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Review

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## A review on levels of polychlorinated naphthalenes in matrices with emphasis on knowledge and research gaps priorities in Africa

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#### Abstract

Polychlorinated naphthalenes (PCNs) were listed as Persistent organic pollutants in the Stockholm Convention, in May 2015, because of their adverse health and environmental effects. PCNs production began in the early 1900s when they were used extensively in several consumer goods as fire retardants. However, because of their health and environmental implications, the production and use of PCNs chemicals were voluntarily banned in many countries in the 1970s and 1980s. However, PCNs are still detected in different environmental samples including air, water, sediments, soil, indoor dust, biota, consumer products, human diet, blood and serum today, as a result of their historical use and unintentional production. Thus, PCNs can be released into the environment throughout their life cycle. It becomes, therefore, crucial to monitor them in different environmental compartments. To date, about 163 reports on PCNs levels in several matrices have been published in different parts of the world. It was reported that toxic PCNs such as chloronaphthalenes 66, 67 and 73 are prevalent in most samples; thus, there is a need to continuously monitor these congeners in our environment. However, there are sparse studies related to PCNs levels, not only in consumer products, leachates and sediment samples from landfill sites in Africa but also in other matrices, leaving a huge research gap that must be prioritized. To date, only about 3 studies on PCNs have been published in Africa, bearing in mind that there is no documented evidence of any known production of PCNs



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Page 2 of 22

in the continent. Thus, a wide research gap in PCNs studies still exists in Africa. There is an urgent need, therefore, to conduct studies and establish robust PCNs inventories in Africa. The present review examines the existing knowledge on PCNs levels and trends in Africa, and identifies research gaps that ought to be addressed so that the scale of PCNs distribution in the global environment can be known.

**Keywords:** Persistent organic pollutants (POPs), polychlorinated naphthalenes (PCNs), concentrations, congeners, matrices, Africa

#### INTRODUCTION

Polychlorinated naphthalenes (PCNs), commonly known as chloronaphthalenes, are among the chlorinated polycyclic aromatic hydrocarbons comprising 75 congeners, with two-ringed aromatic compounds containing 1 to 8 chlorine atoms per naphthalene molecule as shown in Table 1<sup>[1-3]</sup>. PCNs, are lipophilic and semi-volatile, and are synthesized by reacting molten naphthalenes and chlorine gas at a temperature that is slightly above the melting point of the desired product in the presence of iron (III) or antimony(v) chloride catalysts<sup>[4]</sup>. This reaction gives rise to complex liquids and waxes of naphthalenes with high melting points<sup>[5]</sup>. The synthesis of PCNs was authorized in 1909, and their applications grew during World War  $I^{[4]}$ . According to Falandysz et al.<sup>[6]</sup> PCNs were produced under different trade names such as Halowax, Nibren wax, Perna wax and Basileum, and Seekay waxes, Clonacire, Cerifal materials, and N-oil and N-wax. Furthermore, PCNs were the second largest high volume halogenated organic chemicals after hexachlorobenzene<sup>[7]</sup>. About 150,000-400,000 metric tons of different technical PCN-mixtures were produced from large-scale producers in countries including Germany, the USA, France, Italy, Japan, Poland and the United Kingdom<sup>[8,9]</sup>. However, because of their health and environmental implications, the production and use of PCNs chemicals were voluntarily banned in many countries in the 1970s and 1980s<sup>[10]</sup>. Despite the banning, PCNs are still detected in different matrices hitherto. In Africa, no production of PCNs has been reported yet. However, Babayemi et al.<sup>[11]</sup> pointed out that large volumes of PVC and other polymers with additives that may contain chlorinated paraffins (CPs) have been imported in large quantities by some African countries, which can also be considered a potential source of PCNs.

Given their physicochemical properties such as good thermic balance, water resistance, mucus repellent, insulating properties, flame-retardance and inertness, PCNs were earlier applied in large quantities as flame-retardants in various consumer products<sup>[3,12]</sup>. Thus, many products may contain 5%-30% by weight of PCNs<sup>[3]</sup>. Most of PCNs were widely used as technical mixtures in cable insulation, plasticizers, paints, textile and paper industries, wood preservation, engine oil additives, electroplating masking compounds, dye carriers, and capacitors<sup>[6]</sup>. PCNs can be discharged into the environment throughout their life cycle during the manufacture, use and disposal of PCN-containing consumer products, coking plants, metallurgical plants and waste incinerators<sup>[13,14]</sup>. Other sources of PCNs discharge in the environment include historical usage of technical PCB formulations, which exist in small quantities of up to 1%<sup>[9,15,16]</sup>. The burning of fuels such as biomass and forest fires, metal smelting and sintering, and the formation of PCNs during cooking process are also among other sources<sup>[3,17]</sup>.

Because of their toxic health effects on both humans and animals, PCNs were included as Persistent organic pollutants (POPs) in the Stockholm Convention Annexes A and C in May 2015<sup>[9]</sup>. Moreover, PCNs were added to the protocol on POPs under the Convention on Long-Range Transboundary Air Pollution in December 2009<sup>[18]</sup>. The major pathway of human intake of PCNs is via dietary intakes such as eggs, milk, and fish, which is accounted for about 90% of their daily individual intake<sup>[19]</sup>, although other routes such as inhalation and dermal contact are also possible<sup>[3,17]</sup>. The toxic effects of PCNs in both animals and humans include mortality, embryotoxicity, hepatotoxicity, immunotoxicity and induction of dermal lesions,

Congener group	Acronym	Molecular formula	No. of individual congeners
Monochloronaphthalenes	MonoCN	C <sub>10</sub> H <sub>7</sub> Cl	2
Dichloronaphthalenes	DiCN	$C_{10}H_6CI_2$	10
Trichloronaphthalenes	TriCN	C <sub>10</sub> H <sub>5</sub> Cl <sub>3</sub>	14
Tetrachloronaphthalenes	TetraCN	$C_{10}H_4CI_4$	22
Pentachloronaphthalenes	PentaCN	C <sub>10</sub> H <sub>3</sub> Cl <sub>5</sub>	14
Hexachloronaphthalenes	HexaCN	C <sub>10</sub> H <sub>2</sub> Cl <sub>6</sub>	10
Heptachloronaphthalenes	HeptaCN	C <sub>10</sub> HCl <sub>7</sub>	2
Octachloronaphthalenes	OctaCN	C <sub>10</sub> Cl <sub>8</sub>	1

#### Table 1. PCNs homologues

Adapted from data compiled by Agunbiade et al.<sup>[3]</sup>. PCNs: Polychlorinated naphthalenes.

teratogenicity and carcinogenicity<sup>[3,20,21]</sup>. Consequently, studies have reported PCNs levels in human adipose tissue, liver, breast milk and blood serum<sup>[22-24]</sup>. In Canada, a screening exercise reported PCNs levels with 2-8 chlorine atoms were released into the environment at levels that may have immediate or long-term harmful effects on the environment. Therefore, PCNs met the criteria outlined in the persistence and bioaccumulation regulation under the Canadian Environmental Protection Act 1999<sup>[25]</sup>. It is, however, noteworthy to consider that currently, there are no PCNs regulations in the continent of Africa.

Hitherto, efforts have been made to characterize POPs chemicals, including CPs, in several matrices such as atmosphere, river, sediments, soil, indoor dust, biota, consumer products, human diet, blood and serum in Africa<sup>[26-41]</sup>. However, in the African continent, studies on PCNs in environmental matrices are yet to be investigated, hence the limited available information<sup>[3,10,42,43]</sup>. Furthermore, according to Hogarh *et al.*<sup>[10]</sup>, PCNs are one of the least researched halogenated organic pollutants in Africa. Electronic gadgets and industrial wastes that may contain PCNs are exported from developed countries to developing countries, and this can serve as a source of transferring the PCNs pollution burden from industrialized nations to developing ones<sup>[44]</sup>. Additionally, most developing countries lack safety measures and regulations for the exposed population<sup>[44]</sup>. Currently, few studies have reported the PCNs levels in consumer products, leachate and sediment samples from landfill sites. The present review, therefore, examines the existing knowledge on PCNs levels and trends in the continent of Africa, and identifies knowledge gaps that should be addressed so that the scale of PCNs distribution in the global environment can be known.

## PRODUCTION, USES AND RELEASES OF PCNS

#### Production

Historically, the synthesis of PCNs was authorized in 1909, and their applications grew during World War I<sup>[4]</sup>. However, the production of PCNs declined after World War II when polychlorinated biphenyl (PCBs) were introduced, yet, they remained high volume chemicals until the  $1970s^{[9,45]}$ . PCNs were synthesized by reacting molten naphthalenes with chlorine gas at a temperature that is slightly above the melting point of the desired product in the presence of iron (III) or antimony (v) chloride catalysts<sup>[3-5]</sup>. The crude product was further treated with sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) or sodium hydroxide (NaOH) to give a final product of complex mixtures of naphthalenes that range from liquids to waxes with high melting points<sup>[3,5,46]</sup>. PCNs were produced via chlor-alkali and metal productions<sup>[47]</sup>. According to Falandysz *et al.*<sup>[6]</sup>, PCNs were (France) and Halowax (USA). Other trade names include Perna wax, Basileum and N-oil [Table 2]<sup>[9]</sup>.

Trade name		Composition	Manufacturer
Halowax	1031	mono-diCN (22-70% CI)	Koppers Co Pittsburg, PA, USA
	1000	mono-diCN (26% Cl)	
	1001	di-penta (50% CI)	
	1099	di-pentaCN (52% Cl)	
	1013	tri-pentaCN (56% CI)	
	1014	tetra-hexaCN (62% CI)	
	1051	hepta-octaCN (70% CI)	
Basileum	SP-70	mono-diCN (80% Cl)	Desowag Bayer, Germany
Nibren wax	D88	(50% CI)	Bayer Leverkusen Germany.
	D116 N	(50% Cl, estimated from melting point)	
	D130	(60% Cl, estimated from melting point)	
Seekay wax	R68	(46.5% CI)	ICI Runcorn, UK
	R93	(50% CI)	
	R123	(56.6% CI)	
	R700	(43% CI)	
	RC93	(50% CI)	
	RC123	(56.5% CI)	
Clonacire wax	95	(50% CI)	Prodelec, Paris, France
	115		
	130		

Table 2. Trade names, composition and manufacturers of technical PCN mixtures\*

Adapted from UNEP Draft guidance documents for inventories of PCNs<sup>[9]</sup>, \*Mono-CNs are not listed as POPs in the Stockholm Convention. Mono-CN products might, however, contain higher chlorinated PCNs listed in the Convention. UNEP: United Nations Environmental Programme; PCNs: polychlorinated naphthalenes; POPs: persistent organic pollutants.

Because of the health and environmental issues associated with PCNs, the majority of countries in North America and Europe prohibited the manufacture and application of PCNs in the 1980s<sup>[48,49]</sup>. According to Hayward, between 50,000 and 150,000 tons were produced in the USA from 1910 to 1960<sup>[50]</sup>. In Japan, the total production volume of PCNs w about 5,000 tons between 1940 and 1976<sup>[51]</sup>. Although the production of PCNs was ceased in the mid-1960s in the UK, small quantities of PCNs were still manufactured in the 1970s<sup>[52]</sup>. PCNs were manufactured as additives in products until the early 2000s, where PCN-containing consumer products were still found in the Japanese market<sup>[9]</sup>. Except for some small-scale production of octachloronaphthalenes, China is reported to have never produced technical PCN formulations<sup>[10]</sup>. There are no documented records of any PCNs production in Africa. However, a publication in 2015 showed that about 10,000 tons of CPs were produced per year in South Africa, indicating the existence of production of PCNs in the continent<sup>[53]</sup>.

#### Industrial uses

Because of their physicochemical properties, such as stability, flame retardation, electrical insulating, fungicidal and insecticidal properties, PCNs were used as additives in different consumer products [Table 3 ]<sup>[9,14]</sup>. PCNs were predominantly used in cable insulation, fluids and impregnate in capacitors or condensers, wood treatment, additive in paints and dye carriers, dye feedstock, production of engine oils and transformer fluids<sup>[9]</sup>. Tri- to octa-CNs were mainly used in different mixtures, as shown in Table 3. PCNs mixtures consisting of mono- and di-CNs were used in gauges and instrument seals, fluids in heat exchangers, solvents for colour dispersion, vehicle crankcase additives, fluids in motor tune-up and dyes. Moreover, Helm *et al.*<sup>[54]</sup> also pointed out that the use of PCNs in fire retardation and as dielectric fluids in capacitors was authorized in the 1900s. Other uses include wood, textile and paper treatment for fungal protection, plasticizers, additives in oil, casting materials for alloys and lubricants for graphite electrodes;

Sector	Application
Transformers and Capacitors	Capacitor impregnates Transformer and capacitor fluids
Batteries	Separator in storage batteries
Plastics and cables	Cable covering compositions Additive in plastic Intermediate for polymers and fire-retardants in plastics
Rubber	Additive in Neoprene
Sealants	Water proofing
Paints, lacquers, dyes/dye carrying agents	Anti-corrosion/underwater paints and lacquers Raw material/feedstock dye carriers
Wood preservative / fungicide	Impregnation of wood
Textile and paper industry	Water proofing of paper and textiles Binders in paper coating and impregnation
Oil additives and lubricants	Oil additives for gear and machinery lubrication Oils in the mining sector Vehicle oil additive Oils for refracting index testing
Military use	Fogg ammunition; smoke grenades Inert artillery and mortar projectiles Paper filter for gas masks in WW1 Paints for ships and metals Military vehicles and equipment

 Table 3. Former PCNs uses in consumer products

Adapted from UNEP Draft guidance document for inventories of PCNs<sup>[9]</sup>. UNEP: United Nations Environmental Programme; PCNs: polychlorinated naphthalenes.

electronic and automotive applications, paper binding, coating and impregnation; ceramic binding, lubricants for grinding and cutting, moisture proofing and sealant<sup>[45]</sup>.

In Europe, PCNs were used in paints until the 1980s, but their use declined considerably after the 1980s<sup>[55]</sup>. The most recent available information on PCNs application in casting material was reported in Germany and the former Yugoslav Republic of Macedonia until 1989<sup>[56]</sup>. It was further reported that PCNs were used as additives in chloroprene rubber until early 2000. About 12.6 tons of PCNs were used to produce 259 tons of synthetic chloroprene rubber (Neoprene FB), of which 207 tons were for export and the remainder used in Neoprene FB rubber belts and sealants production<sup>[9]</sup>. Sumitomo 3M Co. Ltd in 2002, imported 54 tons of Acoprene FB rubber compounds from Canada, which was used in manufacturing more than 210,000 cans of aerosol adhesives<sup>[57]</sup>. Manufacturers in Japan were directed to stop exporting and recall all PCNs-containing products<sup>[57]</sup>. Some uses of PCNs include fog ammunition and inert artillery and mortar projectiles for military operations<sup>[9]</sup>. In 1981, about 15 tons/year were used as capacitors dielectrics and refractive index tests in the USA<sup>[9]</sup>. In consideration of the aforementioned manufacture of CPs and the importation of polymers into Africa, the presence of PCNs in different applications becomes quite clear. These prompt the need to develop robust PCNs inventories and regulations in Africa.

#### **Environmental releases**

PCNs are ubiquitous in the environment. Studies have shown that PCNs are conveyed from their production sites to far distances globally either by wind, water or living organisms resulting in their bioaccumulation over a long period in the environment<sup>[9]</sup>. Of all the sources via which PCNs are released into the environment, combustion has been identified as the major source. Above 80% of PCNs is estimated to have been emitted into the European atmosphere from this source<sup>[12]</sup>. According to Helm and Bidleman, the present PCNs concentrations in the environment are attributed to sources from past uses of technical

mixtures and combustion from WEEE, waste incinerators, metal refining and steel production<sup>[58]</sup>. The following PCNs congeners PCN-20, -17/25, -26, -13, -18, -44, -36/45, -29, -27/30, -39, -35, -52/60, -50, -51, -54, -66/67, and -73 are related to combustion<sup>[54]</sup>. In the UK, elevated concentrations of polychlorinated naphthalene congeners-24 and -50 in the atmosphere have been attributed to coal and wood combustion<sup>[59]</sup>. Research reports have shown that the part played by combustion sources in the PCN burden on the environment has been increasing<sup>[60]</sup>. For example, Pan *et al.*<sup>[61]</sup> conducted a study on PCNs in dated sediment cores from Jiaozhou Bay in the Yellow Sea region (East of China). The results showed that PCN flux maxima occurred in the mid-1970s and late-1990s outside and inside the bay, respectively. This observation was attributed to the influence of different sources of PCN pollution in the Yellow Sea region. The chronology of PCN pollution elucidated from characteristic congener patterns from thermal sources indicated that PCN pollution from the 1970s to 1990s. The congener patterns in the uppermost layers of the cores suggested that the contribution from municipal solid waste combustions may have become more significant in recent years<sup>[61]</sup>.

#### Industrial processes and inadvertent production of PCNs

Moreover, Liu *et al.*<sup>[14]</sup> and Bidleman *et al.*<sup>[12]</sup> reported that PCNs are still released into the environment through different industrial and other thermal processes such as refuse burning, manufacturing of iron and steel, nonferrous melting procedures, cooking processes and manufacturing of cement despite the prohibition of their production in most countries since the 20<sup>th</sup> century<sup>[62-66]</sup>. Secondary copper smelting processes from a Chinese factory were recently reported to emit about 65%, 27% and 8% of PCNs into the environment during the three different stages of production, respectively- feeding fusion, oxidation and de-oxidation<sup>[3,64]</sup>. PCNs concentrations in the stack gas samples for the three stages ranged from 477.0-762.5 ng/m<sup>3</sup>. Polychlorinated naphthalenes can also be released into the environment from sites of production [Table 4]<sup>[9]</sup>. High releases and contamination at former PCN-production sites to air (25-2900 ng/m<sup>3</sup>), water (up to 5500 ng/L) and soil (up to 1300 mg/kg) have been reported, which indicates past pollution and possible current contamination at and around PCN-production sites<sup>[9]</sup>.

Another important source of PCNs in the environment is their inadvertent occurrence as contaminants in other similar industrial chemicals such as commercial PCB mixtures, Aroclors, Kanechlors, Phenoclors and Sovol<sup>[17]</sup>. Profiles of PCN congeners (tri- to octa) in 18 different commercial PCB mixtures have been presented, and an estimation of global inadvertent by-production of approximately 169 tonnes was reported<sup>[15]</sup>. PCNs concentrations ranged from 5.2-67  $\mu$ g/g in Aroclors and 731  $\mu$ g/g in Sovol. PCN congener profiles in PCB mixtures varied depending on the type of mixture and the chlorine content, but also on other conditions such as selective volatilisation of the lower chlorinated congeners (mono-, di- and tri-CNs)<sup>[15]</sup>. PCNs are also released into the environment during the cooking process<sup>[3,17]</sup>. In a study on potential dietary sources, Dong et al.<sup>[67]</sup> reported on the potential for direct formation of PCNs in food during the cooking process. The study involved heating commonly used cooking oils (peanut and olive) known to be free of PCNs in the presence of sucralose (a synthetic sweetener) at elevated temperatures. Sucralose thermally decomposed at high temperatures and acted as a chlorine source during the formation of a range of PCN congeners, which were detected in the fumes emitted during the experimental process. The total concentrations of PCNs found in the peanut and olive oil fumes were 490 pg/g and 240 pg/g, respectively<sup>[67]</sup>. Moreover, according to Ren et al. [68] municipal solid waste (MSW) incineration is a widely adopted technology for treating waste. During incineration, PCDD/Fs, PCBs and PCNs, can be formed and released into the ambient environment unintentionally. The emission of these chemicals is of public concern because of their toxic health effects.

Sample matrix	Levels of PCNs
Soil at former PCN production site	1300,000 μg/kg
Soil at chloralkali plant	7400-18,000 μg/kg
Soil at electric arc furnace	10 μg/kg
Soil background	0.003 µg/kg
Sediment at hot spot	100,000 µg/kg
Sediment at chloralkali plant	260-23,000 μg/kg
Sediment background	0.2 µg/kg
Sewage sludge China	1-11 µg/kg
Surface water production site	up to 5500 ng/l
Air at workplace PCN production	14,500,000 ng/m <sup>3</sup>
Ambient air at PCN production site	25-2900 ng/m <sup>3</sup>
Ambient air at electric arc furnace	1.6 ng/m <sup>3</sup>
Ambient air across Ghana	0.027-0.095 ng/m <sup>3</sup>
Air at e-waste recycling,Ghana	0.38 ng/m <sup>3</sup>
Air background	0.001-0.040 ng/m <sup>3</sup>

Adapted from UNEP draft guidance document for inventories of PCNs<sup>[9]</sup>. UNEP: United Nations Environmental Programme; PCNs: polychlorinated naphthalenes.

#### Landfills and open dumping

Landfills with wastes containing PCNs can be considered contaminated sites with the potential to release PCNs into the environment through landfill leachates and gas<sup>[69]</sup>. In Spain, Martí and Ventura analysed groundwater samples from four boreholes in the Llobregat aquifer, a study area that previously served as a dumping site<sup>[70]</sup>. The levels PCNs ranged from 0.0005-79.1 µg/L, while tetra-CNs were the dominant congeners. The Basel Convention, Annex VIII, has classified waste containing PCNs as hazardous and low POP content threshold for PCNs was set at 10 mg/kg or 50 mg/kg<sup>(9)</sup>. It was further stated that wastes containing PCNs above this concentration should be handled in a sound environmental manner to destroy the POP content or irreversibly transformed according to the methods described in the Basel Convention technical guidelines<sup>[9]</sup>. Nonetheless, in Africa, most polymeric wastes are disposed of with MSW with minimal formal recycling of approximately 10% either by landfilling or open dumping<sup>[29,53]</sup>. There is hardly any thermal or energy recovery from waste (incinerators or cement kilns) in Africa. Thus, by far, the largest share of polymeric waste ends up in dumpsites or landfills, which may serve as a source of PCNs emissions into the environment<sup>[11,53]</sup>. Moreover, the open burning of solid waste, inclusive of polymeric products, is prevalent in most African countries<sup>[68]</sup>. As a result of the lack of effective solid waste management, mixed wastes, including polymers, end up in dumpsites where they are burnt, resulting in the release of POPs into the environment<sup>[53]</sup>. Polymeric products normally contain a wide range of additives such as plasticizers, flame-retardants, antioxidants, acid scavengers, light and heat stabilizers, lubricants, pigments, antistatic agents, slip compounds, and thermal stabilizers, which are used for various purposes<sup>[71-74]</sup>. Many of these additives are classified as endocrine disrupting chemicals. Several other chemicals listed as endocrinedisrupting POPs include PBDEs, HBB, HBCD, SCCPs, and PFOA<sup>[11]</sup>. These releases of POPs from aforementioned products can, therefore, be regarded as sources of PCNs to air, soils, biota industrial areas and in-house dust, resulting in human exposure.

#### ROUTES OF EXPOSURE AND TOXICITY

The principal route via which humans are exposed to PCNs is through dietary intake<sup>[13,17]</sup>. According to Martí-Cid *et al.*<sup>[75]</sup> and Llobet *et al.*<sup>[76]</sup>, dairy products are the major sources of given population exposure, amounting to about 90% of ingestion of PCNs/day/person. The presence of PCNs in sea and fish has been

reported globally<sup>[77-80]</sup>. In addition, PCN congeners with high masses have also been detected in drinking water(79,81]. During the 1930s and 1940s, a study by Hayward reported occupational health hazards associated with PCNs exposure, and these included chloracne as a result of severe skin rashes and liver disease that may have resulted in the deaths of some workers<sup>[50]</sup>. The toxic effects of PCNs in both animals and humans include mortality, embryotoxicity, hepatotoxicity, immunotoxicity and induction of dermal lesions, teratogenicity and carcinogenicity<sup>[3,20,21]</sup>. A set of thermodynamic data obtained by Falandysz et al.<sup>[82]</sup> indicated that continuous deleterious effects of 75 PCN congeners on living organisms steadily increase from mono-CN to octa-CNs. All PCN congeners are planar compounds, which dissolve easily in lipids (lipophilic), and they structurally resemble the highly poisonous 2,3,7,8 -tetrachlorodibenzo-p-dioxin (TCDD)<sup>[3]</sup>. The brominated or chlorinated counterparts are expected to show similar properties, although structural distortion due to the higher mass and size of bromine may influence the degree of planarity. The structural similarity of these molecules to the highly toxic TCDD molecule suggests an aryl hydrocarbon (AhR)-mediated mechanism of toxicity, also commonly referred to as dioxin-like toxicity<sup>[8]</sup>. Thus, some PCNs are included in the toxicity equivalency factor concept. It uses the relative effect potency (REP) determined for individual PCDD, PCDF, and PCBs compounds for producing toxic or biological effects relative to a reference compound, usually 2,3,7,8-TCDD. The total toxic equivalent is operationally defined by the sum of the products of the concentration of each compound multiplied by its TEF value and is an estimate of the total 2,3,7,8-TCDD-like activity of the mixture<sup>[83]</sup>. Suzuki et al.<sup>[83]</sup> also explained that PCN congeners cause dioxin-like effects due to the interaction of planar molecules with AhR, resulting in toxicological effects comparable to those of PCDD/Fs. Furthermore, the dioxin-like toxicity of PCNs depends on the planar structure and substitution of chlorine at lateral ( $\beta$ ) positions (2,3,6,7) of the naphthalene ring<sup>[6]</sup>. Based on this assertion, there are seven PCN congeners which have their lateral positions filled with chlorine; CNs- 48 (2,3,6,7-TetraCN), 54 (1,2,3,6,7-PentaCN), 66 (1,2,3,4,6,7-HexaCN), 67 (1,2,3,5,6,7-HexaCN), 70 (1,2,3,6,7,8-HexaCN), 73 (1,2,3,4,5,6,7-HeptaCN), 75 (1,2,3,4,5,6,7,8-OctaCN). Although CNs-68 (1,2,3,5,6,8-HexaCN) and -69 (1,2,3,5,7,8-HexaCN) showed reasonably high dioxin-like toxicity, they both have one carbon at the  $\beta$ -position which is not substituted with chlorine<sup>[3]</sup>.

Additionally, of the PCN congeners, studies have revealed that hexachloronaphthalenes (hexa-CNs) are the most dangerous, particularly hexa-CNs 66, and 67<sup>[6]</sup>. Effects including oxidative stress, accumulation of fats in the liver (hepatic steatosis), blood disorders (hematological disturbances), liver damage (hepatotoxicity) and loss of appetite (anorectic effect) were observed in rats administered with hexa-CNs<sup>[84,85]</sup>. Chicken oedema (characterized by loss of feathers) and X-disease (bovine hyperkeratosis) in cattle's characterized by symptoms such as vitamin A deficiency, hypersalivation, skin thickening (Pachyderma), hair loss, and on rare occasions, may result in death, have all been linked to PCNs exposure in animals<sup>[3]</sup>. Additionally, other health effects of PCNs on humans include eye irritation, tiredness, headache, loss of appetite, constipation leading to severe abdominal discomfort<sup>[86]</sup>.

#### PCNS STUDIES IN DIFFERENT MATRICES

Like many other persistent organohalogenated compounds, PCN congeners are lipophilic in nature and can be transferred from one matrice to another, leading to bioaccumulation via the food chain<sup>[84]</sup>. Globally, biotic and abiotic matrices are usually contaminated with relatively small amounts of PCNs<sup>[6,58,78,85-88]</sup>. While reports on PCNs are slowly emerging from different regions of the world, information on the studies conducted so far in different matrices is discussed below.

#### Atmosphere

One of the main sources of POPs in the human body is the inhalation of particles with a diameter of less than 2.5  $\mu$ m<sup>[89,90]</sup>. About 90% of these particles can enter the alveoli, and this can lead to heart and lung

diseases and even death<sup>[90]</sup>. PCNs can be adsorbed strongly by particles with large specific surface areas<sup>[91-93]</sup>. Mao *et al.*<sup>[94]</sup> analysed atmospheric background levels of PCNs in East China. The  $\sum_{39}$ PCNs levels ranged from 5.9-143 pg m<sup>-3</sup>, slightly lower than the concentrations obtained from studies conducted across China but higher than those obtained from Japan and Korea<sup>[95,96]</sup>. Tri-CNs were the most predominant congeners accounting for 65%  $\Sigma$ PCNs, while tetra-CNs and penta-CNs recorded 22% and 11% of  $\Sigma$ PCNs, respectively. However, hexa-CNs to octa-CNs exhibited 2% of  $\Sigma$ PCNs. Compared with other studies, the observed composition profile is in agreement with the observations in Ghana, India, Japan, Korea and Pakistan, where tri-CNs and tetra-CNs exhibited more than 80% of  $\Sigma$ PCNs<sup>[10,97]</sup>. In another study, PCNs levels were determined in atmospheric particulates from secondary copper smelters surroundings in China<sup>[98]</sup>. The observed PCNs levels ranged from 4.76-9.89 pg m<sup>-3</sup>. In comparison with other studies, the PCNs concentrations differed significantly from the levels observed in industrial areas in Shanghai, Taiwan and Beijing<sup>[96-100]</sup>. Zhu *et al.*<sup>[101]</sup> reported atmospheric PCNs concentrations in gas and particle samples in Beijing, China, and  $\Sigma$ PCNs concentrations in gas and particle fractions in the urban environment ranged from 6.77-25.90 pg m<sup>-3</sup> and 0.17-2.78 pg m<sup>-3</sup>, respectively. Table 5 is a summary of atmospheric PCNs studies worldwide.

#### Aquatic environment

#### River

Mahmood *et al.*<sup>[102]</sup> determined PCNs concentrations in water samples from River Chenab tributaries in Pakistan. The observed PCNs concentrations ranged from 178-489 ng/L, with polychlorinated naphthelene-75 as the most prevalent congener among  $\sum_{39}$ PCNs. Furthermore, PCNs concentrations among congeners decreased in the following order: PCN-75 (37%) > PCN-32 (10%) > PCN-39 (8%) > PCN-51 (6%) > PCN-16 and -23 (5%). These results were lower than the levels noted by Espadaler *et al.*<sup>[103]</sup>. Ishaq *et al.*<sup>[104]</sup> reported mean PCNs concentrations that ranged from 14-410 ng/L in water samples from Grenlandsfjords in Norway<sup>[104]</sup>.

#### Sediment

According to Cetin and Odabasi, PCNs are likely to be deposited in reservoirs and rivers sediments, where they are subjected to partitioning, decomposition and transportation according to their physical and chemical properties<sup>[105]</sup>. Previously, research studies have indicated that sediment is a major sink for POPs and PCNs show high accumulation potential in sediment and biota<sup>[106,107]</sup>. Dat *et al.*<sup>[108]</sup> analysed PCNs concentrations in three core sediment samples from Feitsui Reservoir and one surface sample from Laojie River in Northern Taiwan<sup>[108]</sup>. PCNs concentrations in sediment samples from Feitsui Reservoir and Laojie River ranged from 0.012-0.05 ng/g<sup>-1</sup> and 0.408-1.47 ng/g, respectively. In comparison with other studies [Table 6], PCNs concentrations were relatively lower. In Canada, McGoldrick *et al.*<sup>[18]</sup>conducted a study on suspended sediment samples, which were collected at selected locations within the GreatLakes, their connecting channels, and the St. Lawrence River in 2012. Of the selected sampling locations, the highest PCN concentration of about 264,000 ng g<sup>-1</sup> was detected in suspended sediment samples from the Detroit River, which was attributed to very high concentrations of PCNs at the monitoring stations in the Trenton Channel (DR1159 & DR1161). In addition, hexa-CNs were the most abundant PCN congeners present in suspended sediments from the Detroit River (32%) and surficial sediments in the western basin of Lake Erie (35%) and Niagara Bar in Lake Ontario (23%).

#### Fish

According to Cui *et al.*<sup>[109]</sup>, the presence of PCNs in fish is an indication of contamination as well as the transfer of contaminants throughout the food chain<sup>[109]</sup>. Moreover, studies have indicated that although fish is an important source of protein for humans, however, the PCNs concentrations in fish appear to be significantly more than in other foods. Therefore, fish is an important contributor to PCNs intake by

Country	Sampling year	Concentration pg m <sup>-3</sup>	Dominant homologue	Ref.
Arctic and Scandinavia	1994	10-46		[84]
Northern Atlantic Ocean	1994	29-71		[84]
British Isles	1994	34-340		[84]
Europe	1994	22-170		[84]
Chicago, IL, USA	1994	24-180		[84]
British Isles	1998	22-160		[84]
British Isles	1999	27-140		[84]
British Isles	2001	85-100 (31-310)		[84]
Toronto, Canada	2001	7-84		[84]
Toronto, Canada	2001	31-78		[84]
India and Pakistan	2006 and 2011	4.9-140	Tri- and Tetra-CNs	[97]
East China	2012-2015	5.9-143	Tri-CNs	[94]
Northern Taiwan	2017	172 ± 111	Tri- and Tetra-CNs	[100]
Dalian, China	2022	0.05-0.43 (summer) 0.08 -1.42 (winter)	Tetra- and Hexa-CNs	[144]

Table 5. Concentrations of PCNs in the troposphere reported in different parts of the	ne world
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PCNs: Polychlorinated naphthalenes; CNs: chloronaphthalenes.

Country	Concentration (ng/g dw)	Dominant homologue	Sampling year	Ref.
Liaohe River Basin, China	0.33-12.5	Tri-CNs and tetra-CNs	2010	[145]
East China	0.60-4600	Octa-CN	2009	[118]
North China	0.12-5.10	Tri- to Penta-CNs	2009	[146]
Lake Ontario	21-38	Hexa- to Octa-CNs		[81]
Barcelona (Spain)	0.17-3.27	Tetra-CNs	2003	[147]
Pakistan	8.94-414	Tri- to Penta-CNs	2012	[103]
Italy	ND- 0.053	Tri- to Penta-CNs	1995	[103]
Baltic sea, Sweden	0.27-2.8	Tetra-CNs	1991-1993	[78]
Qingdao, China	212-1209	Tri-, Tetra- and Penta-CNs	1997 and 1999	[148]
Taiwan	0.012-0.055 (reservoir) 0.408-1.47 (river)	Tetra- to Penta-CNs	2017	[108]

PCNs: Polychlorinated naphthalenes; CNs: chloronaphthalenes.

humans<sup>[17]</sup>. Recently, Zacs *et al.*<sup>[13]</sup> analysed PCNs concentrations in 15 fish samples from Latvia, and the highest  $\Sigma$ PCN concentration of 45.7 pg/g was detected. The obtained results were in general agreement with the POP-like properties of PCNs and other studies on PCNs occurrence in food. The result also indicated that aquatic biota had been subjected to PCNs bioaccumulation from historically used technical PCN formulations or from industrial emissions<sup>[17]</sup>.

Kim *et al.*<sup>[109]</sup> reported PCNs concentrations in Crucian Carp obtained from upstream and midstream rivers in South Korea. PCNs concentrations ranged from 1.46-3.08 pg/g ww, 20.6-31.6 pg/g ww, 14.8-40.7 pg/g ww and 7.57-18.0 pg/g in muscles, livers, gonads and blood of Crucian Carp, respectively. However, the PCNs concentrations in muscle and liver tissues were lower than those reported in previous studies<sup>[110-112]</sup>. Penta-CNs were dominant in both muscles and gonads, constituting 55.6% and 39.8%, respectively, similar to the results from previous studies on various fish samples<sup>[81,108,113,114]</sup>. Zhihua *et al.*<sup>[115]</sup> also analysed PCNs concentrations in 75 different fish species from UK, Ireland and France. PCNs concentrations observed

ranged from 0.7-265 ng/kg ww, with the highest mean concentrations recorded at 67 ng/kg ww and 68 ng/kg ww for Sardine and Mackerel, respectively. Though similar findings were obtained in other studies, Fernandes *et al.*<sup>[116]</sup> and Zhihua *et al.*<sup>[115]</sup> pointed out that size, age and seasonal changes may also have influenced the findings. Additionally, higher concentrations were observed for penta- and hexa-CNs (PCNs 52, 53 and 66/67). McGoldrick *et al.*<sup>[18]</sup> determined PCNs concentrations in Trout and Walleye samples collected from 11 locations in the Canadian Great Lakes. Across the Great Lakes,  $\Sigma$ PCNs concentrations ranged from 171-7660 pg/g ww, and Penta-CNs were the most predominant congeners<sup>[18]</sup>.

#### Soil and dust

Niu*et al.*<sup>[117]</sup> determined PCNs concentrations in the soil from WEEE recycling sites in Nanyang, Shanglian, Huamei, Longmen, and Yaocuowei) of Southeast China. The total concentrations of  $\sum_{18}$ PCN congeners differed considerably from one location to another, with concentration range covering three orders of magnitude from 1.22-4.00 × 10<sup>3</sup> ng/g dw. Overall, the frequencies of detection of tetra-, hexa-, and penta-CNs congeners were 85%, 79%, and 52%, respectively. The mono-, di-, and tri-CNs congeners were detected at > 90% in soil samples, but at relatively low concentrations (N.D. to 350 ng/g). In comparison with other similar studies, the observed congener profiles in the aforementioned study were different from those observed in the natural environment<sup>[99,118]</sup>. The observed profile indicated differences in potential sources of PCNs in e-waste recycling areas and natural areas. Waheed *et al.*<sup>[43]</sup> collected 250 indoor dust samples from five major e-waste hubs in Pakistan. PCNs concentrations in overall indoor dust samples ranged from 0.25-697 ng/g, with tetra-CNs (38%) and tri-CNs (26%) being the most dominant congeners<sup>[43]</sup>. Compared with other studies, PCNs concentrations in soil samples revealed a similar pattern of the tetra- and tri- CNs congeners' dominancy in Pakistan, China, Ghana and other countries<sup>[39,95,104,119-122]</sup>.

#### Eggs

Vorkamp *et al.*<sup>[123]</sup> determined PCNs concentrations in addled eggs collected during field studies on the South Greenland peregrine falcon in Denmark<sup>[123]</sup>. The  $\Sigma$ PCN levels in the eggs of peregrine falcon were 21 ng/g lipid weight (lw). This level is considered high for PCNs in bird eggs compared to other studies<sup>[12,124-126]</sup>. Another study by McGoldrick *et al.*<sup>[18]</sup> analysed PCNs concentrations in Herring Gull (*Larus argentatus*) eggs, which were collected annually as part of the Great Lakes Herring Gull Contamination Monitoring Program in April-May<sup>[18]</sup>. The highest PCNs concentrations were detected at 3020 pg/g ww in eggs from the colony on Middle Island, and the most abundant PCNs congener was hexa-CNs, which comprised 39-79% of the  $\Sigma$ PCNs measured.

#### **Consumer Products**

In Japan, Yamamoto *et al.*<sup>[127]</sup> conducted a preliminary study to monitor PCNs in waste. PCNs were detected at 36,000 mg/kg in Neoprene FB samples and 97-2000 mg/kg in rubber printer belts<sup>[127]</sup>. Additionally, levels of PCNs in refuse derived fuel and automotive shredder residues were 0.01-0.086 mg/kg<sup>[128]</sup>. In addition to the provided information on the levels of PCNs in consumer products, Table 7 summarizes levels of PCNs or PCBs in selected applications and some waste fractions.

#### Humans

Human exposure to PCNs can occur via oral, inhalation and dermal routes. However, dietary intake is the most significant route of exposure for the general population<sup>[17]</sup>. Despite the scarcity of data on the occurrence of PCNs in human tissues, several studies from Japan, Canada, Sweden, Russia, Kazachstan and Germany showed PCNs levels in blood, breast milk, adipose tissue and liver<sup>[129-133]</sup>. Studies have further indicated that human milk is considered one of the core monitoring matrices of the United Nations Environmental Programme' on POPs monitoring programme focusing on testing the efficiency of executing the Stockholm Convention<sup>[23]</sup>.

Product/sample	POPs measured	PCNs or PCBs content (mg/kg)	Ref.
Neoprene rubber	PCNs	36,000-45,000	[7,127]
Rubber coated plastic	PCNs	1000	[7]
Rubber belt for printers	PCNs	41-2000 (3/21)	[127]
Rubber belt for printers	PCNs	0.001-0.1 (17/21)	[127]
Aerosol adhesives	PCNs	1150-1200	[7]
Sealants	PCBs*	28,00 -224,000	[128]
Paints	PCBs*	30,000 -160,000	[149]
Cable sheathing and coating	PCBs	30,000-200,000	[150]
Automotive shredder residue	PCNs	0.026-0.040	[127]
Refused derive fuel	PCNs	0.011-0.086	[127]
PCN-technical mixture	PCNs	930,000-1,000,000	[7]
Transformer oils	Askarel PCB*	ca. 600,000**	[150]
Contaminated transformer oil	PCB*	50 - 100,000	[150]
Capacitor/condensers	PCB*	ca. 600,000**	[150]
Transformer oils	unintentional PCNs	1000-9000	[15]
Automotive shredder residue	PCNs	0.026-0.040	[127]
Refused derive fuel	PCNs	0.011-0.086	[127]

Table 7. Concentrations of PCNs (or PCBs)\* in selected applications and some waste fractions

\*For these applications, only PCB data were available. Due to the use in the same application and similar chemical properties, the levels of PCBs used might reflect if PCNs were/are used; \*\*The PCBs are normally mixed with ca. 300,000 mg/kg PCBs. PCNs: Polychlorinated naphthalenes; PCBs: polychlorinated biphenyl; POPs: persistent organic pollutants.

#### Human diet

Recently, Zac *et al.*<sup>[13]</sup> determined PCNs in food products from Latvia. The following selected food products, milk, meat, eggs, fish, cod liver, bread and cereal, vegetable oils, fish oil and baby food were analyzed. The highest  $\Sigma$ PCN concentration detected was 45.7 pg/g in fish samples, which reflected the exposure of aquatic biota to PCNs bioaccumulation from the historical use of technical PCN formulations. Other types of food products also showed a wide range of PCN levels. However, there was less contamination observed in the following order of mean  $\Sigma$ PCN concentrations: bread - 9.49 pg/g; dairy products - 5.29 pg/g; vegetable oil - 3.53 pg/g; meat - 3.13 pg/g; baby food - 1.40 pg/g; eggs - 1.14 pg/g. The observed PCNs concentrations in the selected foods were broadly similar to those reported from other countries<sup>[20,21,50,77-88,115-117,125-127,134,135]</sup>. In addition to the provided data, Table 8 summarizes concentrations of PCNs in the human diet.

#### Breast milk and serum

Li *et al.*<sup>[136]</sup> analysed levels of PCNs in Chinese human milk, which ranged from 164.4-2497.4 pg/g lw with the mean and median of 514.3 pg/g lw and 382.4 pg/g lw, respectively. In comparison with other studies, the concentration of PCNs in human milk was about 4 to 5 magnitude higher than the PCDD/Fs and one order of magnitude lower than dioxin-like PCBs reported by Zhang *et al.*<sup>[137]</sup>. Li *et al.*<sup>[23]</sup> analysed 3790 human milk samples in 2017-2019 from 77 cities around China. PCNs were present in the pooled samples that were analysed. The obtained results were compared with the available data on PCNs levels in human samples. PCNs levels were lower than the levels in adipose tissue samples from some developed countries<sup>[130,132,133]</sup>. PCNs concentrations in human blood samples from Korea were comparable to the ones obtained by Li *et al.*<sup>[23]</sup> but higher in blood samples from an industrial site in China<sup>[24,132]</sup>. Another recent study determined PCNs concentrations in workers, children and residents ranged from 1.12-401 pg/g lipid, 0.25-302 pg/g lipid and 0.15-313 pg/g lipid, respectively. Moreover, the highest  $\Sigma$ PCN concentration was recorded in workers, followed by residents and children with tetra- and penta-CNs as the dominant congeners, reflecting

Country	Type of sample	Sampling year	Quantitation type	PCNs concentrations (ng/kg)	Ref.
Great Lakes & inland Michigan. N America	Fish	1996-1997	Homologue totals tri-octa	19-31,400	[77]
Catalonia, Spain	Fish	2000	Total congener tetra-octa	39 (average)	[151]
altic sea	Fish	2001-2003	Sum of 16, tetra-octa congeners	1-190	[152]
altic sea	Fish	2001-2003	Sum of 16, tetra- octa congeners	20-450	[152]
emote lakes, Finland	Fish	2001-2003	Sum of 16, tetra-octa congeners	2-66	[152
ast & South China sea	Fish	2003-2004	Homologue totals tri-octa	137-545 (lipid wt, average	[153
atalonia, Spain	Fish	2005	Homologue totals tetra- octa	13-227	[76]
atalonia, Spain	Fish	2006	Homologue totals tetra	12.8-226.9	[154
hina	Fish	2006	Homologue totals congeners	25-640 (lipid wt, average)	[155
Inited Kingdom	Fish	2007	Sum of 12 penta-octa congeners	0.73-37.3	[156
eland	Fish	2007-2008	Sum of 12, penta-octa congeners	2.08-59.3	[157
cotland	Fish	2008	Sum of 12, penta-octa	0.3-63	[116]
cotland	Fish	2008	Sum of 12, penta-octa congeners	2.5-103	[116]
Inited Kingdom fresh vaters	Fish	2008-2009	Sum of 12, penta-octa congeners	0.7-265	[158
Inited Kingdom marine vaters	Fish	2013-2014	Sum of 12, penta-octa congenersSum of 12, penta-octa congeners	0.7-265	[159
atvia	Fish	2019-2020	26 PCN congeners, tetra-octa congeners	45.7	[13]
ast & South China sea	Shell fish	2003-2004	Homologue totals tri-octa	94-1300 (lipid wt, average)	[153
eland	Shell fish	2007-2008	Sum of 12, penta-octa congeners	0.18-2.34	[157
hanghai, China	Crab	2019	Di-hepta congeners	5.46-43.8 ww	[160
hanghai, China	Feed	2019	Tri-octa congeners	20.1-758 WW 30.3-92.6 ww	[160
atalonia, Spain	Eggs	2000	Homologue totals tetra-octa	23 (average)	[151
atalonia, Spain	Eggs	2006	Homologue totals tetra-octa	1.7-4.3	[154
hina	Eggs	2006	Total congeners	43.8 (lipid wt., average)	[155
eland	Eggs	2007-2008	Sum of 12, penta-octa congeners	0.23-2.22	[157
atvia	Eggs	2019-2020	26 PCN congeners, tetra-octa congeners	1.14	[13]
atalonia, Spain	Milk	2000	Homologue totals tetra- octa	0.4 (average)	[157
atalonia, Spain	Milk	2006	Homologue totals tetra- octa	0.5-1.2	[151
eland	Milk	2007-2008	Sum of 12, penta-octa congeners	0.09-0.38	[154
orth China	Raw cow milk	2019-2020	Mono-octa-CNs	89.6-2050	[161]
atalonia, Spain	Dairy food	2000	Homologue totals tetra- octa	36 (average)	[151]
atalonia, Spain	Dairy food	2006	Homologue totals tetra- octa	0.8-22.7	[154
Inited Kingdom	Dairy food	2007	Sum of 12, penta- octa congeners	0.52-6.09	[156
eland	Dairy food	2007-2008	Sum of 12, penta- octa congeners	0.68-3.13	[157
hina	Dairy food	-	-	5.6-103 (cheese) 5.0-199 (butter)	[162
atvia	Dairy food	2019-2020	26° PCN congeners, tetra-octa congeners	5.9	[13]
atalonia, Spain	Meat	2000	Homologue totals tetra-octa	18 (average)	[151]
atalonia, Spain	Meat	2006	Homologue totals tetra-octa	1.8-5.8	[154
nited Kingdom	Meat	2007	Sum of 12, penta-octa congeners	0.19-5.69	[156
ibet-Qinghai Plateau, China	Meat	2007	Tri-octa individual congeners	13.6	[163
Catalonia, Spain	Cereals & bread	2000	Homologue totals tetra- octa	3-71 (average)	[151]
Catalonia, Spain	Cereals &	2006	Homologue totals tetra- octa	5.3-15.1	[154

#### Table 8. A summary of PCNs studies in food

	bread				
United Kingdom	Cereals & bread	2007	Sum of 12, penta-octa congeners	0.28	[156]
Ireland	Cereals & bread	2007-2008	Sum of 12, penta-octa congeners	0.25-0.77	[157]
Catalonia, Spain	Fruits & vegetables	2000	Homologue totals tetra-octa	0.7-4 (average	[151]
Catalonia, Spain	Fruits & vegetables	2006	Homologue totals tetra-octa	0.9-3.9	[154]
Ireland	Fruits & vegetables	2007	Sum of 12, penta-octa congeners	0.16-2.84	[157]
United Kingdom	Fruits & vegetables	2007	Sum of 12, penta-octa congeners	0.15-0.16	[156]

PCNs: Polychlorinated naphthalenes.

exposure time, intensity and distance from the e-waste sites. Comparing the obtained data with previous studies, penta-, hexa- and tetra- CNs congeners were reported as predominant congeners detected in human plasma, liver, milk and fat tissue<sup>[64,133,138]</sup>. Penta- and hexa-CNs and, to a lesser extent, tetra-CNs congeners were the most prevalent observed in human tissue samples, showing some consistency with the normally observed profiles in animal tissues<sup>[3]</sup>.

#### PCNS STUDIES IN AFRICA

According to the UNDP, Africa covers over 30 million km<sup>2</sup>, including over 54 countries and a population of about 1.17 billion people<sup>[137]</sup>. However, it remains the least studied continent in the world with respect to PCNs studies in different matrices. In fact, only three studies on PCNs have been published in different matrices<sup>[3,10,42]</sup>. Jaward *et al.*<sup>[42]</sup> analysed 55 air samples for PCNs along the north to south Atlantic transect in 2001, as the Pelagia traveled from the Netherlands (1.06° N, 1.43° E) to South Africa (33.88° S, 18.3° E). The reported mean PCN concentrations ranged between 0.3-86 pg/m<sup>3</sup>. The European samples exhibited the highest levels. However, fairly high values were also detected off the West African coast, as well as in samples taken closest to South Africa. Jaward et al.<sup>[42]</sup>. further reported that there are limited data on regional or global usage and emission of PCNs. However, emissions from halowaxes and high-temperature combustion processes were identified as the major sources. Additionally, although inventories have been developed for Europe, almost no data are available for Africa<sup>[42]</sup>. Another study determined the levels of atmospheric POPs in Ghana between May and July  $2010^{[10]}$ . PCNs levels averaged  $49 \pm 5.4$  pg/m<sup>3</sup>, with a high impact on the southern coastal zone of Ghana, where uncontrolled open burning of electronic waste, industrial emissions, and harbour environment were identified among possible emission factors. Tri- and tetra-CNs were the most abundant congeners, altogether constituting approximately 90% of total PCN homologues composition<sup>[10]</sup>. It was concluded that the study brought to the fore the emerging problems of the occurrence of organohalogens in matrices that might be facing African nations like Ghana<sup>[10]</sup>. Agunbiade et al.<sup>[3]</sup> reviewed data on the occurrence and analytical procedures for the evaluation of PCNs in human and environmental matrices in South Africa. The study was conducted as a result of PCNs being listed as POPs at the Stockholm Convention in May 2015. It was reported that highly toxic congeners (CNs 66, 67 and 73) are prevalent in most samples; thus, there is a need for continuous monitoring in our environment<sup>[3]</sup>. In comparison with the reviewed PCNs studies from other continents, very little has been done with regard to PCNs studies in Africa. There is an urgent need to conduct more research studies in the different matrices such as atmosphere, river, sediments, soil, indoor dust, biota, consumer products, landfills, human diet, blood and serum in order to cover this huge omission. Africa then becomes an important study area for PCNs studies.

**RESEARCH GAPS PRIORITIES ON PCNS STUDIES IN AFRICA** 

#### Matrices to be prioritized

Among the different matrices, Akinrinade *et al.*<sup>[139]</sup> pointed out that the atmosphere is particularly an important matrix to be prioritized and monitored for POPs since it is the key route via which contaminants are distributed over long distances beyond the original source of emission. Again, with the high temperatures in the African content, volatilisation of POPs from both primary and secondary sources will be more facile. Consequently, the atmosphere may become a proportionally greater reservoir of POPs in the continent<sup>[140]</sup>. Marek *et al.*<sup>[141]</sup> and Wemken *et al.*<sup>[142]</sup> pointed out that the contribution to overall human exposure to POPs in Europe and North America from outdoor air is minor. In contrast, greater emissions of POPs into the atmosphere may arise in many parts of Africa due to factors including poor handling of waste materials and weak environmental laws enforcement, leading to open waste dumping and burning of waste materials<sup>[139]</sup>. In 2001, Jaward et al.<sup>[42]</sup> detected elevated levels of PCNs in the atmosphere from locations off the coasts of West and South Africa. Although precise sources were not fully resolved, these pollutants might have emanated from countries bordering the west and south coasts of Africa<sup>[10]</sup>. These may have been as results of combustion or from toxic wastes exported to the continent<sup>[10]</sup>. Both issues constitute grave environmental challenges on the continent. For instance, a substantial amount of MSW generated in the African continent 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 release unintentional POPs into the atmosphere<sup>[10,29,31,143]</sup>. Although sources of PCNs in the African continent are not well documented, presumably, there are potential hotspots of PCNs emissions in certain African countries that should be investigated. Since the atmosphere is a key vector through which contaminants are distributed over long distances, the occurrence of PCNs in other matrices such as rivers, sediments, soil, indoor dust, biota, consumer products, landfills, human diet, blood and serum becomes obvious. It is, therefore, crucial to prioritize the monitoring and investigation of the occurrence of PCNs not only in consumer products, landfill leachate and sediments but also in other different matrices.

#### **Research gaps direction**

While studies on POPs are emerging in Africa, it is, however, noteworthy that very few studies on PCNs in various matrices have been conducted. To date, only three studies on PCNs have been published<sup>[3,10,42]</sup>. Nonetheless, despite the scarcity of published data on environmental contamination with PCNs in Africa, about 163 studies on PCN levels in different environmental departments in Asia, Europe and America have been published. Given the large African population, increasing industrialization, urbanization and the increasing demand for imported goods, this is an important omission. In addition, information about environmental levels of PCNs in Africa is essential for guiding efforts to reduce health implications associated with the contaminant in order to achieve the United Nations' Sustainable Development Goals on healthy lives and the promotion of well-being for all at all ages by 2030. There is, therefore, a critical need to study environmental concentrations of PCNs in Africa as well as to expand sampling sites to include landfill leachates, consumer goods and other matrices. Historical sources, current sources, as well as Africa's characteristics, prevailing global warming, make Africa an important study area. In Africa, there are need to assess the presence, use and lifecycle of PCNs in the continent, as well as to develop a National Implementation Plan with specific activities in order to develop PCNs inventories. In view of the effects of PCNs globally, their use needs to be legally restricted or banned. Robust PCNs inventories are overdue in Africa and, therefore, require some attention. It is, therefore, important to gather comparable data on concentrations of PCNs in consumer products and other matrices in all the continents in order to have a global overview of the state PCNs. It is also crucial to study PCNs in Africa in order to understand the impacts of the Stockholm Convention to reduce POPs in Africa and assess their distribution and influence on other continents on the environmental burden of PCNs in Africa, and vice versa.

#### Page 16 of 22

#### CONCLUSION

From the few PCNs studies conducted in Africa, it can be concluded that not much is known about the environmental pollution effects of these pollutants on the African continent. Further research studies on levels of PCNs in matrices can assist in addressing these research gaps. Thus, the expansion of sampling sites not only includes landfill leachates, sediments and consumer goods but also other matrices such as atmosphere, rivers, sediments, soil, indoor dust, biota, human diet, blood and serum, should be prioritized. The effect of temperature on the emission of PCNs has been observed to be very important. Considering the fact that the African continent experiences high temperatures, any increase in temperature coupled with global warming will directly lead to enhanced volatilization of PCNs from their sources, thereby exposing a large population. In addition, foodstuffs imported from other countries might be another pathway for Africa's exposure to PCNs. Currently, there is no published information on the production, use and regulations of PCNs in Africa. Considering the global effects of PCNs, their use should be strictly controlled with robust PCNs inventories developed in Africa. It is also important to collate comparable data globally on concentrations of PCNs in a wider number of matrices in order to have a global overview of PCN distribution. It is of paramount importance to study PCNs in Africa so that a better understanding of the impacts of the Stockholm Convention to reduce POPs in Africa can be achieved; and to assess their distribution, influence on other continents on the environmental burden of PCNs in Africa, and vice-versa.

#### DECLARATIONS

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#### Author's contribution

Prepared the draft manuscript: Nevondo V

Edited and proofed read the manuscript before submission for consideration for publication: Okonkwo JO All authors read and approved the final manuscript.

### Available data and materials

Not applicable.

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#### **Conflicts of interest**

All authors declared that there are no conflicts of interest.

# **Ethical approval and consent to participate** Not applicable.

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