal for PCBs. Their findings showed significant levels of PCBs in mangrove sediments in the range 0.3–19.1 ng/g of dry weight. The investigators reported that POP levels and patterns were in good agreement with literature data available for other tropical countries of the South. Higher levels of PCBs were observed in sediments after the rainy season. Bodin et al. (2011) observed significantly higher concentrations of PCBs in shellfish soft tissues. The investigators concluded that POPs in sediments from the two Senegalese study stations would not cause toxic effects and impairments in molluscs, and that no potential risk exists for the local population via the mangrove shellfish consumption.

Studies have been conducted in Ghana using human breast milk, fish, and cow milk samples aiming to assess the levels and congener profiles of PCBs and evaluating human health risk via breast milk and fish consumption. Human milk samples (n=42) were collected from primiparous mothers in 2009 from three locations in Ghana: Accra (coastal), Kumasi (forest zone), and Tamale (savannah). Samples were taken from both urban and rural areas at each location. Twenty-five samples collected from Accra in 2004 were also analyzed to assess the temporal variation. Forty tilapia fish samples were obtained in August 2010 from some lakes and lagoons as well as an aquaculture pond. Cow milk was also sampled in March 2009 from some kraals in Accra (urban) and Asutuare (rural) (Asante 2012).

PCBs were detected in all analyzed matrices from Ghana, indicating ubiquitous contamination in the Ghanaian environment as well as human exposure to this contaminant. Total PCBs concentration (sum of 62 congeners) in all the human milk samples varied between 15 and 160 ng/g lipid weight (ng/g lw), with a mean of 62 ng/g lw (Asante et al. 2011). At the three locations, concentrations averaged 82 ng/g lw in Accra, 65 ng/g lw in Kumasi, and 30 ng/g lw in Tamale. Statistically significant differences were found between Accra and Tamale (p<0.001) as well as Kumasi and Tamale (p=0.002). The authors explained that the relatively high concentrations obtained from mothers in Accra suggest that inhabitants of Accra are more exposed, probably due to their higher preference for food and varied sources of PCBs. The food sources include fish (marine and freshwater) and fish products, meat, poultry-derived products, eggs, and milk and milk products. Although the use of PCBs in Ghana has been banned, the past use of PCB oils in transformers, electrical equipment, ship painting, and other industrial uses was common, and these are some of the sources of PCBs in Ghana. The dominant congeners in the Ghanaian breast milk were CB-153, CB-138, and CB-180 (Fig. 1). The predominance of these higher chlorinated congeners is a consequence of the increase in the accumulative properties of PCB congeners with the number of chlorine atoms on the biphenyl rings and the resulting increase in their lipophilicity. Especially, congeners having chlorines at 2, 4, and 5 positions in one or both rings were reported to have slower metabolism, which lead to their persistency and bioaccumulative properties (Chiu et al. 2004). In order to know the magnitude of contamination, the mean concentration of total PCBs in

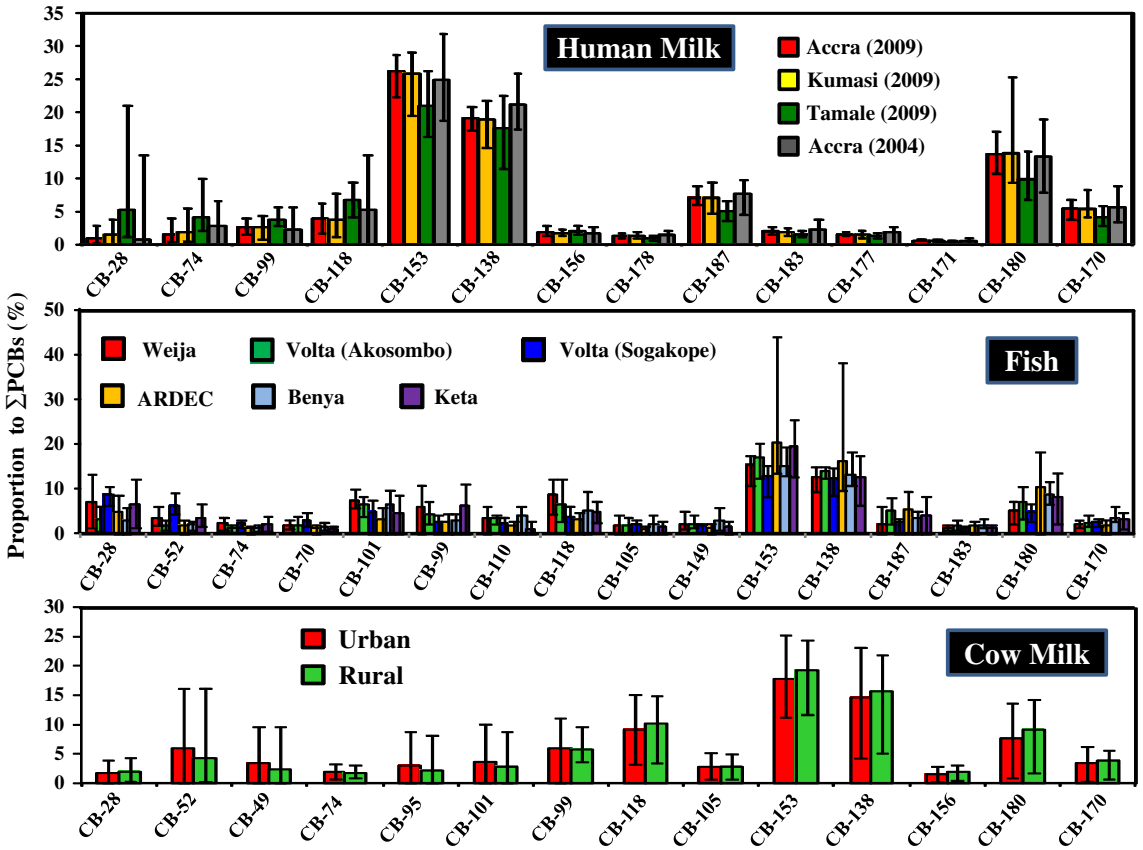

Fig. 1 PCBs congener profiles in sample matrices from Ghana (*vertical bars* show the range and mean of each congener to the total PCBs concentration). *Weija* and *Volta* are lakes, *Benya* and *Keta* are lagoons, and *ARDEC* is an aquaculture pond

human breast milk from Ghana was compared with those reported in other countries. There are only few studies reporting PCBs in breast milk from Africa, and the mean level (62 ng/g lw) in Ghana was higher than those observed in SA (10 ng/g lw; Darnerud et al. 2011) and Zimbabwe (26 ng/g lw; Chikuni et al. 1997), but fivefold lower than those reported in Tunisia (331 ng/g lw; Hassine et al. 2012). The levels were also higher than those recorded in some Asian countries but lower than levels in China, Japan, USA, and Europe (Asante et al. 2011). This indicates the necessity to extensively investigate PCBs pollution and its potential sources as well as to eliminate and properly dispose of PCBs in African countries. The total mean PCBs concentration in Accra in 2009 (82 ng/g lw) was statistically higher ($p<0.001$) than in 2004 (34 ng/g lw), possibly suggesting that PCBs increased in the Ghanaian environment within the 5-year period.

PCBs' concentrations in fish displayed a significant variation among the sampling locations. In addition to the differences in physicochemical properties of PCB congeners, different uptake and metabolic rates which is species dependent may influence the accumulation of pollutants in fish. The detection of PCBs in all the samples indicates human exposure to this contaminant via fish consumption in Ghana. Total concentration of PCBs varied between 1.1 and 300 ng/g lw, with a mean of 62 ng/g lw for all the sampling sites, with Benya lagoon being the most polluted water body (Asante et al. 2013). The predominant congeners in fish samples were CB-153, CB-138, and CB-180. Global comparison of PCBs confirms that the countries of the North were more contaminated by PCBs than the countries of the South, although comparison between results is sometimes difficult because of the variability of PCB congeners that have been analyzed in the different surveys and other differences concerning the way results were reported (i.e., wet weight, dry weight, or lipid weight). Nevertheless, the levels in fish from Ghana indicate a notable contamination by PCBs which may be associated with anthropogenic activities.

Estimated hazard quotients (HQs) (calculated as the daily intake of PCBs divided by the reference dose) via human breast milk showed that all the PCB values exceeded the threshold of one, indicating potential health risk for the newborns. On the other hand, estimated HQs through fish consumption were below one, suggesting that it is unlikely there could be a risk to human health via fish consumption. However, since some HQ values for PCBs (through fish) were close to one, and a few samples were analyzed, a continuous monitoring is warranted. As for the urban cow

milk samples, PCBs varied from 2.5–87 ng/g lw with a mean of 27 ng/g lw for the $\sum_{62}$PCBs, while the rural cow milk samples had a mean level of 14 ng/g lw ($\sum_{62}$PCB), ranging from 2.1–45 ng/g lw (Asante et al. 2010). The homologues pattern followed the order: Hexa > Penta > Hepta > Tetra, and the overall dominating congener pattern was: CB-153 > CB-138 > CB-118 > CB-180 > CB-99 > CB-52. Comparison of the cow milk results reported in other studies is limited by the few available data. $\sum_{62}$PCBs reported in Ghana exceeded levels reported for Slovenia (Cerkvenik et al. 2000), the UK (Stewart and Jones 1996), and Siberia (Mamontova et al. 2007), but it was lower than that of a Polish study (Pietrzak-Fiecko et al. 2005).

According to the report by EPA, Ghana (2007), plasticizers constitute the largest source of PCBs in Ghana with other open applications including certain paints, fire retardants, and lubricants. The report also emphasized that the main potential sources of PCB-containing applications at electric distribution networks, industrial facilities, residential, and commercial buildings were found to be transformers and capacitors in Ghana. Although it is still not confirmed, it has also been reported that PCB oils referred to as "dirty oil" finds its way into small-scale industries, where they are used to produce pomade (a greasy or waxy substance that is used to style hair) and sold on the local markets. There is also an indication that workers in some industries have been exposed to PCBs as a result of bad practices such as using empty transformer oil drums for drinking water storage. Comparing the profiles of PCBs in Ghana (Fig. 1) to the composition of the PCBs technical mixtures provided by Ishikawa et al. 2007 suggests that technical PCB mixtures (e.g., Clophen A60) have been used in Ghana. PCBs in "dirty oils" and obsolete equipment could also be potential sources in Ghana. In a related study in Ghana, Buah-Kwofie et al. (2011) determined levels of PCBs in transformer oils, and reported that the total chlorine content of the positive samples varied between 71 and 266 μg g^{-1}. Furthermore, all the samples that tested positive from the PCB test kits that were analyzed using instrumental neutron activation analysis indicated that they were PCB contaminated with total chlorine concentration above 50 μg g^{-1} based on US EPA regulations. Legislation on the importation/dumping of used electronic and electrical equipment and associated e-waste activities should be given the needed attention by African governments if the related problems of e-waste are to cease.

Aerobic biodegradation studies for PCBs in tropical regions

Microbial metabolism of PCBs is complicated because they are produced as complex mixtures, consisting of a number of congeners, which differ in the number and distribution of chlorines on the biphenyl ring. As a consequence, they pose a particularly difficult challenge to be biotransformed by microorganisms. The range of PCBs transformed by the biphenyl/PCB metabolic pathways is highly dependent upon the bacterial strain. Some organisms do not transform PCBs that contain more than three chlorines, whereas, other strains such as *Burkholderia xenovorans* LB400, *Rhodococcus* sp. RHAI, and *Alcaligenes eutrophus* H850 transform up to hexachlorobiphenyls (Bedardet al. 1987; Bedard and Harberl 1990; Seto et al. 1995). In general, the degradation rate of PCBs decreases as chlorine substitution increases, while congeners with more than five chlorine substitution are practically recalcitrant to aerobic cometabolism (Adebusoye 2006). Additionally, PCBs containing all chlorines on a single ring are generally degraded faster than those containing the same number on both rings (Furukawa et al. 1978). While this generalization holds firm for the majority of PCB-degraders isolated thus far, current studies have shown that some may not be true for newly characterized bacterial strains (Adebusoye et. al. 2007, 2008c).

After more than 30 years microbial degradation of PCBs has been investigated; scientists have only been able to isolate bacteria that are able to aerobically grow on monochlorobiphenyls (CBs) as a sole source of carbon (Abramowicz 1990; Pieper 2005; Adebusoye 2006). As a consequence, several investigators believed that only CBs function as growth substrates for aerobic organisms. Others were of the opinion that earlier claims of isolation of PCB-mineralizing or dichlorobiphenyl (diCB)-degrading organisms must be viewed as equivocal as a result of reasons highlighted by Brenner et al. (1994). Potrawfke et al. (1998) was the first to report that natural organisms (*B. xenovorans* LB400) are capable of utilizing a PCB, bearing two chlorines on one or both rings. In a parallel investigation however, Kim and Picardal (2001) documented aerobic growth of two bacterial strains, SK-3 and SK-4, isolated from a contaminated sludge on 2, 4'- and 2, 2'-diCB. In these studies the organisms exhibited a very limited range of PCB congeners used as a sole source of carbon, and the isolated strains occurred in temperate industrialized nations of the world (i.e., Europe, North America, and Japan). There is a paucity of data on the environmental fate and microbial degradation of PCBs in tropical environments especially in sub-Saharan Africa, despite the fact that environmental matrices are becoming more and more contaminated by these chemicals.

It is unlikely, however, that identical xenobiotic degrading organisms are uniformly distributed around the globe due to differing environmental conditions, soil composition, organic carbon content in soil, etc. In a review on diversity of prokaryote culture collected at the American Type Culture Collection, Floyd et al. (2005) reported that only 2.8 % of the strains

collected in the database came from Africa. Knowledge of environmental prokaryotes is clearly based on the disproportionate number of microorganisms isolated in North America (24.1 %), Europe (14.7 %), and Asia (11.5). According to Adebusoye et al. (2007), it is reasonable to hypothesize that additional bacteria with new metabolic capabilities may be present among the microbial populations of tropical soils. Adebusoye et al. (2007) was the first to isolate and characterize multiple bacterial strains, SA-1 to SA-6, capable of degrading PCBs in tropical African contaminated matrices. Molecular characterization revealed that SA-3, SA-4, and SA-5 belonged to the genus *Ralstonia*, SA-1 and SA-6 to the genus *Pseudomonas*, and SA-2 to the genus *Enterobacter*. A summary of the catabolic competences of these organisms are shown in Table 1; the isolated strains could utilize CBs used as growth substrates with the accumulation of respective chlorobenzoic acids (CBAs) as primary metabolic products, although evidences shows that CBAs may not be dead-end products of the metabolism (Adebusoye et al. 2008a). With the exception of *Pseudomonas cepacia* P166 described by Arensdorf and Focht (1994), SK-3, SK-4, and all the SA strains, no other natural organism has been described to date to utilize all CB isomers as growth substrates.

Adebusoye and co-workers (2007; 2008a; b; c) also demonstrated that the organisms were capable of metabolizing more extensively diCBs substituted on both rings than those substituted on one ring. For instance, 2, 2'-, 2, 4'-, and 3, 3'-diCB were degraded more extensively than 2, 3-diCB or 3, 5-diCB. It is also interesting to note that the organisms show extensive dissimilation of PCB congeners substituted at the *ortho* position of one ring or both rings; a degradation pattern that many confer resistance to aerobic degradation via 2, 3-hydroxylation; a clear deviation from popularly held views (Furukawa et al. 1978; Abramowicz 1990; Dai et al. 2002). The uniqueness and the most fascinating properties of three of the tropical strains, SA-4, SA-5, and SA-6 is their unusual *ortho*-substituted trichlorobiphenyls (triCBs) (substituted on both rings) catabolic functions (Adebusoye et al. 2008c). Growth could not be sustained on triCBs isomers containing chlorines on only one ring. It is noteworthy that the group of triCB isomers (i.e., 2, 2', 4-, 2, 2', 5-, and 2', 3, 4-triCB) utilized by the three strains are cometabolically poorly degraded by most bacterial strains so far characterized (Furukawa 1982; Maltseva et al. 1999). Although a mass balance of products was not obtained, production of 2, 4-diCBA and 2, 5-diCBA together with the lack of 2-CBA recovery suggest growth at the expense of the 2-chlorophenyl ring. In addition, the concentration of chloride recovered from the culture media (Table 1) was approximately equal to the triCB transformed which also suggested dechlorination, and perhaps mineralization, of the least substituted ring.

Table 1 Comparison of the PCB-metabolic competence of bacterial strains isolated from African contaminated soils

PCB congener[a]	SA-2			SA-4			SA-5			SA-6		
	% Degradation	% CBA recovered	% Cl⁻released[b]	% Degradation	% CBA recovered	% Cl⁻released	% Degradation	% CBA recovered	% Cl⁻released	% Degradation	% CBA recovered	% Cl⁻released
2-CB	96±5	34±2.7 (2-CBA)	27±13.6	99±1.2	34±5.7 (2-CBA)	39±2.3	88±16	22±16 (2-CBA)	14±6.8	94±1	20±8.8 (2-CBA)	50±22.7
3-CB	91±7.5	30±8.2 (3-CBA)	0	97±1.3	19±2.6 (3-CBA)	29±5.7	86±9.2	64±19 (3-CBA)	23±14.3	93±7.7	6.4±2 (3-CBA)	14±2.9
4-CB	88±9.1	98±5.3 (4-CBA)	0	97±1.3	73±13 (4-CBA)	0	98±1.4	92±52 (4-CBA)	0	90±6.3	85±13 (4-CBA)	0
2,3-diCB	69±12.3	82±11.7 (2,3-CBA)	3±0	84±3.8	71±10.1 (2,3-CBA)	7±0	65±4.1	92.8±37.6 (2,3-CBA)	6±4.1	68.5±17.3	96.3±1.4 (2,3-CBA)	3±0
2,2'-diCB	92±8	45±4.3 (2-CBA)	13±0	95±4.8	98±18 (2-CBA)	63±26.3	96±4.5	65±13.5 (2-CBA)	22±3.9	86±5.6	93±38 (2-CBA)	63±13.2
2,4'-diCB	100±0	45±13 (4-CBA)	58±0	97±1	7±4 (4-CBA)	26±12.8	97±0.1	74±32.9 (4-CBA)	4±1	97±4.2	47±22 (4-CBA)	26±0
3,3'-diCB	N/A[b]	N/A	N/A	84±1.3	64±3.5 (3-CBA)	41±5.3	89±6.1	36±23.8 (3-CBA)	26±11.2	89±1.6	40±3.9 (3-CBA)	20±2.6
3,5-diCB	N/A	N/A	N/A	90±7.5	21±3.8 (3,5-CBA)	0	N/A	N/A	N/A	91±2.5	100±17.1 (3,5-CBA)	0
2,2',4-triCB	N/A	N/A	N/A	71±2.4	23±7.1 (2,4-CBA)	23±2	81±7.8	4±2.5 (2,4-CBA)	11±1	86±3.2	70±15 (2,4-CBA)	28±3
2,2',5-triCB	N/A	N/A	N/A	79±9.4	64±7.3 (2,5-CBA)	26±2.9	85±1.8	105±2.7 (2,5-CBA)	29±4.3	93±3.2	62±19.4 (2,5-CBA)	30±1.4
2',3,4-triCB	N/A	N/A	N/A	93±5.5	78±14 (3,4-CBA)	25±1.2	93±5.5	74±8.3 (3,4-CBA)	21±4.8	79±1.5	66±2.8 (3,4-CBA)	26±1.2

N/A not applicable

[a] Data were compiled from Figures and Tables from Adebusoye et al.2007; 2008a; b; c; d

[b] Determined on the basis of the expected amounts of chloride if the congener were to be totally mineralized

Ilori et al. (2008a, b) were able to isolate an additional PCB degrading strain, *Achromobacter xylosoxidans* IR08, from the same site, where strains SA-2, SA-4, and SA-6 were obtained. The catabolic functions of this organism appear to be similar to other isolated strains in its ability to grow on all three CBs. However, it differs not only in its capacity to mineralize all CBs but also in the utilization of 4, 4'-diCB without noticeable production of respective CBA metabolites. Furthermore, strain IR08 also demonstrates a rare and quite unusual metabolic functionality, in that its growth was poorly supported by biphenyl and benzoate. It shows that chlorine substitution rather than impeding growth obviously aided it. Significantly, the findings show that the enzymes of both the upper and lower chlorobiphenyl pathways were particularly evolved to metabolize substituted compounds at the expense of their unsubstituted analogs. This inference is further reinforced by the data obtained during simultaneous adaptation experiments (Ilori et al. 2008b). It is apparent, therefore, that enzymatic reactions other than those widely reported for PCB-degrading organisms are likely to occur in IR08. According to these authors, such catabolic anomalies have implications in the evolution of catabolic pathways. The acquisition of simple dehalogenation steps to convert xenobiotic compounds to their nonhalogenated derivative may not be the primary mode of evolution of pathways for the biodegradation of such compound as believed by several workers (Janssen et al. 1994; Abraham et al. 2002).

Overall, the metabolic properties of strains IR08, SA-2, SA-3, SA-4, SA-5, and SA-6 are quite remarkable. It is likely that these strains use new catabolic pathways, possess a greater ability to attack chlorinated rings without steric hindrance, have a reduced level of enzyme specificity or otherwise differ enzymatically from other reported PCB degraders. The elucidation of the biochemistry and genetics of PCB metabolism in these organisms will determine the factors responsible for their substrate versatility. The mode of regulation of various biocatalytic reactions and their genetic structure leading to their diversities or similarities will provide some common denominators affecting the evolution of these new catabolic functions and give essential information for engineering of organisms with even greater degradative competence.

Application of bioremediation technique for PCB-contaminated systems in tropical regions

The difficulties of microbial degradation of PCBs originate from the requirement of a nonchlorinated ring for microbial growth, the incompatibility between biphenyl degraders and chlorobenzoate degraders, and the biodegradability of recalcitrant *ortho*-chlorinated di- or trichlorobiphenyls as well as highly substituted congeners. Bearing this in mind, it is not surprising that effective bioremediation strategies have not yet been developed for PCB-polluted matrices despite the extensive body of knowledge on microbial degradation of PCBs. Nearly 80 % of studies on PCB degradation focus on aerobic metabolism, but the largest reservoir of PCBs in lakes and rivers are anaerobic sediments, which are not suitable for the growth of aerobic microorganisms. Effective microbial transformation of PCBs in these matrices can only occur through anaerobic reductive dechlorination processes. Consequently, the use of a sequential anaerobic–aerobic treatment has often been proposed as a potential bioremediation strategy for treatment of PCB contaminated sites (Abramowicz 1990; Tiedje et al. 1993; Adebusoye et al. 2008c; Bedard 2008). An anaerobic treatment would be used to reductively dechlorinate highly substituted congeners. The lightly chlorinated congener products would then be degraded aerobically. One difficulty associated to this sequential treatment is that aerobic biodegradation is thought to require a primary growth substrate, e.g., biphenyl, as it has been generally believed that congeners containing more than one chlorine cannot serve as an aerobic growth substrate and must therefore be cometabolically degraded. This presents additional problems as biphenyl is expensive, difficult to disperse throughout a contaminated matrix, and can be subject to regulatory restriction (Adebusoye et al. 2008c).

Similarly, most reports on aerobic degradation of commercial mixtures of PCBs recorded extensive degradation of the mixtures only in the presence of biphenyl as an inducer of the 2, 3-biphenyl dioxygenase (Baxter et al. 1975; Bedard et al. 1987; Seto et al. 1995). Because of their abilities to attack a wide range of PCB congeners, strain LB400 and RHA1 are two of the more promising strains that have been advocated for use in the aerobic stage of a PCB biotreatment process. However, owing to the problems of biphenyl amendment and their limited ability to grow on PCBs, repeated additions (bioaugmentation) would be required for such biotreatment. The use of aerobic tropical strains described by Adebusoye et al. (2007, 2008a, b, c, d) might therefore be excellent candidates compared to LB400 or RHA1. These strains are able to utilize four dichlorobiphenyl isomers as growth substrate including those chlorinated on one ring i.e., 2,3-, 3,5-diCB, and those with chlorine substitution on both rings i.e., 2, 2'-, 2, 4'-, and 3,3'-diCB relatively rapidly. In addition to these congeners, 2, 2', 4, 2, 2', 5-, and 2', 3, 4-triCB as well as all three monochlorobiphenyls can also serve as growth substrates. Data obtained from a parallel study (Adebusoye et al. 2008d) showed these organisms hold good promise for use in the aerobic stage of the sequential anaerobic–aerobic treatment for PCB contaminated systems. Although their effectiveness in a contaminated soil as bioaugmentation candidates remains to be ascertained, the strains exhibited superior degradation in terms of total transformation, transformation of

Table 2 Analysis of the transformation of Aroclor 1242 components by bacterial strains isolated from African contaminated soils

			Percent degradation[a]							
			SA-2		SA-3		SA-5		SA-6	
Peak no.	No. of chlorine	Congener assignment	Without biphenyl	With biphenyl	Without biphenyl	With biphenyl	Without biphenyl	With biphenyl	Without biphenyl	With biphenyl
[1]	1	3	67.5 (46.2)	98.5 (7.5)	100 (0)	100 (0)	71.0 (20.4)	70.5 (12.5)	100 (0)	100 (0)
[2]	1	4	41.3 (3.9)	100 (0)	40.3 (12.4)	100 (0)	100 (0)	100 (0)	100 (0)	100 (0)
[3]	2	2,2'; 4,4'	92.3 (3.4)	73.9 (9.3)	82.1 (10.6)	70.4 (17.8)	77.1 (17.3)	86.0 (4.0)	34.0 (8.0)	85.3 (1.4)
[4]	2	2,5; 2,4	87.2 (11.2)	81.0 (10.7)	100 (0)	100 (0)	–[b]	–	27.1 (11.5)	89.6 (16.8)
[5]	2	2,3'	91.7 (1.7)	78.8 (15.8)	80.2 (11.5)	70.3 (16.0)	91.9 (1.5)	89.4 (4.2)	26.5 (12.6)	90.6 (6.5)
6	2	2,4'; 3,4	94.6 (1.6)	80.3 (18.0)	–[b]	–	93.7 1.3)	92.5 (4.6)	33.1 (11.5)	88.6 (2.0)
7	2	2,3; 2,6	96.4 (1.9)	94.0 (3.3)	82.7 (15.0)	54.7 (10.8)	98.9 (1.4)	89.7 (7.3)	95.0 (2.5)	88.0 (1.5)
8	2, 3	2,2',4	92.6 (0.9)	75.9 (20.4)	81.1 (8.5)	70.5 (15.6)	89.6 (2.8)	87.5 (4.6)	37.1 (12.3)	87.9 (3.3)
9	2, 3	3,3'; 2,4,6	100 (0)	75.0 (15.3)	9.3 (3.5)	56.2 (1.1)	100 (0)	82.7 (24.5)	33.1 (10.5)	81.8 (15.8)
11	3	2,'2,5	66 (6.4)	68 (10.5)	36 (3.4)	63 (12.5)	98.1 (14.3)	76.2 (6.7)	31.4 (10.9)	77.4 (4.3)
12	3	2,3',6	94.3 (1.2)	88.0 (5.2)	80.8 (15.1)	65.4 (14.3)	91.0 (2.5)	88.4 (5.3)	37.5 (12.8)	84.6 (5.2)
14	3	2,2',3	91.4 (2.0)	76.6 (19.7)	81.2 (11.0)	70.5 (16.7)	90.0 (2.6)	87.2 (4.8)	28 (13.0)	87.8 (3.7)
15	3	2',3,5	94.1 (1.0)	88.5 (4.3)	81.2 (14.5)	66.7 (13.8)	91.3 (1.8)	87.9 (5.1)	35.8 (13.2)	86.8 (4.9)
16	3	2,3,4	94.0 (10.4)	75.8 (16.3)	85.7 (9.2)	72.5 (9.0)	100 (0)	100 (0)	33.6 (15.4)	87.4 (4.3)
17	3, 4	2,4,5; 2,2',4,6	53.1 (7.3)	49 (4.1)	63.6 (17.3)	69 (15.1)	69.8 (11.1)	71.1 (15.6)	19.7 (9.3)	67.2 (5.8)
18	3	2,3'4	95.0 (0.8)	90.2 (2.9)	83.6 (11.5)	70.8 (12.5)	92.7 (2.0)	89.4 (4.7)	17.1 (10.3)	89.2 (3.6)
19	3, 4	2,4,4'	94.1 (0.8)	78.5 (21.1)	83.8 (10.6)	72.0 (12.3)	92.2 (2.1)	89.8 (4.8)	17.3 (5.0)	89.8 (3.4)
20	3	2',3,4; 2,3,3'	91.8 (0.2)	74.8 (22.3)	–	–	90.3 (2.4)	96.8 (9.4)	15.5 (8.9)	85.7 (4.8)
21	3	2,2',3,6	96.0 (0.7)	89.0 (3.2)	82.6 (16.1)	66.6 (12.9)	94.8 (1.2)	88.7 (5.5)	44.5 (7.6)	86.8 (4.6)
22	3, 4	2,2',3',6	91.2 (0.7)	71.8 (19.6)	71.3 (14.7)	72.1 (11.3)	89.6 (2.5)	83.3 (4.2)	38.6 (12.1)	80.4 (2.2)
23	3, 4	2,2'5,5'; 2,3',6,5'	93.9 (0.2)	90.1 (2.3)	82.2 (11.5)	69.8 (12.4)	91.3 (2.2)	85.5 (6.1)	39.6 (11.4)	88.7 (4.0)
24	4	2,2',4,5'	53.6 (4.1)	67 (12.3)	–	–	80.3 (6.8)	81.0 (12.2)	–	–
25	4	2,2',4,4'	–	–	55.1 (7.4)	63.2 (15.3)	91.6 (12.4)	83.1 (10.2)	24.6 (5.1)	79.3 (11.5)
27	3, 4	3,3',4	92.1 (1.4)	86.3 (3.4)	80.3 (11.2)	67.4 (12.7)	90.2 (2.3)	85.7 (4.6)	42.1 (8.2)	85.7 (4.4)
28	4	2,2',3,6	91.4 (1.4)	86.4 (3.0)	80.2 (10.7)	67.9 (12.5)	90.0 (2.4)	85.3 (4.5)	42.1 (16.5)	86.0 (4.2)
30	4	2,2',4,5	93.4 (0.3)	74.5 (17.2)	80.3 (12.7)	67.8 (14.8)	90.4 (2.0)	86.0 (5.1)	14.2 (9.9)	85.7 (5.0)
32	4	2,2', 3,5'	45 (3.2)	57.2 (11.2)	67.9 (11)	57.4 (11.4)	–	–	18.4 (6.7)	60.3 (10.4)
34	3, 4	3,4,4'; 2,2',3,4'	52.5 (13.2)	53.2 (6.2)	74.3 (15.1)	72.2 (16.6)	84.1 (7.4)	86.1 (4.3)	19.5 (3.2)	66.7 (11.5)
35	4	2,2'3,5'	92.5 (1.4)	88.4 (3.4)	82.1 (10.6)	67.9 (9.2)	91.6 (2.1)	87.3 (4.7)	25.3 (7.6)	87.7 (4.3)
36	4	2,2',3,4	67.2 (10.6)	60.3 (9.5)	59.3 (5.5)	53.4 (3.6)	83.0 (4.8)	86.1 (9.1)	23.7 (9.7)	76.5 (13.2)
37	4	2,2',3,3'	65.3 (15)	63.4 (6.6)	61.3 (11.5)	56.4 (4.6)	–	–	27.8 (8.2)	71.5 (7.1)
38	4	2,4,4',5	91.5 (0.1)	87.8 (2.3)	81.1 (10.8)	68.3 (12.7)	91.0 (2.0)	86.1 (4.8)	41.8 (11.5)	86.8 (4.4)
39	4	2,3',4',5	91.7 (0.3)	75.5 (18.7)	66.5 (14.2)	71.3 (15.2)	90.2 (2.1)	87.3 (6.5)	21.2 (8.4)	85.5 (4.8)
41	4	2,3',4,4'	67.8 (6.3)	65.3 (13.1)	56.1 (6.4)	53.3 (4.4)	80.4 (3.4)	82.0 (11.1)	18.4 (7.6)	70.5 (6.8)
43	4, 5	2,2'3,4',6	91.7 (0.1)	76.6 (19.9)	–	–	91.3 (2.0)	90.8 (13.3)	18.3 (8.0)	86.9 (4.1)

Table 2 (continued)

Peak no.	No. of chlorine	Congener assignment	Percent degradation[a]							
			SA-2		SA-3		SA-5		SA-6	
			Without biphenyl	With biphenyl	Without biphenyl	With biphenyl	Without biphenyl	With biphenyl	Without biphenyl	With biphenyl
45	4, 5	2,2',4,4',5	47.9 (11)	47.4 (6.4)	50.5 (7.3)	51.2 (8.1)	–	–	15.1 (3.1)	73.4 (15.3)
46	5	2,2',3',4,5	87.2 (6.3)	72.8 (15.3)	73.1 (13.2)	69.4 (11.2)	89.0 (1.3)	91.3 (4.5)	19.5 (3.0)	83.7 (1.8)
47	4, 5	2,2',3,4,5'	72.3 (41.2)	59.4 (21.5)	90.3 (13.7)	77.6 (19.7)	100 (0)	92.9 (6.5)	31.2 (10.9)	78.8 (16.9)
48	5	2,2',3,4,4'	50.0 (21.1)	50.0 (13.3)	50 (9.3)	50.0 (5.7)	50 (3.9)	86.8 (3.6)	80.0 (0)	50.0 (13.9)
50	4, 5	3,3',4,4'; 2,3,3',4',6	43.8 (7.6)	46.2 (10.2)	60 (12.3)	61.0 (10.7)	–	–	34.3 (5.0)	50.1 (11.2)
52	5	2,2',3,3',4	91.2 (0.3)	85.8 (1.9)	80.9 (10.7)	67.0 (11.6)	91.1 (1.9)	85.5 (4.6)	15.8 (9.6)	85.1 (4.2)
53	4, 5	2,2',3,5,5'6	45.4 (9.7)	50.2 (11.1)	62.1 (5.5)	73.7 (14.6)	62.3 (11.3)	79.3 (6.4)	–	–
55	5	2,2',4,4'5,5'	40 (4.3)	37.2 (5.5)	57.2 (10)	55.2 (10.5)	63.1 (15.1)	81.1 (9.8)	–	–
56	5, 6	2,2',3,3'4,6	87.0 (1.1)	63.5 (21.4)	75.7 (10.7)	67.5 (18.1)	92.6 (6.8)	80.8 (2.9)	21.8 (10.9)	79.5 (6.2)
57	5, 6	2,3,3',4,4'; 2,2',3,3',4,6'	91.2 (0.4)	86.1 (1.8)	80.8 (10.1)	72.0 (15.6)	91.3 (2.0)	85.6 (3.2)	33.2 (12.7)	85.2 (4.4)

[a] Data are compiled from Adebusoye (2006) and Adebusoye et al. (2008d)

[b] Peaks that were not reproducible from one GC run to another

specific congeners, and diversity of congeners attacked (Table 2).

In addition to the above difficulties, anaerobic–aerobic treatment is also impeded by the chemical physicochemical characteristics as well as various microbiological factors. With the exception of few cases, reductive dechlorination of PCBs rarely occurs at the *ortho* positions, thus, resulting in the accumulation of *ortho*- or *ortho*- and para-substituted congeners (Bedard et al. 1987; Furukawa 1982; Abramowicz 1990; Bedard 2008). Unfortunately, ortho-substituted congeners are known to elicit a wide range of toxic responses (van der Plas et al. 2000) and are also often resistant to chemical and aerobic (bio)degradation (Dai et al. 2002). While this could pose a formidable metabolic challenge to the well-characterized temperate PCB degraders such as LB400, H850, and RHA1, recent findings have revealed that SA strains particularly SA-4, SA-5, and SA-6 have the requisite enzymic and genetic machineries to handle this group of congeners either as growth substrates or cometabolically. Studies further indicated that the presence of chlorine at the ortho positions of those congeners analyzed did not result in obvious patterns of recalcitrance.

Concluding remarks

There are indications of continuing shift in primary emission sources of PCBs from source regions to the countries of the South such as Africa, where PCBs have not been produced and used. This is supported by PCB levels in abiotic and biotic matrices in Africa, which clearly show an increase of PCBs concentrations during the last 5–10 years, suggesting potential health risks especially for the newborns. Major sources of PCBs in Africa include transformers, continuing import of e-waste from the countries of the North, shipwreck, and biomass burning. Little remains known about the amounts of PCBs exported outside former use regions as different types of wastes because of the often illicit nature of these operations. This can result in a challenge for global emission inventories and control strategies. More research is needed to investigate how much of the reduction of PCBs in former use regions is occurring at the expense of countries receiving PCBs as obsolete products and wastes such as Africa. Further efforts are needed to mitigate the export of obsolete products and waste from the countries of the North to the countries of the South as well as sound waste management and solution for elimination and remediation of PCBs from the environment in Africa.

A first step in managing such waste is identification, marking, and safe storage. Identification and marking require preliminary analysis, to establish the status of the waste, while safe storage involves containment, i.e., using marked and closed containers, as well as impervious floors

and treatment of exhaust air, to remove PCBs as well as diluents. PCBs proper are generally eliminated by incineration in adequately equipped and duly licensed incinerators. Incineration is also applied to PCB-contaminated paper, rags, pastes, paints, and plastics. PCB waste can be disposed of by a variety of methods, such as chemical landfill or incineration.

The isolation of tropical strains has shown that they exhibited a high degradation capacity of PCBs in terms of total transformation, transformation of specific congeners, and diversity of congeners attacked. The successful characterization of strains IR08 and SA from African contaminated soils is an indication that diCBs or triCBs utilizing bacteria may be more widely distributed than previously believed, and that novel or more extensive metabolic pathways may be evolving in response to selective pressure of long-term exposures. Harnessing this microbial expansion will greatly improve the understanding of the breadth of PCB-metabolic capability that exists naturally. This improvement will doubtlessly prevent accumulation of *ortho*-substituted congeners in natural systems and offer the hope for development of effective sequential anaerobic–aerobic biotreatment techniques. Successful application of this sequential treatment may enable the cleanup of all types of PCB contamination in soil and sediments in Africa and worldwide.

The threat that PCBs pose to the environment and the fragile health of Africans is a real problem and may become overwhelming in view of prevailing poverty, poor resource allocation and management, strive, and lack of vital infrastructures. Africa needs all the help it can get from developed nations in order to make appreciable progress and success in the race to reduce the sources of PCBs and POPs in general. The buildup of PCBs in the continent will significantly add to the disease burden with consequent hindrance of the desired economic and social development. The individual has little control over this type of exposure. This is where governments and international forces come into play. It is therefore suggested that a concerted effort is put in place by governments in Africa in conjunction with nongovernmental organizations, civil society, and relevant international organizations to facilitate and sustain public awareness on PCBs and potential for adverse effects on human health and the environment, enhance capacity for monitoring and enforce effective regulations for the use and disposal of old legacy and new toxic chemicals.

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