Atmospheric Polychlorinated Naphthalenes in Ghana

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ABSTRACT: A nationwide monitoring of atmospheric POPs (persistent organic pollutants) was conducted in Ghana between May and July 2010, applying polyurethane foam (PUF) disk passive air samplers (PAS). Reported here are preliminary findings on PCNs, an industrial organic contaminant currently under review for possible listing under the global chemical treaty. The present results constitute the first set of nationwide data on air PCNs from a West African country. Contrary to expectation, air PCNs levels were quite high in Ghana, at an average of 49 ± 5.4 pg/m³. The coastal (southern) zone of Ghana appeared the most impacted, with crude open burning of waste, industrial emissions, and the harbor environment identified among possible emission factors. Tri- and tetra-CNs (the lowly chlorinated homologues) predominated in the atmosphere, altogether constituting approximately 90% of total PCN homologues composition. Increased volatilization under tropical conditions was presumed a key factor that contributed to this high atmospheric input of lowly chlorinated homologues. We further observed a significant level of fractionation of PCN homologues across the breadth of the country. The percentage composition of the lowly chlorinated homologues increased northwards, probably because of their transportation in the direction of prevailing winds. From congener profile analysis, PCN-45/36 is proposed as a possible source marker for emissions preempted by uncontrolled waste burning activities. Dioxin-like toxicity of air PCNs in Ghana was estimated to range 0.49–5.6 fg TEQ/m³. This study brought to the fore the emerging problems of nonagricultural organohalogens that covertly might be confronting the environment in African nations like Ghana.

INTRODUCTION

Persistent organic pollutants are a group of organohalogens considered undesirable in the environment because of their high level of persistence, toxicity, and bioaccumulativeness. Emissions of POPs have been reported at various sites in the world, from the tropics to polar regions.¹⁻⁴ They are distributed partly by long-range atmospheric transport (LRAT), hypothesized to occur in a grasshopper-like fashion.⁵,⁶ Notable sources of POPs in the environment can be categorized into three—agricultural, industrial, and unintentional formation. For most African countries, much of the information available on POPs concerns residues from agrochemicals such as DDT, endosulfan, hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), dieldrin, etc.,⁷⁻¹¹ perhaps a reflection of the agricultural-base economy operated in many African countries. On the contrary, information is scanty on POPs generated from industrial sources or by unintentional formation in Africa. The few studies conducted so far nevertheless suggest that these categories of POPs are of contemporary relevance in African countries.¹²⁻¹⁶ In the West African region, emissions of polychlorinated biphenyls (PCBs) for instance were recently reported to be relatively high, a situation blamed on factors such as illegal dumping of PCB containing wastes, uncontrolled burning of wastes, and the breakup of old ships.¹² Analysis of human breast milk from Ghana for certain organic contaminants has further revealed impacts from industrial organohalogens such as PCBs and polybrominated diphenylethers (PBDEs), which otherwise have no known production or usage history in Ghana.¹⁶

Polychlorinated naphthalenes (PCNs) remain one of the least scrutinized organohalogens on the continent of Africa. PCNs constitute a complex mixture of 75 congeners, some of which are planar in structure with similar biochemical toxicity behavior as polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDDs/PCDFs) and coplanar PCBs.¹⁷⁻²¹ PCNs are currently under review for possible listing under the global chemical treaty. They were initially manufactured as high volume chemicals under various trade names such as Halowax (in Japan), Nibren wax, Perna wax, and Basileum (all in
Germany), Seekay wax (in Great Britain), Clonacire (in France), Cerifal materials (in Italy), and N-oil and N-wax (in the USA) have been used as insulators, lubricants, dielectrics, flame-retardants, plasticizers, etc. However, since the 1970s to 1980s, most countries voluntarily avoided production and new application of PCNs formulations, in response to the environmental health dangers that later became associated with these compounds. PCNs nevertheless continue to be detected in the environment. Industrial combustion and waste incineration are key source factors identified in the contemporary emissions of these compounds. A variety of pathways have been suggested for combustion byproduct PCNs. These include chlorination of already present naphthalenes, de novo synthesis from polycyclic aromatic hydrocarbons (PAHs), and chlorophenol condensation. The mechanisms involved are thought to be closely linked to PCDDs/PCDFs formation. In 2001, elevated levels of air PCNs were picked up from locations off the coasts of West and South Africa. This is the most significant detection of air PCNs closest to the African continent. Although precise sources were not fully resolved, these pollutants might have emanated from countries bordering the west and south coasts of Africa in taking into consideration the movement directions of air mass which reached the respective offshore sampling locations. Presumably, there are hotspots of PCNs emissions in certain African countries that should be investigated. These may arise as combustion byproduct or from toxic wastes exported to the continent. Both issues constitute grave environmental challenges in Ghana. For instance, substantial amount of the municipal solid waste (MSW) generated in Ghana is burnt uncontrollably in the open at waste dumpsites, as incineration and proper landfill facilities are lacking. Putrescible fractions, plastics, metals, papers, etc. in the waste stream are all burnt together. Potentially, this could generate unintentional POPs. On the issue of e-waste, Ghana and indeed many African countries have the unenviable status of ranking among the major dumping grounds in the world. Various toxics contained in obsolete electronics and gadgets and industrial wastes continue to be illicitly shipped to developing countries from rich nations. Parallel with this, might be a shifting of POPs burden from industrialized nations to poor ones. The quantum of e-waste that reaches the shores of Africa is difficult to quantify. Conservative figures from Nigeria however suggest that a volume of e-waste equivalent to about 100,000 computers or CPUs or 44,000 Cathode Ray Tube TVs enter Africa through Nigeria alone each month. The estimate for Ghana, we assume, is not any less. The environmental risk associated with e-waste in Ghana is compounded by the crude means of retrieving various valuable metals from these obsolete gadgets. Metal wires retrieved from e-wastes are usually burnt to remove their polyvinyl chloride (PVC) protective covering. These activities are accompanied by lots of emissions into the atmosphere, some of which may be toxic. Presumably, old POPs contained in some of these e-wastes could be released or unintentional ones could be formed.

In this report, we focused on atmospheric contamination from PCNs in Ghana, considering the contemporary and future relevance of this group of pollutants as POPs. The spatial distribution of air PCNs was highlighted for the first time across the country. Pertinent source factors of ambient PCNs were subsequently characterized and the extent of dioxin-like toxicity by PCNs estimated.

**MATERIALS AND METHODS**

**Study Area, Sampling Process, and Pretreatment.** The study was conducted in Ghana deploying polyurethane foam (PUF) disk passive air samplers (PAS) at 13 sites across the country (Figure 1). The PUF disk PAS has been described elsewhere. They were deployed continuously for 8 weeks, starting in May 2010. The exact start date though varied slightly from site to site, as it took different traveling days to reach the various sites spread across the country, some very remotely located. The first sampler was deployed 5th May, 2010 and final...
pm 3, with a mean value of 0.01 and standard deviation. For 24 different congeners/coeluents quantified as the mean congener concentration plus three (MDLs) were derived from laboratory blank PUFs and particular congener in trace amount. Method detection limits discarded but considered as indicating the presence of a of retention time and fair height above noise level, were not discarded but considered as indicating the presence of a particular congener in trace amount. Method detection limits (MDLs) were derived from laboratory blank PUFs and quantified as the mean congener concentration plus three times standard deviation. For 24 different congeners/coeluents measured in blanks, the MDLs ranged between 0.001 and 0.03 pg/sample, with a mean value of 0.01 and standard deviation 0.008 pg/sample.

**RESULTS AND DISCUSSION**

**Spatial Distribution of Atmospheric PCNs in Ghana.** Table S2 shows air PCN congener concentrations at various locations in Ghana. \( \sum_{\text{congeners}} \) PCNs ranged between 27 and 95 pg/m\(^3\) with a national average of 49 ± 5.4 pg/m\(^3\) (Figure 1), applying a sampling rate of 3.5 m\(^3\)/day.\(^{36,39}\) These concentrations were unexpectedly high but were included within the range of value (0.3–86 pg/m\(^3\)) of air PCNs, which was reported by Jaward et al. along the north–south Atlantic transect near West Africa in 2001.\(^{31}\) They not only reported the existence of hotspots off the coasts of West and South Africa. In the present study, we found PCNs to be highest along the coastal stretch of Ghana, which somehow might imply that these coastal areas are the emission sources of these pollutants (Figure 1). The highest concentration (95 pg/m\(^3\)) was detected at Teshie near Accra (the national capital) and the lowest (27 pg/m\(^3\)) at Kumasi (the second largest city). We did not find much evidence of rural-urban gradient of ambient PCNs in Ghana. Rather, a south–north gradient was observed, with concentrations in the southern belt almost twice as those in the middle and northern belts (Figure 1). Averagely, ambient PCN levels were similar between the middle and northern belts.

**Homologue Composition and Fractionation.** Clearly, tri-CNs and tetra-CNs (the lowly chlorinated homologues) predominated in Ghana’s atmosphere (Figure 2). These two homologues constituted approximately 90% of total PCN homologues composition in the atmosphere in Ghana in comparison to about 80% in East Asian countries.\(^{40}\) The relatively greater composition of lighter homologues in the atmosphere in Ghana probably is a manifestation of strong volatilization effect under high tropical temperatures. There was a progressive increase in ambient composition of tri-CNs and decrease in tetra-CNs as one traversed from south to north of the country (Figure 2). As deduced from Figure 1, the bulk of the PCN emissions occurred in the southern belt. We presumed a northward atmospheric transport of aerial PCNs from the southern parts of Ghana. This study was conducted between May and July, when the West African monsoon, the major wind system that affects this region, blows southwesterly (i.e., from southwest to northeast).\(^{41}\) Indeed, back trajectory analysis (applying METEX – Meteorological Data Explorer) showed movement of air masses from the coastal south to the northern parts of Ghana (Supporting Information 3). This seemed to have triggered air PCN homologue fractionation across the breadth of the country. Much of tri-CNs, being lighter and more susceptible to atmospheric transport, appeared blown and accumulated further north than the tetra-CNs (Figure 2). Generally, less of the heavier homologues were transported up north.

In Sunyani, Wa, and Tumu, the PCNs were blown from the southern parts of neighboring Cote d’Ivoire (Supporting Information 3). Yet, the homologue compositions at these sites were consistent with the identified trend of homologue fractionation (Figure 2). On this score, it is assumed that the southern parts of Ghana and Cote d’Ivoire share similar characteristics of PCN emission factors. It is worth noting that the southern parts of Cote d’Ivoire had a major encounter with illegally dumped hazardous waste in 2006.\(^{42}\) PCN homologue profiles at the Teshie and Tema sites were strikingly dominated by tetra-CNs, constituting about 80% and 60% of their respective homologue compositions (Figure 2). Samples from Teshie were collected from the point close to a
solid waste dumpsite where uncontrolled waste burning activities were observed. Tema on the other hand is the industrial city of Ghana and at the heart of Ghana’s industrial development plan. Industrial activities at Tema include oil refinery, metal smelting, steel production, manufacturing of plastic products, cement, paints, etc.; in all of which energy are expended intensively, with combustion byproducts. Tema also hosts a shipping harbor. Our sampling site in the Tema district was close to the Tema Oil Refinery. With such point sources of combustion identified, it was assumed that the high tetra-CNs at these two sites was a direct impact from combustion. We are unsure if local practices of burning such waste items as plastics, PVC coatings of copper wires, and car tires has in any way influenced the air PCN homologue pattern in Ghana. Noma et al., however, have shown through laboratory-scale incineration experiment that incinerating certain synthetic rubber products emitted PCNs with tetra-CNs constituting nearly 60% of the homologue composition.29 There is also evidence suggesting that petrochemical activities, for instance, might generate PCNs with relatively high levels of tetra-CNs (judging from the amounts measured in surrounding soils); the researchers however did not report on tri-CNs.

**Congener Profiles for Source Characterization.** Out of 63 PCN congeners screened, 58 were routinely detected and quantified (Table S2). The congener patterns from the various sampling points are presented in Figure 3. PCN-21/24/14, -26/25, and -23 generally dominated the tri-CNs, accounting for 31%, 23%, and 24% of average tri-CNs composition, respectively; together contributing approximately 78% of total tri-CNs composition. Averagely, the tetra-CNs were dominated by PCN-37/33/34 (15%) and -45/36 (30%); penta-CNs by PCN-52/60 (18%) and -59 (19%); and hexa-CNs by PCN-66/67 (42%). Many of these congeners that dominated in the atmosphere in Ghana (PCN-14, -21, -26/25, -37/33/34, -45/36, -52/60, and -66/67) are reportedly enrich in combustion sources,23,25 making combustion a key factor of PCN emissions in Ghana.

The PCN congener profiles appeared different between the Takoradi, Teshie, and Tema sites but fairly consistent in the remaining sites within the southern zone (Figure 3). Profiles were, however, generally consistent in the middle zone and variable in the northern zone. The profile for Teshie was overwhelmingly dominated by PCN-45/36, constituting nearly 60% of total congener composition (Figure 3a). The Teshie site is proximate to a solid waste dumpsite, so it is presumed that congener profile at this site reflected directly the impact from such a source, and PCN-45/36 might qualify as a marker for this source. Indeed, the PCN congener profile at the Teshie site is consistent with the pattern reported in MSW by Noma et al., as one dominated by PCN-45/36.29 Thus, the general prominence of this particular congener in various profiles provides the possibility that many sites might have been impacted by MSW related sources. Open waste dumpsites are widespread in Ghana and often characterized by a complex mixture of waste materials that include e-wastes, plastics (including PVCs), car tires, and metals,33,34 all of which provide...
ingredients for possible de novo synthesis of organohalogens such as PCNs.\textsuperscript{25} PCN-66/67, which constituted approximately 42\% of average hexa-CN composition, provides further evidence of combustion source, considering that this congener is generated mainly as a combustion byproduct.\textsuperscript{23}

As atmospheric POPs generally show congener specific variations between seasons, we assume that the present data which reflect PCN congener patterns in the rainy season might differ from data obtained in the dry season.\textsuperscript{27,43}

**Principal Component Analysis (PCA).** Applying STATISTICA \textsuperscript{7} software, three major principal components (PC1 – PC3) were extracted as underlying PCN emissions in Ghana. These accounted for 49\%, 22\%, and 11\%, respectively, of total variance. The factor loadings plot in Figure 4 indicates the three significant congener clusters. Group 1 cluster of congeners correlated with PC1, Group 2 with PC2, and Group 3 with PC3. In Group 1, we find notable combustion markers of PCNs such as PCN-52/60, -50, -51, -54, and -66/67.\textsuperscript{1,18,27,29,44} In addition, PCN-45/36 and -39 occurring in this group are reportedly among the most abundant tetra-CNs in fly ashes from MSW.\textsuperscript{1,29} From the factor scores plot in Figure 4, the Tema and Teshie sites relate to the Group 1 set of congeners. This implies that the sources of PCN emissions at Tema and Teshie were most likely related to combustion predominantly. As expressed earlier, Tema is an industrial city, as such combustion byproduct were anticipated; while at Teshie, we assumed the aforementioned factor of waste burning.

Some of the most enrich congeners included in Halowax (technical PCN formulations) as characterized by Falandyzs et al. (e.g., PCN-23, -37/33/34, -48/35, -46, and -61) clustered into Group 2.\textsuperscript{45} But these congeners are also fairly prominent among trace PCN contaminants present in technical PCB formulations.\textsuperscript{46} It is, therefore, difficult to indicate precisely which formulations might have emitted them. Considering the factor scores plot, however, Group 2 could be associated with the Takoradi site, where PAS were placed close to the Takoradi shipping harbor. Thus, this cluster possibly suggests an impact from the harbor environment. As an old harbor, possible factors of PCN emissions might include old applied paints as well as broken down/abandoned ships. Thus far, the implication of the PCA is that such point sources contributed the most to air PCNs at Takoradi closest to the coastal line.

Majority of the sites located in the mid to northern regions e.g. Kumasi, Sunyani, Ejura, Tamale, and Wa related to PC3, which is associated with Group 3 cluster of congeners. This cluster is dominated by highly chlorinated congeners (PCN-63, -69, -71/72, -73, -74, and -75). As heavier congeners with relatively poor traveling capacity in air, our immediate impression was that the cluster expressed a certain element of marginal local influence at several sites, most of which are quite distant from the important sources identified in the southern regions. It is suggested that the sites in the mid to northern regions were not important emission points of the lowly chlorinated congeners that accumulated in these regions but might have received these congeners following LRAT from the southern zone.

**Potential Toxicity.** The toxicological significance of the levels of PCNs measured in air was assessed considering their dioxin-like equivalency (Figure 5). As PCNs toxicity is mediated via a similar mechanism as the dioxins, toxic equivalent factors (TEFs) have been determined for some of the PCN congeners, weighing their toxicity against the most toxic dioxin 2,3,7,8-TCDD, which is assigned the TEF of 1.\textsuperscript{1,19,21,47,48} In this study, 17 PCN congeners with known TEFs were used to assess overall PCN toxic equivalency (TEQ) (Table S3). These congeners are within the tetra- to octa-CN homologue groups, as the tri-CN homologues have no
or low dioxin-like activities and TEFs. The highest value was applied among multiple TEFs for a particular congener. In addition, if TEF is available for only one of coexisting congeners (usually the congener with greater content), this factor was assumed applicable for both congeners. For the 17 PCN congeners (coexisting congeners considered as a unit), TEQ was estimated as \( \sum_{i=1}^{n} C_i \times TEF_n \) where \( C_i \) and \( TEF_n \) are concentration and TEF of the \( n \)th congener, respectively. We estimated PCN TEQ concentrations to range between 0.49 and 0.80 fg TEQ/m\(^3\), respectively. The worst case scenario of dioxin-like toxicity by PCNs via inhalation in Ghana could be estimated at Legon as follows: \( \text{TEQ}_{\text{Legon}} \times \text{approximate air volume inhaled per day} = 5.6 \text{ fg TEQ/m}^3 \times 15 \text{ m}^3/\text{day} = 84 \text{ fg TEQ/day}. \) The tolerable daily intake (TDI) of dioxin toxicity as stipulated by the WHO is 1–4 pg TEQ/kg body weight/day.\(^{48}\) For any adult of body weight 60 kg, maximum WHO-TDI of dioxin toxicity is estimated as 4 pg TEQ/kg/day × 60 kg = 240 pg TEQ/day. Thus, it is estimated that a daily exposure to the highest dioxin-like toxicity by air PCNs in Ghana might account for about 0.04% of the maximum WHO-TDI of dioxin toxicity.

In summary, the present study has revealed an emerging burden of air PCNs in Ghana and reiterates the need for thorough monitoring of industrial and unintentional POPs in Ghana and other West African countries. The fraction of dioxin-like toxicity by air PCNs was low, but other routes of exposure such as by food and water and other dioxin-like compounds in these media should be monitored to help evaluate the total dioxin-related burden in Ghana.

**ASSOCIATED CONTENT**

Supporting Information

Additional experimental details, data, and back trajectory information. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We are very thankful to the following colleagues for the immense help they provided during sampling in Ghana: Mr. Eric A. Amoako (Department of Urban Roads, Accra), Mr. John Terlari (Department of Theoretical and Applied Biology, Kwame Nkrumah University of Science and Technology, Kumasi), Mrs. Nora N. Terlari (Ghana Food and Drugs Board, Kumasi), Prof. Derick Carboo (Department of Chemistry, University of Ghana, Legon, Accra), Dr. Noah Adamey (formerly of Ghana Atomic Energy Commission, Kwenanya, Accra), Dr. Kwabenya Ofosu-Budu (University of Ghana Agricultural Research Centre, Kade), and Mr. Gordon Foli (Department of Geological Engineering, Kwame Nkrumah University of Science and Technology, Kumasi).

This study was supported by the International Environmental Leadership Program in Sustainable Living with Environmental Risk (SLER) at the Yokohama National University funded by Japan Science and Technology Agency and the Global Center of Excellence (GCOE) Program “Global Eco-Risk Management from Asian Viewpoints” of the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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