Preliminary inventories of selected POPs by Tier I and II in Brazil and research needs towards Tier III inventory for Polychlorinated naphthalenes (PCNs) and Short-chain chlorinated paraffins (SCCPs)

The report was developed within the Project on "Supporting inventories development and priority setting as part of the process to develop, review and update NIPs -National Implementation Plans- for POPs listed after the entry into force of the Stockholm Convention" financed by the European Union

12/2019

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Abbreviations and Acronyms

ABIQUIN	*Associação Brasileira da Indústria Química* (Brazilian Chemical Industry Association)
CAS	Chemical Abstracts Service
CP	Chlorinated paraffins
DDT	Dichlorodiphenyltrichloroethane
decaBDE	Decabromodiphenyl ether
ECD	Electron Capture Detector
ECNI	Electron capture negative ionization
ESM	Environmentally Sound Management
EU	European Union
FISPQ	*Ficha de Informação de Segurança para Produtos Químicos* (Chemical Safety Data Sheet)
FR	Flame Retardant
GC	Gas chromatography
HBB	Hexabromobiphenyl
HBCD	Hexabromocyclododecane
HCB	Hexachlorobenzene
HCBD	Hexachlorobutadiene
HCH	Hexachlorocyclohexane
HS	Harmonized System
IBAMA	*Instituto Brasileiro do Meio Ambiente e dos Recursos Naturais Renováveis* (Brazilian Institute of Environment and Renewable Natural Resources)
LCCPs	Long-chain chlorinated paraffins
MCCPs	Medium-chain chlorinated paraffins
MDIC	*Ministério do Desenvolvimento, Indústria e Comércio Exterior* (Ministry of Economy, Industry, Foreign Trade and Services)
MMA	*Ministério do Meio Ambiente* (Ministry of the Environment)
MS	Mass spectrometer
MWF	MetalWorking Fluid
NCM	*Nomenclatura Comum do Mercosul* (MERCOSUR Common Nomenclature)
NIP	Nation Implementation Plan
PBDEs	Polybrominated diphenyl ethers
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzo-*p*-dioxins
PCDFs	Polychlorinated dibenzofurans
PCNs	Polychlorinated naphthalenes
PCP	Pentachlorophenol
PeCB	Pentachlorobenzene
PFHxS	Perfluorohexanesulfonic acid
PFOA	Penta-decafluoro-octanoic acid
PFOS	Perfluorooctane sulfonic acid
PFOS-F	Perfluorooctane sulfonyl fluoride
POPs	Persistent Organic Pollutants
PVC	Polyvinylchloride

RAPEX	Rapid Alert System for Non-Food Consumer Products (EU)
SC	Stockholm Convention
SCCPs	Short chain chlorinated paraffins
UNECE	United Nations Economic Commission for Europe
UNEP	United Nation Environment Program
VCM	Vinyl chloride monomer

1 INTRODUCTION

1.1 Background on the Brazilian POP activities and current project

Brazil signed the treaty of the Stockholm Convention (SC) on Persistent Organic Pollutants (POPs) in the Act of its creation, in May 2001, and ratified its text on June 16, 2004, becoming part of that global commitment. As a signatory country of this Convention, the Brazilian State acknowledges its obligation, in accordance with article 7° (seventh) of the Stockholm Convention and its internal legal order, which was made via Decree No. 5,472 of 20 June 2005, of I) to develop a National Implementation Plan (NIP), indicating how the obligations laid down in the treaty are met, defining priorities and strategies; and II) Review and update the NIP-Brazil periodically, with the aim of assisting the Government to identify the necessary measures to control POPs in the country.

The first NIP of the Stockholm Convention was published in the year 2015 (NIP-Brazil-2015). This publication presents the conclusions of an initial investigation into the situation of the implementation of the Stockholm Convention on Persistent Organic Pollutants in Brazil, the use of these chemicals in the country, the management of its residues and stocks, the areas contaminated by POPs, as well as the installed national capacity (MMA, 2015a). In addition, the NIP-Brazil 2015 identified the legislative and administrative measures already underway, to protect human health and the environment from the effects of POPs, and pointed out the gaps that need to be overcome, offering an action plan for the Brazilian State to meet the obligations of the Stockholm Convention. In the first NIP were approached the initial 12 (twelve) POPs, the 9 (nine) new POPs added to the annexes of the Convention in 2009, the endossulfam, listed in 2011 in COP 5 (five) and hexabromocyclododecane (HBCD), listed during COP 6 (six), in 2013.

After the publication of NIP-Brazil 2015, new chemical compounds were listed by the Stockholm Convention. During COPs 7 (seven), 8 (eight) and 9 (nine), seven groups of chemicals entered the list of POPs from the Stockholm Convention: hexachlorobutadiene (HCBD); pentachlorophenol (PCP); polychlorinated naphthalenes (PCNs); decabromodiphenyl ether (decaBDE); short-chain chlorinated paraffins (SCCPs) and products that may contain this substance with a percentage above 1% of its mass; penta-decafluoro-octanoic acid, its salts and related compounds (PFOA) and dicofol. Table 1 highlights all substances listed as POPs by the Stockholm Convention by the year 2019. Besides, three more chemicals are currently under review by the POPs Review Committee (PFHxS, Dechlorane Plus and methoxychlor).

Brazil is currently developing the review and update of its first NIP, published in 2015. Therefore, the country, through its Ministry of the Environment, is working to update and revise the information regarding some of the previously addressed in the National Inventory of New POPs of Industrial Use (MMA, 2015a,b), with exception of the hexabromobiphenyl (HBB) and the pentachlorobenzene (PeCB), since it was stated in the National Inventory of New POPs of Industrial Use that there was no stockpiles or articles containing HBB or PeCB in the country. The inventory (MMA, 2015b) also highlighted that no information was found on the production or use of HBB and PeCB in the past and the specific use of PeCB as an intermediate in the production of quintozene was investigated at the only company that was registered to trade this product. But the company informed that it had not used PeCB. Hence, only the perfluorooctane sulfonic acid (PFOS) and perfluorooctane sulfonyl fluoride (PFOS-F) its salts and related compounds, polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) are being addressed in this review to be updated and the not mentioned, pentachlorophenol, its salts and esters (PCP), polychlorinated naphthalenes (PCNs), hexachlorobutadiene (HCBD), decabromodiphenyl ether (decaBDE), short-chlorinated paraffins

(SCCPs) are now having their inventories built. However, dicofol and PFOA should soon be included in this same project.

Table 1: Persistent Organic Pollutants under Stockholm Convention, detailed according to date and the Conference of the Parties (COP) in which had been regulated, its potential emission source and the annex of listing

Compound	Conference and year	Source
Aldrin [A]	COP 1 - 2001	Pesticide
PCBs [A]* [C]	COP 1 - 2001	Industrial-Unintentional
Chlordane [A]	COP 1 - 2001	Pesticide
DDT [B]	COP 1 - 2001	Pesticide
Dieldrin [A]	COP 1 - 2001	Pesticide
Endrin [A]	COP 1 - 2001	Pesticide
Dioxins (PCDD) [C]	COP 1 - 2001	Unintentional
Furans (PCDF) [C]	COP 1 - 2001	Unintentional
Heptachlor [A]	COP 1 - 2001	Pesticide
HCB [A] [C]	COP 1 - 2001	Industrial-Pesticide-Unintentional
Mirex [A]	COP 1 - 2001	Pesticide
Toxaphene [A]	COP 1 - 2001	Pesticide
α- HCH [A]	COP 4 - 2009	Pesticide
β- HCH [A]	COP 4 - 2009	Pesticide
PFOS, PFOSF its salts and derivates [B]	COP 4 - 2009	Industrial-Pesticide
Chlordecone [A]	COP 4 - 2009	Pesticide
Hexa and hepta-BDE [A]	COP 4 - 2009	Industrial
HBB [A]	COP 4 - 2009	Industrial
γ-HCH [A]	COP 4 - 2009	Pesticide
PeCB [A] [C]	COP 4 - 2009	Industrial-Pesticide-Unintentional
Tetra and penta-BDE [A]	COP 4 - 2009	Industrial
Endosulfan technical and isomers [A]	COP 5 - 2011	Pesticide
HBCDD [A]	COP 6 - 2011	Industrial
HCBD [A] [C]	COP 7/8 - 2015/2017	Industrial-Unintentional
PCP and its salts and esters [A]	COP 7 - 2015	Pesticide
PCNs [A] [C]	COP 7 - 2015	Industrial-Unintentional
DecaBDE [A]	COP 8 - 2017	Industrial
SCCPs [A]	COP 8 - 2017	Industrial
PFOA [A]	COP 9 - 2019	Industrial
Dicofol [A]	COP 9 - 2019	Pesticide

Annex [A], elimination, with prohibited use and production (*-with some specific restrictions); Annex [B], restriction (and perspective of elimination); Annex [C], unintentional production

Moreover, the country is involved in the pilot project for the inventory of PCBs, PCNs and SCCPs in open-application. Pursuant to Article 10 of the SSFA No. BRS-SSC-SSFA-1741 that entered into force on April 2018 between SSC/UN Environment Programme and the Brazilian Partner, on “Supporting inventories development and priority setting as part of the process to develop, review and update NIPs for POPs listed after the entry into force of the Stockholm Convention”. The activities to be carried out by the Partner with the support of the small-scale funding from the Stockholm Secretariat and the European Union (EU):

a. To organize a 3 (three)-day training workshop in Brazil, from 19 to 21 June 2018;

b. To facilitate pilot-testing of the draft guidance on preparing inventories of Polychlorinated Naphthalenes (PCNs) in Brazil, which includes:

i. In coordination with SSC/UN Environment Programme, to contact and follow-up with the authorities in Brazil for the piloting of the inventory of one of the two above-mentioned POPs;

ii. Undertaking inventory of PCN, PCB and SCCPs in open application in major products in accordance to the "Terms of Reference for developing inventory of PCNs, PCBs in open application and SCCPs in major products" (Annex E);

iii. To assist in organizing the inventory validation meeting.

1.2 Background on PCNs and link to PCBs

In May 2015, by decision SC-7/14, the Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants amended Annex A to the Convention to list polychlorinated naphthalenes (dichlorinated naphthalenes to octachlorinated naphthalenes, referred to as PCNs). In order to attend the Russian request, which stated a demand of PCNs as intermediates on the production of polyfluorinated naphthalenes (including octafluoronaphthalene), this application was established as a specific exemption. In the same decision, PCNs were also listed as unintentional POPs, therefore being included in Annex C to the Convention. PCNs were first produced for technical use around 1910 with major production from 1930s to 1960s and declining production in the 1970s, as they were gradually replaced by PCBs for some applications (HAYWARD, 1998). The production of PCN mixtures continued during a longer period for some specific applications as wood protection until 1987 (JAKOBSSON & ASPLUND, 2000) and as additives on chloroprene rubber until 2000 (YAMAMOTO, 2016). Since then, the production of PCNs is assumed to have ended, with the exception of production of PCNs as intermediate for the production of polyfluorinated naphthalenes (PFNs) and for laboratorial analytical purposes.

Major uses of PCNs were in cable coatings, rubber, paints, sealants, lubricants and capacitors (Table 2). Considering that most of the PCN-containing products had short service lives (Table 2), it is likely that the largest number of products to which they have been applied have already been disposed. However, for some other long-term uses, mainly outdoor applications, like sealants in buildings and outdoor paints (such as construction) and in capacitors, some PCNs might still be present. Also, for the more recent use in rubber (until 2000) some treated products might still be in use and they are also expected to be found in areas where PCNs have been used in the past.

Only a few measurements on PCNs in open applications have been published, such as PCNs in Neoprene FT rubber (YAMASHITA et al. 2003); or PCNs in waste wood (KOYANO ET AL., 2019) and there was no specific monitoring of PCNs in closed applications such as capacitors or transformers. However, some measurements of technical PCB oils from transformers showed that PCBs contain unintentional produced PCNs (YAMASHITA et al., 2000).

The main uses of PCNs were practically identical to those of PCBs in both closed applications (e.g. capacitors, transformers) and open applications (e.g. cables, paints/coatings, sealants) (Table 2, 3). However, the total production of PCBs were approx. 10 times higher (ca. 1.5 million tonnes) compared to PCNs (ca. 150,000 t). Therefore, the inventory of PCNs should be linked or combined with the inventory of PCBs.

Table 2: Former PCN uses in closed and open applications (UNEP 2017a)

Sector	Application
Transformers and Capacitors	• Capacitor impregnates (JACOBSSON & ASPLUND, 2000) • Transformer and capacitor fluids (UNECE, 2007; IPCS, 2001)
Batteries	• Separator in storage batteries (JACOBSSON & ASPLUND, 2000)
Plastics and cables	• Cable covering (flame-retardants) (JACOBSSON & ASPLUND, 2000) • Additive in plastic (JAKOBSSON & ASPLUND, 2000)
Rubber	• Additive in Neoprene and possibly other chloroprene with use in printer belts (YAMASHITA et al., 2003; YAMAMOTO et al., 2016)
Sealants	• Water proof sealants (NICNAS 2002)
Paints, lacquers, dyes/dye carrying agents	• In anti-corrosion/underwater paints and lacquers (JACOBSSON AND ASPLUND, 2000)
Wood preservative/fungicide	• Impregnation of wood (IPCS 2001; JAKOBSSON & ASPLUND, 2000)
Textile and paper industry	• Coating/impregnation of paper and textiles for water proofing (Van de PLASSCHE and SCHWEGLER, 2002, JAKOBSSON & ASPLUND, 2000)
Oil additives and lubricants	• Additives in oils for lubrication in gear and machinery (JAKOBSSON & ASPLUND, 2000; US DEPARTMENT OF AGRICULTURE 1954) • Oils in mining sector (POPP ET AL., 1997) • Cutting oils (JAKOBSSON AND ASPLUND, 2000) • Engine oil additive (Van de PLASSCHE and SCHWEGLER, 2002) • Refracting index testing oils (Van de PLASSCHE and SCHWEGLER 2002)
Military use	• Fogg ammunition; smoke grenades (GENERALSTAB SCHWEIZER ARMEE, 1945; EMPA 2006). • Inert artillery and mortar projectiles (HEWITT et al., 2011; CLAUSEN et al., 2004; FALANDYSZ, 1998) • Paints for ships (REDFIELD et al., 1952) and possibly other metal surfaces of military vehicles/equipment.

A draft inventory guidance for PCNs has been developed by the Secretariat of the Stockholm Convention and it contains information on PCBs in open application (UNEP 2017a, UNEP 2019a). PCNs and PCBs are also formed as unintentional POPs in certain processes of the organochlorine (e.g. production of chlorinated paraffins; TAKASUGA et al., 2012) and chlorine industries and in incineration processes and are therefore listed also in Annex C. PCNs and PCBs were later substituted in many open applications by chlorinated paraffins (CPs) which are still produced and where short chain chlorinated paraffins (SCCPs) have been listed as POP in 2017. Therefore, the most appropriate approach is an assessment/inventory of PCN combined with an assessment of PCBs and SCCPs.

Table 3: Concentration of PCNs (or PCBs)* in selected application and some waste fractions

Product/sample (POPs measured)	Level of PCN or PCB (mg/kg)	References
Neoprene rubber (PCN)	36,000 – 45,000	YAMAMOTO et al. 2005 YAMASHITA et al. 2003
Rubber coated plastic (PCN)	1000	YAMASHITA et al. 2003
Rubber belt for printers (PCN)	41 to 2000 (3/21)	YAMAMOTO et al. 2005
Rubber belt for printers (PCN)	0.001 – 0.1 (17/21)	YAMAMOTO et al. 2005
Aerosol adhesives (PCN)	1150 – 1200	YAMASHITA et al. 2003
Sealants (PCB)*	28,000 – 224,000	KOHLER et al., 2005
Paints (PCB)*	30,000 – 160,000	WEBER et al., 2018
Cable sheathing and coating (PCB)	30,000 to 200,000	MUELLER, 2017

Product/sample (POPs measured)	Level of PCN or PCB (mg/kg)	References
Cables coatings in recycling (PCB)*	10 – 325	LEHNIK-HABRINK et al. (2005)
Automotive shredder residue (PCN)	0.026 – 0.040	YAMAMOTO et al. 2005
Refused derive fuel (PCN)	0.011 – 0.086	YAMAMOTO et al. 2005
PCN (technical mixture)	930,000 – 1,000,000	YAMASHITA et al. 2003
Transformer oils (Askarel PCB)*	ca. 600,000**	MUELLER, 2017
Contaminated transformer oil (PCB)*	50 – 100,000	MUELLER, 2017
Capacitor/condensers (PCB)*	ca. 600,000**	MUELLER, 2017
Transformer oils (unintentional PCNs)	1000 – 9000	YAMASHITA et al. 2000

*For these applications only PCB data were available. Due to the use in the same application and similar chemical properties, the levels of PCB use might reflect levels if PCN was/are used.
**The PCBs are normally mixed with ca. 300,000 mg/kg Pentachlorobenzene.

1.3 Background on SCCPs and link to PCBs and PCNs

Short-chain chlorinated paraffins (SCCPs) (chain length C10 to C13) together with medium- and long-chain chlorinated paraffins (MCCPs and LCCPs, respectively) have substituted PCBs and/or PCNs in a range of open applications (e.g. cables/PVC, sealants/adhesives, paints/coatings, cutting oils, rubber) since the 1970s (HOWARD, 1975). SCCPs have been listed as POPs in the Stockholm Convention in 2017. In May 2017, by decision SC-8/11, the Conference of the Parties amended Annex A to the Convention to list short-chain chlorinated paraffins (SCCPs) with various specific exemptions (Table 4). As Brazil did not deposit any notification with the depositary, it was the responsibility of the Brazilian Government to comply with the obligations that lead to the elimination of the SCCPs throughout the national territory from 18 December 2018.

Table 4: Specific exemptions for short-chain chlorinated paraffins listed in the Stockholm Convention

Chemical	Activity	Specific exemption
Short-chain chlorinated paraffins (Alkanes, $C_{10\text{-}13}$, chloro)$^{+}$: straight-chain chlorinated hydrocarbons with chain lengths ranging from C_{10} to C_{13} and a content of chlorine greater than 48%, by weight For example, the substances with the following CAS numbers may contain short-chain chlorinated paraffins: CAS No. 85535-84-8; CAS No. 68920-70-7; CAS No. 71011-12-6; CAS No. 85536-22-7; CAS No. 85681-73-8; CAS No. 108171-26-2; CAS No. 63449-39-8.	Production	As allowed for the Parties listed in the Register
	Use	• Additives in the production of transmission belts in the natural and synthetic rubber industry; • Spare parts of rubber conveyor belts in the mining and forestry industries; • Leather industry, in particular fat-liquoring in leather; • Lubricant additives, in particular for engines of automobiles, electric generators and wind power facilities, and for drilling in oil and gas exploration, petroleum refinery to produce diesel oil; • Tubes for outdoor decoration bulbs; • Waterproofing and fire-retardant paints; • Adhesives; • Metal processing; • Secondary plasticizers in flexible polyvinyl chloride, except in toys and children's products.

Parties of the Convention for which the amendments to list PCNs and SCCPs have entered into force shall meet the obligations under the Convention leading to the elimination of those chemicals. According to Article 7 of the Convention, each Party shall develop a NIP within two years from the date of entry into force. The establishment of inventories is one of the important phases in the development of NIPs. Furthermore, Article 6, paragraph 1 (a), of the Stockholm Convention requires each Party to develop appropriate strategies for the identification of products and articles in use and wastes consisting of, containing or contaminated with POPs.

MCCPs and LCCPs are not listed in the Convention and not restricted in countries however it is cautioned by science that that also MCCP are bioaccumulative, toxic to the aquatic environment, and that they are also persistent in the environment (GLÜGE et al. 2018).

The total global production volume of all CPs is more than 1 million tonnes per year, in a minimum scenario (GLÜGE et al. 2016). It is estimated that this includes production and used of about 165,000 t of SCCPs (GLÜGE et al. 2016). The major use is in open applications such as plasticizer or flame retardant in PVC/other plastic, rubber, paints, sealants/adhesives, leather fat-liquoring, lubricants and metalworking fluids. Many of these uses were exempted in the Stockholm Convention listing (Table 4). These were also the major historic uses and therefore over the last 50 years stockpiles (products in use) and wastes have accumulated over time.

SCCPs (chain length C10 to C13) can be impurities of MCCPs (C14 to C18). If the SCCP content in MCCPs is above 1%, this mixture is considered also a POP. Therefore, for an inventory of SCCPs, also MCCPs and LCCPs need to be assessed and analysed. For that, monitoring and chemical analysis are needed, since only by this approach it can be decided if a chlorinated paraffin in a use or product contain SCCPs or is contaminated by SCCPs or if it contains other chlorinated paraffins not listed in the Convention.

Due to the concerns on the persistence and bioaccumulation of MCCPs (GLÜGE et al. 2018), also the exposure and release of MCCP need to be controlled. Recent studies have shown that MCCPs and to a lower extent SCCPs are released in 50% of baking ovens in Germany (n=20) and are released from many kitchen/food-blenders (GALLISTL et al. 2018; YUAN et al. 2017). Therefore, it would be wise from the industry to support the control of release of MCCPs to minimize these releases to the environment and human exposure to avoid that MCCPs become legally restricted as suggested e.g. from Swedish Kemi for electronic equipment by suggested listing into the RoHS list (KEMI 2018). Since MCCP uses need to be monitored within the assessment of SCCPs to clarify the SCCP contribution in MCCP to clarify on the POPs properties an assessment of MCCP use and substance flow is needed for SCCP assessment. Such an assessment can lead to a more sustainable use of MCCPs and the improvement of its current use. A sustainable and controlled use of MCCPs that reduce and possibly minimize releases of MCCP (and associated SCCPs) to the environment and avoiding high exposure to humans and biota which is likely the best basis to avoid future restriction of MCCPs.

1.4 Science-Policy Support - monitoring and assessment of PCNs, PCBs and SCCPs

1.4.1 Background

The science-policy interface is of key relevance for science-based decision making which is stressed by the Basel, Rotterdam and Stockholm Convention with a road map from science to action presented at COP 2017 and 2019 (UNEP 2019b).

The science base for policy making includes e.g. inventories and material and substance flow analysis, quantitative data on pollution, or science-based limits for exposure or regulatory action. The integration of research groups or governmental institutions with analytical capacity in the development and implementation of the NIP is therefore of key importance. For a range of POPs, the assessment/inventory and the implementation of the convention need monitoring and measurement data.

There is relatively good information on PCBs in open applications in industrial countries (JARTUN et al. 2009; UNEP 2019c; WAGNER et al. 2014) including the relevance of contamination of environment, food and humans (WEBER et al. 2017; 2018). There are hardly any data and information on PCBs in open applications in developing countries. Most PCB data from developing countries are from GEF projects on measuring of PCBs in closed applications in particular transformers. However, after more than 10 years inventory work still many developing countries have to screen transformers and often have not yet addressed capacitors.

As described above, PCNs have also been used in the same open and closed applications as PCBs (UNEP 2017a, 2019a). However, there are only a few measurements on PCNs in open application (e.g. Neoprene FT, YAMASHITA et al. 2003) and there are no data on PCNs in closed applications other than as unintentional POPs in PCB oils (YAMASHITA et al. 2000).

Also, for SCCPs (including SCCPs in MCCPs) only initial monitoring data have been generated in some monitoring projects in Europe (GALLISTL et al. 2018; UNEP 2018; YUAN et al. 2017) but data on SCCP in products are missing from South America and other world regions.

Therefore, it needs some screening and monitoring and a strategic use of research/monitoring capacity to assess and understand the presence of PCNs and PCBs and the substitute SCCPs in the different uses and waste and recycling flows. For PCNs an inventory guidance has been developed to support assessment (UNEP 2017a, 2019a) This guidance also includes information on PCBs in open application. For SCCPs in 2019 an inventory guidance has been developed (detailed version UNEP 2019d).

1.4.2 Need of monitoring data and approach

PCNs in open applications need to be analysed to finally confirm their presence in a product as highlighted for PCBs in open applications (UNEP 2019c). Otherwise it is not possible to confirm if a sealant or a rubber contain these POPs pollutants or not. There is a global GAP on information of the presence of PCNs in open application worldwide even in industrial countries where now the first monitoring studies are conducted and published e.g. for Japan (KOYANO et al. 2019, YAMAMOTO et al. 2018; YAMASHITA et al. 2003). However, there is no single dataset of PCNs or PCBs in open application in developing countries.

Also, there is a complete knowledge gap on PCBs in open applications in developing countries including Brazil. Since PCBs have been used in higher volumes than PCNs in history but in basically the same uses, it is wise and practical to combine the screening of PCBs and PCNs for POPs inventories. Since SCCPs, listed as a POP in 2017, have substituted PCNs and PCBs in open applications, the most appropriate approach is a combined assessment of PCNs, PCBs and SCCPs. Since CPs contain PCNs and PCBs as unintentional POPs (TAKASUGA et al. 2012; 2013), this also should address the unintentional PCNs and PCBs in SCCPs and other CPs with appropriate measurements. Also, the assessment of SCCPs in CP mixtures to decide on POPs categorisation need analytical assessment.

A useful inventory of PCNs, PCBs and SCCPs, therefore need monitoring and analysis (Tier III assessment). Therefore, for a reasonable inventory analytical capacity need to be involved either by cooperation with existing laboratories or by the development of analytical capacity.

1.4.3 Steps to establish analytical capacity and get data in the current project, the following approach and steps were taken

A) Contact/involvement of research groups with experience in PCN and SCCP analysis

In the preparation of the country pilots research groups with capacity to analyse PCNs and SCCPs were contacted and asked for support. The very limited budget of this project did not allow a budget for analytical cost but only voluntary contributions. Research groups were contacted for discussion including Dr. Natsuko Kajiwara (Japanese National Institute for Environmental Science); Prof. Takeshi Nakano (Osaka University, Japan); Professor Walter Vetter and Jannik Sprengel (Hohenheim University, Germany); Dr. Guroi Liu (Chinese Academy of Science); Professor João Torres and Yago Guida (Federal University of Rio de Janeiro, Brazil).

B) Involvement of research groups for inventory and assessment of respective POPs

One bottleneck of POPs assessment and management in developing or transition economies is the lack of analytical capacity. Therefore, the approach in this project was the establishment of analytical and research capacity for PCNs and SCCPs in the country. Such capacity and involvement of research groups contributes to the improvement of knowledge in the science community of a country and the science-policy dialogue with related strengthening of the Science-Policy interface. In the pilot countries the research groups were assessed for potential partners which were thus selected to work on the project.

C) Capacity building and research development in the respective country and development of a PhD

To get reliable results, a robust monitoring and analytical method need to be established. This was done by selecting cooperation partners developing the standard procedures in respective industrial countries. In South Africa and Brazil, the research group start to establish a PhD or integrated the topic in an ongoing PhD. The Brazilian student (MSc. Yago Guida) had already been trained in Germany (within Prof. Walter Vetter group) for SCCP analysis in the frame of another project and was capable to establish the SCCP and PCN analysis at the Federal University of Rio de Janeiro in Brazil. The Brazilian group (MSc. Yago Guida) together with the group of Professor Vetter (Jannik Sprengel) developed Standard Operation Procedure for the GC/LRMS analysis of PCN (see Annex 2) and SCCPs (See Annex 3).

1.5 Approach for developing a preliminary inventory and building the bases for detailed assessment

1.5.1 Involvement of research groups and building knowledge and analytical capacity

In Brazil several research groups possess some capacity for POPs analysis. However, the only group able to perform PCN and SCCP analyses is the group of the Federal University of Rio de Janeiro, due to the collaboration with the German group (Prof. Walter Vetter). Although the Brazilian group has implemented analytical capacity for PCN and SCCP analyses and were already able to perform PCB, OCP and PBDE analyses, the group is still trying to manage an XRF equipment for sample screening, which would optimize the number of analysed samples for PCB, PCN and SCCP quantification.

1.5.2 Gap analysis and developing research/monitoring project proposal for next inventory phase

This initial study did not have the time, resources and capacity to develop a detailed inventory of SCCP and PCN which are addressed for the first time in a developing country and need monitoring and analysis. Even for industrial countries such inventories do not exist yet. Only initial monitorings of selected product categories are currently conducted e.g. in Japan where recently the first study on PCNs in waste wood was conducted and published (KOYANO et al. 2019) and PCN contaminated rubber was destroyed (YAMAMOTO et al. 2018). Therefore, the Terms of Reference of this project included the request to conduct a gap analysis and the need of future screening and monitoring of PCBs, PCNs and SCCPs in Brazil.

1.6 Structure of the report

In this report information on the potential and likely uses of PCBs, PCNs and SCCPs (in open application) have been compiled. Also, a gap analysis is conducted and a compilation of samples for monitoring of SCCPs and PCNs in import and export, productions, products including consumer products and products used in industry as well as end of life management and recycling has been conducted and information compiled.

1.6.1 Support for establishing PCN and SCCP analysis for Tier III inventory

As support for the establishment of PCN and SCCP analysis contacts were established to experienced research group for PCN and SCCP analysis including the research group of Professor Vetter supervising a PhD on the development of SCCP analysis for the national European food and feed laboratories and to Dr. Natsuko Kajiwara responsible for development of PCN and SCCP analysis for Japan.

The Federal University of Rio de Janeiro group (MSc. Yago Guida) in cooperation with Hohenheim University (Professor Vetter; Jannik Sprengel) developed a Standard Operation Procedure for setting up analysis of SCCPs (Annex 3). For the SOP for PCNs (Annex 2) the Stockholm Convention guidance for monitoring POPs in products were considered (UNEP 2017b).

2 INVENTORY DEVELOPMENT

2.1 Approach for Tier I and II

Polychlorinated biphenyls (PCBs) are listed in Annexes A and C, which means they must be phased out from use by 2025 and be given final disposal by 2028 (according to Annex A). Unintentional releases must also be controlled (Annex C). The Brazilian Government already published an inventory of PCBs aiming to identify the existing stockpiles, PCB-containing equipment (in and out of use), and amount (in number of devices and in volume, when appropriate) (MMA, 2015a,c). To gather this information, production and commercial sectors in Brazil likely to have PCB-containing equipment were consulted, particularly those related to the use of electrical energy (small electrical substations, transformers and capacitors). This inventory (MMA, 2015c) included areas at risk, such as schools, shopping centres, hospitals, and universities (high-traffic areas) according to the priorities set forth in Annex A, Part II of the Stockholm Convention. The food and beverages sector were also of concern, since the use of PCB-containing equipment is banned from food production areas and drinking water areas. No consultations were carried out regarding the unintentional production of PCBs (Annex C), since this information is included in the National

Inventory of Sources and Estimative of Dioxins and Furans Releases (MMA, 2013). Furthermore, the National Inventory of PCBs is complemented by the Inventory of POP Contaminated Sites (MMA, 2015d) and thus, we focused on the new inventories of PCNs and SCCPs, still to be done to the development of this project and to the review and update of the NIP-Brazil-2015. However, in this project, chemical confirmation analysis for open application uses must be performed targeting the three of them, PCBs, PCNs and SCCPs.

The first action developed in order to construct the inventories of PCN and SCCPs in Brazil, following their respective guides, published by the Stockholm Convention (UNEP, 2019a,d) and after studying deeply the topic, was to identify the potential information holders at national level and to carry out a consultation on the entire life cycle of PCNs and SCCPs. The inventories of PCNs and SCCPs are presented separately, however, they were addressed together in many steps due to their similar application and potential crossed contamination.

Firstly, a consultation was made to the governmental institutions such as the departments of the Ministry of the Environment (*MMA – Ministério do Meio Ambiente*), the Brazilian Institute of Environment and Renewable Natural Resources (*IBAMA – Instituto Brasileiro do Meio Ambiente e dos Recursos Naturais Renováveis*), that is the national authority for the import of some substances controlled by the Stockholm Convention, the actual Ministry of Economy, Industry, Foreign Trade and Services (*MDIC – Ministério do Desenvolvimento, Indústria e Comércio Exterior*) and all environmental secretariats and industrial federations from the 26 Brazilian states.

The MDIC was officially consulted online via its unified database portal for the international trade, *Comex Stat* (http://comexstat.mdic.gov.br). The IBAMA was officially consulted, by e-mail, regarding the control information of the substances studied and through the Electronic System of Information Service to Citizen. The IBAMA declared to carry out its control searches in the same general government database, but by the platform Single Portal of Foreign Trade (Siscomex*).* Both the IBAMA and the technical team of the project carried out data collection through codes of the MERCOSUR Common Nomenclature (*NCM – Nomenclatura Comum do Mercosul*). However, most NCMs are generic codes that can encompass a variety of substances and thus lead to an overestimation of the quantities of commercialization of the compounds studied. In addition, some substances may have been marketed within different NCMs depending on the period evaluated and the data search systems do not allow the collection of data referring to a cancelled NCM code. The IBAMA reported to do not have any control over the volumes of PCNs or SCCPs international trade.

In parallel, industrial/business associations and individual private companies, potentially involved in some stage of PCNs and/or SCCPs lifecycle – production, import and export, uses and final destination of PCNs and/or SCCPs or products that can contain PCNs and/or SCCPs – in national territory were listed for further inquiry. From the exhaustive search on the web, 1599 institutions were listed within 21 sectors of interest (Table 5).

From then on, the institutions were consulted via an official questionnaire sent by the MMA (circular craft n ° 171), sent by e-mail – when available – or directly through their web pages. However, approximately 15% of the institutions could not be contacted by the website or by e-mail, having 1357 (85%) institutions been actually contacted. Approximately 6% of this amount was composed of associations (n = 78) that together can add thousands more to the 1280 (94.3%) individually consulted companies for PCNs and SCCPs.

Table 5: List of institutions potentially involved in some stage of the life cycle of short-chain chlorinated paraffins (SCCPs) consulted by the Ministry of the Environment: number of questionnaires sent, number of private companies, number of associations and number of responses

Sector	Institutions	Questionnaires	Companies	Associations	Positive answer	Negative answer
Acrylic	22	22	22	0	0	0
Adhesive & Sealant	119	114	114	0	0	5
Additive	13	10	9	1	0	0
Rubber	32	31	27	4	0	2
Chloroprene rubber	10	9	10	0	0	1
Cables	104	88	86	2	0	1
Capacitor	19	16	15	1	0	0
Fire-fighting	3	3	0	3	0	0
Civil engineering	41	37	28	9	0	0
Electronics	396	283	276	7	0	7
Cutting oil	36	35	35	0	0	1
Lubricant	115	91	91	0	0	1
Plastic	11	9	2	7	0	0
Polymer	120	100	95	5	0	0
PVC	123	117	113	4	0	0
Chemical	30	26	24	2	3	7
Recycling	12	12	1	11	0	0
Textile	154	136	124	12	0	2
Paints & coating	72	66	62	4	2	2
Transformer	58	56	56	0	0	2
Transport	109	96	90	6	0	2
Total	**1599**	**1357**	**1280**	**78**	**5**	**41**

This consultation aimed to emphasize the obligations of the Brazilian State to the international treaty of the Stockholm Convention and to request any information about any stage of the life cycle of PCNs and SCCPs – production, import and exports, uses and final destination of PCNs and/or SCCPs and the products that can contain them. Moreover, the economic importance of the maintenance and the good development of these inventories was emphasized in order to identify the needs of the Brazilian industry to be presented to the secretariat of the Convention and in relation to the international trade of Brazilian products. Because even products that are not directly involved in the life cycle of POPs can be affected by the presence of them in the environment, mainly the agricultural exports, since the environmental contamination by POPs, even at low concentrations in soil, water and air, can lead to high contaminations in commodities, mainly in animal meat (TORRES et al., 2013; WEBER, 2017; WEBER et al., 2018). With this, several trading partners could impose sanctions or blockages on products contaminated by POPs and it is important to highlight that the European Union, one of the main consumers of Brazilian commodities, recently lowered the limits of daily/weekly intake acceptable for substances such as dioxins (now seven times lower), PFOS (now 80 times lower) and PFOA (now 1500 times lower) (EFSA, 2018a; 2018b).

Furthermore, the Brazilian MDIC had already accused – in response to previous questions about SCCPs sent by the MMA – the adoption of restrictive measures, within the framework of the World Trade Organization's Technical Barriers to Trade Committee (WTO) – long before the list of SCCPs as POPs by the Stockholm Convention – by countries such as Belgium (G/TBT/Notif. 99.518, 1999), Netherlands (G/TBT/Notif. 99.195, 1999), Switzerland (G/TBT/N/CHE/37, 2004), Canada (G/TBT/N/CAN/127, 2005) and Norway (G/TBT/N/NOR/17, 2007).

3 PCN INVENTORY

3.1 PCN production

Parties to the Stockholm Convention shall prohibit and/or eliminate the production of PCNs, except if they have notified the Secretariat of their intention to utilize the time-limited specific exemption for production and use of PCNs as intermediate for the production of polyfluorinated naphthalenes, as provided in Annex A to the Convention (UNEP 2017a). The Party registering the specific exemptions should provide to the Secretariat the information on the production and use of PCNs. Only Russia has asked for exemption for production of PCNs for PFN production.

Among all the industries and associations contacted directly through circular craft sent by the Brazilian Ministry of Environment, only one answer concerning the category of PCNs was received. This means less than 0.1 % of the institutions replied the 1357 circular crafts sent by the Ministry of the Environment. The response, sent by the Ministry of Infrastructure, stated that the extinct Federal Railway System had been a user of paraffinic and naphthenic thermal insulating oils, in addition to polychlorinated biphenyls (PCBs), until the date of its closure, in 1999. The statement, besides not providing a concrete estimation of the volumes of the referred substances during the period of operation of the company, is not conclusive concerning the applied compounds. There is currently a wide variety of non-chlorinated naphthenic oils which are used for similar applications to CPs, PCBs, and PCNs, such as transformers, lubricant oils, cutting oils, oils for compressors, and also as rubber plasticizers. Therefore, the single answer that was obtained does not provide clear information of whether the substances applied refer to the PCNs or are similar to the current naphthenic compounds.

3.2 PCN trade

To investigate the availability of technical mixtures of PCNs on the national market, searches were conducted via Google platform using various keyword combinations between synonyms related to the compound (“PCN”, “chloronaphthalene”, “chlorinated naphthalene”, “polychlorinated naphthalene”, and their trade names) plus the words “buy”, “sell” or “Brazil”. The online searches did not show any data pointing for the commerce of PCNs in the country.

The Brazilian Government provides the import and export data of international trade through its MDIC. This database can be accessed through the Comex Stat portal (http://comexstat.mdic.gov.br), and searches must be done by the goods registration Code, MERCOSUR Common Nomenclature (NCM – *Nomenclatura Comum do Mercosul*). In order to obtain information relative to the import and export volumes of PCNs in Brazil, the historical series from 1997 to 2019 provided by the MDIC, through the Comex Stat online platform were consulted. Two registry trade numbers (NCMs) listing “chloronaphthalenes” were identified: the first NCM: 29.03.69.15 was used between 1997 and 2011 and the second NCM: 29.03.99.15 from 2012 to 2019 (Figure 1). During the analysed period (1997-2019) there were no records of export of chlorinated naphthalenes, which may indicate inexistence or little national production. Concerning the import records, the purchase of small quantities was verified between the years 2001 and 2012, whose total amount for the period was 75 net kg. The years 2013 and 2015 stood out in relation to the pattern observed until then, with 230 and 215 net kg respectively, while in 2017 a peak import of the product was verified, registering the purchase of 930 net kg in a single year. The imported volume was significantly reduced in the following year (46 kg net), however, between the months of January and August of 2019, it is already registered 172 net kg of the substance, retaking the increasing seen in 2017. From the total volume of 1,705 kg imported liquids, 53% are from the United States (which contributed 881 kg of imports of 2017), 32% from China, 14% from India, and the remaining 1% is divided between Switzerland, Italy, Germany and Spain.

It is noteworthy that the NCM, as a generic code, does not provide individualized information about each of the products that may be listed under the same classification. Therefore, it is not possible to distinguish how much of the total verified imports corresponds to the mono-CN, not listed by the Convention, and how much refers to the other 7 homologous groups (di-CNs to octa-CNs) covered by the classification of POPs. There are no records for which purposes the imported products have been acquired.

There was not detected any NCMs relative to the polyfluorinated naphthalenes, for which the use of PCNs is allowed on the manufacturing process, in accordance with the Convention. Thus, it is assumed the absence of a national demand for production and acquisition of this class of compounds, which could in turn generated an indirect demand for the production and use of PCNs.

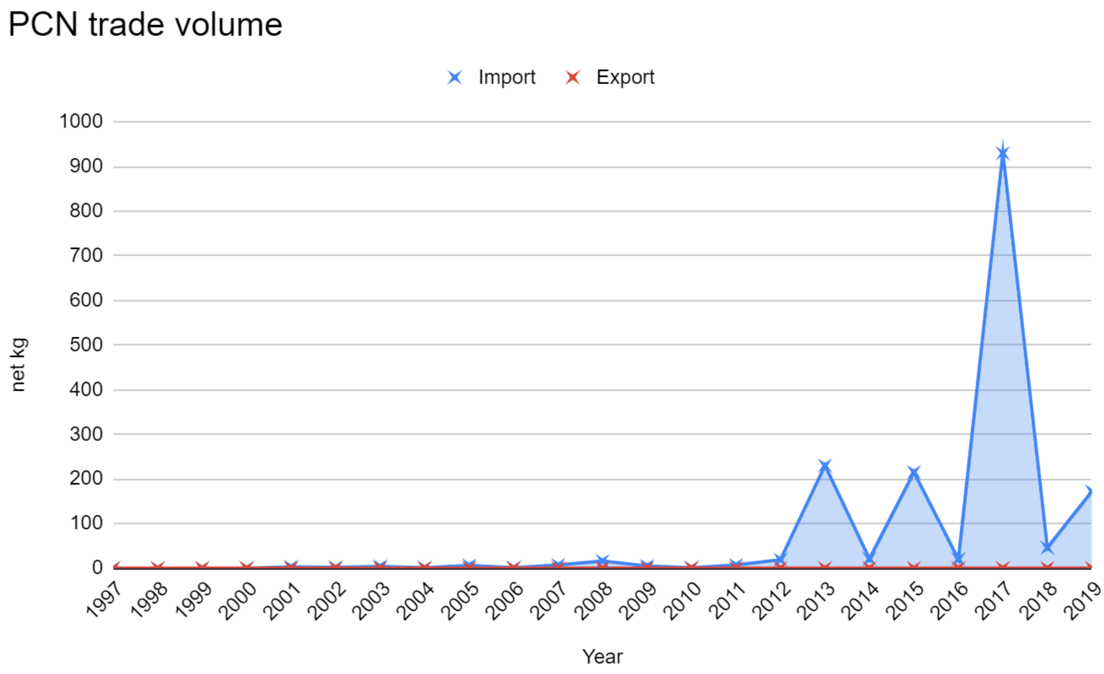

Figure 1: Total Brazilian PCN international trade (import and export volumes in net kilogram) from January 1997 to March 2019 in net kilograms, listed under both NCMs: 29.03.69.15 and 29.03.99.15. Source: Comex Stat (http://comexstat.mdic.gov.br)

As the production of PCNs is considered to have ended in the years 1980/90 – with the exception of chloroprene, which extended to 2000 – and considering they are no longer intentionally present in the products in which they used to be applied, the import and export of goods are no longer considered the entry and exit routes of the contaminant in the country. For this reason, the data on trade flows related to products previously carriers of PCNs were not considered for this inventory. As an exception, we present the data related to chloroprene rubber (NCM 40.02.49.00 – Other chloroprene rubbers (chlorobutadiene), in plates, etc.) (Figure 2), whose the maximum of imports was precisely in the year 2000 (over 10 thousand net tonnes), when the material could possibly contain PCNs in its composition and, subsequently, would have been replaced by other compounds and data related to chloroprene rubber latex (NCM 40.02.41.00 - Chloroprene rubber latex (chlorobutadiene) (Figure 3). In general, PCNs are not expected to be found in products currently circulating in the market, but rather in secondhand goods or largely as waste or recycled material, since most of them have relatively low durability and would have already been disposed.

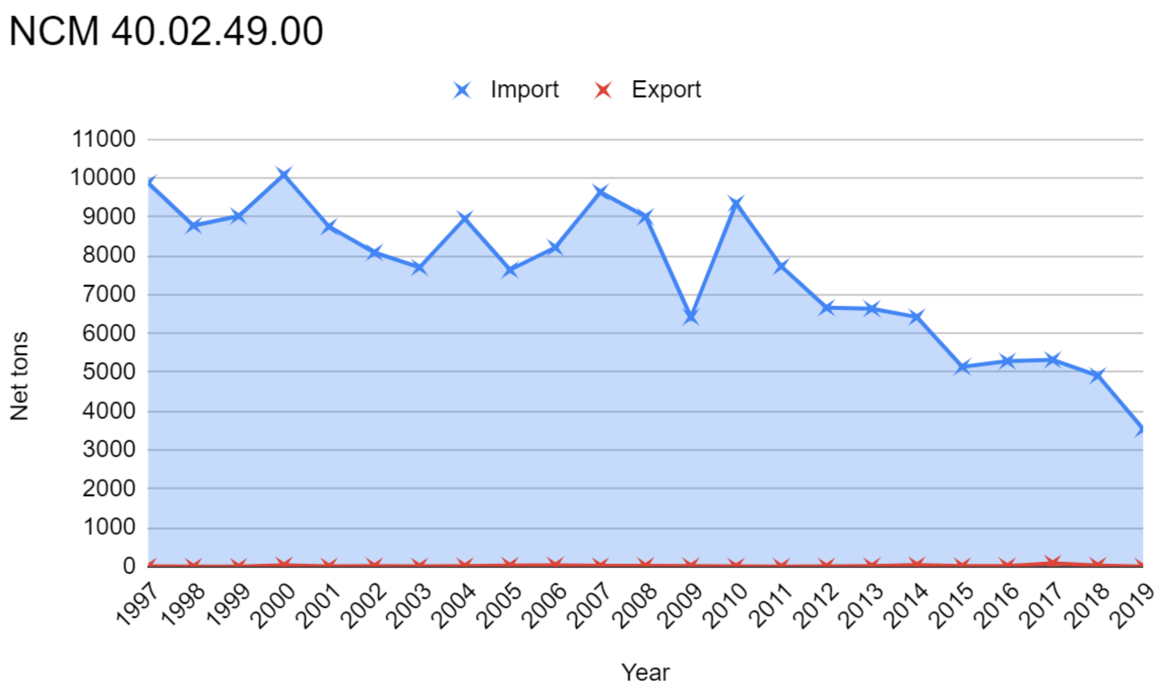

Figure 2: Brazilian commercial balance (import and export volumes in net tonnes) of products registered under NCM 40.02.49.00 – Other chloroprene rubbers (chlorobutadiene), in plates, etc; from January 1997 to March 2019. Source: Comex Stat (http://comexstat.mdic.gov.br)

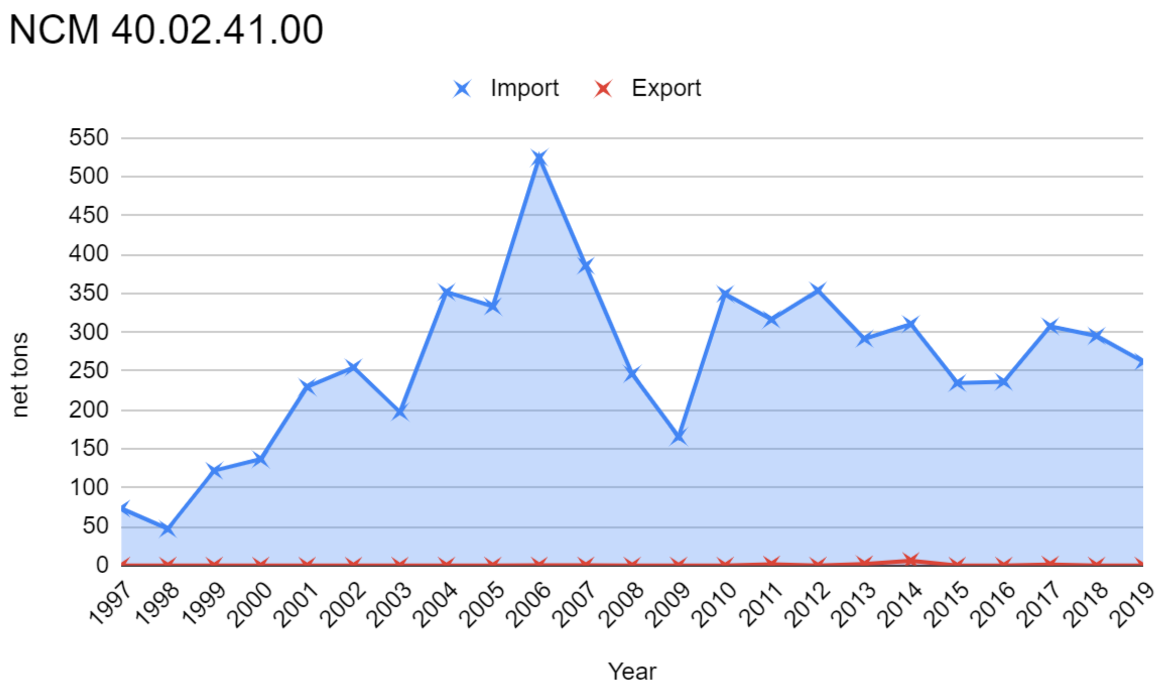

Figure 3: Brazilian commercial balance (import and export volumes in net tonnes) of products registered under NCM 40.02.41.00 - Chloroprene rubber latex (chlorobutadiene), from January 1997 to March 2019. Source: Comex Stat (http://comexstat.mdic.gov.br)

3.3 Non-intentional PCNs in PCBs ad other chemicals

According to information compiled in the PCN inventory guidance (UNEP 2017a, 2019a), PCNs not intentionally produced may be present in commercial mixtures of PCBs in concentrations ranging between 40 and 1,300 mg/kg. In a previous national inventory of PCBs, carried out in 2015, the total number of PCB-containing equipment in the country was compiled – active and out-of-use – which resulted in an estimation of 823,886 liters of PCB based oil in the country. Based on this, we can estimate that there could be an amount of PCNs in the country ranging between 33 g and 1,071 kg contained in PCB-containing equipment. However, it should be pointed out that such numbers are certainly underestimated, given the representative quantity of companies contacted who did not respond to the questionnaires sent. Furthermore, considering that PCBs have been widely used in the country, with emphasis on Ascarel oil, it can be assumed that a representative contribution of unintentional PCNs to the environment has occurred.

Unintentional PCNs have also been reported in chlorinated paraffins in high levels in Asia and might be present in other chemicals. Also processes in the chemical industry might have generated PCNs. Therefore, chemical analyses are necessary to detect its occurrence and abundance in technical products and biotic and abiotic environmental matrices in the country.

3.4 Preliminary considerations on Action plan for PCNs

Considering that most of the uses of PCNs were interrupted about three decades ago and that there is no evidence that Brazil has at some point acted as a producer of these substances, the most important step of the inventory for this compound should focus on chemical analysis to clarify if PCN related to PCBs could be an environmental issue, since PCBs have been reported in extremely high concentrations in environmental samples from Brazil. At this stage, the evaluation of open-application materials, such as building sealants in the 1960/70-decade buildings, external paints and coatings (waterproof and anticorrosive), is of high importance, considering that they have longer useful lives and may still be present in external structures. This analysis will allow to assess how representative were the entry routes of PCNs in the country through products to which they were added. In addition, it is necessary to search for recycling and waste disposal companies for the evaluation of products of lower life cycle and already out of use, such as wires and cables, for the collection of data and eventual samples of products potentially containing PCNs and which have already been disposed. The method for chemical analysis of PCN based on gas chromatography coupled to mass spectrometry (GC-MS) was already developed and implemented in the Federal University of Rio de Janeiro, following the Draft Guidance on Sampling Screening Analysis of POPs in Products and Articles of the Stockholm Convention (UNEP, 2017b).

4 SCCP INVENTORY

4.1 SCCP production

In 2007, the Brazilian government, via the Department of Environmental Quality and Waste Management of the Environmental Quality Secretariat (*Departamento de Qualidade Ambiental e Gestão de Resíduos da Secretaria de Qualidade Ambiental*) of its Ministry of Environment, reported to the secretariat of the Stockholm Convention that Brazil was among the countries producers of SCCPs, with a production of approximately 150 tonnes per year and a two-fold higher consumption (300 tonnes per year), which would be remedied by importing the same volume produced internally (BRAZIL, 2007). This information was passed on to the MMA by the Brazilian Chemical Industry Association (ABIQUIN – *Associação Brasileira da Indústria Química*), which stated that the national production of SCCPs reached 360 tonnes per year in the past and that, in Brazil, the main application of the SCCPs is given as flame retardant additive in rubber artefacts, being widely used in the manufacture of automotive carpets and other components of motor vehicles, except in tires. Yet according to national producers, the application of CPs in metalworking fluids, paints, varnishes and leather processing are negligible. According to the Convention guide, Brazil is listed among the countries that have produced SCCPs in the past and still produce other CPs today (UNEP, 2019d). However, although the number of responses to the questionnaires sent to institutions operating in the Brazilian territory has been tiny – only 46 (3%) of the 1357 contacted institutions returned with any type of response and only 4 of them (0.3%) provided relevant information regarding SCCPs – no information raised up to the present time indicates the existence of national production of any type of CP in the last ten years.

In the year 2010, when consulted by MMA, the MDIC reported that, according to the Brazilian Chemical Industry Association guide of 2010, there was only one company producing SCCPs in Brazil. This information was confirmed by the ABIQUIN in our current questionnaire and the producer company itself responded to some of the issues raised in the craft sent by the Ministry of the Environment, assisting in the clarification of some important points, although it is still necessary to establish a dialogue with the company to clarify all matters of interest to the Brazilian inventory of SCCPs. According to this company, the production of CPs was initiated in the decade of 1980 and lasted until August 1994. However, despite the information presented by the Brazilian Government to the Secretariat of the Stockholm Convention (2007) and subsequently published in other studies and documents (GLÜGE et al., 2016; UNEP, 2019d), the company did not mention the type of CP produced and processed by it. The company only informed that that the CP produced was sold under the trade name "Clorax" and that it was marketed mostly for application as plasticising for most of the synthetic rubbers. The company also presented the letter sent to the supervisory body of the Government of São Paulo, CETESB – Environmental Sanitation Technology Company (present-day Environmental Company of the State of São Paulo and Regional Centre of the Stockholm Convention on POPs for Latin America and the Caribbean) – and reported that the production of Clorax was interrupted with the closing of the production unit in São Paulo, in 1994, due to the unfeasibility of production. The company also reported that its last sales occurred in 2011, for a feedstock company for the rubber industry, with a volume of 1,159 kg.

Although this was the only report of CP production in the Brazilian territory, both by the company itself and by the Brazilian Chemical Industry Association (ABIQUIN), three other companies reported the trade of CPs. A paint and coating company in the state of São Paulo reported to import approximately seven tonnes of Celeclor 48 (CAS N °: 063449-39-8) with the frequency of purchases twice a year. But without any further clarification so far.

Another company located in the state of São Paulo reported that it used CPs in the period 2011 to 2018 as feedstock for the manufacture of a lubricant (Gardolube L 6083) for the use of special steels. Thanks to the information presented, it was also possible to identify the main buyers of the lubricant in question, based on CP. This company declared that it had no prior knowledge of the listing of SCCPs by the Stockholm Convention. And, although it has not reported the CP volumes used or the proportion of CP in its lubricant product, it has reported that, according to the Chemical Safety Information Sheet (FISPQ - *Ficha de Informação de Segurança para Produtos Químicos*) of its supplier, the feedstock used by it is a medium-chain CP, Celeclor S 52 (MCCP; CAS NO.: 85535-85-9). The company appointed as the supplier of Celeclor S 52 had been contacted by e-mail and through the website, but there was no response from it. In any way, it was possible to verify on its website, in its portfolio of products, the supply of chlorinated paraffin – 42 to 60% of chlorine – for application as: Flame retardant additive, secondary plasticizer in PVC, plasticizer in paints, lubricants and extreme pressure lubricant additives (cutting/metalworking oils), sealing agent and adhesives and softeners.

The third company that responded to the MMA office, reported commercializing CP-52, which on its website is "chlorinated paraffin 50-52%" and made available its history of purchase and sale of CP from the last five years. Based on the commercial balance sheet of this company, from January 2014 to March 2019, it was possible to identify 50 other companies that use the product at some stage of their processes at national level, because they were among their real consumers and more 12 companies on the balance sheet with acquisition lower than five kilograms. It is noteworthy that both this trading company and all its buyers are also located in the state of São Paulo. According to the data presented, more than 95% (540,000 kg) of all CP acquired by the company in the last five years (563,750 kg) was imported from an Indian company. The remaining 4.4% (23,750 kg) were acquired with other companies that also appear among its buyers. The chart below (Figure 1) illustrates the variation in the quantity of CP (kg) acquired by the company in the last 5 years, where it is possible to notice that the highest volume of CP purchases took place in the years 2016 and 2014.

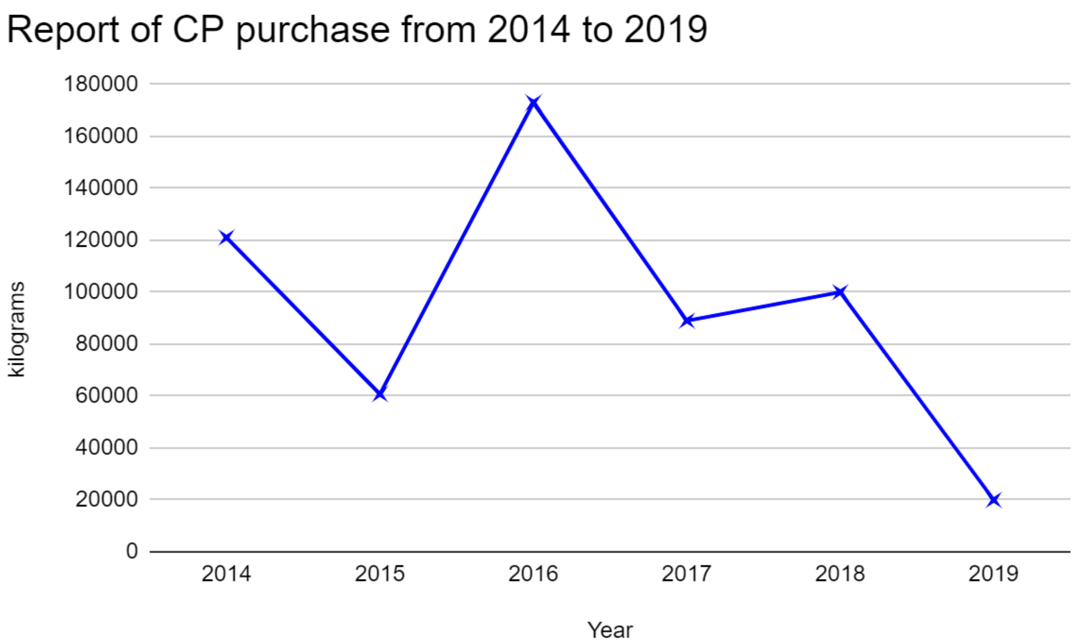

Figure 4: Quantity of chlorinated paraffin (CP) acquired by a paint and coating company in Brazil between January 2014 and March 2019 in kilograms

Among the 50 companies that have appeared in the list of buyers of the last five years, most are companies producing lubricant oils and chemical companies which use CPs as additives in many products, with various purposes. However, companies were grouped into six distinct categories. The category of grouped companies that most acquired CPs from the company in question, in the last five years, was the polymer industry, with the highest representativeness of the plastics industry, followed by the lubricant industry, mostly focused on the metalworking oils, but also for automobiles (Table 6). It is also noteworthy that the total sale volume is lower than the total acquisition of the company in question, which may suggest that it uses part of its stock of CPs for the manufacture of products manufactured by itself.

Table 6: Sales values of chlorinated paraffin (CP-52) in kilograms (kg) of the last 5 years, reported by one of the companies that responded to the questionnaire submitted

Category	2014	2015	2016	2017	2018	2019	Category total
Civil engineering	0	0	1250	500	0	0	**1750**
Lubricant	51000	10000	19440	23000	5050	0	**108490**
Chemical	16250	1250	12750	20500	9750	500	**61000**
Paints & Coatings	500	1000	1250	2750	1750	250	**7500**
Rubber	6750	7250	4250	4000	2000	5700	**29950**
Polymers (plastic, PVC, polyurethane)	12500	60250	94550	35020	71750	16000	**290070**
Total annual	**87000**	**79750**	**133490**	**85770**	**90300**	**22450**	**488760**

4.2 SCCP trade

The international trade (import and export) of industrial POPs has shown to be challenging since most of them do have a specific classification. Many national controls are based on the Harmonized System (HS) of the United Nations Trade Statistic Database (Comtrade database). Currently, there is no specific HS codes for SCCP trade and even general CPs could be traded under generic HS codes which include a broad range of chemicals (UNEP, 2019d). The Brazilian Government provides the import and export data of international trade through its MDIC. This database can be accessed through the Comex Stat portal (http://comexstat.mdic.gov.br), and searches must be done by the goods registration Code, MERCOSUR Common Nomenclature (NCM). NCM codes are based on HS codes and, therefore, an initial issue to be highlighted is that NCMs tend to be generic codes where several products can be framed, just as HS codes. Therefore, HS or NCM codes cannot be reliably used for assessing the international trade data of SCCPs at the moment. But they can give an indication (Tier I) and can be used for further assessment by Tier II and III approaches. The detailed guidance on preparing inventories of SCCPs (UNEP, 2019d) mentions that CPs are imported under different HS codes, such as follows:

HS Code 27.12.20.10 – Synthetic paraffin wax of a molecular weight of 460 or more but not exceeding 1560

HS Code 27.12.90.90 – Paraffin waxes

HS Code 38.12.20.90 – Plasticizers, compound; for rubber or plastics

HS Code 38.24.90.90 – Chemical products and preparations of the chemical or allied industries, not elsewhere specified or included

In Brazil, this control is similarly generic. The Brazilian Federal Revenue, when consulted in 2010, highlighted that the classification of the SCCPs is quite complex and that they can be found within three distinct NCMs, depending on their characteristics. However, the three NCMs appointed by the Federal Revenue also encompass several other products and their evaluation can generate an overestimation of the actual import and export values of CPs. Even so, the Comex Stat portal was surveyed based in the following three NCMs:

NCM 29.03.19.90 – Other saturated derivatives of acyclic hydrocarbons:

Chlorinated paraffin consisting of molecules of a single size and all with the same amount of chlorine atoms, that is, with defined chemical constitution.

NCM 34.04.90.19 – Other artificial waxes:

Chlorinated paraffin in solid form (powder, granules, etc.) With characteristics of wax and constituted by the mixture of molecules of various different sizes, that is, with 10 to 13 carbon atoms and 3 to 12 chlorine atoms.

NCM 38.24.90.89 – Other products and preparations based on organic compounds, not elsewhere specified or included:

Chlorinated paraffin in liquid form and constituted by the mixture of molecules of different sizes, that is, with 10 to 13 atoms 13 carbon atoms and 3 to 12 chlorine atoms. If it's solid, it can't have wax characteristics.

As both HS and NCM are generic codes and NCMs are supposedly based on HS codes, data of the international trade (import and export) of CPs in Brazil was only compiled using NCM codes. The procedures were the same for the data collection of import and export: In each search was selected the entire period available ("Initial year" 1997 and "final year" 2019), with selection of the "initial month" in January and "final month" in December, for each of the three NCMs (29.03.19.90; 34.04.90.19; 38.24.90.89) (Table 7). However, it should be emphasized that for the year 2019 the values were compiled only until the month of March (03/2019).

Table 7: Import and export values of chlorinated paraffins (CPs) in a net kilogram, from January 1997 to March 2019. Data available on the Comex Stat platform (http://comexstat.mdic.gov.br) for the three Mercosur common Nomenclature codes (NCM) appointed by the Brazilian Federal Revenue as possible to have CP included.

	NCM 29.03.19.90		**NCM 34.04.90.19**		**NCM 38.24.90.89**	
Year	**Import**	**Export**	**Import**	**Export**	**Import**	**Export**
1997	145,898	18,269	1,256,665	1,446,797	1,817,857	132,812
1998	109,072	8,778	1,407,585	1,975,730	3,003,099	1,511,106
1999	89,283	1,120	1,442,298	1,373,862	2,236,693	4,028,908
2000	52,602	1,547	1,100,529	1,732,793	2,315,953	4,115,471
2001	92,769	416	1,209,298	1,123,483	3,491,401	5,939,247
2002	46,674	2,203	2,250,021	1,528,234	5,297,861	5,993,880
2003	21,141	NA	3,162,440	1,442,747	33,621,170	10,759,578
2004	79,785	2,314	3,896,265	1,263,177	62,943,346	9,779,671
2005	89,200	104	4,813,820	1,147,245	42,076,531	5,624,679
2006	223,485	2,438	5,629,501	994,681	34,237,798	7,324,595
2007	511,843	674	5,301,113	1,644,025	40,702,901	8,364,307
2008	317,277	24,580	6,950,606	2,938,852	58,722,704	6,126,037
2009	577,573	21,835	5,984,554	1,783,698	33,856,573	12,010,805
2010	479,715	44,25,212	5,069,405	716,429	41,622,766	12,260,968
2011	753,576	14,987,302	5,084,661	510,966	44,082,176	12,964,111
2012	300,865	17,449,689	5,661,579	654,963	44,568,440	6,477,360
2013	529,388	14,615,152	5,570,970	635,029	40,802,946	5,712,837
2014	567,278	15,180,754	4,972,633	358,966	35,452,191	7,751,267
2015	398,699	17,162,939	4,379,439	371,567	28,962,465	7,118,743
2016	538,434	14,664,513	4,818,380	360,493	28,563,190	8,214,340
2017	365,477	18,060,222	7,398,021	634,963	47,731	24,991
2018	542,790	16,722,501	6,254,034	623,983	NA	NA
2019	293,370	9,465,069	4,126,276	215,823	NA	NA
Total	**7,126,194**	**142,817,631**	**97,740,093**	**25,478,506**	**588,425,792**	**142,235,713**

NCM 29.03.19.90 – Other saturated derivatives of acyclic hydrocarbons; NCM 34.04.90.19 – Other artificial waxes; NCM 38.24.90.89 – Other products and preparations based on organic compounds, not elsewhere specified or included. NA = not available.

The consultation conducted through the MDIC database revealed that Brazil imported about 7,126 net tonnes of products listed under the NCM 29.03.19.90 (other saturated derivatives of acyclic hydrocarbons) and exported about 142,818 tonnes of the same, indicating that there is a higher internal production than the volume imported by the country (Figure 5).

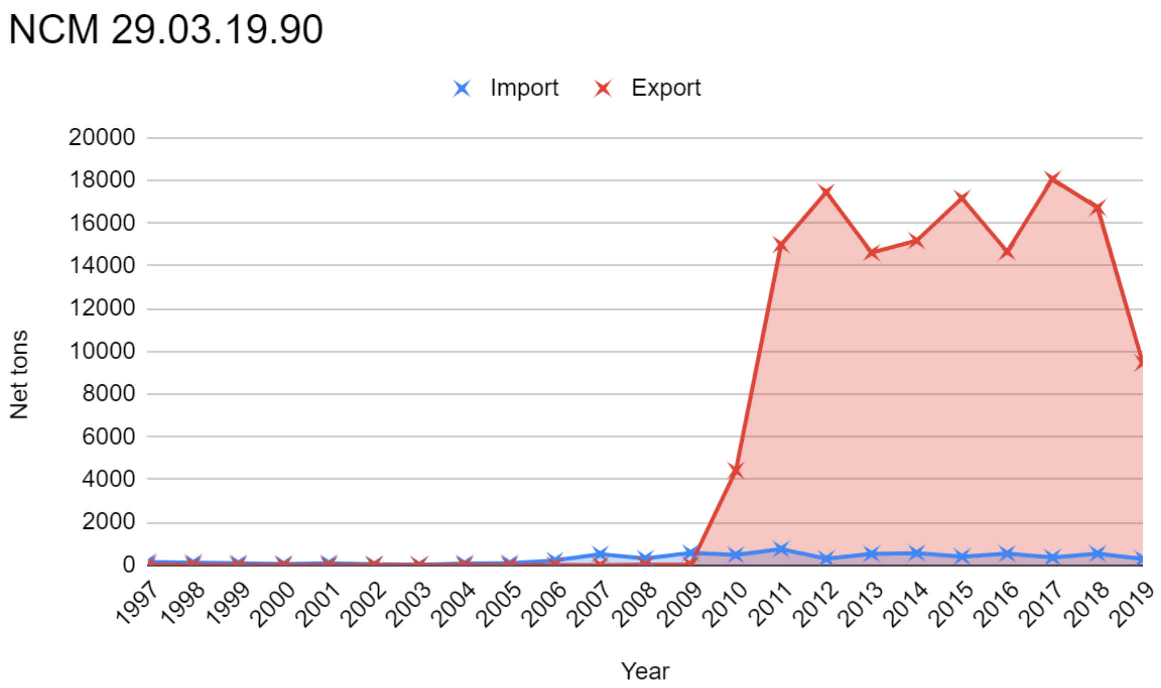

Figure 5: Brazilian commercial balance (import and export volumes in net tonnes) of products registered under the NCM 29.03.19.90 – Other saturated derivatives of acyclic hydrocarbons. Source: Comex Stat (http://comexstat.mdic.gov.br)

For the NCMs 34.04.90.19 (other artificial waxes) (Figure 6) and 38.24.90.89 (other products and preparations based on organic compounds, not elsewhere specified or included) (Figure 7), data collection has shown that there is a higher consume than the national production capacity, resulting in higher import values than export values. Brazil imported 97,740 and exported 25,478 net tonnes of products under the NCM 34.04.90.19 and imported 588,425 and exported 142,235 net tonnes of products under the NCM 38.24.90.89. However, as previously mentioned, the survey of the total volume of import and export for the available period does not allow to evaluate the actual amount of the entry flow of CPs in the Brazilian territory, being at most one overestimation of 382,7760 net tonnes of many chemicals traded under these three NCMs that have entered and stayed in the country and where an unknown share of CPs is hidden.

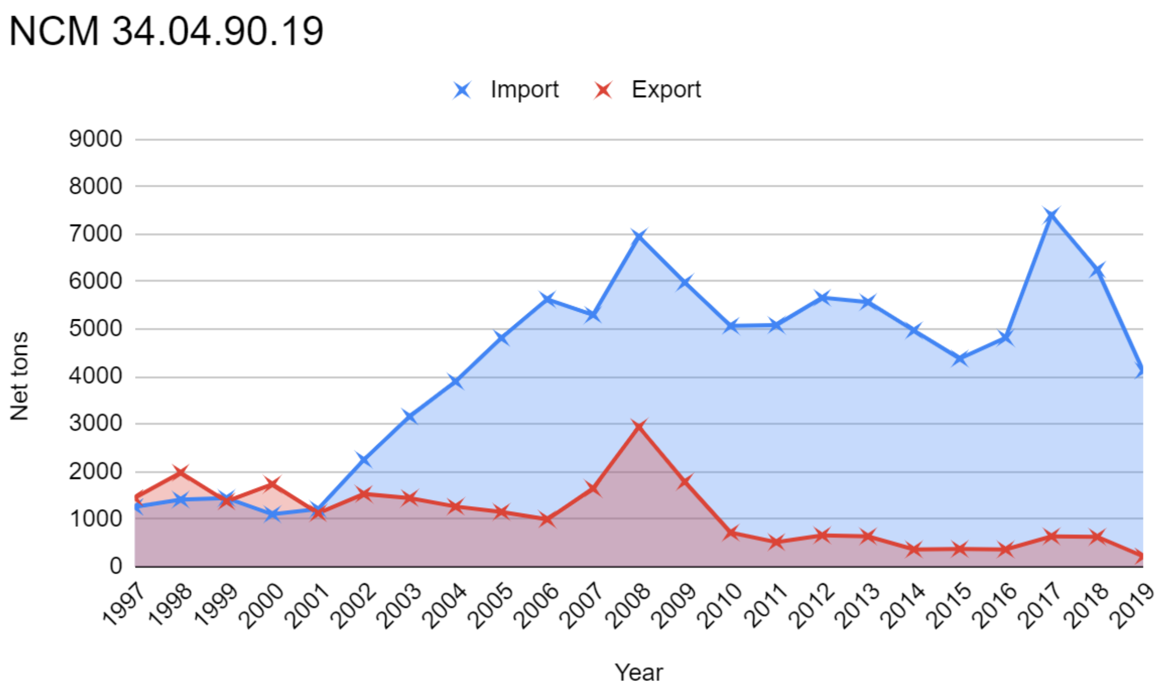

Figure 6: Brazilian commercial balance (import and export volumes in net tonnes) of products registered under the NCM 34.04.90.19 – Other artificial waxes in net tonnes. Source: Comex Stat (http://comexstat.mdic.gov.br)

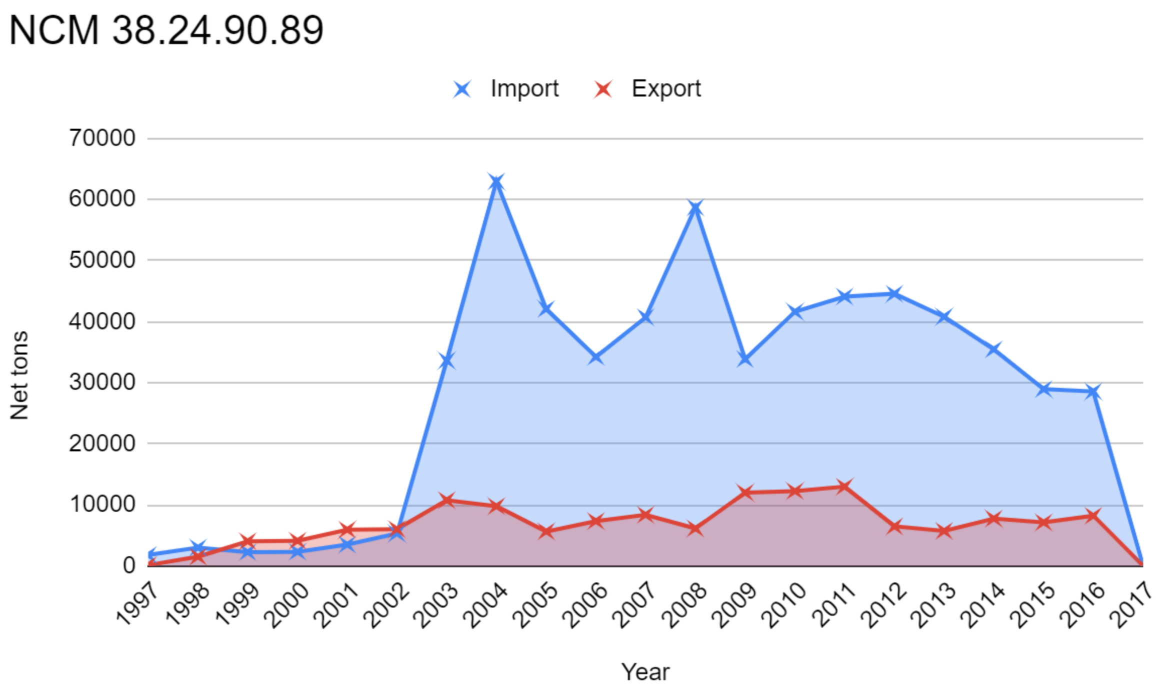

Figure 7: Brazilian commercial balance (import and export volumes in net tonnes) of products registered under the NCM 38.24.90.89 – Other products and preparations based on organic compounds, not elsewhere specified or included. Source: Comex Stat (http://comexstat.mdic.gov.br)

As the control of international trade by the Brazilian Government does not allow a specific evaluation of the imports and exports of CPs and, although no institution has reported the production of CPs in Brazil and the only clear import information was the one in the commercial balance of a paint and coating company, indicating the importation of 540 tonnes of CP-52 from an Indian company, a search was made on websites that disclose data on the commercialization of CPs from India. However, referring to the websites: https://www.zauba.com/export-chlorinated+paraffin+wax/fp-brazil-hs-code.html and https://www.infodriveindia.com/india-export-data/chlorinated-paraffin-export/fc-brazil/unit-kgs-report.aspx, it was not possible to make a more accurate evaluation of the volume of CPs imported from India to Brazil, since the websites do not present continuous data and the available values are lower than the values reported by a single company that reported to import CPs from India for commercialization in Brazil. According to the first website, (https://www.zauba.com/) 103,400 kg of chlorinated paraffin wax (paraffin wax – CP 51-55%) were exported from India to Brazil in the period 2013 to 2016. The data available on the second website (https://www.infodriveindia.com/) for a period of three months (September to November) of the year 2016, 120,000 kg of CP 50-52% were imported from India to Brazil.

4.3 SCCPs in products

Even if there was a specific NCM code for CPs, or even for its subcategories (SCCP, MCCP and LCCP), it would also be necessary to keep track of the volumes of imported and exported products that might contain CPs and the amount of CP added in each product to finally assert the actual amount of CPs entering and leaving the Brazilian borders. And, as CPs can be applied in proportions of around 20%, but can reach up to 70% (Table 8) of the mass of certain products, the volume of international marketing of products in which CPs are applied may represent an expressive rate of total CPs everywhere, even if the national industry does not make use of them.

Table 8: Some examples of applications and content of SCCPs in their uses.

Uses	**SCCPs content in mg/kg**	**Source**
PVC	Up to 100,000 (10%)	BTHA, 2016; KEMI, 2016
EVA Foam	Up to 70,000 (7%)	BTHA, 2016
Rubber	Up to 170,000 (17%)	ECB, 2008; RPA, 2010
Paints/coatings	Up to 200,000 (20%)	ECB, 2008; RPA, 2010
Leather	Up to 200,000 (20%)	ECB, 2008; RPA, 2010; ESWI, 2011
Adhesives/sealants	Up to 300,000 (30%)	ECB, 2008; Danish EPA, 2014
Metalworking fluids	Up to 150,000 (15%)	RPA, 2010; BTHA, 2016
Lubricants	Up to 700,000 (70%)	MSDSs Sloan, 1986

In order to evaluate the entry of CPs associated with other products in the national territory, the commercial balance of some products typically known to contain CPs in their formulation, taking into account their percentage of application, can serve as a gross estimation of interborder transit of CPs. With this, using the same criteria adopted for the survey of CPs through the generic NCMs that may contain technical formulations of CPs – from January 1997 to March 2019 – a new survey was made via Comex Stat of the trade volumes of products that may contain CPs in their formulation, being presented in the graphs below (Figures 8, 9, 10, 11, 12, 13, and 14).

According to the survey of the commercial balance (import and export) made for the NCM 38.09.93.11 (Waterproofing of the types used in the leather industry or similar industries, paraffin-based or fatty acid derivatives), via the Comex Stat platform, Brazil imported 4,578,437 net kg of these products in the period 1997 to 2019 and exported only 59,291 net kg in the same period. Italy (50%), Germany (27%) and Argentina (17%) were the main suppliers of these products registered under this NCM in question for Brazil and the Dominican Republic (42%), Chile (18%) and Argentina (17%) were the main buyers. In a scenario in which the entire volume of imported products within the NCM 38.09.93.11 is considered of products based on CP and that the CP percentage of the waterproofing formulation used in the leather industry can reach 20% (Table 8), we could estimate that between 1997 and 2019 entered around 916 net tonnes of CPs, of which about 12 tonnes would have left the country in the same period.

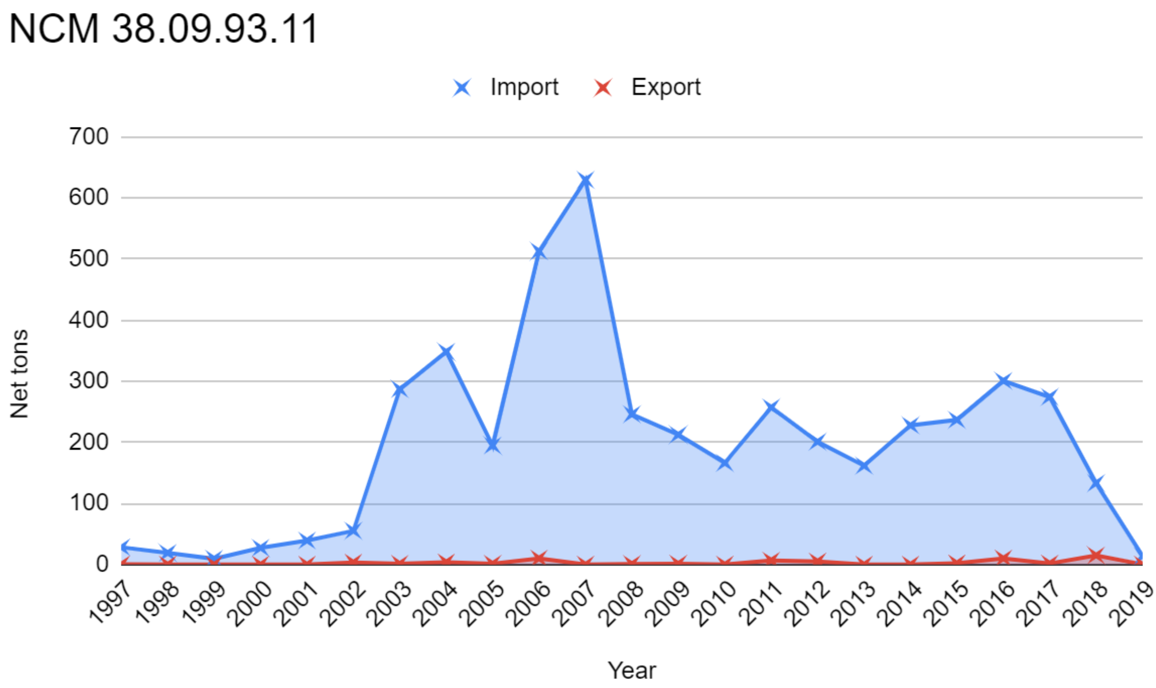

Figure 8: Brazilian commercial balance (import and export volumes in net tonnes) of products registered under the NCM 38.09.93 – Waterproofing of the types used in the leather industry or similar industries, paraffin-based or fatty acid derivatives, from January 1997 to March 2019. Source: Comex Stat (http://comexstat.mdic.gov.br)

According to the survey of the commercial balance (import and export) made for the NCM 38.09.92.11 (Waterproofing of types used in the paper industry or similar industries, paraffin-based or fatty acid derivatives), via the Comex Stat plataform, Brazil imported 454,395 net kg of these products in the period 1997 to 2019 and exported 96,829,545 net kg in the same period. Being United States (61%), Chile (29%) and Austria (5%) the main suppliers of the products registered under this NCM for Brazil and Argentina (48%), Ecuador (16%) and Venezuela (15%) the main buyers. In a scenario in which the entire volume of imported products within the NCM 38.09.92.11 is considered of products based on CP and that the percentage of CP of the formulation of waterproofing used in the paper industry or similar is also around 20% (Table 8), we could estimate that between 1997 and 2019 entered about 91 net tonnes of CPs, of which about 19,4 net tonnes would have left the country.

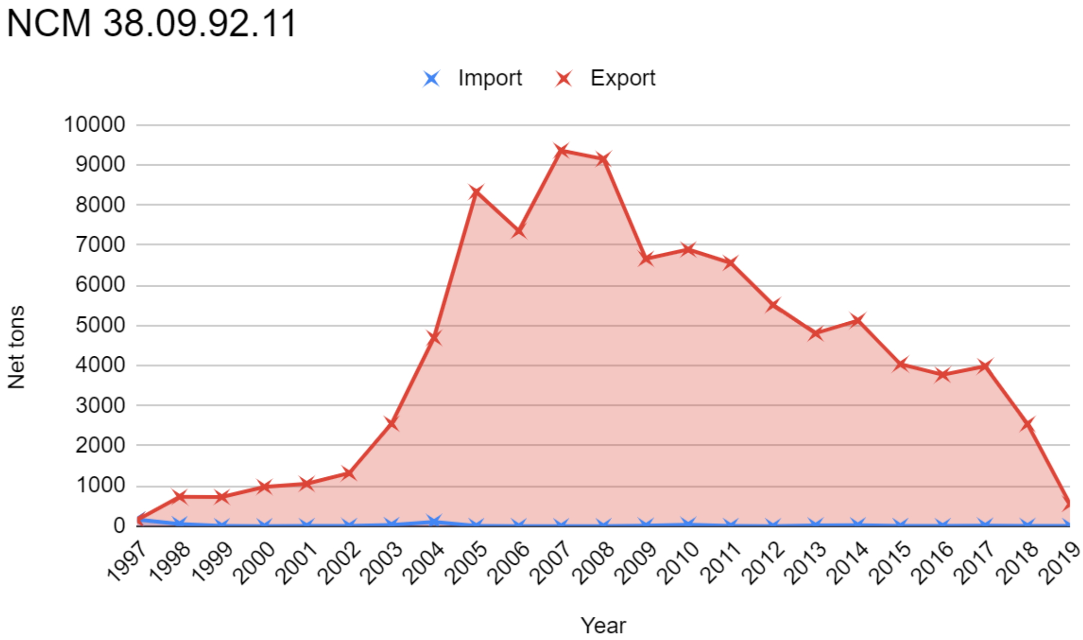

Figure 9: Brazilian commercial balance (import and export volumes in net tonnes) of products registered under the NCM 38.09.92.11 – Waterproofing of types used in the paper industry or similar industries, paraffin-based or fatty acid derivatives, from January 1997 to March 2019. Source: Comex Stat (http://comexstat.mdic.gov.br)

According to the survey of the commercial balance (import and export) made for the NCM 38.09.91.41 (paraffin-based waterproofing or fatty acid derivatives), via the Comex Stat platform, Brazil imported 1,036,583 net kg of these products in the period 1997 to 2019 and exported only 42,835 net kg in the same period. Germany (45%), Italy (26%), Taiwan (12%) and Argentina (10%) were the main suppliers of the products registered under this NCM in question for Brazil and Argentina (58%), United States (12%) and China (7%) were the main buyers. In a scenario in which the entire volume of imported products within the NCM 38.09.91.41 is considered of products based on CP and that the CP percentage of the formulation of waterproofing the basis of CPs can reach 20% (Table 8), we could estimate that between 1997 and 2019, 207 net tonnes of CPs would have entered in the country and about 8.5 tonnes would have left the country in the same period.

Considering only waterproofing products that could be based on CPs summing up to 20% of their mass volume, 1,174 net tonnes of CPs would have entered and stayed in Brazil from January 1997 to March 2019. However, we consider it an overestimation due to uncertainty of the products listed under those NCMs and the percentage of CPs.

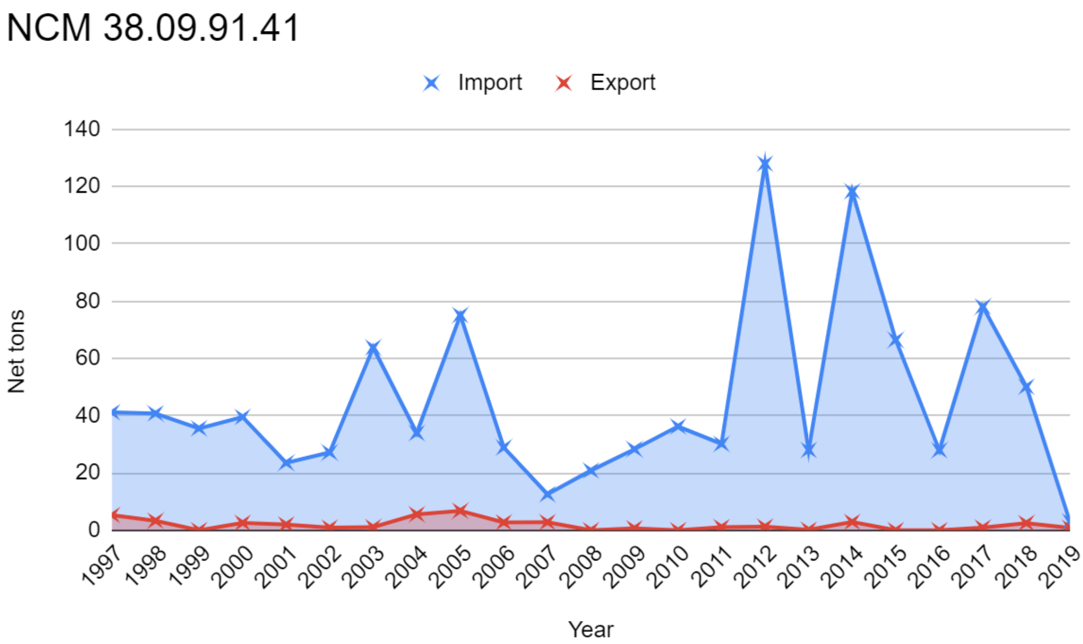

Figure 10: Brazilian commercial balance (import and export volumes in net tonnes) of products registered under the NCM 38.09.91.41 – Paraffin-based waterproofing or fatty acid derivatives, from January 1997 to March 2019. Source: Comex Stat (http://comexstat.mdic.gov.br)

According to the survey of the commercial balance (import and export) made for the NCM 39.13.90.11 (chlorinated or chlorhydrate rubber, in pieces, lumps, etc.), via the Comex Stat platform, Brazil imported 1,094,437 kg net of these products in the period 1997 to 2019 and exported only 4,037 kg net in the same period. Almost all of the imported volume (98%) From Germany and India (1.7%). The main buyers were Argentina (45%), Uruguay (31%) and Colombia (13%). In a scenario in which the entire volume of imported products within the NCM 39.13.90.11 is considered of products based on CP and that the CP percentage of the formulation of chlorinated rubbers varies around 10% (Table 8), we could estimate that between 1997 and 2019 entered 109 net tonnes of CPs, of which about 404 net kg would have left the country.

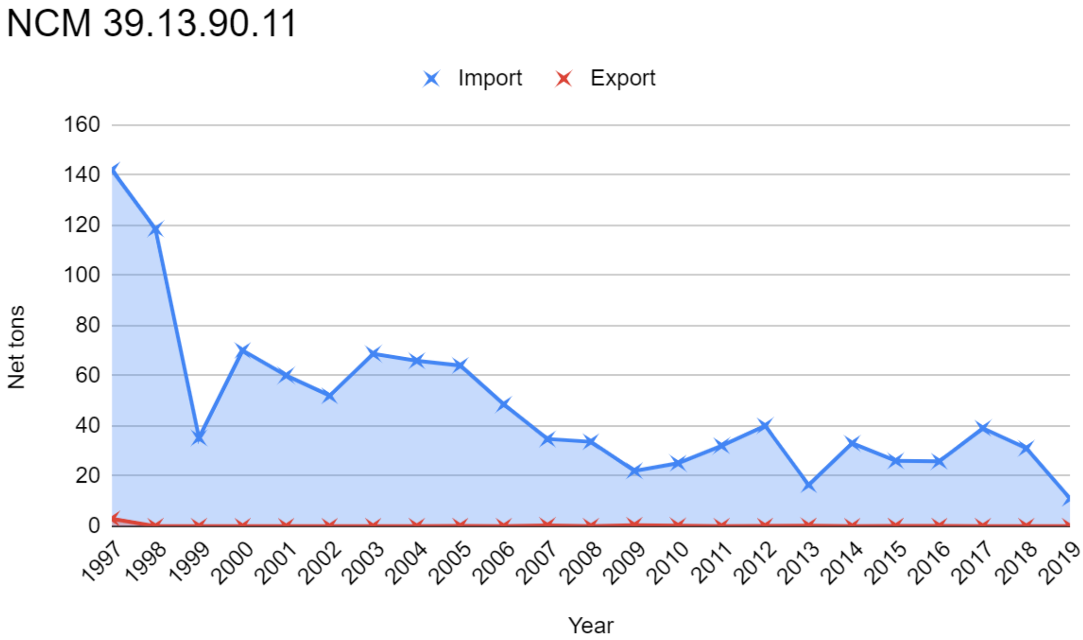

Figure 11: Brazilian commercial balance (import and export volumes in net tonnes) of products registered under the NCM 39.13.90.11 – Chlorinated or chlorhydrate rubber, in pieces, lumps, etc; from January 1997 to March 2019. Source: Comex Stat (http://comexstat.mdic.gov.br)

According to the survey of the commercial balance (import and export) made for the NCM 39.13.90.12 (chlorinated rubber in other primary forms), via the Comex Stat platform, Brazil imported 9,581 net kg of these products in the period from 1997 to 2019 and exported only 908 net kg in the period from 1999 to 2019. Being United States (74%), Germany (14%) and France (12%) the main suppliers of the products registered under this NCM in question for Brazil. In a scenario in which the entire volume of imported products within the NCM 39.13.90.12 is considered of products based on CP and that the CP percentage of the formulation of chlorinated rubbers varies around 10% (Table 8), we could estimate that between 1997 and 2019 entered about 958 kg net of CPs, of which about 10 net kg would have left the country.

Moreover, considering the NCMs 40.02.49.00 (other chloroprene rubbers (chlorobutadiene), in plates) (Figure 2) and 40.02.41.00 (chloroprene rubber latex (chlorobutadiene) (Figure 3), Brazil imported 173,176,384 net kg of the products under the NCM 40.02.49.00 and 6,024,472 net kg of the products under the NCM 40.02.41.00 in the period 1997 to 2019 and exported only 340,035 net kg of the products under the NCM 40.02.49.00 and 10,488 net kg of the products under the NCM 40.02.41.00 in the same period. Being the United States (39%), Japan (27%) and Germany (26%) the main suppliers of the products registered under the NCM 40.02.49.00 and Germany (40%), United States (37%) and Japan (12%) the main suppliers of the products registered under the NCM 40.02.41.00 for Brazil. Colombia (17%), Chile (11%), Uruguay (11%) and Argentina (10%) were the main buyers of the products under the NCM 40.02.41.00 and Germany (73%), Mexico (9%) and Peru (8%) were the main buyers of the products under the NCM 40.02.41.00. In a scenario in which the entire volume of imported products within the NCMs 40.02.49.00 and 40.02.41.00 are considered of products based on CP and that the CP percentage of the formulation of chlorinated rubbers varies around 10% (Table 8), we could estimate that between 1997 and 2019 entered 17,318 and 602,447 net tonnes of CPs, of which about 34 and 1,050 net tonnes would have left the country, respectively.

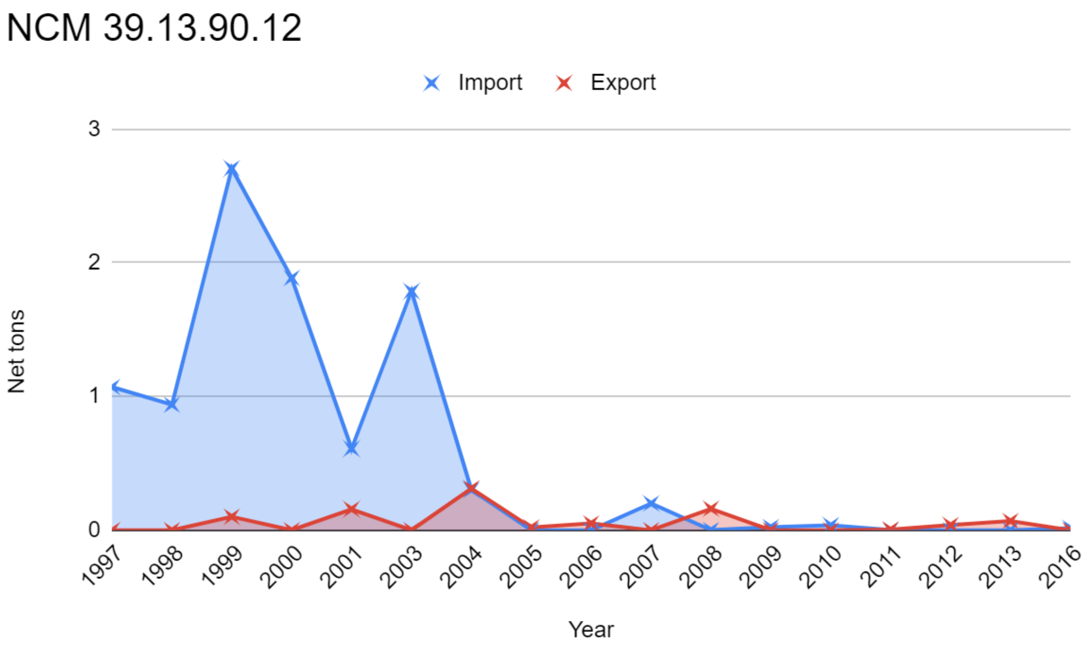

Figure 12: Brazilian commercial balance (import and export volumes in net tonnes) of products registered under the NCM 39.13.90.11 – Chlorinated rubber in other primary forms, from January 1997 to March 2019. Source: Comex Stat (http://comexstat.mdic.gov.br)

According to the survey of the commercial balance (import and export) made for the NCM 38.24.90.39 (other mixtures and preparations for rubber or plastics and other mixtures and preparations to harden synthetic resins, glues, paints or similar uses), via the Comex Stat platform, Brazil imported 146,165,048 net kg of these products in the period 1997 to 2017 and exported 61,618,247 net kg in the same period. Being United States (36%), Germany (23%) and Spain (8%) the main suppliers of the products registered under this NCM in question for Brazil and Argentina (45%), Chile (22%), Indonesia and Cambodia (10% each) the main buyers in the same period. In a scenario in which the entire volume of imported products within the NCM 38.24.90.39 is considered of products based on CP and that the CP percentage of the formulation of this type of product can reach 20% (Table 8), we could estimate that between 1997 and 2017 entered around 29,233 net tonnes of CPs in Brazil and about 12,323 tonnes would have left the country.

Whether all material traded under these five NCMs could be considered of products based on CPs summing up to 10% of their mass volume, approximately 635,592 net tonnes of CPs would have entered and stayed in Brazil from January 1997 to March 2019. However, we consider it an overestimation due to uncertainty of the products listed under those NCMs and the percentage of CPs and highlight the need of a specific code to registry POP substances.

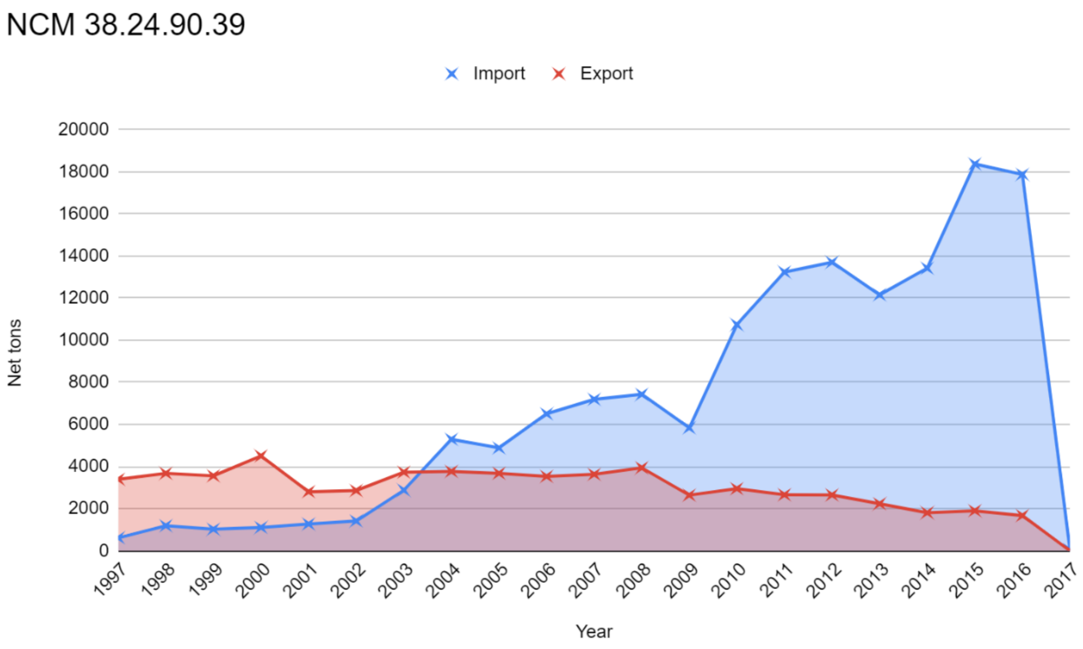

Figure 13: Brazilian commercial balance (import and export volumes in net tonnes) of products registered under the NCM 39.13.90.11 – Other mixtures and preparations for rubber or plastics and other mixtures and preparations to harden synthetic resins, glues, paints or similar uses, from January 1997 to March 2019. Source: Comex Stat (http://comexstat.mdic.gov.br)

According to the survey of the commercial balance sheet (import and export) made for the NCM 39.04.22.00 (Polyvinyl chloride (PVC), plasticised, in primary form), via the Comex Stat platform, Brazil imported 326,426 net tonnes of these products in the period 1997 to 2019 and exported 157,035 net tonnes in the same period. Argentina (49%), United States (18%) and Uruguay (13%) were the main suppliers of the products registered under this NCM in question for Brazil and Bolivia (32%), Argentina (24%) and Paraguay (22%) were the main buyers. In a scenario in which the entire volume of imported products within the NCM 39.04.22.00 is considered of products based on CP and that the CP percentage of the formulation of this type of product can reach 10% (Table 8), we could estimate that between 1997 and 2017 entered around 32,642 net tonnes of CPs, of which about 15,703 tonnes would have left the country.

Based on all these gross estimations related to paraffin-based waterproofing, rubber and PVC trade, we overestimate that the total volume of CPs that may have entered Brazil associated with products containing CPs in its formulation, between the years 1997 and 2019, is approximately 654,000 net tonnes. However, while we expect this value to be overestimated, there are several other products that may contain CPs – such as cables, paints, coatings, metalworking fluids, lubricants, sealants and adhesives – catalogued within other NCMs that have not been evaluated due to more uncertainty regarding their classification and control. Therefore, even overestimating the total amount of CPs entering in Brazil associated with some products that might contain them, this value of 654,000 net tonnes can be just wrong for more or less.

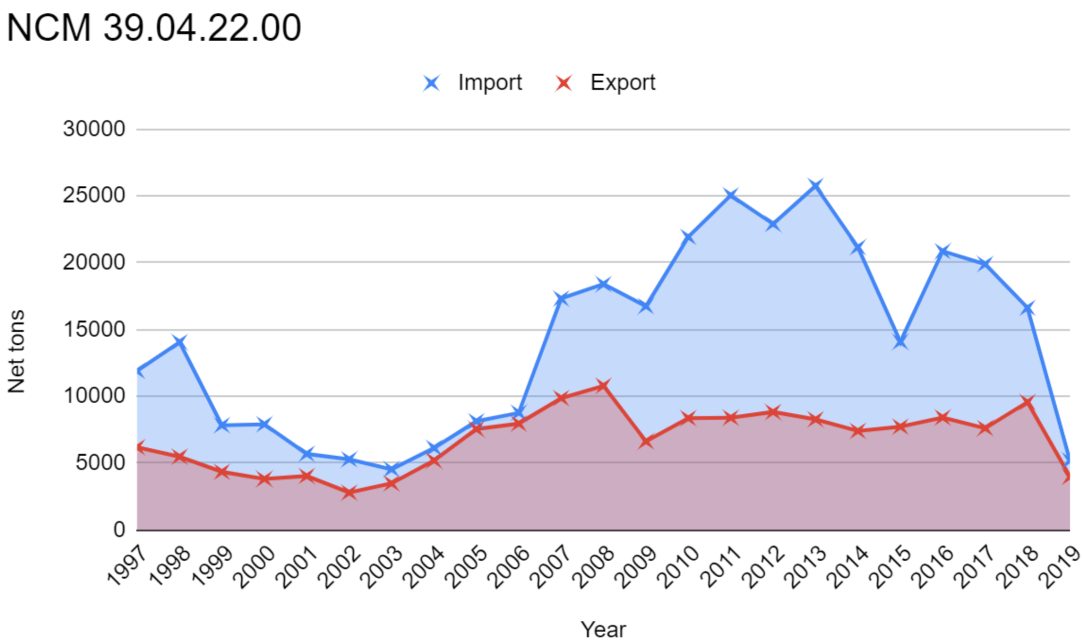

Figure 14: Brazilian commercial balance (import and export volumes in net tonnes) of products registered under the NCM 39.13.90.11 – Polyvinyl chloride (PVC), plasticised, in primary form, from January 1997 to March 2019. Source: Comex Stat (http://comexstat.mdic.gov.br)

4.4 Action plan for SCCPs

Considering all the information raised up to the present time and also the processes by which we obtained (or did not obtain) the information, we emphasize the need to think of a new approach, encouraging the industrial sector to provide information in good faith for the development of the NIP-Brazil. We suggest that not just national governments propose a way to incentive the participation of their industries but also that the Stockholm Convention itself could provide kind of a stamp to state which companies helped in the processes of NIP developments and so customers could be aware of the affirmative behave of those companies to the Stockholm Convention implementation and for the environment protection. Although the circular crafts were clear about the need of the Country-Parties to manifest their interest for the maintenance of specific exceptions, there seems to be no understanding from the institutions consulted or even from governmental secretariats that the NIP is a tool that can help to predict and avoid economic catastrophes stemming from a possible blockade of Brazilian commodities, especially for the European Union, which has recently radically lowered the limits of acceptable daily/weekly intake for POP substances.

It will also be necessary, as a next step, to contact the institutions that responded the questionnaires or that were mentioned in some reply, for further clarification. As well, try to sample some of the mentioned products for evaluating the percentage of SCCPs and other CPs and their homologous profiles (percentage of each chain length and chlorine content). It is important to emphasize that the method for identification and quantification of SCCPs and MCCPs have already been implemented in the Laboratory of Radioisotope Eduardo Penna Franca, of the Biophysical Institute of the Federal University of Rio de Janeiro, as one of the fundamental steps for the development of the new NIP-Brazil and this pilot project. In addition, it is foreseen a literary review and evaluation of studies that report the presence of CPs in any type of sample in the Brazilian territory. Further, we shall compare the data available in the Brazilian database (Comex Stat) using the NCM codes with the database of the World Trade Organization (Comtrade) using the Harmonized System (HS) codes.

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Annexes

Annex 1: Consumer products containing SCCPs on the EU market

Consumer products assessed in European Union members states and Norway between 2013 and 2017 and found to contain SCCPs levels above regulatory limits (1500 mg/kg) in the Rapid Alert System for Non-Food Consumer Products (EU) (RAPEX).

Table A1. Consumer products containing SCCPs on the EU market 2013-2017 (UNEP 2018b)

2017	Sports equipment: Boxing gloves	4400
	Sports equipment: Gym ball	8500
	Toy pistol (plastic cord)	7000
	Bathtub pillow	17 000
	Electric shaver (cable)	9800
	Hobby/sports equipment: Hot pack	4000
	Hobby/sports equipment: Exercise tube	90 000 (handles)
	Speaker (cord)	10 000
	Radio controlled car (tires)	17 000
	Claw hammer (Handle)	7000
	In-ear headphones (USB cord)	3000
	LED candle (cord)	13 000
	Power cord	26 000
	Table cloth	6 000
	Selfie stick (cord)	45 700
	USB cable	16 000
	Bath toy	13 400
	Game controller	43 000
	Plastic doll	8 600
	Babies' sleeping bag/footmuff (packaging)	40 000
	Babies' sleeping bag (anti-slip knobs)	18 000
	Handle (cycle parts)	3 500
	Breastfeeding pillow (packaging)	60 000
	Hammer (handle)	2 800
	Sports equipment: Yoga mat	8 000
	Erotic article	4 400
2016	Lighting chain (cord)	7 000
	Sports equipment: Yoga mat	2 300
	Sports equipment: Abs trainer	4000

	Steering wheel cover	4 600
	Long sleeved sweater (print)	2 300
	Steering wheel cover	3 000
	Motor vehicle sidelight (cable)	2 600
	USB-cord	2 570
	Selfie Stick	1 600
	Digital thermometer (cable)	1 100
	Stickers (toys)	9 000
	Stickers (toys)	14 000
	Mobile phone case	4 400
	Sports equipment: Baseball glove	13 600
	All-purpose mat	3 600
	Sports equipment: Yoga mat	6 400
	Sports equipment: Yoga mat	5 400
	Sports equipment: Yoga mat	32 000
	Sports equipment: Yoga mat	69 000
	Sports equipment: Yoga mat	3 500
	Sports equipment: Fitness gloves	1 800
	Rain cover for pushchair	7 300
	Extension lead	47 000
	Extension lead	17 000
2015	Kettle (cable)	36 400
	Game Controller (cable)	19 000
	Rubber knife	2 600
	Mobile phone cover	2 600
	Cloche cover (garden equipment)	4 000
	Toilet seat for children	710
	Plastic doll	3 170
	Toy doctor set (stethoscope)	49 100
	Electric kettle (cord)	5 000
	Beach ball	3 100
	Bouncy toy	5 000
	Bathmat	5 200
	Shower curtain	4 900
	Stickers (toys)	15 000
	Stickers (toys)	2 000

	Bathmat	5 300
	Shower hose	47 000
	Earphones	2 800
2014	Wallet (artificial leather)	1 300
	Handbag (artificial leather)	14 000
	Mobile phone bag (artificial leather)	1 100
	Brush case black (artificial leather)	3 500
	Toiletry bag	11 700
	Handbag (artificial leather)	3 800
	Handbag (artificial leather)	3 200
	Bag (artificial leather)	2 700
	Small bag / purse (artificial leather)	1 700
	Wallet case for smartphones (artificial leather)	1 800
	Purse (artificial leather)	2 000
	Pencil case (artificial leather)	5 000
	Handbag (artificial leather)	10 000
	Toiletry bag (artificial leather)	1 300
	Toy car (tires)	8 300
	Sports equipment: Exercise mat	16 000
	Sports equipment: Exercise mat	49 000
	Sports equipment: Jump rope	22 000
	Plastic cooking set (plastic bag)	8 800
2013	Beauty case	12 000
	Squeeze toy (chicken)	100 000
	Plastic bath toy	71 000
	Pirate slap-on bracelet	31 000
	Doll with accessories	15 000
	Police costume (transparent plastic pocket)	57 000
	Replaceable wall decorative stickers	18 000
	Pirate costume for children	2 800 (belt) and 1900 (vest)
	Plastic toy figures	83 000

Annex 2: GC/MS analysis of PCNs (instrumental setting; chromatogram)

GC/MS conditions for PCNs (example) (Secretariat of the Stockholm Convention 2017b)

An example of instrumental setting for the GC/MS analysis of PCNs is given in Table A2 and the exact masses of native and ^{13}C-labled PCNs in Table A3.

A chromatogram of PCN homologues from GC/MS analysis is shown in Figure A1.

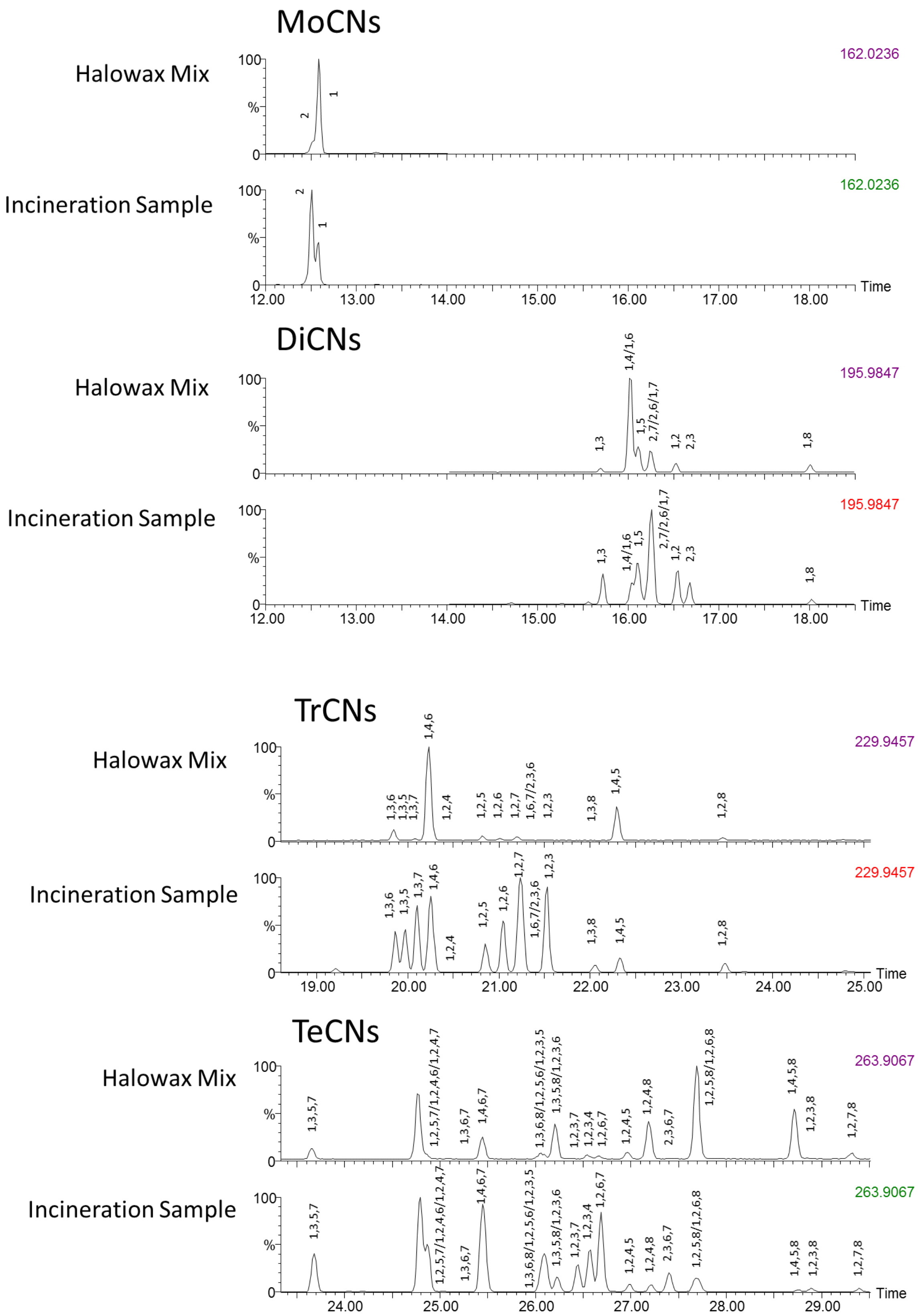
Table A2: PCP GC/MS conditions (example)

GC column	DB-5MS（Agilent Technologies/J&W）fused silica capillary column ID 0.32 mm, length 60 m, thickness 0.25 µm
Oven Temp.	90°C (2 min hold) - (20°C/min)→160°C - (3°C /min) →245°C -(5 C/min) →310°C（2 min hold）
Injection	On-column or Split less
Injector Temp. (On-column)	90 C(1 min hold)ー（100 C/min）→300 C
Injection volume	1〜2 µL
HRMS condition	Autospec Ultima （Waters/Micromass）
Ionization	EI
Ionization voltage	35 V(35〜70 V)
Ionization current	500 µA
Accelerating voltage	8 kV
Ion source Temp.	290〜300 °C
Interface Temp.	290〜300 °C
MS resolution	10 000

Table A3: Masses of detected ions (*m/z*'s) and isotope ratio for PCNs

	CL degree	M^+	$(M+2)^+$	$(M+4)^+$
Native PCN	*MoCNs (not listed)*	*162.0237(100)*	*164.0208(32.6)*	
	DiCNs	195.9847(100)	197.9818(64.5)	
	TrCNs	229.9457(100)	231.9428(96.5)	
	TeCNs	263.9067(77.8)	265.9038(100)	
	PeCNs		299.8648(100)	301.8619(64.3)
	HxCNs		333.8258(100)	335.8229(80.3)
	HpCNs		367.7869(100)	369.7839(96.3)
	OcCN		401.7479(89.1)	403.7450(100)
Internal Standard for PCN	$^{13}C_{10}$-DiCN	206.0183(100)	208.0152(64.0)	
	$^{13}C_{10}$-TeCNs	273.9402(78.2)	275.9373(100)	
	$^{13}C_{10}$-PeCNs		309.8983(100)	311.8954(64.0)
	$^{13}C_{10}$-HxCNs		343.8593(100)	345.8564(80.0)
	$^{13}C_{10}$-HpCN		377.8204(100)	379.8174(95.9)
	$^{13}C_{10}$-OcCN		411.7814(89.4)	413.7785(100)
	$^{13}C_{12}$-DiCB*,**	234.0406(100)	236.0376(65.6)	
	$^{13}C_{12}$-TrCB*	268.0016(100)	269.9986(98.0)	
	$^{13}C_{12}$-TeCB**	301.9626(78.2)	303.9597(100)	
	$^{13}C_{12}$-PeCB*		337.9207(100)	339.9177(65.3)
	$^{13}C_{12}$-HxCB*		371.8817(100)	373.8788(81.5)
	$^{13}C_{12}$-OcCB*		439.8038(87.8)	441.8008(100)

Up to now, not sufficient of $^{13}C_{10}$-PCN for internal standard, so alternatively used $^{13}C_{12}$- PCB


MoCNs
Halowax Mix
162.0236
Incineration Sample
162.0236
DiCNs
Halowax Mix
195.9847
Incineration Sample
195.9847
TrCNs
Halowax Mix
229.9457
Incineration Sample
229.9457
TeCNs
Halowax Mix
263.9067
Incineration Sample
263.9067
Time
%
1,4/1,6
2,7/2,6/1,7
1,4,6
1,2,7
1,2,3
1,4,5
1,2,5,7/1,2,4,6/1,2,4,7
1,3,6,8/1,2,5,6/1,2,3,5
1,3,5,8/1,2,3,6
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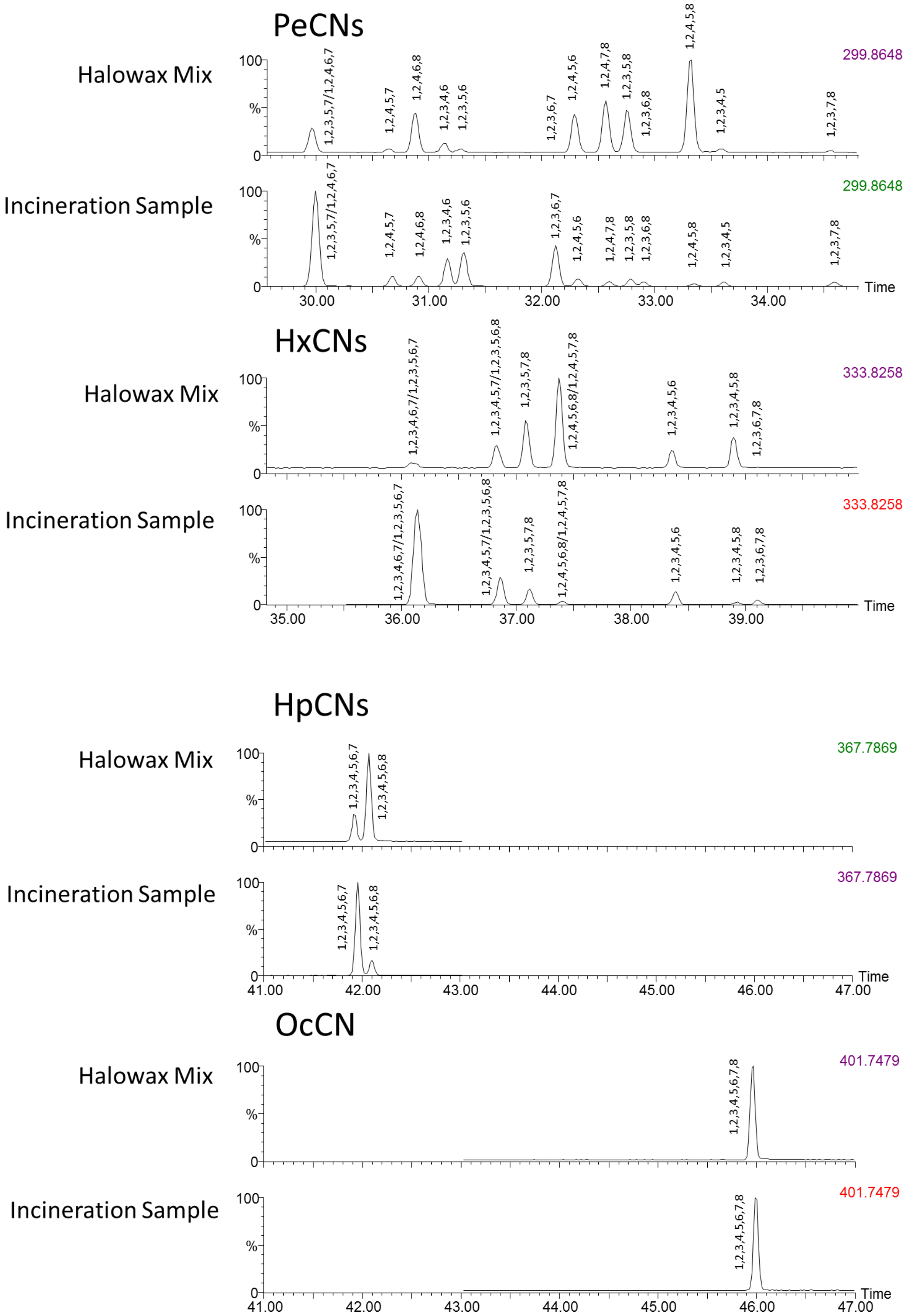
1,4,6,7
1,2,6,7
1,3,5,7



※Halowax Mix： Halowax 1000,1001,1013,1014,1031,1051,1099 mixture

Incineration sample：flue gas sample

Figure A1: Chromatogram of PCN congeners from technical mixtures and waste incineration[1]

[1]Noma Y, Yamamoto T, Sakai S (2004) Congener-specific composition of polychlorinated naphthalenes, coplanar PCBs, dibenzo-p-dioxins, and dibenzofurans in the Halowax series. Environ Sci Technol. 38, 1675-80.

Takasuga T, Inoue T, Ohi E, Senthil Kumar K (2004) Formation of Polychlorinated Naphthalenes, Dibenzo-p-Dioxins, Dibenzofurans, Biphenyls, and Organochlorine Pesticides in Thermal Processes and Their Occurrence in Ambient Air. Arch. Environ. Contam. Toxicol. 46, 419-431.

Operating Protocol for Polychlorinated Naphthalenes Analysis

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[2]POPs Environmental Consulting, Schwäbisch Gmünd, Germany, 73527

This protocol is mainly based on the "Guidance on preparing inventories of polychlorinated naphthalenes (PCNs)" and on the "Draft Guidance on Sampling Screening and Analysis of Persistent Organic Pollutants in Products and Articles"; both available on the following links:

1- http://chm.pops.int/Implementation/NationalImplementationPlans/Guidance/NewlyDevelopedGuidance/GuidanceforPCN/tabid/6231/Default.aspx

2- http://chm.pops.int/Implementation/NationalImplementationPlans/GuidanceArchive/guidanceonsampling,screeningofPOPs/tabid/5333/Default.aspx

This protocol was created to help to implement analysis of polychlorinated naphthalenes (PCNs) by gas chromatography coupled with electron impact positive ion mass spectrometry operated in selected ion monitoring mode (GC/EI-MS-SIM).

PCNs have been used by some companies until around 2000 (Yamashita et al., 2000; Yamamoto et al., 2016). However, commercial mixtures of PCNs were mainly produced and used between 1920 and 1970 (UNEP, 2017). The total production volume of commercial PCNs is estimated to 150,000 (UNEP, 2017). Similarly, to PCBs and SCCPs, PCNs have been used in closed applications (e.g. capacitors and transformers) and in a wide range of open applications including cable insulation, wood preservation, as additive in paints and dye carriers, feedstock for dye, and in engine oils (UNEP, 2017). Since the production of PCNs has largely been phased out in the 1980s and 1990s, most articles and products containing PCNs have reached end of life or have already been disposed. However, some PCNs are unintentionally formed in the production of organochlorine chemicals and in thermal processes (UNEP, 2017).

PCN screening could be enough to distinguish isomer specific assignments among different technical products and thermal by-products. This is important to evaluate PCN sources in the environment and also the risks posed by the more toxic isomers. However, PCNs can form 75 different congeners, varying from one to eight chlorine atoms around the planar naphthalene molecule and to securely quantify specific isomers a standard containing a broad range of specific isomers is needed.

PCN screening could be done in the full-scan mode on a low-resolution GC/EI-MS, however, it may not be sensitive enough when dealing with PCN low concentrations. Therewith, this protocol was created to help in the implementation of a more sensitive screening in selected ion monitoring mode by GC/EI-MS. Thereby, after the differentiation of isomer specific assignments, the best fitted standard for PCN quantification could be selected and the critical isomers could be traced.

The quantification of one isomer of each homologue group was also developed from the PCN-MXA standard (Wellington Lab. ON, Canada)

Step 1: Standard preparation

A serial dilution of the standard mix solution should be performed covering the range of PCN concentration expected to be measured in the samples, adding the injection/internal standard (ISTD)*, which must match the same concentrations in the standards and in the sample extracts to be analysed.

** In this case 2,4,5,6-tetrachloro-m-xylene (TCMX - 100 ng mL^{-1}), from Sigma-Aldrich Brasil Ltda. was used as ISTD.*

Dilutions of 5, 10, 25, 50, 75 and 100 ng mL^{-1}, with 100 ng mL^{-1} of TCMX were used for the calibration curve.

Step 2: Instrument setup

A first screening in the full-scan mode (30-700 amu) was carried out using a dilution of 1000 ng mL^{-1}, in order to know the retention times of each homologue and set up the ion monitoring windows.

The analysis should be carried out using the following general setup:

- 60 m column with **DB-5** phase; 0.25 mm id, 0.25 µm film thickness (or equivalent)
- Temperature program: 50°C (1 min) – 25 °C/min - 130 °C (3 min) – 5 °C/min - 280 °C (10 min) – 2 °C/min - 290 °C (15 min)
- Ion source: 230 °C; Quad: 150 °C; transfer line: 300 °C
- Splitless injector: 290 °C

Exemplary GC/EI-MS-SIM setup

------- -----------

Sample Inlet : GC

Injection Source : GC ALS

Mass Spectrometer : Enabled

Oven

Equilibration Time 0 min

Oven Program On

50 °C for 1 min

then 25 °C/min to 130 °C for 3 min

then 5 °C/min to 280 °C for 10 min

then 2 °C/min to 290 °C for 15 min

Run Time 67,2 min

Front Injector

Syringe Size 10 µL

Injection Volume 2 µL

Solvent A Washes (PreInj) 2

Solvent A Washes (PostInj) 4
Solvent A Volume 8 µL
Solvent B Washes (PreInj) 2
Solvent B Washes (PostInj) 4
Solvent B Volume 8 µL
Sample Washes 1
Sample Wash Volume 8 µL
Sample Pumps 4
Dwell Time (PreInj) 0 min
Dwell Time (PostInj) 0 min
Solvent Wash Draw Speed 300 µL/min
Solvent Wash Dispense Speed 6000 µL/min
Sample Wash Draw Speed 300 µL/min
Sample Wash Dispense Speed 6000 µL/min
Injection Dispense Speed 6000 µL/min
Viscosity Delay 0 sec
Sample Depth Disabled
Injection Type Standard
L1 Airgap 0,2 µL

Sample Overlap
Sample overlap is not enabled

Front SS Inlet He
Mode Splitless
Heater On 290 °C
Pressure On 13,573 psi
Total Flow On 53,8 mL/min
Septum Purge Flow On 3 mL/min
Gas Saver On 20 mL/min After 2 min
Purge Flow to Split Vent 50 mL/min at 1 min
Thermal Aux 2 {MSD Transfer Line}
Heater On
Temperature Program On
250 °C for 0 min
Run Time 67,2 min
Column #1
DB-5MS
325 °C: 60 m x 250 µm x 0,25 µm
In: Front SS Inlet He

Out: Vacuum
(Initial) 50 °C
Pressure 13,573 psi
Flow 0,8 mL/min
Average Velocity 23,05 cm/sec
Holdup Time 4,3385 min
Flow Program On
0,8 mL/min for 0 min
Run Time 67,2 min

Aux EPC 1 He
Excluded from Affecting GC's Readiness State
Aux EPC 2 He
Excluded from Affecting GC's Readiness State
Aux EPC 3 He
Excluded from Affecting GC's Readiness State

Signals
Test Plot Save Off
50 Hz
Test Plot Save Off
50 Hz
Test Plot Save Off
50 Hz
Test Plot Save Off
50 Hz

MS ACQUISITION PARAMETERS

General Information
------- -----------
Tune File : atune.u
Acquistion Mode : SIM

MS Information
-- -----------
Solvent Delay : 5.00 min

EMV Mode : Gain Factor

Gain Factor : 1.00
Resulting EM Voltage : 1588

[Sim Parameters]

GROUP 1
Resolution: Low
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
(207.00, 100) (209.00, 50) (244.00, 50)
(162.00, 100) (164.00, 50)
GROUP 2
Resolution: Low
Group Start Time: 14.00
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell)
(196.00, 100) (198.00, 50)
(230.00, 100) (232.00, 50)
GROUP 3
Resolution: Low
Group Start Time: 25.00
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell)
(264.00, 50) (266.00, 100)
(300.00, 100) (302.00, 50)
GROUP 4
Resolution: Low
Group Start Time: 35
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell)
(334.00, 100) (336.00, 50)
(368.00, 100) (370.00, 50)
(402.00, 50) (404.00, 100)
[MSZones]

MS Source: 230 C maximum 250 C
MS Quad: 150 C maximum 200 C

END OF MS ACQUISITION PARAMETERS

TUNE PARAMETERS for SN: US94344155

Trace Ion Detection is OFF.

EMISSION : 34.610
ENERGY : 69.922
REPELLER : 34.814
IONFOCUS : 90.157
ENTRANCE_LE : 12.500
EMVOLTS : 1364.706
Actual EMV : 1588.23
GAIN FACTOR : 1.02
AMUGAIN : 2551.000
AMUOFFSET : 121.188
FILAMENT : 1.000
DCPOLARITY : 1.000
ENTLENSOFFS : 20.329
MASSGAIN : -310.000
MASSOFFSET : -36.000

END OF TUNE PARAMETERS

END OF INSTRUMENT CONTROL PARAMETERS

Step 3: Quantification

After the method development, a calibration curve was set up in the software “Data Analysis” for the quantification of PCNs 2, 6, 13, 28, 52, 66, 73, 75 (PNC-MXA; Wellington). Basically, the standard serial dilution was injected, the peaks were labelled and the ions selected. A linear regression was performed from the dilutions and the constant ISTD. Therefore, those congeners could be identified by specific ion masses, their ratio (Table 1) and the standard comparable retention time and the quantification was done considering the peaks’ area.

Annex 3: Standard Operation Protocol for SCCP/CP analysis by GC/ECNI-MS

Operating Protocol for Chlorinated Paraffin Determination by GC/ECNI-MS-SIM

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[2]University of Hohenheim, Institute of Food Chemistry, Garbenstr. 28, D- 70599 Stuttgart, Germany

This protocol is mainly based on the following literature:

Reth M, Zencak Z, Oehme M. **New quantification procedure for the analysis of chlorinated paraffins using electron capture negative ionization mass spectrometry**. *J. Chromatogr. A* 2005; 1081 (2): 225–231. doi: 10.1016/j.chroma.2005.05.061;

Reth M & Oehme M. **Limitations of low-resolution mass spectrometry in the electron capture negative ionization mode for the analysis of short- and medium-chain chlorinated paraffins**. *Anal. Bioanal. Chem.* 2004; 378 (7): 1741–1747. doi: 10.1007/s00216-004-2546-9;

Sprengel J & Vetter W. **Synthesis and characterization of eight single chain length chlorinated paraffin standards and their use for quantification**. *Rapid Commun Mass Spectrom*. 2019; 33: 49-56. doi: 10.1002/rcm.8310.

Sprengel J, Wieselmann S, Kröpfl A, Vetter W. **High amounts of chlorinated paraffins in oil-based vitamin E dietary supplements on the German market**. *Env. Int*. 2019; 128: 438-445. doi: 10.1016/j.envint.2019.04.065.

This protocol was created to help to implement analysis of short- and medium-chain chlorinated paraffins (CPs) by gas chromatography coupled with electron capture negative ion mass spectrometry operated in selected ion monitoring mode (GC/ECNI-MS-SIM) and it is divided in three steps. However, you must read the references above to fully understand the method (preferentially in the order they were presented).

Rio de Janeiro, July, 2019

Step 1: Standard preparation

CP homologs with different chlorine contents are needed (**at least five different Cl% should be used**). Thus, starting with 3 CP homologs with different chlorine content (**SCCP 51.1% Cl; SCCP 55.5% Cl and SCCP 63% Cl**), you just need to make a 1 + 1 mixture of them and you will have two additional chlorine contents, which is enough to make a linear regression (SCCP 51.1% Cl + SCCP 55.5% Cl = **SCCP 53.3% Cl** and SCCP 55.5% Cl + SCCP 63% Cl = **59.25% Cl**). The same should be made with MCCP standards. **MCCP 42% Cl; MCCP 52% Cl and MCCP 57% Cl** can originate **MCCP 47% Cl (42% + 52%) and MCCP 54.5% Cl (52% + 57%).**

Once all CP homologs with different chlorine content are prepared, you can make a work dilution according to the concentrations you expect to measure in the analysed samples, adding the injection/internal standard (ISTD)*, which must match the same concentrations in the standards and in the sample extracts you aim to analyse. CP homologs concentrations do not need to vary. The linear regression shall be made with the chlorine content variation of the homologs.

** In this case 6'-MeOH-BDE 66 (BCIS), synthesized by Prof. Vetter's work group, is used as ISTD.*

Step 2: Instrument setup

CPs can be quantified by monitoring the two most abundant isotopes of the $[M\text{-}Cl]^-$ ions of CPs in the SIM mode. All m/z values used for CP-analysis are listed in Table A4. It is necessary to make a SIM run for each CP chain-length. Thus, a total of 8 SIM runs will be necessary to quantify SCCPs and MCCPs by GC/ECNI-MS-SIM*. The analysis should be carried out using the following setup:

- 30 m column with **DB-5** phase (or equivalent)
- Temperature program: 50°C (1 min) – 10 °C/min - 300 °C (14 min)
- Ion source: 150 °C; Quad: 150 °C; transfer line: 300 °C
- PTV or split/splitless injector

Table A4: *m/z* values monitored in GC/ECNI-SIM runs.

	Used for	measured ions (*m/z*)	Dwell time [ms]
SIM 01	C_{10}-CP quantification	243; 245; 279; 277; 313; 315; 347; 349; 381; 383; 417; 415; 451; 449 + ***ISTD ions****	28
SIM 02	C_{11}-CPs quantification	257; 259; 293; 291; 327; 329; 361; 363; 395; 397; 431; 429; 465; 463 + ***ISTD ions****	28
SIM 03	C_{12}-CPs quantification	271; 273; 307; 305; 341; 343; 375; 377; 409; 411; 445; 443; 479; 477 + ***ISTD ions****	28
SIM 04	C_{13}-CPs quantification	285; 287; 321; 319; 355; 357; 389; 391; 423; 425; 459; 457; 493; 491 + ***ISTD ions****	28
SIM 05	C_{14}-CPs quantification	299;301; 335; 333; 369; 371; 403; 405; 437; 439; 473; 471; 507; 505 + ***ISTD ions****	28
SIM 06	C_{15}-CPs quantification	313; 315; 349; 347; 383; 385; 417; 419; 451; 453; 487; 485; 521; 519 + ***ISTD ions****	28
SIM 07	C_{16}-CPs quantification	327; 329; 363; 361; 397; 399; 431; 433; 465; 467; 501; 499; 535; 533 + ***ISTD ions****	28
SIM 08	C_{17}-CPs quantification	341; 343; 377; 375; 411; 413; 445; 447; 479; 481; 515; 513; 549; 547 + ***ISTD ions****	28

**Whether using BCIS as ISTD, add ions 79; 81; 261; 259 in each SIM run.* Dwell time can be changed to optimize the resolution of the chromatogram according to your needs.

Exemplary GC/ECNI-MS-SIM setup

Sample Inlet: GC
Injection Source: GC ALS
Mass Spectrometer: Enabled

Oven

Equilibration Time	0,5 min
Oven Program	On
50 °C for 1 min	
then 10 °C/min to 300 °C for 14 min	
Run Time	40 min

Front Injector

Syringe Size	10 µL
Injection Volume	1 µL
Solvent A Washes (PreInj)	5
Solvent A Washes (PostInj)	5
Solvent A Volume	8 µL
Solvent B Washes (PreInj)	5
Solvent B Washes (PostInj)	5
Solvent B Volume	8 µL
Sample Washes	0
Sample Wash Volume	8 µL
Sample Pumps	6
Dwell Time (PreInj)	0 min
Dwell Time (PostInj)	0 min
Solvent Wash Draw Speed	300 µL/min
Solvent Wash Dispense Speed	6000 µL/min
Sample Wash Draw Speed	300 µL/min
Sample Wash Dispense Speed	6000 µL/min
Injection Dispense Speed	6000 µL/min
Viscosity Delay	0 sec
Sample Depth	Disabled
Injection Type	Standard
L1 Airgap	0,2 µL

Sample Overlap
Sample overlap is not enabled

Front PTV Inlet He*

Mode	Pulsed Splitless

Heater On 80 °C
Pressure On 9,7853 psi
Total Flow On 104,2 mL/min
Septum Purge Flow On 3 mL/min
Temperature Program On
80 °C for 0,01 min
then 500 °C/min to 300 °C for 2 min
then 10 °C/min to 260 °C for 0 min
Run Time 40 min

** If you don't have a Front PTV inlet injector, you won't be able to setup the temperature program. In this case, setup the temperature as 280 °C.*

Gas Saver On 20 mL/min After 2 min
Injection Pulse Pressure 25 psi Until 1 min
Purge Flow to Split Vent 100 mL/min at 2 min
Cryo Off

Thermal Aux 2 {MSD Transfer Line}
Heater On
Temperature Program On
300 °C for 0 min
Run Time 40 min

Column #1
HP-5MS 5% Phenyl Methyl Siloxane: 1077.58889
HP-5MS 5% Phenyl Methyl Siloxane
325 °C: 30 m x 250 µm x 0,25 µm
In: Front PTV Inlet He
Out: Vacuum

(Initial) 50 °C
Pressure 9,7853 psi
Flow 1,2 mL/min
Average Velocity 39,923 cm/sec
Holdup Time 1,2524 min
Flow Program On
1,2 mL/min for 0 min
Run Time 40 min

Signals
Test Plot Save Off
50 Hz
Test Plot Save Off

50 Hz
Test Plot Save Off
50 Hz
Test Plot Save Off
50 Hz

MS ACQUISITION PARAMETERS

General Information
Tune File : ncich4.u
Acquistion Mode : SIM

MS Information
Solvent Delay : 8.00 min
EMV Mode : Gain Factor
Gain Factor : 14.00
Resulting EM Voltage : 1541

[Sim Parameters]
GROUP 1
Group ID : 1
Resolution : Low
Plot 1 Ion : 261.00
Ions/Dwell In Group (Mass, Dwell) (Mass, Dwell) (Mass, Dwell) (Mass, Dwell)
Example: BCIS ions (79.00, 28) (81.00, 28) (259.00, 28) (261.00, 28)
This step will change for each SIM run. You must select the ions according to the CP chain-length as shown in Table A4. In the end you will have 8 different injection methods, in which you will run each sample. Do not forget to save all SIM runs as different methods.

[MSZones]
MS Source : 150 C maximum 300 C
MS Quad : 150 C maximum 200 C

TUNE PARAMETERS for SN: US94343906
Trace Ion Detection is OFF.

EMISSION : 49.443
ENERGY : 119.076
REPELLER : 3.988
IONFOCUS : 96.800
ENTRANCE_LE : 15.500
EMVOLTS : 1294.118
Actual EMV : 1541.18

GAIN FACTOR : 13.50

AMUGAIN : 1742.000

AMUOFFSET : 128.625

FILAMENT : 1.000

DCPOLARITY : 0.000

ENTLENSOFFS : 21.082

MASSGAIN : -782.000

MASSOFFSET : -32.000

CI Flow Rate: 40

CI A/B Gas : 1

Step 3: Quantification

After the setup of the instrument and method development you will be ready to inject your standards and sample extracts in each SIM run. Starting with the standards, every different Cl content (SCCPs 51.5%, 53.3%, 55.5%, 59.25%, 63% and MCCPs 42%, 47%, 52%, 54.5% 57%) have to be inject in the different SIM runs. Therefore, the 5 SCCPs with different Cl% have to be inject four times each, being one in each method (SIM runs 01, 02, 03 and 04; according to Table A4) and the 5 MCCPs with different Cl% have to be inject four times each, being one in each method (SIM runs 05, 06, 07 and 08; according to Table A4). After a total of 40 runs, 20 runs for SCCPs and 20 runs for MCCPs, you are ready to start sample injections. The samples will be injected 4 times for SCCPs and 4 times for MCCPs, just like the standards. Once you have the chromatograms, you will open one by one and extract the selected ions (you might have to do it more than once for each CP chain-length, cause generally you can only extract 6 ions per time).

Beginning with the standards, each ion of the ISTD and CP with different Cl% have to be integrated and their area computed for the next step in an Excel file. The computed area of each ion will be typed in the Excel file "CP_quantification", which is ready to use. The "Sample" sheet in the file can be duplicated for every sample you need to quantify. CP concentrations in ng μL^{-1} and chlorine content (Cl%) will be given. Then, CP concentrations can further be corrected according to the sample mass/volume analysed.

It is extremely important, especially for setups using LRMS, to ensure a precise integration of the correct CP humps. Therefore, it is elementary that you get to known the typical hump shapes of CPs, especially as they appear on your system. Be careful if you have any peak which do not match the standard chromatogram. If there is any clearly discernible peak on top of the CP hump, the interference must be integrated separately afterwards and its area have to be deducted from the integration of the total area (CP + interference). Starting with the standards will make you familiar with its chromatogram, which is necessary to recognize any interference afterwards. For some examples of CP shapes, please check the chromatograms in Figure A2.

Additionally, you have to consider the interferences between the CPs themselves. On LRMS systems, especially CPs which are 2 and 5 carbon atoms apart can lead to big interferences. On a 30 m column, CPs which are 5 C apart can be separated via retention time. By comparing the retention times of the samples with the respective standards, the overlapping hump peak in the sample can generally be sharply separated between the two CP species. However, overlaps between CPs that are 2 C apart cannot be separated via retention time. Here, it is important to know which CP chain length (+2 or -2) is causing the interference. In this case, the peak area contribution of the desired chain length can be calculated from the measured isotope ratio, and the theoretical isotope ratios of the desired CPs and the interference. Generally, one can say:

- If **$C_{(x+2)}$-CPs are much more abundant**, than the **Cl_{8-10} homologs** of C_X-CP are affected and need correction
- If **$C_{(x-2)}$-CPs are much more abundant**, the **Cl_{5-7} homologs** of C_X-CPs are affected and need correction

Be careful, as sometimes additional interferences of another origin can occur in your sample that also need arithmetic correction.

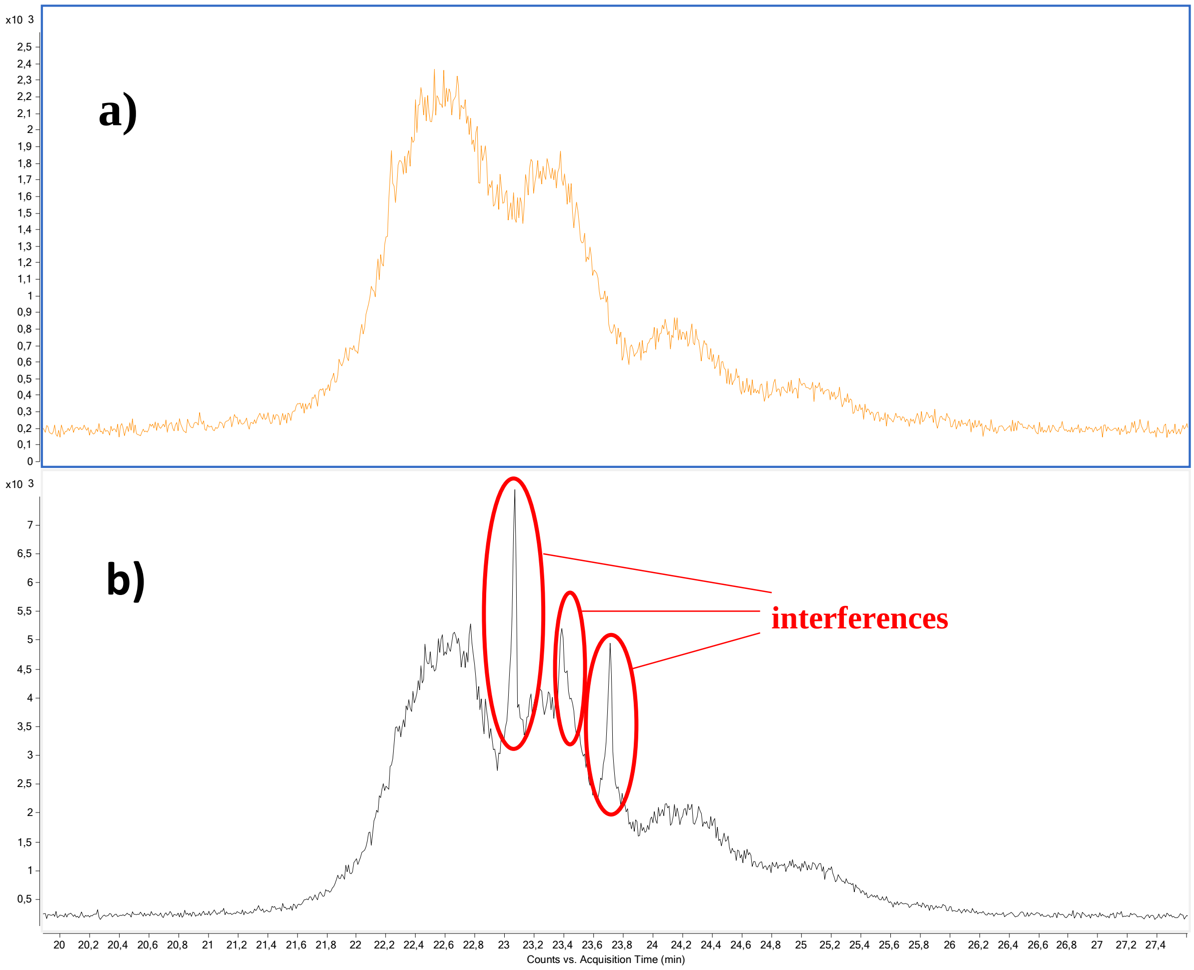

Figure A2: examples of **a)** CP-only hump and **b)** CP hump with interference peaks.

This document must come with the Excel file “CP_quantification” and the four references in which it is based.

Don’t hesitate to contact me if you have any question.

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Skype: yagoguidarj

Annex 4: Short Paper for global POPs Conference 39th International Symposium on Halogenated Persistent Organic Pollutants (Dioxin2019), 25-30 August, Kyoto, Japan

DEVELOPMENT OF ANALYTICAL CAPACITY IN BRAZIL FOR TIER III INVENTORY DEVELOPMENT FOR SCCPs AND PCNs IN BRAZIL

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Introduction Polychlorinate naphthalenes (PCNs) were listed as POPs in the Stockholm Convention in 2015. More recent in 2017 short-chain chlorinated paraffins (SCCPs; C10 to C13 and a content of chlorine greater than 48% by weight.) were listed as POPs in the Stockholm Convention on Persistent Organic Pollutants (POPs). Additionally, a limit for the presence of SCCPs in other chlorinated paraffin mixtures was set at 1% by weight. SCCPs are listed with a wide range of specific exemptions for production and use. Brazil as a Party of the Stockholm Convention need to assess the use and lifecycle of SCCP in the country. In this contribution steps towards developing an inventory of PCNs and SCCPs in Brazil is presented starting with the development analytical capacity.

Materials and Methods: SCCP and PCN analysis were developed based on GC-MS. The SCCP draft inventory guidance and draft PCN inventory guidance of the Stockholm Convention was considered for developing a draft inventory and gap analysis. Both SCCP and PCN mixtures were analysed with a 7890A gas chromatograph coupled to a 5975C mass spectrometer (Agilent, Waldbronn, Germany) equipped with an HP-5MS capillary column (30 m x 250 mm internal diameter x 0.25 µm film thickness) containing 95% methyl, 5% phenyl polysiloxane from Quadrex Corporation (Agilent Technologies, U.S.A.). SCCPs were quantified according to Reth et al. (2004; 2005) using a linear calibration curve of area over chlorine content by means of GC/ENCI-MS-SIM. SCCP standard was synthetized by Sprengel & Vetter (2018) and donated to our group. Native PCN mixture (WELL-PCNMXA) standard was purchased from Wellington Laboratories (Ontario, Canada) and was quantified using a linear calibration curve of 6 different concentrations by means of GC/EI-MS-SIM.

Results: Within the activity the development of SCCP and PCN inventory, instrumental analysis could be established at Rio University. An initial assessment of the presence of products and waste fractions potentially contaminated with SCCPs and/or PCNs were in development. The major products/waste include soft PVC, rubber belts, lubricants, waterproofing and fire-retardant paints; metalworking fluids, adhesives, and fatliquoring of leather. Since SCCP have substituted technical PCNs mixtures in many applications, these two POPs should be assessed in products and wastes respectively. Brazil had formerly produced SCCP. In an initial assessment it could be confirmed that the SCCP production started in the 1980's and stopped in 1994, then it started to be imported from the USA and its trade lasted until 2011, when the stockpiles were finished.

Contact has been established to the Japanese National Institute of Environmental Studies (NIES) which develop a standard analysis for products/wastes containing PCNs and SCCPs for cooperation and quality assurance.

Conclusions: A wide range of products and waste fractions in Brazil likely contain SCCPs and some of the waste fractions might contain PCNs used in the past. An analytical capacity to assess these products and waste have been established and South-North cooperation will be used for quality assurance of analytical results.

Acknowledgements:
Part of the activity has been financed by the European Union and supported by the Secretariat of the Stockholm Convention.

References:
1. Reth M & Oehme M. (2004) *Analytical and Bioanalytical Chemistry*. 378(7): 1741-7.
2. Reth M, Zencak Z, Oehme M. (2005) *Journal of Chromatography A*. 1081(2): 225-31.
3. Sprengel & Vetter (2018) *Rapid Commun. Mass Spectrom.* 2019(33): 49-56

Annex 5: General comments on using the guidance documents of the Stockholm Convention

All Parties of the SC are encouraged to use the available guidance and invited to provide comments based on their experience in using them. Therefore, some aspects of the new available guidance (UNEP, 2019d) and its previous draft guidance on preparing inventories of SCCPs were considered within this project.

The detailed guidance showed to be more complete and therefore more useful to provide the working team responsible for the inventory with a better understanding about the lifecycle of SCCPs and their relation with other CP chain lengths and even with other POPs. In the context of the NIP development or update, the detailed guidance on SCCPs showed to be the most complete one if compared to the other POP guidance documents due to its questionnaires models and its given information on how to deal with the industrial sectors and to request information from them and, finally, due to its proposed integrated approach of its Tier III considering the potential occurrence of other POPs, such as PCNs and PCBs. However, although the presence of HCB and PeCB are also highlighted in the studies that found unintentional POPs in CP and CP-containing products, the guidance seems to do not give the deserved attention to these POPs.

To conclude, we do suggest the use of the detailed guidance instead of the draft version. However, some improvements could be considered, such as:

- Consider HCB and PeCB in the proposed integrated approach of Tier III.
- Review the references of Yuan et al., 2017. There are two different studies of the same author in that year and both are cited in the guidance without differentiation along the text. It should be differed in Yuan et al., 2017a and Yuan 2017b.
- Chapter seven should be “Inventory of SCCPs in products, products in use and stocks” instead of “Inventory of SCCPs in products, use and stock”
- References should also be listed in the Appendix 3 on analyses as follows:

BTHA (British Toys and Hobby Association). 2016. Short Chain Chlorinated Paraffins (SCCP) CAS 85535-84- 8 Regulation (EU) 2015/2030 amending Regulation (EC) 850/2004 (POPS). http://www.btha.co.uk/wp-content/uploads/2016/08/SCCP-Guide.pdf Accessed 27 January, 2019.

ESWI. 2011. Study on waste related issues of newly listed POPs and candidate POPs. Consortium ESWI (Bipro, Umweltbundesamt and Enviroplan) for the European Commission.

Gallistl C, Sprengel J, Vetter W. 2018. High levels of medium-chain chlorinated paraffins and polybrominated diphenyl ethers on the inside of several household baking oven doors. Sci Total Environ. 615, 1019-1027. doi: 10.1016/j.scitotenv.2017.09.112.

Reth M, Zencak Z, Oehme M. 2005. New quantification procedure for the analysis of chlorinated paraffins using electron capture negative ionization mass spectrometry. *J. Chromatogr. A*; 1081 (2): 225–231. doi: 10.1016/j.chroma.2005.05.061.

Sprengel J & Vetter W. 2019. Synthesis and characterization of eight single chain length chlorinated paraffin standards and their use for quantification. Rapid Commun Mass Spectrom; 33: 49-56. doi: 10.1002/rcm.8310.

UNEP. 2018b. Draft technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with short-chain chlorinated paraffins. UNEP/CHW/COP.14/7/Add.2

UNEP. 2018d. Draft Guidance on Sampling, Screening and Analysis of Persistent Organic Pollutants in products and articles. UNEP/POPS/COP.7/16/analysis, revised 2018.

Yuan B, Strid A, Darnerud PO, de Wit CA, Nyström J, Bergman Å. 2017a. Chlorinated paraffins leaking from hand blenders can lead to significant human exposures. Environ Int. 109, 73-80.

- The following references are missing in appendix 3: (Tommy et al., 1997); (Yuan et al., 2017c); (Krätschmer et al., 2018) and the reference (Yuan et al., 2018) should be (Yuan et al., 2017a)

Annex 6: Draft TOR for the scientific group supporting initial inventory activities

Draft TORs to develop an initial inventory of the presence of PCNs, PCBs in open application and SCCPs in major products, wastes and recycling

1. BACKGROUND

The Stockholm Convention on Persistent Organic Pollutants is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have harmful impacts on human health or on the environment. In response to this global problem, the Stockholm Convention, which was adopted in 2001 and entered into force in 2004, requires its parties to take measures to eliminate or reduce the release of POPs into the environment. As set out in Article 1 of the convention, the primary objective of the Stockholm Convention is to protect human health and the environment from persistent organic pollutants.

In May 2015, by decision SC-7/14, the Conference of the Parties amended Annex A to the Convention to list polychlorinated naphthalenes (dichlorinated naphthalenes to octachlorinated naphthalene, referred to as PCNs). PCNs were listed with specific exemptions for production of those chemicals as intermediates in production of polyfluorinated naphthalenes, including octafluoronaphthalene, and the use of those chemicals for the production of polyfluorinated naphthalenes, including octafluoronaphthalene. PCNs were also listed as unintentional POPs in Annex C to the Convention.

In May 2017, by decision SC-8/11, the Conference of the Parties amended Annex A to the Convention to list short-chain chlorinated paraffins (SCCPs) with various specific exemptions.

Parties to the Convention for which the amendments to list PCNs and SCCPs have entered into force shall meet the obligations under the Convention leading to the elimination of those chemicals. According to Article 7 of the Convention, each Party shall develop a NIP within two years from the date of entry into force. The establishment of inventories is one of the important phases in the development of NIPs. Furthermore, Article 6, paragraph 1 (a), of the Stockholm Convention requires each Party to develop appropriate strategies for the identification of products and articles in use and wastes consisting of, containing or contaminated with POPs.

A draft inventory guidance for PCNs has been developed by the Secretariat of the Stockholm Convention and it contains information on PCBs in open application (UNEP 2017a). A draft inventory guidance for SCCPs is scheduled to be available in May 2019.

The main use of PCNs were practically identical to the uses of PCBs in closed applications (e.g. capacitors, transformers) and open applications (e.g. sealants, paints/coatings). Therefore, the inventory of PCNs should be linked or combined with the PCB inventory. Only a few measurements on PCNs in open applications have been published (e.g. Neoprene FT Yamashita et al. 2003) and there are no data on PCNs in closed applications other than in PCB oils (Yamashita et al. 2000).

SCCPs together with medium- and long-chain chlorinated paraffins (MCCPs and LCCPs) have substituted PCBs and PCNs in a range of open applications (sealants, paints/coatings, cutting oils). Therefore, the inventory of SCCPs should also be linked or combined with the inventory PCBs and PCNs.

The total global production volume of chlorinated paraffins is more than 1 million tonnes per year (Glüge et al. 2016). It is estimated that still about 165,000 t of SCCPs are produced/used

(Glüge et al. 2016). The use of SCCPs in open applications such as PVC/plastic additives, rubber additives, paints, sealants, leather fatliquoring, lubricants and metalworking fluids are listed as specific exemptions. These are also the major historic uses and therefore stockpiles and wastes have been accumulated from these and possibly other uses over time.

SCCPs (chain length C10 to C13) can be present in MCCPs as impurities (C14 to C18). If the SCCP content in MCCPs is above 1%, this mixture is considered as a POP. Therefore, MCCPs should also be analysed and assessed when developing the inventory for SCCPs. SCCP and in higher levels MCCP were recently detected at high levels in backing ovens (Gallistl et al. 2018) and kitchen blenders (Yuan et al 2017). In these studies it was not clarified if SCCPs were impurities of MCCPs or if they were independently applied.

It is important to integrate researchers' groups or governmental institutions with analytical capacity in the development and implementation of the NIP. For example, to identify and manage PCBs in open applications, PCNs and SCCPs (including SCCPs in MCCPs), monitoring and analysis are essential.

Screening, monitoring and a strategic use of research/monitoring capacity to assess and understand the presence of PCNs, together with PCBs in open application and SCCPs in different uses, waste and recycling flows are needed.

For the initial inventory of the current situation of PCNs/PCBs in open application and SCCPs in the country, an initial assessment need to be conducted. Also the presence of PCNs in closed applications of PCBs should be assessed within the PCB assessment in transformers and capacitors. At the same time, the draft inventory guidance on PCNs should be tested and evaluated.

2. SCOPE OF WORK, RESPONSIBILITIES AND DESCRIPTION OF THE PROPOSED REPORT WORK

The task for the research group is to gather information and data for the development of a preliminary inventory of PCNs, PCBs in open applications and SCCPs in selected applications. Also compile current information gaps and respective monitoring needs. Initial collection of relevant samples and analyse selected samples for PCBs, PCNs and SCCPs/MCCPs to the extent feasible.

During the activities, the current situation of the management of materials potentially containing PCNs, PCBs and SCCPs should be briefly described. All activities will be conducted with online-support of Roland Weber.

For the activities, the respective inventory guidance, technical guidelines and other materials supporting inventory development should be considered such as:

- The Stockholm Convention inventory guidance for PCNs. http://chm.pops.int/Implementation/NationalImplementationPlans/Guidance/tabid/2882/Default.aspx
- Presentations from the regional workshop introducing the links between PCNs, PCBs and SCCPs (will be provided).
- Basel Convention Technical Guidelines on PCBs, PCTs and PCNs
- Further useful literature reviews on SCCPs and MCCPs (will be provided).

The detailed duties of the consultant/research group will include, but not limited to, the following specific responsibilities:

- Define the detailed objectives and scope of a (preliminary) qualitative inventory on PCNs, SCCPs and PCBs in open applications in the country considering the objectives and scope setting proposed in the inventory guidance for PCNs, in close communication with Dr. Weber.
  1) Open applications (see Chapter 6 of PCN inventory guidance)
     a) PVC cables and recycled PVC (PCN, SCCP, PCB)
     b) Paints/coatings e.g. Ships[2], swimming pools (PCN, SCCP, PCB)
     c) Sealants/caulks and putty (PCN, SCCP, PCB)
     d) Rubber (Chloroprene and other rubber) (PCN, SCCP, PCB)
     e) (Waste) Oils (see 2) below)

     Representative samples should be gathered and analysed as time and capacity allows. The selection of samples should be discussed with Dr. Weber. A list of samples should be compiled, and those samples which cannot be analysed in the first phase, could be analysed in a next phase of the assessment.
  2) Closed applications (chapter 5 of PCN inventory guidance)
     a) Propose an approach for integrating PCN monitoring in ongoing or planned PCB monitoring
     b) If feasible, collect samples of mixed waste oils from sectors with possible impact by PCNs and SCCPs.

  3) Initial assessment of potential generation of unintentional PCNs in the country (see Chapter 7 of PCN inventory guidance)
     a) Identify which of the sources might be present in the country
     b) Compile initial information

  4) Summarize initial findings on potentially PCN (if possible also SCCP) contaminated sites (Chapter 8 of PCN inventory guidance)
     a) Assess which of the potentially PCN contaminated sites might be present in the country. Analogous compilation of SCCP contaminated sites along the lifecycle of production, use in industry/products and end of life
     b) If feasible, prepare an initial description of some of these sites

  5) Evaluate and provide comments on the PCN inventory guidance (UNEP 2017a)
     a) Is the background information given in chapter 1 to 3 appropriate? What is missing? Suggestion for modification and additions or shortening?
     b) Are the chapters on inventory development (4 to 8) appropriately structured and clear? Do you have suggestions for additions, modifications or shortening?

For addressing the above points:

- Develop a work plan on the above listed activities and revise it based on comments received from Dr. Weber and Stockholm Convention Secretariat.

[2] The removal of ship paints can generate large wastes of sand blasted paints.

- In cooperation with Dr. Weber, prepare a report:
  - On findings of the assessment of the presence of products, wastes and recycling of materials potentially containing PCNs/PCBs and/or SCCPs (considering chapter 5 to 7 of the PCN inventory guidance).
  - Compile a list of potentially contaminated sites/hot spots of PCNs/PCBs[3] (and SCCP) considering chapter 8 of the PCN inventory guidelines.
  - Conduct a gap analysis and assess the need of future screening and monitoring of PCNs/PCBs and SCCPs in the country.
- Develop a list of sampling and analysis necessary for identifying the presence of PCNs/PCBs and SCCPs in products, wastes and recycling. Prioritize samples for assessment. Conduct initial screening, sampling and analysis to the extent feasible.
- Provide comments on the PCN inventory guidance.

3. Deliverables

Item	%age	Deadline for deliverable
Work plan/methodology submission and approval of the assignment.	5%	Within 1 week of assignment
Report on information and data collection from identified sectors/areas of POPs (PCNs/PCBs, and SCCPs) in products, wastes, recycling and contaminated sites including gap analysis.	40%	Within 12 weeks of the assignment
List of samples and analysis which would be necessary to identify the presence and amount of PCNs/PCBs and SCCPs in products, wastes and recycling. Results from initial screening, sampling and analysis of selected samples.	40%	Within 15 weeks of the assignment
Comments and suggestions to improve the Stockholm Convention PCN inventory guidance	15%	Within 15 weeks of the assignment

4. REQUIREMENTS FOR EXPERIENCE AND QUALIFICATIONS

- University Degree in Chemistry, Environmental Science/Engineering, or other relevant discipline.
- At-least five (05) years of professional work experience in related areas of the project including POPs analysis, inventory & management, Stockholm Convention on POPs, hazardous chemicals & waste, environmental management, programme evaluation and coordination.
- Scientific knowledge and good understanding of the national environmental/ developmental technical issues related to POPs and hazardous chemicals & waste.
- Previous work experience with international agencies/ projects is an asset.

Functional Competencies:

- Advanced computer skills in Excel, Word processing, Database management
- Excellent report writing skills;
- Knowledge of research designs are desirable;

[3] Since the use of PCNs were in the same use as the PCBs, the PCB contaminated sites possibly compiled in the NIP

- Excellent communication and writing skills both verbal and written in English (Knowledge of local languages will be an additional asset).

References

Gallistl C, Sprengel J, Vetter W (2018) High levels of medium-chain chlorinated paraffins and polybrominated diphenyl ethers on the inside of several household baking oven doors. Sci Total Environ. 615, 1019-1027. doi: 10.1016/j.scitotenv.2017.09.112. Epub 2017 Oct 17.

UNEP (2017a) Draft guidance on preparing inventories of polychlorinated naphthalenes (PCNs). Draft March 2017. UNEP/POPS/COP.8/INF/19

Yuan B, Strid A, Darnerud PO, de Wit CA, Nyström J, Bergman Å (2017) Chlorinated paraffins leaking from hand blenders can lead to significant human exposures. Environ Int. 109, 73-80.

Yamashita N, Kannan K, Imagawa T, Miyazaki A, Giesy J P (2000) Concentrations and Profiles of Polychlorinated Naphthalene Congeners in Eighteen Technical Polychlorinated Biphenyl Preparations. Environ. Sci. Technol. 34, 4236-4241.

Yamashita N, Taniyasu S, Hanari N, Falandysz J (2003) Polychlorinated naphthalene contamination of some recently manufactured industrial products and commercial goods in Japan. J Environ Sci Health A 38:1745–1759.