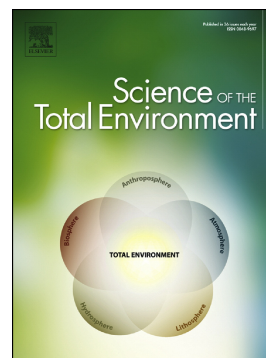


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**Analytical procedures for short chain chlorinated paraffins determination - how to make them greener?**

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**Abstract**

The aim of the following paper was to gather current scientific information about the analytical protocols dedicated to measuring the content level of short-chain chlorinated paraffins (SCCPs) in various types of environmental samples. Moreover, the data about the basic validation parameters of applied procedures for SCCPs determination are listed. The main issue which is highlighted in the paper is the possibility of the application of green analytical chemistry (GAC) principals in the SCCPs measuring process to reduce the environmental impact of the applied methodology. Analytical methods dedicated to SCCPs determination contain a significant number of steps and require advanced analytical equipment during the quantitative and qualitative analysis. In addition, there is a substantial issue associated with the reliability of the obtained results, especially in the case of the quantification of individual SCCPs in the studied samples. Due to this fact, the paper attempts to discuss the various stages of the analytical procedure, in which appropriate changes in the formula or equipment solutions might be introduced to ensure a better quality of the analytical results, as well as to meet the requirements of the philosophy of green analytical chemistry. The most important case which concerns this subject is finding an optimal consensus between the economic and logistic aspects and the quality and “greenness” of the analytical procedure employed in SCCPs determination process.

**Keywords:** short-chain chlorinated paraffins; green analytical chemistry; sample preparation techniques; environmental samples; gas chromatography; results quality



**Alphabetical list of abbreviations and acronyms**

APCI	Atmospheric Pressure Chemical Ionization
ASE	Accelerated Solvent Extraction
CPs	Chlorinated Paraffins
GAC	Green Analytical Chemistry
GAPI	Green Analytical Procedure Index
GC/ECNI- MS	Gas Chromatography/Electron Capture Negative Ionization Mass Spectrometry
GC/ECNI-HRMS	Gas Chromatography/Electron Capture Negative Ionization High Rating Mass Spectrometry
GC/ECNI-LRMS	Gas Chromatography/Electron Capture Negative Ionization Low Rating Mass Spectrometry
GC/ECNI-TQMS	Gas Chromatography/Electron Capture Negative Ionization Triple Quadrupole Mass Spectrometry
GC/EI-LRMS/MS	Gas Chromatography/Electron Ionization Low Rating Tandem Mass Spectrometry
GC-ECD	Gas Chromatography With Electron Capture Detector
GC-GC/ECNI-HRTOF-MS-TIC	Two-Dimensional Gas Chromatography/Electron Capture Negative Ionization Time-Of-Flight High-Resolution Mass Spectrometry
GC-GC/ECNI-MS	Two-Dimensional Gas Chromatography/Electron Capture Negative Ionization Mass Spectrometry
GC-GC/TOF-MS	Two-Dimensional Gas Chromatography/Time-Of-Flight Mass Spectrometry
GPC	Gel Permeation Chromatography
HRGC/ECNI- LRMS	High Rating Gas Chromatography/Electron Capture Negative Ionization Low Rating Mass Spectrometry
HSE	Hot Solvent Extraction
LC-MS	Liquid Chromatography/Mass Spectrometry
LLE	Liquid-Liquid Extraction
LOD	Limit Of Detection
LRGC/ECNI-MS	Low Rating Gas Chromatography/Electron Capture Negative Ionization Mass Spectrometry
MCDA	Multicriteria Decision Analysis
MIP	Molecularly Imprinted Polymer
PBDEs	Polybrominated Diphenyl Ethers
PCA	Polychlorinated Alkanes
PM	Particulate Matter
PUF	Polyurethane Foam
SCCPs	Short-Chain Chlorinated Paraffins
SE	Solvent Extraction
SFE	Supercritical Fluid Extraction
SFS	Separatory Funnel Shaker
TDI	Tolerable Daily Intake
SOM	Self-Organizing Maps
SPE	Solid-Phase Extraction
SPM	Solid Phase Matter
TOPSIS	Technique for Order Preference by Similarity to Ideal Solution
UAE	Ultrasound-Assisted Extraction
UV	Ultraviolet
LCCPs	Long-Chain Chlorinated Paraffins
MCCPs	Medium-Chain Chlorinated Paraffins
POPRC	Persistent Organic Pollutants Review Committee
POPs	Persistent Organic Pollutants
PVC	Polyvinyl Chloride
NEMI	National Environmental Methods Index



## 1. Introduction

The chemical compounds defined as chlorinated paraffins (CPs), also known as polychlorinated alkanes (PCA), are a complex mixture of different chlorinated hydrocarbons with variable composition, first introduced on the global market in the 1930s. This group contains many congeners with carbon chain length from  $C_{10}$  to  $C_{30}$ , diverse chlorination degree from 40% to 70% by weight, as well as structural and spatial isomers (De Boer, 2010). The classification of CPs in general is based on chain length and is divided into three general groups: (i) short-chain CPs (SCCPs – chain length ranged from  $C_{10}$  to  $C_{13}$ ); (ii) medium-chain CPs (MCCPs – chain length from  $C_{14}$  to  $C_{17}$ ); (iii) long-chain CPs (LCCPs – chain length above  $C_{17}$ ). However, some CP products derived from the Chinese market (CP-42, CP-52, CP-70) are described by chlorination degree rather than chain length, and they contain on average 42%, 52% and 70% of chlorine by weight. Thus, the carbon chains length of chlorinated hydrocarbon in these products is diverse (van Mourik et al., 2016; Li et al., 2018; Schinkel et al., 2018). Industrial synthesis of CPs is conducted by way of chlorination of petroleum-based n-alkanes/paraffins and rarely olefin or alkyne fractions. The main reaction which occurs during this process is radical chlorination of hydrocarbons initiated by high temperature and/or light irradiation (Li et al., 2018; EPA, 2008). In the case of olefins and alkynes, the electrophilic addition of chlorine to unsaturated bonds or radical chlorination in allylic position is also possible. During radical chlorination, hydrogen chloride is composed as a by-product, and together with the excess chlorine they should be removed from final products. The high ranges of used feedstocks, as well as the low specificity of the chlorination reaction caused that CPs mixtures include a lot of congeners, and this makes their identification and quantification a tremendous challenge. The analytical methods for the determination of CPs involve standards which can be divided into four groups: (i) complex CP mixtures with different ranges of carbon chain lengths and chlorination degrees, (ii) single



chain CP mixtures containing only one type of congener with a specific carbon chain length and different chlorination level, (iii) CPs with a defined carbon chain length and chlorination position, (iv) isotopically labelled CPs. The detailed characterization of CP analytical standards is given by Schinkel et al. (2018a). The main method of CP standards synthesis is based on radical chlorination of pure n-alkanes or their defined mixtures. This low selective method is useful for the standards preparation belonging to the first and second groups. The reaction is usually performed in chlorinated organic solvents under UV light irradiation in the presence of chlorine or sulfuryl chloride, which is a more convenient source of chlorine/chlorine free radicals for the laboratory scale. This method was utilized for the synthesis of CP standards from n-decane to n-heptadecane (Tomy et al., 2000; Sprengel and Vetter, 2019). On the other hand, n-alkenes are good substrates for the synthesis of standards with a defined chlorination position (third group). It is shown in the synthesis of polychlorodecane analogues containing from five to nine chlorine atoms (Laitinen, 1973; Coelhan, 2003; Beaume et al., 2006). The standards were obtained by the electrophilic addition of chlorine or hydrogen chloride to the double bonds of appropriate decatrienes with a combination of bromination in allylic position followed by hydrolysis of allyl bromide, and finally replacement of the hydroxyl group to the chlorine atom in the reaction with phosphorus pentachloride. For the two highest substituted polychlorodecanes the appropriate alkenes were produced in the Wittig reaction followed by chlorination. Alkenes can also be used in the free radical addition of tetrachloromethane or compounds containing the trichloromethyl group to the terminal double bond of an alkene. This method is known as Kharasch addition and results in the elongation of the carbon chain length of polychlorinated alkanes. For more detailed information about the synthesis of CPs, as well as analytical standards, the Handbook of Chlorinated Paraffins, edited by De Boer (2010) is recommended.



Among CPs, special attention has been paid mainly in the field of the occurrence, environmental fate and health risks of SCCPs in various types of samples characterized by the complex and very often nonhomogeneous composition of the matrix. Following the information gathered using the SCOPUS scientific papers database, it can be noticed that the number of papers published from 2008 to 2018, associated with the analytical procedures employed in studies of content levels, environmental fate and health risk of SCCPs, is constantly growing (Figure 1). SCCPs are industrial products which were (or in some cases still are) commonly used as metal-working fluids and flame retardants for various types of plastic materials and rubber (Harada et al., 2011). Mainly, they have been produced in China, the USA, Canada, India, Japan and Europe. As an example, in 2007 the production volumes of SCCPs were 600 kilotons in China and 11.3 kilotons in the European Union region (Fridén et al., 2011). SCCPs are characterized by significant persistence in the environment, high potential for bioaccumulation, biomagnification, and a tendency to transport transgenically. Taking into consideration their physicochemical properties, such as hydrophobic behaviour, high values of octanol/water partition coefficients ( $\log K_{o/w}$  from 3.82 to 7.75), and vapour pressures ranged from  $2.8 \cdot 10^{-7}$  to  $6.6 \cdot 10^{-2}$  Pa, SCCPs might be adsorbed on the components of outdoor (particulate matter, sediments, sewage sludge, plants) and indoor (house dust, fly ash and particulate matter) environments (Eljarrat and Barcelo, 2006). The main environmental issue associated with SCCPs is the fact that they exhibit toxic effects on aquatic organisms (Rubirola et al., 2018). In 2017, members of the Persistent Organic Pollutants Review Committee (POPRC) of the Stockholm Convention classified SCCPs as Persistent Organic Pollutants (POPs) (van Mourik et al., 2018). Moreover, SCCPs have also been qualified by members of the International Agency for Research on Cancers as compounds belonging to group 2B - potentially possessing carcinogenic properties for humans (Wang et al., 2014). In addition, despite the fact that SCCPs are characterized by high persistence in the environment,



under special environmental conditions they might be considered as an additional emission source of chlorine to various components of the environment. As a result, several international and national law regulations on the manufacturing process and application of SCCPs have been introduced. In Figure 2 information about the most important milestones in the field of law regulations about SCCPs' compounds in various components of the environment is presented. Due to this, the presence and the content level of these harmful chemical compounds should be constantly monitored in almost every component of the environment.

Nevertheless, the determination of the content level of SCCPs during the analysis of sample materials characterized by the complex composition of the matrix is not an effortless process. Mainly, it is caused by the diversified composition of the employed technical mixtures during the manufacturing process, and the complex analytical procedures which should be used to obtain reliable analytical information about the SCCPs' content level. Generally, a significant number of analytical procedures employed in SCCPs determination (see Table 1) consist of the sample collection stage, a two-step sample preparation process containing the extraction procedure and the clean-up process of obtained extracts, and finally the extensive determination process (including quantitative and qualitative analysis). Following the recent literature data, it might be found that there are several reliable prepared review articles which contain detailed information about analytical procedures and analytical devices which were applied to determine SCCPs in various types of environmental samples (Berton et al., 2016; van Mourik et al., 2015; Zeng et al., 2013; Zencak and Oehme, 2006). Having regard to the above-mentioned factors and considering the information listed in the current review articles, it might be noticed that the optimal determination of the content level of SCCPs in environmental samples is very time and labour consuming, and requires a lot of financial resources.



There is also an important issue associated with the sufficient chromatographic separation of SCCP mixtures into selected congeners in proper extracts of studied samples. This is caused by the fact that SCCPs might occur in the studied samples in a significant homologues and isomers. Because of this, there are several types of quantification methods developed by authors to obtain the most reliable analytical information about the type and the amount of SCCPs present in studied environmental samples. However, there is still a lack of a clearly defined, optimized and validated analytical methods which might be implemented in everyday analytical laboratory practice in studies of SCCPs' occurrence and their environmental fate (Aamir et al., 2019). The main reason for this is the fact that performing the quantification analysis of SCCPs it is necessary to select the appropriate SCCPs certificate standard mixture with a defined chlorinated degree which has a significant impact on the response of employed chromatographic detectors (Gandolfi et al., 2015; Muscalu et al., 2017).

The main aim of the following paper is not only to update and present the current information about the analytical equipment applied in the sample preparation, separation, identification and quantitative determination of SCCPs in environmental samples. The most important issue discussed in this paper will contain the problems and challenges which might be encountered during everyday analytical practice associated with the determination of SCCPs in samples characterized by the complex composition of the matrix. Moreover, an important aspect of this work will be the possibility of evaluating those points of analytical procedures in which it is possible to implement the aspects of the philosophy of green analytical chemistry (GAC). Taking into consideration the SIGNIFICANCE mnemonic of green analytical practices developed by Gałuszka et al. (2013), an attempt was made to propose some alternative solutions to make SCCPs analytical methodologies more "green", environmentally friendly and less time and labour consuming. However, it should be kept in mind that it is difficult to apply all of the 12 principals of GAC in laboratory practice. As a consequence, in this paper



the proposition of the employment of some of the GAC principals in selected steps of the analytical procedures for the determination of SCCPs in environmental samples is discussed.

## **2. The main occurrence areas of SCCPs in environmental samples**

Due to the toxicity of SCCPs, their capacity for bioaccumulation, and their persistence in the environmental mediums, SCCPs have become an important environmental issue, mainly in countries such as China, India, Russia, and the USA (van Mourik et al., 2015; van Mourik et al., 2016; Liu et al., 2017). Following the information listed on the Scopus web site, from 2010 to 2018 the number of scientific papers considering the occurrence of SCCPs in the China region was 91, and the number of papers in this period was characterized by constant growth. As a consequence, Wei et al. (2016) published a review paper which concerns the most important information about the occurrence, environmental fate, and potential ecological risk of all types of CPs (including SCCPs) in various types of samples collected in the Asia region. Because of this, there is a constant need to develop and apply such analytical procedures which give reliable information about SCCPs' concentration, especially in samples originating from various components of the environment. The majority of the currently performed research is focused on the occurrence and distribution of SCCPs in the China region, because of the fact that currently it is the largest manufacturer and consumer of CPs in the world. In addition, China is one of the most intensive producers of various types of plastic materials (mainly products made of PVC and textiles) to which the CPs might be added (Li et al., 2012; Xu et al., 2014; Wei et al., 2016). Due to the fact that CPs might be transported over long distances and be deposited in the area of other countries and regions, the number of articles concerning the analysis of environmental samples derived from Europe, North America or even the Antarctica region has been steadily increasing due to the interest in their environmental fate and the potential ways of emission (Reth et al., 2006; Li et al., 2016;



Kobetičová and Černý, 2018). Moreover, considering the CPs' physicochemical properties, it might be noticed that they are similar to another group of chemical compounds used in the plastic materials manufacturing process as flame retardants - polybrominated diphenyl ethers (PBDEs). As a consequence, the CPs' migration pathways in the environment might be similar to PBDEs and concern parallel components of the environment – from atmospheric and indoor air, through the aquatic environment, ending in the soil and sediment (Król et al., 2012; Śmiełowska and Zabiegała, 2018).

### **3. The major components of the environment containing SCCP compounds**

Aerosols, dust and particulate matter (PM) are among the most often investigated types of environmental samples analyzed for the presence of SCCPs in atmospheric, urban or indoor air. Due to the persistence of SCCPs, as well as their wide and, until recently, completely unrestricted use, they are usually detected in various types of air samples throughout the world, though based on the available data it can be concluded that the overall concentration of SCCPs is higher in the Asia region than in North America or Europe (Wei et al., 2016). The exact levels of SCCPs in certain regions may vary depending on various factors, such as (i) proximity to local sources, (ii) meteorological variables, or (iii) the physiochemical properties of the CPs themselves. Moreover, the concentration of SCCPs might differ significantly from summer to winter, mainly because of seasonal temperature differences. In addition, the levels of SCCPs in the particle phase are also subjected to intra-seasonal changes, though to a lesser extent. This is probably caused by the fact that the occurrence of higher temperatures during summer may facilitate the volatilization of SCCPs already present in the environment, or those from commercially used products. Conversely, during periods of lower temperatures, particularly winter, the binding of SCCPs to the particles is favoured in lieu of volatilization. A similar relationship between the temperature and atmospheric partition can also be found in



the case of various parallel semi-volatile compounds (Wang et al., 2012; Wang et al., 2013). As for atmospheric air, the presence of SCCPs is caused by their emission directly during the manufacturing process of the plastic materials and from the e-waste areas – areas for depositing discarded electrical or electronic devices. In the case of indoor air, the main emission sources of SCCPs are electronic devices and various types of plastic indoor equipment. However, one of the most important factors that might be considered as a potential source of information about human exposure to SCCPs in indoor environment is house dust. Considering the literature data, it was noticed that SCCPs are characterized by higher content levels in offices and public utilities than in residential buildings and dormitories. Furthermore, the content level of SCCPs in the indoor environment is much higher than in outdoor/urban air (Shi et al., 2017). In the case of indoor air in enclosed areas, SCCP compounds adsorbed on house dust, PM, and the surfaces of indoor equipment are considered to be more stable in the indoor environment, mainly due to their negligible oxidative degradation phenomenon caused by the minor levels of potential hydroxyl radicals (Li et al., 2014).

Since waterways may be one of the pathways of SCCPs' long-distance transport, samples of water from different sources are often analyzed in order to establish on what levels CPs are present in streams, rivers, etc. The general emission sources of SCCPs into the aquatic environment are industrial production of plastic domestic goods, their disposal, and recycling and sewage treatment. As a consequence, SCCPs might migrate to the groundwater and municipal wastewater network. Moreover, e-wastes and microplastics are additional emission sources which might affect the presence of SCCPs in the aquatic environment (Cole et al., 2011; Wei et al., 2016). Special emphasis has been put on SCCPs' determination in samples of wastewater, since effluents may constitute another important transport path of SCCPs to the aquatic environment, and affect their content level not only in water, but also due to





SCCPs' ability to accumulate in soil, sediments and suspended particulate or organic matter (Castells et al., 2008; Li et al., 2018). Based on the already existing data, it is possible to conclude that even though sewage treatment is routinely performed, it may still be considered as one of the major SCCP pathways for the contamination of the aquatic environment. However, it should be highlighted that the analysis of water samples aimed at the determination of SCCPs is very difficult due to the low solubility of SCCPs in water.

Other types of samples commonly investigated for the presence of SCCPs are solid samples, mainly soil and sediment. SCCPs have been found in samples collected from various parts of the world, e.g. the Arctic area and Western Europe. However, their concentrations vary depending on the land-use type, proximity to industrial sources and, in case of soil and sediment samples, soil profile/body or distance from the coast, respectively. Nonetheless, the highest levels of SCCPs and other CPs have been observed in the area of e-waste dismantling in China, which seems to corroborate the importance of the industrial sources' impact on their concentration (Wang et al., 2014; Halse et al., 2015; Yuan et al., 2017; Qiao et al., 2016). Moreover, based on the already existing literature information associated with the SCCPs content, it can be concluded that, their high levels in sediments is caused mostly by wastewater releases. Considering the content level of SCCPs in soils, their presence may be generally caused both by air mass transport and deposition, though air mass exchange seems to be more compelling in rural areas, where lighter congeners constitute a bigger contribution to the overall concentration of SCCPs (Wei et al., 2016; Wang et al., 2013).

### **3.1 The content levels of SCCPs in environmental samples**

The levels of SCCPs in different samples vary significantly depending on various factors, such as the type of sample, and are affected considerably by the presence of local SCCP sources. Their concentration in all types of environmental samples differs according to the



proximity of their major production and consumption areas. Results of SCCP determination in various environmental samples, and information about the basic method's validation parameters are shown in Table 2.

Content levels of SCCPs in samples of urban air are typically higher than in those sampled in rural areas. Moreover, as has been mentioned before, it seems that the levels of SCCPs in summer and winter differ significantly. According to the results on the SCCPs' determination in urban areas in Beijing, their concentration ranged from 1.9-33.0  $\text{ng}\cdot\text{m}^{-3}$  during wintertime to 112-332  $\text{ng}\cdot\text{m}^{-3}$  during summertime (Wang et al., 2012). However, there is not enough information concerning intraseasonal variance of SCCP levels in different parts of the world to draw a definitive conclusion on the seasonal fluctuation of CPs' concentration. It is worth noting, though, that the results obtained in Beijing in summer are much higher than those thus far obtained in Europe (Barber et al., 2005), which may be caused both by the differences in meteorological conditions as well as the presence of multiple sources of CPs in Asia. Following the information listed by Wei et al., (2016), and research papers enclosed there, the fluctuations of the SCCPs' content level in atmospheric air over the Asia region ranged from 0.28–14.2  $\text{ng}\cdot\text{m}^{-3}$  and 0.37–14.2  $\text{ng}\cdot\text{m}^{-3}$  for Japan and Pakistan, respectively, up to 13.5–517  $\text{ng}\cdot\text{m}^{-3}$  for China. It is also worth noting that due to their potential for long-range atmospheric transport, they have also been detected in air samples collected from the Arctic (Li et al., 2017), Shergyla Mountain (total SCCPs from 0.030 to 1.300  $\text{ng}\cdot\text{m}^{-3}$ ) and Lhasa (total SCCPs from 1.10 to 14.44  $\text{ng}\cdot\text{m}^{-3}$ ) (south-eastern Tibetan Plateau) (Wu et al., 2017) and the Antarctica region (total SCCPs from 9.6 to 20.8  $\text{pg}\cdot\text{m}^{-3}$ ) (Ma et al., 2014). As for the house dust samples on which SCCPs might be adsorbed, the general issue is associated with direct human exposure (via dermal adsorption or inhalation) to those harmful compounds, especially for children and employees working in CP production plants. According to the information published by Wang et al. (2018), the average daily occupational exposure to SCCPs



(calculated based on the measured SCCP content) of employers of CP production plants was approx.  $21.8 \mu\text{g}\cdot\text{day}\cdot\text{kg}^{-1}$ , and it was much higher in comparison to tolerable daily intake (TDI), which is equal to  $10 \mu\text{g}\cdot\text{day}\cdot\text{kg}^{-1}$ . Taking this into consideration, it might be noticed that dust might impose a great adverse health risk for people working there or living in the close neighbourhood of CP production plants.

SCCPs have also been found in water samples from various areas. Their concentration varies depending on the type of sampling area. SCCP levels are higher in sewage treatment plants' effluents and influents, which suggests that they may be one of the sources of their presence both in water and soil nearby. Moreover, the results suggest that riverine transport may play a significant part in SCCPs' distribution. However, there are limited data on their occurrence in aquatic samples, mainly due to their low solubility in water and the possibility that SCCPs accumulate in aquatic organisms and sediments. There might be an important issue with the obtained results which concerns the aquatic samples due to the fact that in most cases SCCPs might be adsorbed on suspended matter and microorganisms present in the studied water samples. As a consequence, the information about the content level of SCCPs might not be directly connected with the aquatic medium.

Nonetheless, SCCPs are often detected in soil or sediments samples. They have been found in various areas and in lands of different use. However, the levels of CPs in e-waste dismantling areas are significantly higher than in any other sampling places. Their levels in sediments from the e-waste treatment area in China ranged from 32.5 to  $1.29 \times 10^4 \text{ ng}\cdot\text{g}^{-1}$  (Xu et al., 2019). Moreover, the concentration of SCCPs in both soil and biota samples from that area is much higher than in those from control areas (Luo et al., 2015). Apart from that, it seems that the concentration of SCCPs increases with the decrease of the proximity of places of e-waste treatment, which suggests that they might be among the most important sources of CPs (Wei et al., 2016). The e-wastes, CP production plants and the plastic materials industry are also



considered as the main sources of emission of SCCPs directly into the soil. The content level of SCCPs in soil samples over the China area vary from 0.22 to 1736 ng·g<sup>-1</sup> (Wang et al., 2014; Yuan et al., 2017; Xu et al., 2019). Comparing the content level of SCCPs measured in sediment and soil samples, it might be observed that a much higher content level of SCCPs was found in the case of sediment samples. This might be caused by the fact that sediment (especially its bottom layer) is mainly the last stage of the transport process of SCCPs in the environment. Moreover, the SCCPs present in soil might be transported by air masses to other areas, affecting the fluctuations of SCCPs content level. Furthermore, the occurrence of precipitation might result in the leaching/washing out of those compounds from the soil, and the transporting of them to the aqueous medium, and in the last stage to the sediment.

#### **4. The extraction techniques and purification solutions employed in analytical protocols for the determination of SCCPs in various types of environmental samples**

The optimal sample preparation process is the most bottleneck of every analytical procedure, and it is the main source of the errors which affect the final determination results. Sample preparation is usually performed in order to remove both the matrix components that may interfere with the final determination results and, generally, non-targeted compounds. Since the types of environmental samples in which SCCPs are determined vary and, thus, their physical and chemical properties are significantly different, selection of the most suitable preparation procedure may prove to be challenging. In order to assess the efficacy of the selected method and also to ensure that there is no contamination, procedures are often monitored with the use of control measures such as procedural and/or field blanks of varying composition. Depending on the type of the analyzed samples, blanks consisted of e.g. pre-extracted PUF disks, unexposed glass or wool filters, as well as samples in which no detectable amount of SCCPs were found (Rubirola et al., 2018; Chaemfa et al., 2014; Gallistl



et al., 2017). Moreover, in a case of solid samples (soil or sediment) which might be collected with the use of a stainless steel hand-held corer, before starting the proper analysis those type of samples should be appropriately characterized (composition, physicochemical properties, pH, particle size distribution or even cation exchange capacity) (Bezchlebová et al., 2007; Halse et al., 2015).

The first step in sample preparation usually consists of the isolation and preconcentration of analytes prior to the step of their identification and final determination. In the majority of cases this step is based on the application of various types of extraction techniques and purification solutions, depending on the type of studied samples. Considering the situation where procedural or field quality control was applied, blank samples were processed and analyzed following the same procedures as the selected environmental samples (Zhu et al., 2017; Wang et al., 2013; Barber et al., 2005). Commonly, after the extraction process, numerous steps of extract clean-up are needed in order to remove interfering compounds and to reduce non-target compounds such as pesticides or polychlorinated biphenyls and other compounds with a similar mass-to-charge ratio that may still be in a sample after extraction (Zeng et al., 2011; Van Mourik et al., 2015). However, due to the high chemical stability of SCCPs, conditions such as strong acidic or alkaline environment may be applied without the risk of the extraction being detrimental to the environmental samples' analysis. The extract purification can be performed using glass clean-up tubes, individually prepared under laboratory conditions or purchased as a ready-to-use commercially available clean-up kit. Silica gel, alumina, Florisil and various combinations of them are the most popular types of adsorbents. However, the choice of particular adsorbent depends mostly on the preference of particular laboratories (Bayen et al., 2006; Chen et al., 2013). Detailed information about the extraction techniques and purification solutions applied in the environmental samples



preparation process for the determination of SCCPs is presented in Figure 3 and listed in Table 1.

### 5. Separation, identification and final determination of SCCPs

Due to the complex matrices in which the SCCPs are determined, and the fact that they have similar retention times, it is difficult to analyze all of them accurately. Different approaches have been applied in terms of the analytical equipment and detecting system usage (Table 1). The most popular approach is the use of single column gas chromatography coupled with appropriate detectors. Usually, a non-polar DB-5MS capillary column (30m x 0.25mm x 0.25 $\mu$ m) is applied, since due to its employment it is possible to perform analysis in a relatively short time and with satisfactory sensitivity. However, in several cases the application of a shorter column (15m x 0.25mm x 0.25 $\mu$ m) also gives sufficient separation results and might be considered for SCCP analysis. Analyzing the information listed in Table 1, it can be concluded that with the use of comprehensive two-dimensional gas chromatography (GC x GC) the results may be obtained with increased overall resolution and selectivity, as well as the possibility of homologue-specific separation. Nonetheless, GC x GC has found its application only in a small number of laboratories that analyze CPs (Huang et al., 2017; Muscalu et al., 2017). This might be caused by the fact that such equipment combination is very expensive and requires a lot of laboratory space and advanced skills for its operation.

Of the detectors that can be coupled with gas chromatography, mass spectrometry is the most often applied for the analysis of SCCPs. Low resolution (LRMS), high resolution (HRMS), and triple quadrupole (TQMS) are mostly employed in the electron capture negative ionization (ECNI) mode, which makes it possible to lessen ion fragmentation and, as a result, enhance the sensitivity of the analysis. Nonetheless, the use of the ECNI mode may result in



underestimation of the compounds with less than five chlorine atoms, since there is a difficulty concerning their detection with ECNI-MS (Van Mourik et al., 2015).

Even though GC is mostly used with HR or LRMS, there have been instances in which high-resolution time-of-flight mass spectrometry (TOF-MS) has been applied in CP analysis (Huang et al., 2017). Moreover, gas chromatography with an electron capture detector ( $\mu$ ECD) has also been used to determinate the levels of SCCPs, since lower CPs are detected with its application with passable sensitivity (Muscalu et al., 2017). The application of GC- $\mu$ ECD is less expensive than a mass spectrometer. However, the main issue during the analysis is the lack of identification of single SCCPs congeners (Yuan et al., 2010). Commonly, in this case, the information about the total amount of SCCPs present in the studied sample is reported. Due to this fact, the mass spectrometry technique equipped with an advanced analyzer (TOF or Orbitrap) is the prevailing analytical equipment, commonly applied in SCCP analysis, and at this time it is going through a stage of intensive technological modifications and improvements. Van Mourik et al. (2018), in their review paper, present a general overview (including the main advantages and the key limitations) of the most frequently employed separation devices equipped with appropriate quantification techniques for analysing SCCPs in various types of environmental samples.

## 6. The quantification methods of SCCPs in environmental samples

The results of CPs analysis are usually reported as total short- ( $\Sigma$ SCCPs), medium- ( $\Sigma$ MCCPs) and long-chain chlorinated paraffins ( $\Sigma$ LCCPs) concentration, as overall CP concentration, or as the concentration of individual homologue groups. Because of that, it may be somewhat difficult to compare results obtained in different laboratories. Moreover, the disparity between the results may also be caused by the method of quantification applied for the environmental samples. Currently, the most commonly employed quantification



techniques are those described in the literature by Tomy et al. (1997), Reth and Oehme (2004), Reth et al. (2005a), and Iozza et al. (2008), and their newest modifications.

Usually, the two most abundant isotopes  $[M-Cl]^+$  are monitored in order to quantify them during the group-specific analysis (Van Mourik et al., 2018). The most commonly used method of SCCP quantification is proposed by Reth et al. (2005b). Its use allows compensating for the effect the degree of chlorination of the reference standard used has on the overall response rate and, in effect, eliminates the necessity to use standards with matching degrees of chlorination. However, there are also alternative approaches such as the use of principal component analysis or multiple linear regression (Nilsson et al., 2012; Geiß et al., 2015).

Since there are no suitable quantification standards for the determination of SCCPs, either mixtures of CPs or congeners of individual CPs are used during the calibration. However, the chemical composition of the CPs depends on the purpose for which they were produced and the various transformations they may be subjected to in the environment, and thus it is unlikely that the ones currently used for calibration may be a suitable standard for all CPs present in environmental samples. Considering the information listed in Table 2, and analyzing the literature data, it might be concluded that the quantitative analysis of SCCPs is mainly performed using commercially available technical SCCPs mixtures prepared in cyclohexane - C<sub>10-13</sub>, 51.5%, 55.5% and 63% chlorine,  $c = 100 \text{ ng}\cdot\mu\text{L}^{-1}$  (Dr. Ehrenstorfer GmbH, Augsburg, Germany). The most frequently used chemical compounds as a recovery or injection standard in analytical procedures for SCCPs analysis are  $^{13}\text{C}_6\text{-HCB}$ ,  $^{13}\text{C}_{10}\text{-}\gamma\text{-chlordane}$ ,  $^{13}\text{C}_6\text{-HCH}$  and  $\epsilon\text{-HCH}$ .

Following the literature data, the appropriate SCCP analysis, especially the reliable quantification process, is an important issue and an analytical challenge. It is caused by the fact that it is a serious problem to perform the optimal separation process of individual SCCP





congeners and to select the appropriate analytical standard for defined congeners. In analytical practice there is a negligible and insufficient number of pure and well characterized analytical standards for individual SCCP congeners. Due to this, in most cases the information about the SCCPs obtained during the analysis of environmental samples is defined as semi-quantitative (van Mourik et al., 2016; Yuan et al., 2016). According to information published by Yuan et al. (2017), in most of the employed analytical procedures for SCCP analysis, the identification of SCCPs' congeners consists of the detection of pseudomolecular ions performed by soft ionization mass spectrometry. However, there is a significant issue which concerns the interferences between SCCPs and, as a consequence, to overlapping the mass spectra. The dissimilarities among the chlorination degree of the SCCPs in the studied samples and in the available analytical standards might affect the dissimilarities of the quantified SCCP content level. Moreover, Schinkel et al. (2018a) highlighted in their paper that there is an urgent need for more specific analytical standards in the field of SCCP, MCCP and LCCP analysis. The authors discussed the main issues associated with the four major solutions which are commonly applied in the analytical procedures to perform reliable CPs quantitative analysis. In Figure 4 the above-mentioned general types of proposed solutions concerning the available analytical standards required for CP analysis are schematically presented. The qualitative and quantitative analysis of CPs has become a significant scientific issue, especially due to the occurrence of mass interferences of CPs and their transformation products, mainly chlorinated olefins (Schinkel et al., 2018a). Facing this analytical challenge, Schinkel et al. (2018b) prepared the analytical guide, in which the authors describe in detail novel solutions in the field of CPs analysis, such as the application of LC-MS systems equipped with three different mass analysers - APCI-qTOF-MS, APCI-Orbitrap-MS and ESI-Orbitrap-MS, and conventional GC-ECNI-Orbitrap-MS, highlighting the problem with the influence of mass resolution and mass accuracy. The authors developed a valuable guide with which to



appropriately interpret and comprehend complex mass spectra of CPs and interfering transformation products.

## **7. Future trends, procedure modifications and possible applications of green analytical chemistry principals**

The introduction of green solutions to the analytical procedure or modification of selected stages of an analytical protocol is always a matter of choosing between economic and logistic factors, and the quality of the obtained results. The rapid development of analytical techniques and advanced analytical devices gives a reason to introduce the screening evaluation of analytical procedures in the field of green analytical chemistry principles. Due to the large number of analytical procedures which might be applied to assess the type and amount of SCCPs in environmental samples, it is necessary to evaluate their potential environmental impact. For this reason, each step of the analytical procedure should be considered, following the 12 main GAC principles, as well as the economic factors, energy consumption and laboratory space (Tobiszewski et al., 2015). To assess the green aspects of selected analytical procedures, in the current scientific literature there are described some mathematical and statistical solutions, which might be divided into main three groups: (i) qualitative, such as National Environmental Methods Index (NEMI labelling), (ii) comparative, including the Multi-Criteria Decision Aid or Analysis (MCDA), self-organizing maps (SOM), and the Technique for Order Preference by Similarity to the Ideal Solution (TOPSIS), and (iii) quantitative, such as the analytical Eco-scale (Astel, 2007; Behzadian et al., 2012; Soltani et al., 2015; Jędrkiewicz et al., 2018). None of the previously described papers was associated with the assessment of environmental nuisance and the personal exposure of analysts during SCCP determination in environmental samples. All these aspects



should be considered and used as additional elements in the evaluation of new analytical procedures being developed.

One of the newest semi-quantitative techniques proposed to assess the green aspects of the selected analytical procedure is the GAPI (Green Analytical Procedure Index) technique (Płotka-Wasyłka, 2018). This approach gives a possibility for screening estimation of the green character of the total analytical protocol, starting from the sampling stage and ending with the separation, identification and final determination of studied chemical compounds. One of the main advantages of the GAPI technique is the fact that there is a possibility to receive qualitative analytical information about the selected analytical methodology. Based on the literature information, three types of analytical procedures for SCCP determination were selected to perform the GAPI analysis. In Figure 5, the results of GAPI analysis for input data collected from selected analytical procedures for SCCPs' determination protocols are presented. The green colour describes the green aspects of the selected stage of the analytical protocol, the yellow moderate green aspect and the red is defined as the minimal green aspect of the selected stage of the analytical method. The circle in the middle defines that the selected analytical protocol is dedicated for qualification and quantification. The screening information shown in Figure 5 gives a possibility to analyze each of the main stages of analytical procedures for SCCP analysis in environmental samples in the context of changes in applications aimed at improving the greenness of a defined stage and in the further perspective the whole analytical procedure.

Taking into account the information listed in Figure 5, it might be observed that the sample preparation stage is characterized by the same environmental impact defined by the same GAPI shape. It is caused by the fact that in most of the analytical procedures dedicated to SCCP analysis the sample collection stage is routine and has the same character as for other persistent organic pollutants. From the green analytical chemistry principles defined by the



SIGNIFICANCE mnemonic guide, there is no space to apply some technical or protocol modifications to increase the green aspect of this stage. There is a lack of the possible application of devices for direct analysis or for performing on-line analysis, due to the complexity of SCCPs and the complex composition of the sample matrix. The only environmentally friendly solution at this stage of the analytical procedure is the use of a passive sampling technique for the isolation and/or pre-concentration of SCCPs from environmental samples. This solution is mainly employed in the case of atmospheric and indoor air quality analysis. The passive sampling technique is considered as a “green sampling technique” mainly due to the lack of energy consumption during the sampling process, reducing the number of samples and their volume. Moreover, there are no specific and regulated conditions for the storage of passive samplers after the sampling stage. In most cases, after the sampling stage, the applied sorption beds (mainly polyurethane foam, XAD-2 or XAD-4 resins) are wrapped with aluminum foil, sealed and stored in a freezer until the next step of analytical procedure (sample extraction, cleanup and final determination of SCCPs) (Wang et al., 2013; Chaemfa et al., 2014; Li et al., 2018). The samples contamination or analytes loss during storage are negligible mainly due to the sorption abilities of the applied sorption medium and the physicochemical properties of SCCPs. In other types of samples (aquatic, solid or biological samples) it is necessary to provide the appropriate sample amount or volume to ensure the quality of the obtained results. Nevertheless, due to the low volatility of SCCPs, there is no need to apply any special treatment associated with sample storage. The proposed future green solution at this stage, mainly concerning the aquatic environment, is to develop such passive samplers (appropriate construction solution, membrane and solvent or sorption medium selection) which might be able to isolate and/or enrich the SCCPs from the aquatic samples.



The bottleneck of every analytical procedure, which is the most solvent-, energy- and time-consuming, is the sample preparation stage. This stage gives a wide spectrum of possibilities and solutions to apply the principals of GAC. In the case of SCCPs' sample preparation stage, the integral part is the necessity to clean up the obtained extracts. Taking into consideration the information presented in Figure 5 and listed in Table 1, it might be observed that the most commonly used sample preparation technique is solvent extraction supported with more or less advanced extraction devices. Following the GAC principles, the greenest solution is the application of the ASE or USA technique, due to the extraction efficiency, analyte recovery and solvent consumption. It is necessary to replace the routine Soxhlet extraction with more advanced solvent extraction techniques to reduce the number of organic solvents and reduce the extraction time without losses in extraction efficiency. However, the main issues that should be considered are the costs of the extraction devices, appropriately skilled laboratory staff, and the costs associated with a single analysis. With the appropriate financial resources and laboratory facilities it is possible to significantly reduce the number of organic solvents and to introduce automation in the extraction process. Nevertheless, in most of the analytical procedures for SCCP determination, at the stage of sample preparation, the Soxhlet extraction is still employed, due to its low operating costs and no special skills requirements. The solution that should be considered in future analytical protocols for SCCP determination to make it much more suitable for the GAC philosophy is the application of the supercritical fluid extraction (SFE) technique (Fabjanowicz et al., 2018). This technique gives a possibility to significantly reduce the number of organic solvents (or even their total elimination) during the sample preparation process. The most important limitation of this technique is the economic factor (the costs of the equipment exploitation) and the repeatability and efficiency of the above-mentioned extraction process. Taking into consideration all the above information about the sample preparation for SCCP analysis, it should be concluded that by



raising financial support for the sample preparation process (mainly supporting the new, more advanced extraction devices) it is possible to ensure the appropriate green character of the whole analytical procedure. However, it should be highlighted that the change in the technique of sample preparation might affect the efficiency of the extraction process, its repeatability, and the proper recovery of analytes.

In the case of SCCP determination in solid and water samples, it is necessary to perform an additional step associated with the extract clean up, employing an appropriate combination of sorption mediums. Generally, this stage is performed in a glass SPE or chromatographic column. It is another step of the analytical procedure in which organic solvents should be used. Moreover, there is a need to appropriately prepare some of the sorption materials and reagents, especially acid  $\text{SiO}_2$  (by  $\text{H}_2\text{SO}_4$ ) and activated copper (using  $\text{HCl}$ ). In addition, the sorption materials and reagents used in the extracts' clean-up process are single use and contain an additional source of solid waste. Gathering this information into one point, it is very hard to find an appropriate solution which will be suitable for the GAC principals. One of the proposed solutions is the application of a sorption material which might be used several times. This gives a possibility to design and develop new sorption materials such as molecularly imprinted polymers (MIPs) which might be able to selectively combine the SCCPs' compounds from the extracts. The MIPs sorption materials are reusable and are resistant to acids and alkalis. The application of MIP sorption materials might reduce the amount of solid waste. Nowadays, it is a serious analytical challenge to develop such sorption materials with a molecular imprint which will be selective to the SCCPs and increase the efficiency of the clean-up process. In the case of MIPs sorption materials, from the GAC principals point of view, the issue that should be considered is the application of MIPs as selective sorbents for SCCPs in the SPE technique. This solution might be possible to obtain in the case of aquatic samples – the introduction of the defined amount of water sample



directly to the sorption medium with the simultaneous process of the isolation and/or pre-concentration of analytes without the need for purification of the extract. This proposition for a more green approach is still the subject of future research, due to the lack of selective MIP sorption materials for SCCPs. Moreover, in the current time of intensive automation of analytical devices, it is possible to employ a device for the automatic SPE process, both at the stage of extract purification and the above-mentioned proposal of the isolation and/or preconcentration process of SCCP analytes from water samples. However, when introducing automatization into the analytical procedure it is necessary to have sufficient financial resources and laboratory space.

Following the next element of GAPI analysis presented in Figure 5 considering the stage of separation, identification and final determination of SCCPs (including qualitative and quantitative analysis) in various types of environmental and biological samples, it might be concluded that the most suitable final determination device which meets GAC requirements is the GC system (single or two-dimension) equipped with  $\mu$ ECD. This is mainly caused by the economic factor (the exploitation of  $\mu$ ECD is less expensive than MSD), the lack of employment of high purity gas (e.g. methane) to perform the chemical ionization, and the lower energy consumption. However, due to the fact that  $\mu$ ECD is mainly sensitive to halogens, it is necessary to perform a precise extraction and clean-up process, and to ensure the appropriate chromatographic separation. As a consequence, the application of a single GC- $\mu$ ECD, which might be recommended following the GAC principles, is not sufficient equipment in the final determination of SCCPs. This equipment solution does not allow the performance of the appropriate qualitative and quantitative analysis of individual SCCP congeners, but only might be the source of screening information about the total amount of SCCPs in analyzed samples ( $\Sigma$ SCCP). To increase the separation resolution in the case of the application of  $\mu$ ECD, and to minimize the sample size, the proposed solution will be the



application of two-dimensional GC (GC x GC). This solution will have a significant impact on the separation process of SCCP analytes, and following the information presented on the GAPI graph, increase the green aspect of the selected analytical procedure. Taking into account the information listed in Table 1, the most commonly used final determination equipment configuration is a GC coupled with an ECNI-MS detector. This configuration gives the most appropriate results in the case of the qualitative and quantitative analysis of SCCP congeners. However, it requires significant financial support, associated with the purchase of a high-quality detection system and high purity gas used for chemical ionization. Moreover, such equipment is very energy-consuming, is characterized by high costs of a single analysis, and requires space in the laboratory. Due to the fact that this type of system is the most commonly used in analytical practice, it is possible to perform interlaboratory studies to compare the obtained results and to validate the developed procedure. One of the propositions from the GAC principals' point of view might be the application of a high purity, high quality and well-characterized reference solution containing a single SCCP congener. Combining it with an efficient extraction and clean-up process, and with appropriately selected separation conditions, it is possible to use the  $\mu$ ECD and receive reliable analytical information.

As a summary, Table 3 was prepared to show possible solutions which might be applied during the analytical procedures for SCCP determination in environmental samples, considering the 12 main principals of GAC. Gathering all the information mentioned above, it might be concluded that the application of new or better quality equipment, or a solution which increase the "greenness" of a defined stage of the analytical procedure for SCCP determination requires significant financial support and appropriate skills from laboratory staff. This phenomenon is mainly associated with the equipment used at the SCCPs' final determination stage. However, an appropriately performed sampling process and well-





optimized sample preparation stage (extraction and clean-up), as well as the application of high quality and fully characterized reference solutions of single SCCP congeners might be a powerful tool in obtaining reliable qualitative and quantitative analytical information about the SCCP content levels in studied environmental samples.

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## 9. Conflict of interest

The authors declare that they have no conflict of interest.

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## 11. Figure Captions

**Figure 1.** The total number of papers dealing with the subject of the presence of xenobiotics from the group of short-chained chlorinated paraffins in different types of studied objects [Scopus web site database from 2008 to 2018].

**Figure 2.** The milestones of the most important international and national law regulations on SCCPs (based on the information published by Glüge et al., 2016 and De Boer, 2010)

**Figure 3.** The general classification of extraction and purification techniques commonly used for the determination of SCCPs in a wide spectrum of environmental samples.

**Figure 4.** The major solutions commonly introduced in the analytical procedures to perform the quantitative and qualitative determination of SCCPs in environmental samples (based on the information published by Schinkel et al., 2018a)

**Figure 5.** The GAPI diagrams for three analytical protocols applied for SCCP determination in environmental samples with different sample preparation techniques and final determination systems consisting of a) GC/ECNI-MS (Luo et al., 2015); b) GC/GC- $\mu$ ECD (Muscalu et al., 2017); c) GC/TOF-MS (Wang et al., 2018).



**Table 1.** General conditions of analytical protocols for determination of SCCPs in environmental samples.

Type of the sample	Sample preparation stage	Clean-up stage	Final determination technique	Column [m x mm x $\mu$ m]	Temperature program	Carrier gas	Ref.
Urban air	Soxhlet extraction n-hexane/dichloromethane (1:1, v/v), 250 mL	I. Multilayer: Na <sub>2</sub> SO <sub>4</sub> , SiO <sub>2</sub> , SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> (44% w/w) II. Basic Al <sub>2</sub> O <sub>3</sub>	HRGC/ECNI-LRMS	DB-5 (15 x 0.25 x 0.25)	100°C for 2 min; 20°C·min <sup>-1</sup> up to 260°C hold for 2 min; 30°C·min <sup>-1</sup> up to 310°C hold for 15 min	helium, constant flow 0.8 mL·min <sup>-1</sup>	Zhu et al., 2017
Urban air	ASE n-hexane/dichloromethane (1:1, v/v), n.r.	Multilayer: Florisil, act. SiO <sub>2</sub> , , SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> (30% w/w), Na <sub>2</sub> SO <sub>4</sub>	GC/ECNI-LRMS	DB-5 (30 x 0.25 x 0.25)	100°C for 1 min; 30°C·min <sup>-1</sup> up to 160°C hold for 5 min; 30°C·min <sup>-1</sup> up to 310°C hold for 17 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Wang et al., 2012
Urban and rural air	Soxhlet extraction n-hexane/dichloromethane (1:1, v/v), n.r.	I. SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> II. Multilayer: Na <sub>2</sub> SO <sub>4</sub> , deact. Florisil, deact. SiO <sub>2</sub> , deact. Al <sub>2</sub> O <sub>3</sub>	GC/ECNI-LRMS	DB-5 (30 x 0.25 x 0.25)	120°C for 1 min; 15°C·min <sup>-1</sup> up to 290 °C hold for 15 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Wang et al., 2013
Urban and rural air	Soxhlet extraction Dichloromethane, n.r.	Multilayer: SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> (50% w/w), Na <sub>2</sub> SO <sub>4</sub>	GC/ECNI-LRMS	DB-5 (30 x 0.25 x 0.25)	120°C for 1 min; 15°C·min <sup>-1</sup> up to 290°C hold for 15 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Li et al., 2012
Urban and rural air	Soxhlet extraction Dichloromethane, n.r.	I. Multilayer: Na <sub>2</sub> SO <sub>4</sub> , deact. SiO <sub>2</sub> (3%), deact. Al <sub>2</sub> O <sub>3</sub> (3%) II. Multilayer: SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> (50% w/w), deact. Florisil (2%), Al <sub>2</sub> O <sub>3</sub>	GC/ECNI-LRMS	DB-5 (30 x 0.25 x 0.25)	120°C for 1 min; 15°C·min <sup>-1</sup> up to 290°C hold for 15 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Chaemfa et al., 2014
Indoor air	UAE I. dichloromethane, 18 mL II. n-hexane, 6 mL	SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> (2:1 w/w)	GC/EI-LRMS/MS	DB-5 (15 x 0.25 x 0.25)	90°C for 2 min; 30°C·min <sup>-1</sup> up to 300°C hold for 5 min	helium, constant flow 1.4 mL·min <sup>-1</sup>	Fridén et al., 2011
Urban air	ASE, Hexane, n.r.	deact. Florisil (1.2%)	GC/ECNI-HRMS	DB-5 (30 x 0.25 x 0.25)	150°C for 1 min; 10°C·min <sup>-1</sup> up to 310°C hold for 15 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Barber et al., 2005



Sediment, SPM	Soxhlet extraction Dichloromethane, n.r.	Multilayer: Na <sub>2</sub> SO <sub>4</sub> , deact. Florisil, deact. SiO <sub>2</sub> , deact. Al <sub>2</sub> O <sub>3</sub>	GC/ECNI-LRMS	DB-5 (30 x 0.25 x 0.25)	120°C for 1 min; 15°C·min <sup>-1</sup> up to 290°C hold 15 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Li et al., 2018
Sediment	HSE, Dichloromethane, 120 mL	deact. SiO <sub>2</sub>	SCGC/ECNI-MS	Microquartz (1.3 x 0.15)	isotherm 270°C	helium, constant flow 1.38 mL·min <sup>-1</sup>	Štejnárová et al., 2005
Sediment	ASE n-hexane/dichloromethane (1:1, v/v), n.r.	Multilayer: Florisil, act. SiO <sub>2</sub> , SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> (30% w/w), Na <sub>2</sub> SO <sub>4</sub>	GC/ECNI-HRMS	DB-5 (30 x 0.25 x 0.25)	100°C for 1 min; 30°C·min <sup>-1</sup> up to 160°C hold for 5 min; 30°C·min <sup>-1</sup> up to 310°C hold for 17 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Zhao et al., 2013
Sediment	ASE n-hexane/dichloromethane (1:1, v/v), n.r.	Multilayer: Florisil, act. SiO <sub>2</sub> , SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> (30% w/w), Na <sub>2</sub> SO <sub>4</sub>	HRGC/ECNI- LRMS	DB-5 (30 x 0.25 x 0.25)	100°C for 1 min; 30°C·min <sup>-1</sup> up to 160°C hold for 5 min; 30°C·min <sup>-1</sup> up to 310°C hold for 17 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Zeng et al., 2011
Sediment	ASE n-hexane/dichloromethane (1:1, v/v), n.r.	I. GPC II. Multilayer: Florisil, act. SiO <sub>2</sub> , SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> (30% w/w), Na <sub>2</sub> SO <sub>4</sub>	GC-GC/TOFMS	DM-5MS (30 x 0.25 x 0.25), BPX-50 (1 x 0.1 x 0.1)	140°C for 1 min; 10°C·min <sup>-1</sup> up to 200°C; 1.5°C·min <sup>-1</sup> up to 310°C hold for 5 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Qiao et al., 2016
Sediment	ASE n-hexane/dichloromethane (1:1, v/v), n.r.	Multilayer: act. Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> , act. SiO <sub>2</sub> , SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> (30% w/w), Na <sub>2</sub> SO <sub>4</sub>	GC/ECNI-TQMS	DB-5 (15 x 0.25 x 0.25)	100°C for 1 min; 30°C·min <sup>-1</sup> up to 160°C hold for 5 min; 30°C·min <sup>-1</sup> up to 310°C hold for 13 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Ma et al., 2014
Sediment	Soxhlet extraction Dichloromethane, 200 mL	Multilayer: deact. Florisil, deact. SiO <sub>2</sub> , SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> (44% w/w), Na <sub>2</sub> SO <sub>4</sub>	GC/ECNI- LRMS	DB-5HT (15 x 0.25 x 0.1)	80°C for 3 min; 25°C·min <sup>-1</sup> up to 160°C hold for 6 min; 20°C·min <sup>-1</sup> up to 280°C hold for 15 min	n. r.	Chen et al., 2011
Sediment	Soxhlet extraction n-hexane/dichloromethane (1:1, v/v), 300 mL	Florisil	GC/ECNI- MS	DB-5 (30 x 0.25 x 0.25)	90°C for 1 min; 15°C·min <sup>-1</sup> up to 180°C; 8°C·min <sup>-1</sup> up to 300°C hold for 10 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Castells et al., 2008
Sediment, soil	ASE n-hexane/dichloromethane (1:1, v/v), n.r.	Multilayer: Florisil, SiO <sub>2</sub> , SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> , Na <sub>2</sub> SO <sub>4</sub>	GC-GC/ECNI-MS	DM-1 (30 x 0.25 x 0.25), BPX-70	100°C for 1 min; 10°C·min <sup>-1</sup> up to 140°C; 1.5°C·min <sup>-1</sup> up to 310°C	helium, constant flow 0.8 mL·min <sup>-1</sup>	Xu et al., 2019



				(1 x 0.1 x 0.1)	hold for 5 min		
Soil	ASE n-hexane/dichloromethane (1:1, v/v), n.r.	Multilayer: Florisil, act. SiO <sub>2</sub> , SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> (30% w/w), Na <sub>2</sub> SO <sub>4</sub>	GC/ECNI-TQMS	DB-5 (30 x 0.25 x 0.25)	100°C for 1 min; 30°C·min <sup>-1</sup> up to 160°C hold for 5 min; 30°C·min <sup>-1</sup> up to 310°C hold for 17 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Yuan et al., 2017
Soil	Soxhlet extraction n-hexane/acetone (1:1, v/v), 200 mL	Multilayer: deact. Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> , Na <sub>2</sub> SO <sub>4</sub>	GC/MS	DB-5HT (15 x 0.25 x 0.1)	80°C for 1 min; 10°C·min <sup>-1</sup> up to 270°C hold for 5 min; 30°C·min <sup>-1</sup> up to 310°C hold for 17 min	helium, constant flow 0.9 mL·min <sup>-1</sup>	Wang et al., 2014
Soil	ASE, n-hexane/acetone (1:1, v/v), n.r.	SiO <sub>2</sub>	GC/ECNI-HRMS	RXI-5MS (15 x 0.25 x 0.25)	90°C for 2 min; 20°C·min <sup>-1</sup> up to 245°C hold for 1 min; 30°C·min <sup>-1</sup> up to 300°C hold for 5 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Halse et al., 2015
Lake water	LLE, Dichloromethane, 450 mL	SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> , Na <sub>2</sub> SO <sub>4</sub>	HRGC/ECNI- LRMS	DB-5 (30 x 0.25 x 0.25)	100°C for 1 min; 30°C·min <sup>-1</sup> up to 160°C hold for 5 min; 30°C·min <sup>-1</sup> up to 310°C hold for 17 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Zeng et al., 2011
Surface and wastewater	LLE, n-hexane, 30 mL	Multilayer: act. Copper powder, act. Florisil, Na <sub>2</sub> SO <sub>4</sub>	GC-ECD	DB-5 (15 x 0.25 x 0.25)	90°C for 1 min; 15°C·min <sup>-1</sup> up to 300°C hold for 5 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Rubirola et al., 2018
Water	SPE, n-hexane/dichloromethane (1:1, v/v), n.r.	Lack of sample clean- up stage	GC/ECNI-TQMS	DB-5 (30 x 0.25 x 0.25)	100°C for 1 min; 30°C·min <sup>-1</sup> up to 160°C hold for 5 min; 30°C·min <sup>-1</sup> up to 310°C hold for 17 min	helium, constant flow 1.2 mL·min <sup>-1</sup>	Wang et al., 2018
Soil, algae, moss, fish	ASE n-hexane/dichloromethane (1:1, v/v), n.r.	Multilayer: Florisil, act. SiO <sub>2</sub> , SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> (30% w/w), Na <sub>2</sub> SO <sub>4</sub>	HRGC/ECNI-MS	DB-5 (30 x 0.25 x 0.25)	100°C for 1 min; 30°C·min <sup>-1</sup> up to 160°C hold for 5 min; 30°C·min <sup>-1</sup> up to 310°C hold for 17 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Li et al., 2016



House dust	Soxhlet extraction n-hexane/dichloromethane (1:1, v/v), n.r.	I. SiO <sub>2</sub> II. Basic Al <sub>2</sub> O <sub>3</sub>	GC/ECNI- LRMS	DB-5 (15 x 0.25 x 0.25)	100°C for 2 min; 20°C·min <sup>-1</sup> up to 160°C hold for 2 min; 30°C·min <sup>-1</sup> up to 310°C hold for 15 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Shi et al., 2017
House dust	SE, n-hexane/dichloromethane (1:1, v/v), 10 mL	Multilayer: deact. Florisil, deact. SiO <sub>2</sub> , SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> (44% w/w), Na <sub>2</sub> SO <sub>4</sub>	GC/ECNI- MS	DB-5 (30 x 0.25 x 0.25)	100°C for 2 min; 10°C·min <sup>-1</sup> up to 280°C hold for 10 min	n. r.	Liu et al., 2017
House dust	Extraction in Schott-Duran bottle with Teflon lined screwcap, n-hexane/acetone (1/1, v/v), 50 mL	Multilayer: deact. SiO <sub>2</sub> , silica gel fortified with 33%, 1 mol/L NaOH, SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> (44%, w/w)	GC/ECNI-MS	ZB-5MS (30 x 0.25 x 0.25)	120°C for 1 min; 15°C·min <sup>-1</sup> up to 310°C hold for 15 min	helium, constant flow 0.95 mL·min <sup>-1</sup>	Hilger et al., 2013
Oven door surface	UAE, n-hexane, 45 mL	deact. SiO <sub>2</sub> , Na <sub>2</sub> SO <sub>4</sub>	GC/ECNI- MS	HP-5 (15 x 0.25 x 0.25)	50°C for 1 min; 10°C·min <sup>-1</sup> up to 300°C hold for 14 min	helium, constant flow 1.2 mL·min <sup>-1</sup>	Gallistl et al., 2018
Window surface film	ASE n-hexane/dichloromethane (1:1, v/v), n.r.	Multilayer: Florisil, SiO <sub>2</sub> , SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> (30% w/w), Na <sub>2</sub> SO <sub>4</sub>	HRGC/ECNI- LRMS	DB-5 (30 x 0.25 x 0.25)	100°C for 1 min; 30°C·min <sup>-1</sup> up to 160°C hold for 5 min; 30°C·min <sup>-1</sup> up to 310°C hold for 17 min	helium, constant flow 1.2 mL·min <sup>-1</sup>	Gao et al., 2016
Polyvinyl Chloride Flooring	UAE n-hexane/dichloromethane (1:1, v/v), 60 mL	Act. SiO <sub>2</sub>	HRGC/ECNI- LRMS	DB-5 (15 x 0.25 x 0.25)	100°C for 2 min; 20°C·min <sup>-1</sup> up to 160°C hold for 2 min; 30°C·min <sup>-1</sup> up to 310°C hold for 8 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Zhan et al., 2017
PM	ASE n-hexane/dichloromethane (1:1, v/v), n.r.	Multilayer: Florisil, act. SiO <sub>2</sub> , SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub> (44% w/w), SiO <sub>2</sub> :H <sub>2</sub> SO <sub>4</sub>	GC-GC/ECNI- HRTOF-MS-TIC	DB-5 (30 x 0.25 x 0.25), BPX-50 (1 x 0.1 x 0.1)	140°C for 1 min; 20°C·min <sup>-1</sup> up to 200°C; 1.5°C·min <sup>-1</sup> up to 310°C hold for 5 min	helium, constant flow 1.0 mL·min <sup>-1</sup>	Huang et al., 2017

ASE – accelerated solvent extraction, UAE – ultrasound-assisted extraction, HSE – hot solvent extraction, LLE – liquid-liquid extraction, SPE – solid-phase extraction, SE – solvent extraction, PM – particulate matter



**Table 2.** Information about the basic validation parameters and concentration ranges of SCCPs determined in environmental samples.

Sample type	Sampling area	Standard solution	SCCPs concentration range	Recovery values	MDL	Ref
Urban air	Dalian, China	Extraction standard: $^{13}\text{C}6\text{-}\delta\text{-HCH}$ Recovery standard: $^{13}\text{C}10\text{-trans-chlordane}$	15.12-66.44 $\text{ng}\cdot\text{m}^{-3}$	78-136%	0.34 $\text{ng}\cdot\text{m}^{-3}$	Zhu et al., 2017
Urban air	Beijing, China	Extraction standard: $\epsilon\text{-HCH}$ Recovery standard: $^{13}\text{C}10\text{-trans-chlordane}$	1.9-33 $\text{ng}\cdot\text{m}^{-3}$ in winter 112-332 $\text{ng}\cdot\text{m}^{-3}$ in summer	73-110%	0.2-0.5 $\text{ng}\cdot\text{m}^{-3}$	Wang et al., 2012
Urban and rural air	Pearl River Delta, China	Recovery standard: $^{13}\text{C}\text{-mirex}$ Extraction standard: $^{13}\text{C}10\text{-trans-chlordane}$	0.95- 26.5 $\text{ng}\cdot\text{m}^{-3}$ in winter 2.01-106 $\text{ng}\cdot\text{m}^{-3}$ in summer	82-96%	0.122 $\text{ng}\cdot\text{m}^{-3}$	Wang et al., 2013
Urban and rural air	China, Japan, South Korea	Recovery standard: $^{13}\text{C}8\text{-mirex}$ Extraction standard: $^{13}\text{C}10\text{-trans-chlordane}$	0.28-517 $\text{ng}\cdot\text{m}^{-3}$	83.2-95.7%	0.18 $\text{ng}\cdot\text{m}^{-3}$	Li et al., 2012
Urban and rural air	India, Pakistan	Recovery standard: $^{13}\text{C}8\text{-mirex}$ Extraction standard: $^{13}\text{C}10\text{-trans-chlordane}$	<LOD-47.4 $\text{ng}\cdot\text{m}^{-3}$	81-90%	2.65 $\text{ng}\cdot\text{m}^{-3}$	Chaemfa et al., 2014
Indoor air	Stockholm, Sweden	n. r.	<LOD-210 $\text{ng}\cdot\text{m}^{-3}$	n. r.	5.0 $\text{ng}\cdot\text{m}^{-3}$	Fridén et al., 2011
Urban air	England	Recovery standard: $^{13}\text{C}8\text{-mirex}$ Extraction standard: $^{13}\text{C}10\text{-trans-chlordane}$	<LOD-9.10 $\text{ng}\cdot\text{m}^{-3}$	n.r.	0.180 $\text{ng}\cdot\text{m}^{-3}$	Barber et al., 2005
Sediment, SPM	Yellow River	Recovery standard: $^{13}\text{C}8\text{-mirex}$ Extraction standard: $^{13}\text{C}10\text{-trans-chlordane}$	11.8-2792 $\text{ng}\cdot\text{g}^{-1}$ for sediment, 213-170038 $\text{ng}\cdot\text{g}^{-1}$ for SPM	70-101.4%	3.84 $\text{ng}\cdot\text{g}^{-1}$ for sediment, 1.63 $\text{ng}\cdot\text{g}^{-1}$ for SPM	Li et al., 2018
Sediment	Czech Republic	n. r.	4.58-180.75 $\text{ng}\cdot\text{g}^{-1}$ d. w.	n. r.	100 $\text{pg}\cdot\mu\text{L}^{-1}$	Štejnarová et al., 2005



Sediment	East China Sea	Recovery standard: $\epsilon$ -HCH Extraction standard: $^{13}\text{C}10$ -trans-chlordane	9-37.2 $\text{ng}\cdot\text{g}^{-1}$ d. w.	81-106%	n. r.	Zhao et al., 2013
Sediment	Beijing, China	Recovery standard: $\epsilon$ -HCH Extraction standard: $^{13}\text{C}10$ -trans-chlordane	1.1-8.7 $\mu\text{g}\cdot\text{g}^{-1}$ d. w.	78.5-92%	100 $\text{ng}\cdot\text{g}^{-1}$	Zeng et al., 2011
Sediment	Yellow River	Recovery standard: $\epsilon$ -HCH Extraction standard: $^{13}\text{C}10$ -trans-chlordane	11.6-9.76 $\cdot 10^3$ $\text{ng}\cdot\text{g}^{-1}$	72.5-93.8%	2.72 $\text{ng}\cdot\text{g}^{-1}$	Qiao et al., 2016
Sediment	Bohai Sea	Recovery standard: $^{13}\text{C}6$ - $\alpha$ -HCH Extraction standard: $^{13}\text{C}6$ -HCB	97.4-1756.7 $\text{ng}\cdot\text{g}^{-1}$	69.5-92.4%	14 $\text{ng}\cdot\text{g}^{-1}$	Ma et al., 2014
Sediment	Pearl River	Recovery standard: $\epsilon$ -HCH Extraction standard: $^{13}\text{C}10$ -trans-chlordane	600-1100 $\text{ng}\cdot\text{g}^{-1}$	90.6-101%	n. r.	Chen et al., 2011
Sediment	Barcelona, Spain	Recovery standard: $^{13}\text{C}6$ -hexachlorobenzene	0.21-2.09 $\mu\text{g}\cdot\text{g}^{-1}$ d. w	95%	1.8 $\text{ng}\cdot\text{g}^{-1}$	Castells et al., 2008
Sediment, soil	China	Recovery standard: $\epsilon$ -HCH Extraction standard: $^{13}\text{C}10$ -trans-chlordane	68.5-2.2 $\cdot 10^5$ $\text{ng}\cdot\text{g}^{-1}$ d. w. in soils 32.5-1.29 $\cdot 10^4$ $\text{ng}\cdot\text{g}^{-1}$ d. w. in sediments	78.5-109.9%	8.2 $\text{ng}\cdot\text{g}^{-1}$	Xu et al., 2019
Soil	Tauzhou, China	Recovery standard: $\epsilon$ -HCH Extraction standard: $^{13}\text{C}10$ -trans-chlordane	30.4-530 $\text{ng}\cdot\text{g}^{-1}$	82-104%	5 $\text{ng}\cdot\text{g}^{-1}$	Yuan et al., 2017
Soil	Shanghai, China	Recovery standard: $\epsilon$ -HCH Extraction standard: $^{13}\text{C}10$ -trans-chlordane	<LOD-615 $\text{ng}\cdot\text{g}^{-1}$	90.6-101%	1.7 $\text{ng}\cdot\text{g}^{-1}$	Wang et al., 2014
Soil	Western Europe	Extraction standard: $^{13}\text{C}10$ -cis-chlordane	<LOD-570 $\text{ng}\cdot\text{g}^{-1}$ SOM	37-68%	0.6 $\text{ng}\cdot\text{g}^{-1}$ SOM	Halse et al., 2015



Lake water Gaobeidian Lake	Beijing, China	Recovery standard: $\epsilon$ -HCH Extraction standard: $^{13}\text{C}10$ -trans-chlordane	162-176 $\text{ng}\cdot\text{dm}^{-3}$	78.5-92%	100 $\text{ng}\cdot\text{g}^{-1}$	Zeng et al., 2011
Surface water and wastewater	Barcelona, Spain	Recovery standard: $\epsilon$ -HCH Extraction standard: PCB-209	0.13-2.36 $\mu\text{g}\cdot\text{dm}^{-3}$ in wastewater, <LOD-0.15 $\mu\text{g}\cdot\text{dm}^{-3}$ in surface water	73-90%	4 $\mu\text{g}\cdot\text{cm}^{-3}$	Rubirola et al., 2018
Water	Beijing, China	Recovery standard: $\epsilon$ -HCH Extraction standard: $^{13}\text{C}10$ -trans-chlordane	<LOD-682 $\text{ng}\cdot\text{dm}^{-3}$	90-135%	18 $\text{ng}\cdot\text{dm}^{-3}$	Wang et al., 2018
Soil, algae, moss, fish, neogastrop oda, arcgeogastr opoda	Fildes Peninsula	Extraction standard: $^{13}\text{C}10$ -trans-chlordane	40.2-256.6 $\text{ng}\cdot\text{g}^{-1}$ d. w. in animal samples, 24.9-97.7 $\text{ng}\cdot\text{g}^{-1}$ d. w. in vegetation samples, 3.5-32.8 $\text{ng}\cdot\text{g}^{-1}$ d. w. in soil samples	81-116%	n. r.	Li et al., 2016
House dust	China	Recovery standard: $^{13}\text{C}6$ - $\delta$ -HCH Extraction standard: $^{13}\text{C}10$ -trans-CD	6.0-361.4 $\mu\text{g}\cdot\text{g}^{-1}$	72.7-119.9%	61 $\text{ng}\cdot\text{g}^{-1}$	Shi et al., 2017
House dust	Northeast China	Recovery standard: $^{13}\text{C}10$ -trans-chlordane Extraction standard: $^{13}\text{C}8$ -mirex	10.1-173.0 $\mu\text{g}\cdot\text{g}^{-1}$	74-106%	0.68 $\mu\text{g}\cdot\text{g}^{-1}$	Liu et al., 2017
House dust	Bavaria, Germany	Injection standard: hexachlorobenzene (HCB)	4 – 27 $\mu\text{g}\cdot\text{g}^{-1}$	68-97%	0.1 – 6.7 $\mu\text{g}\cdot\text{g}^{-1}$	Hilger et al., 2013
Oven door surface	Germany	Recovery standard: $\alpha$ -PDHCH	<LOD-1.9 $\text{mg}\cdot\text{g}^{-1}$ fat	n. r.	5 $\text{ng}\cdot\text{g}^{-1}$ fat	Gallistl et al., 2018
Windows surface film	Beijing, China	Recovery standard: $\epsilon$ -HCH Extraction standard: $^{13}\text{C}10$ -trans-chlordane	337 $\text{ng}\cdot\text{m}^{-2}$ -114 $\mu\text{g}\cdot\text{m}^{-2}$	64-105%	0.25 $\text{ng}\cdot\text{m}^{-2}$	Gao et al., 2016
Polyvinyl Chloride Flooring	China	Recovery standard: $^{13}\text{C}10$ -trans-chlordane Extraction standard: $\delta$ -HCH	63-183 $\mu\text{g}\cdot\text{m}^{-3}$	51.4-135.8%	0.49 $\text{ng}\cdot\text{m}^{-3}$	Zhan et al., 2017



PM	Beijing, China	Recovery standard: $^{13}\text{C}10$ -trans-chlordane Extraction standard: $\epsilon$ -HCH	16.6-28.8 $\text{ng}\cdot\text{m}^{-3}$ outdoor PM10 9.2-19.6 $\text{ng}\cdot\text{m}^{-3}$ outdoor PM2.5 4.1-15.4 $\text{ng}\cdot\text{m}^{-3}$ outdoor PM1.0 38.3-87.7 $\text{ng}\cdot\text{m}^{-3}$ indoor PM10 16.8-49.4 $\text{ng}\cdot\text{m}^{-3}$ indoor PM2.5 6.4-32.5 $\text{ng}\cdot\text{m}^{-3}$ indoor PM1.0	69-105%	0.5 $\text{ng}\cdot\text{m}^{-3}$	Huang et al., 2017
<i>n. r. – not reported, d. w. – dry weight, w. w. – wet weight, SPM – solid particulate matter; SOM - soil organic matter</i>						

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**Table 3.** The general list of solutions which might be introduced in the analytical procedures for SCCPs determination in environmental samples following the 12 principles of GAC.

Green Analytical Chemistry principle	Possibility to introduce into the analytical procedure	Proposed solution
1. Direct analytical techniques should be applied to avoid sample treatment	Impossible	Lack of a possible solution in this field.
2. Minimal sample size and a minimal number of samples are goals	Hardly possible	The application of passive sampling technique in a case of air samples and possible solution in the case of water samples.
3. In situ measurements should be performed	Impossible	Lack of a possible solution in this field.
4. Integration of analytical processes and operations saves energy and reduces the use of reagents	Hardly possible	Application of automatized SPE technique, as a combining of extraction and clean-up tool.
5. Automated and miniaturized methods should be selected	Possible in selected procedure stages	Extraction automatisation – ASE or UAE Application of SPE technique Automatisation of SPE technique
6. Derivatization should be avoided	Possible	Lack of derivatisation process during whole SCCP analytical procedure.
7. Generation of a large volume of analytical waste should be avoided and proper management of analytical waste should be provided	Possible in selected procedure stages	Performing the optimization process using mathematical and statistical modelling for extraction and clean-up stages. Application of advanced extraction techniques – ASE, UAE, SFE or SPE.
8. Multi-analyte or multi-parameter methods are preferred versus methods using one analyte at a time	Possible	The use of advanced detectors such as ECNI- MS, TOF-MS, ECNI-TQMS or Orbitrap GC-MS/MS might give analytical information about the $\Sigma$ SCCPs and individual SCCPs congeners.
9. The use of energy should be minimized	Hardly possible	The application of $\mu$ ECD at the final determination process, followed by the well-performed sample preparation and analytes separation process. Application of SPE technique with properly selected sorption medium instead of ASE or UAE.
10. Reagents obtained from renewable source should be preferred	Hardly possible	The use of MIPs in a SPE technique as a reusable sorption medium.
11. Toxic reagents should be eliminated or replaced	Possible in selected procedure stages	Application of a SFE technique at the sample preparation stage. Application of reference solutions of SCCPs in other than cyclohexane solvents. Possible application of the replacement solvents for dichloromethane.
12. The safety of the operator should be increased	Possible	All of the stages of analytical procedure should be performed by properly skilled laboratory staff, in accordance with the principles of good laboratory practice.



**Highlights**

- The analytical procedures used for SCCPs determination in environmental samples were listed;
- The major components of the environment containing SCCPs and their content levels were shown;
- The application of the principles of green analytical chemistry in SCCPs analytical protocols were discussed;
- The GAPI technique was applied for screening estimation of the green character of the whole SCCPs analytical protocol;
- Possible implementation of “green” solutions during the environmental samples analysis for SCCPs determination were proposed;

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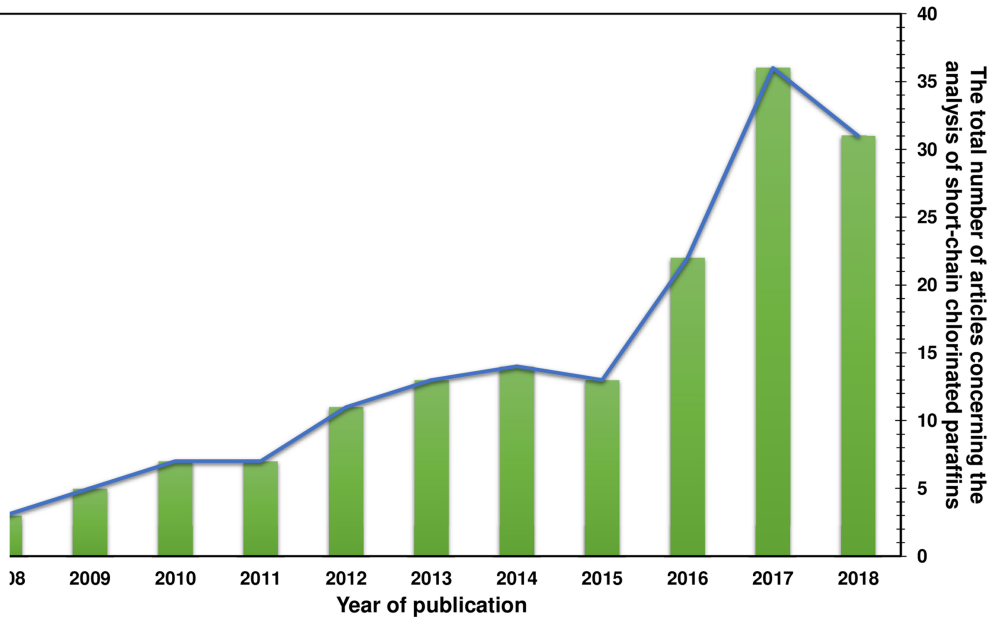
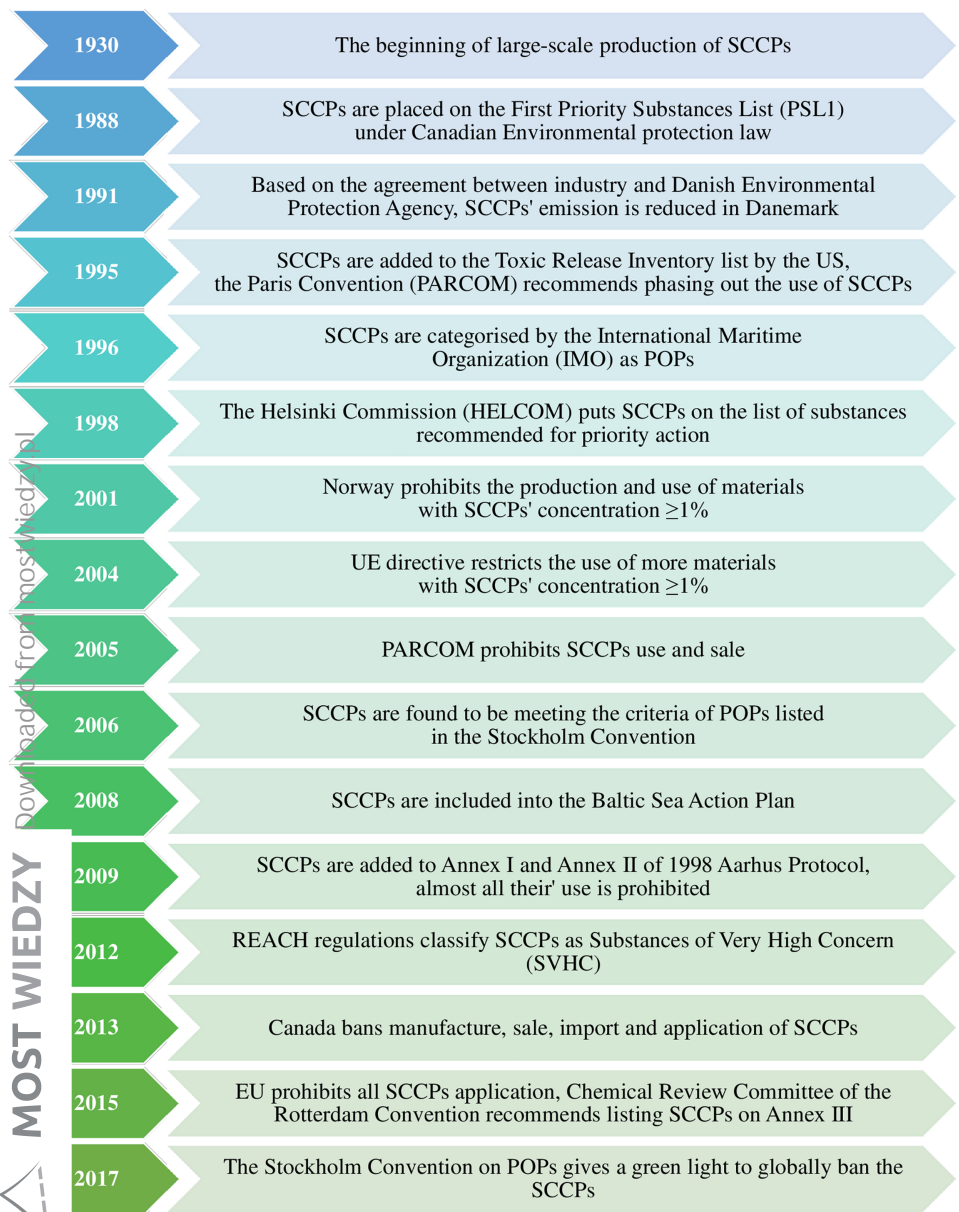


Figure 1



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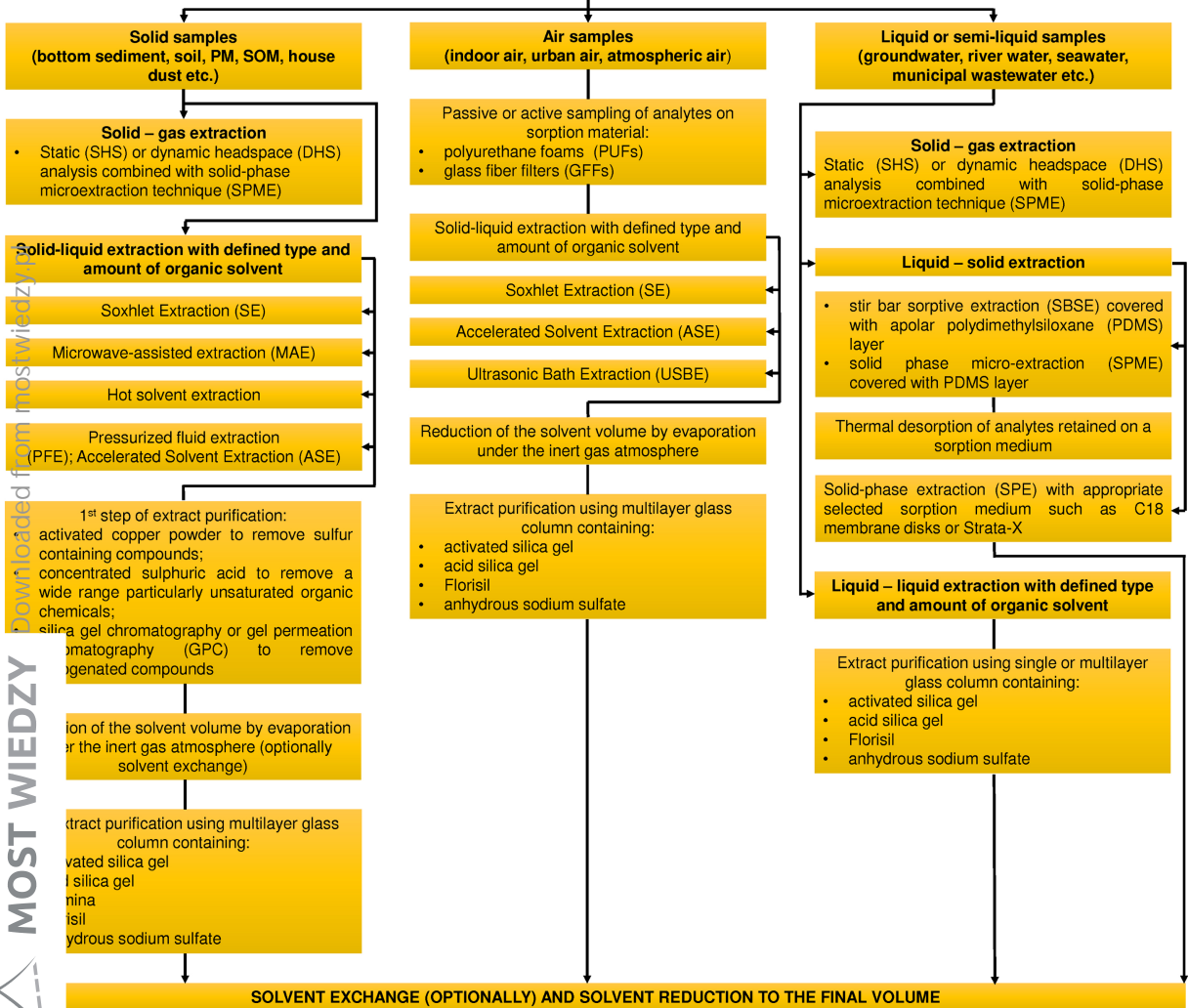
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Figure 2



**EXTRACTION AND PURIFICATION TECHNIQUES COMMONLY USED BEFORE SCCPs FINAL DETERMINATION STAGE**



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Figure 3

**Complex of SCCP mixtures containing the assessed carbon chain length distributions and are available with dissimilar degrees of chlorination**

**Single-chain SCCP mixtures that consist of homologues of only one carbon chain length and are available with dissimilar degrees of chlorination**

**The solutions for SCCPs qualitative and quantitative analysis**

**Constitutionally well-labeled SCCPs that are defined by carbon chain length and specified by chlorine number as well as chlorine position. The application possibility of stereoisomeric mixtures**

**Isotopically labeled SCCPs with a specified constitution**

Figure 4

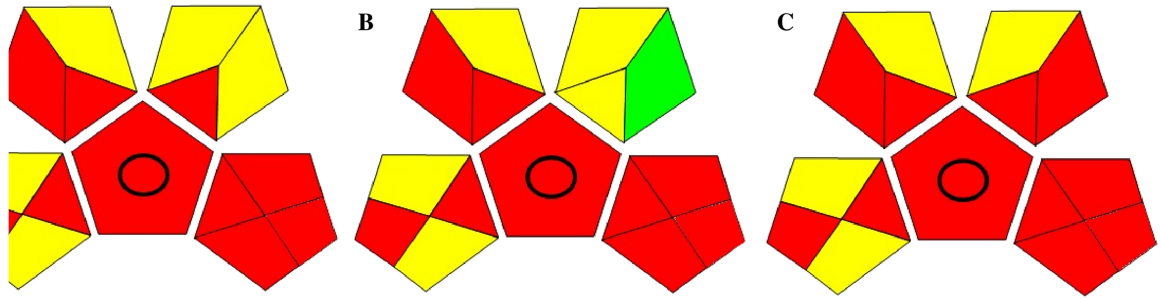


Figure 5