X-RAY FLUORESCENCE SCREENING OF OPEN POLYCHLORINATED NAPHTHALENES (PCNs) AND SHORT CHAIN CHLORINATED PARAFFINS (SCCPs) CONTAING CONSUMER PRODUCTS IN SOUTH AFRICA.

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Introduction

Polychlorinated naphthalenes (PCNs) were listed as POPs in the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2015.[1] More recent in 2017, short-chain chlorinated paraffins (SCCPs; C10 to C13 with a content of chlorine greater than 48% by weight) were listed as POPs in the Stockholm Convention.[2] Additionally, a limit for the presence of SCCPs in other chlorinated paraffin mixtures was set at 1% by weight.[2] SCCPs are listed with a wide range of specific exemptions for production and use. South Africa as a Party of the Stockholm Convention need to assess the presence, use and lifecycle of SCCP and PCNs in the country and develop a National Implementation Plan with specific activities. PCNs are a group of 75 congeners, a family of two-ringed aromatic compounds containing from one to eight chlorine atoms per naphthalene molecule[3-4] (Figure 1) while only DiCNs to OctaCNs are listed in the Convention. PCNs were mainly produced commercially from 1930th to 1970th and for some uses until 2000 and were complex mixtures of PCNs that range from liquids to waxes with high melting points. Short chain chlorinated paraffins (SCCPs) listed as POPs are n-paraffins with more than 1000 congeners that have a carbon chain length of between 10 and 13 carbon atoms and a degree of chlorination of more than 48% by weight. These synthetic compounds are mainly used in metal working fluids, sealants, as flame retardants in rubbers and textiles, in leather processing and in paints and coatings[1,2,6]. Due to the risks caused by the substance to the health and environment the marketing and use of these substances has been restricted in the European Union[6]. There is a weight of evidence that SCCPs are persistent, bioaccumulating and toxic and have potential for long-range environmental transport. The structure of two examples of SCCP compounds ($C_{10}H_{17}C_{l5}$ and $C_{13}H_{22}C_{l6}$) are shown in Fig 2.

Due to their high chemical and thermal stability, inertness, water repellent, flame retardant, and fungus-resistance PCNs and SCCPs have been commercially produced and used as additives in different consumer products. While the use of PCNs have stopped around 2000, the use of SCCP continues with a range of exemptions in the Stockholm Convention listing [1,2,7,8]. Both have been used in the in cables in electrical industry, in textiles, plastic and rubber additives, sealants, oil additives such as hydraulic fluids, lubricants [1,2,9-11]. PCBs were also used in these open applications until 1970s PCNs also occur as trace contaminants in commercial polychlorinated biphenyl (PCBs) mixtures[11]. According to Hogarh PCNs as well as SCCPs remain one of the least researched organohalogens in the continent of Africa[12]. POPs containing products like electronic gadgets and industrial wastes are frequently shipped from developed countries to developing countries which might be a source of shifting of POPs pollution burden from the industrialised nations to developing ones[13].

To date, there is no report on the concentration of PCNs and SCCPs on consumer products in South Africa. The main objective of this study was to develop the PCN and SCCP analysis in South Africa and screen and measure consumer products such as sealants, old paint coatings, PVC products, cable insulation and rubber materials. The presence of chlorine in consumer products may indicate the occurrence of PCNs, SCCPs, PCNs or other chlorinated additives in consumer products.

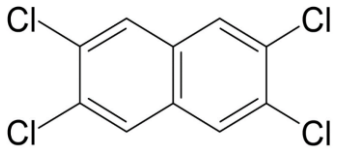

Figure 1. Structure of a polychlorinated naphthalene (PCN)

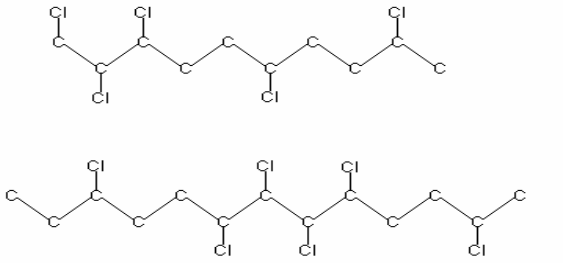

Figure 2. Structures of two examples of SCCPs

Material and methods

Sample collection

A survey was conducted to preliminarily determine the consumer products or articles that are in current use or end of life that may contain PCNs and SCCPs before sample collection was undertaken. For the sample collection strategy the Stockholm Convention inventory guidance documents for PCNs and SCCPs were consulted. The overall aim is to Consumer products samples were obtained from suspected areas where PCNs and SCCPs containing consumer products may be in used. In this first phase of the

X-ray fluorescence (XRF) product testing

Accessible consumer products: sealants, polyvinyl chloride (PVC) cable insulation, plugs and pipes at Tshwane University of Technology, Arcadia campus were subjected to XRF (Olympus Innov-X DELTA XRF analyser) to identify and measure chlorine concentration which may indicate the presence of chlorinated additives in the consumer products. Prior to use, XRF was calibrated using calibration check (pass/fail) 316 stainless steel coupon, followed by the measurement of polymeric check standards (ERM-EC680 and- EC681) through the Mylar window of the plastic cup. The instrument was triggered for 120 s in order to verify the instrument's reliability and accuracy. XRF in the RoHS/WEEE mode triggered for 60 s during each measurement was used to measure chlorine contents of a randomly selected 21 items of consumer products.

Development of PCN and SCCP analysis

For the verification and quantification of PCNs and SCCPs an instrumental analysis needed to be developed. For this PCN mixture standard (PCN-MXA) including PCNs 2, 6, 13, 28, 52, 66, 73 and 75 and SCCP standards were purchased. For the analysis proven standard methods were chosen and established.

Results and discussion

X-ray fluorescence analysis (XRF) is a quick and easy to use tool that can be employed to qualitatively measure different elements in soil, rocks and ores[14] and has been further extended to the screening of elements contained in different consumer products[15]. The XRF results were used as an indicator of the occurrence of PCNs, PCBs, SCCPs or other chlorinated paraffins like medium-chain CPs (MCCPs) or long chain CPs (LCCPs)in various screened consumer products from the laboratory environment (Figure 3).

For products like rubber, sealants or leather, a high chlorine content of several percent is indicative for a chlorinated additive. On the other hand PVC already contains high content of chlorine depending on the additives used. The concentration of chlorine in rigid PVC without plasticiser additives are above 50% while soft PVC contain 50% or more additives and therefore the chlorine content is normally below 30 %. In the screened sealants a high chlorine concentration of 29.79 % was detected. The University was built 1970s and therefore all additives (PCB, PCN or SCCP) could have been used at that time and further instrumental analysis is necessary. For PVC rigid PVC contain normally no softeners and flame retardants and have a chlorine content above 50% chlorine. Soft PVC contain frequently 50 % of softeners often non-chlorinated phthalates and therefore a chlorine content of less than 30 %. SCCPs (or other CP mixtures potentially contaminated with SCCPs[2]) are used as plasticizer or flame retardant in soft PVC with a concentration of up to 15 %. Therefore they might add approx. 8 % of chlorine to soft PVC. Therefore, in the screening of PVC such soft PVC containing SCCPs might have a higher chlorine content compared to soft PVC containing only non-chlorinated plasticizer. Therefore, the need to screen a range of PVC samples using XRF for chlorine content was deemed necessary.

From the PVC samples a blue PVC pipes showed the highest concentration of chlorine 55 % as expected for a rigid PVC material. The concentrations of chlorine in soft PVC like plugs and cables insulators were within the range of 25.89 % to 23.70 %. More screening of soft PVC products and respective analysis of additives need to be performed to see if a chlorine content might be used as indication for a chlorinated additive. Consumer products with chlorine concentrations of less than 1% are not included in the further assessment by instrumental analysis.

Work is underway to screen more consumer products.

Also the development of a standard method for analysis of PCNs and SCCPs by GC-MS are ongoing to confirm quantitatively the presence of PCNs and SCCPs. The method for PCBs has already been established.

For quality assurance, the selected samples with positive SCCPs or PCNs will be sent to the Japanese national laboratory of National Institute of Environmental Studies. This institute has developed a standard analysis for PCNs and SCCPs and is planning an inter-laboratory comparison of industrial POPs in products/waste including PCNs and SCCPs.

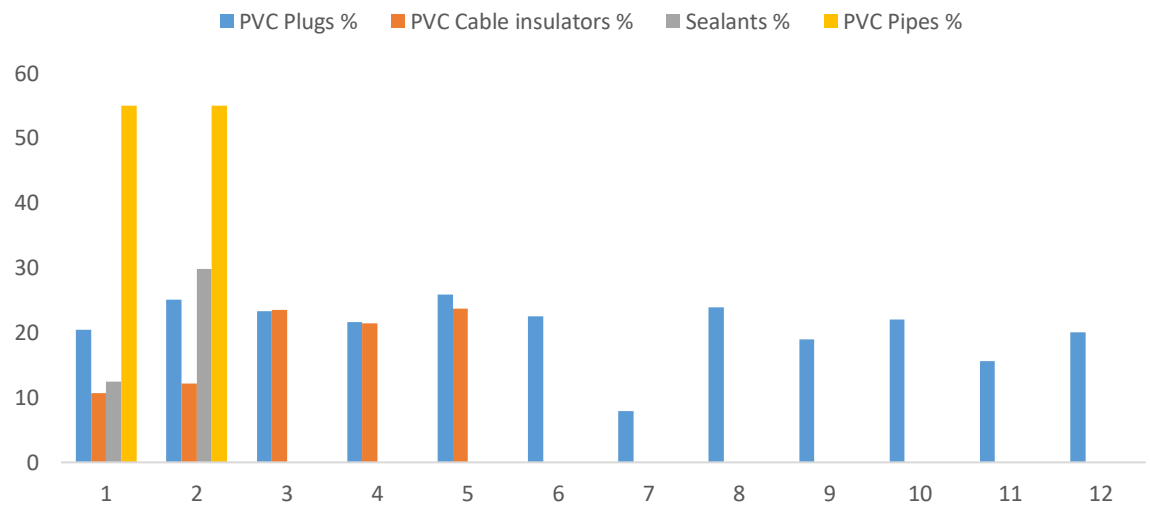

Figure 3**.** Concentrations of chlorine in selected consumer products

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