# Quantitative analysis of polychlorinated *n*-alkanes in environmental samples

E. Eljarrat, D. Barceló

**Polychlorinated *n*-alkanes (PCAs) are persistent organic pollutants of concern due to their toxicological properties, their capability to bioaccumulate and their widespread, unrestricted use. PCAs are classified according to the length of the alkane chain as short-chain chlorinated paraffins (SCCPs), medium-chain CPs (MCCPs) and long-chain CPs (LCCPs). PCAs represent a difficult analytical problem because of the complexity inherent in industrial mixtures. The total number of possible congeners is unknown, but far exceeds 10,000. Many procedures for separation and quantification of these contaminants have been described. However, most relevant works refer to SCCPs, and some others also include MCCPs. But, methodologies for LCCPs are very rare.**

**In this article, we discuss different aspects of current analytical methodology, such as sample preparation, extraction, purification and final determination. Most PCA analyses have been performed by gas chromatography (GC) coupled to electron capture negative ionization (ECNI) mass spectrometry (MS), although alternatives based on the use of electron ionization tandem MS (EI-MS)$^2$ and metastable atom bombardment (MAB) have been reported. New methodologies based on the use of comprehensive two-dimensional GC have also been developed. We discuss the advantages and the disadvantages of the different instrumental techniques, and outline conclusions and perspectives for the future.**


*Keywords:* Chlorinated paraffin; Clean-up; Comprehensive two-dimensional gas chromatography; Extraction; Gas chromatography; Mass spectrometry; Polychlorinated *n*-alkane

*Abbreviations:* APCI, Atmospheric pressure chemical ionization; ASE, Accelerated solvent extraction; CP, Chlorinated paraffin; CRM, Certified reference material; CV, Coefficient of variation; DCM, Dichloromethane; ECD, Electron capture detection; ECNI, Electron capture negative ionization; EI, Electron ionization; GC, Gas chromatography; GCxGC, Comprehensive two-dimensional gas chromatography; GPC, Gel permeation chromatography; HRMS, High-resolution mass spectrometry; iLOD, Instrumental limit of detection; IT, Ion trap; LC, Liquid chromatography; LCCP, Long-chain chlorinated paraffin; LOD, Limit of detection; LOQ, Limit of quantification; LRMS, Low-resolution mass spectrometry; MAB, Metastable atom bombardment; MAE, Microwave-assisted extraction; MCCP, Medium-chain chlorinated paraffin; MS, Mass spectrometry; $MS^2$, Tandem mass spectrometry; NICI, Negative ion chemical ionization; PCA, Polychlorinated *n*-alkane; PCI, Positive chemical ionization; PLE, Pressurized liquid extraction; SCCP, Short-chain chlorinated paraffin; SIM, Selected ion monitoring; SPE, Solid-phase extraction; SPME, Solid- phase microextraction; ToF, Time of flight

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## 1. Introduction

Polychlorinated *n*-alkanes (PCAs) (see above list of abbreviations used), also known as chlorinated paraffins (CPs), are a class of industrially prepared mixtures of the general formula $C_nH_{2n+2-z}Cl_z$. These mixtures have a degree of chlorination between 30% and 70% by weight, and a linear alkane chain with length of $C_{10}$–$C_{13}$ (short-chain CPs, SCCPs), $C_{14}$–$C_{17}$ (medium-chain CPs, MCCPs) or $C_{>17}$ (long-chain CPs, LCCPs). The number of theoretically possible congeners, homologues, diastereomers and enantiomers is unknown, but by far exceeds 10,000 compounds [1].

PCAs have been produced in technical formulations since the early 1930s. Because they are produced with free radical chlorination, a single PCA formulation comprises thousands of different compounds with a range of physical and chemical properties. They are used for a variety of industrial applications, including lubricating additives in plastics, adhesives, sealants, paints, cutting oil additives and flame retardants [2]. The world production of PCAs has shown slow growth over recent decades from ca. 230,000 tons

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per year in 1977–1979 [3] to ca. 300,000 tons in 1997 [4].

PCAs have physical and chemical properties that are similar to other high molecular weight organochlorine pollutants, such as PCBs and DDT. Water solubility has been estimated based on octanol-water partition coefficient ($K_{OW}$) correlations, and an apparent inverse relationship between carbon-chain length and water solubility was noticed with values in the range 0.49–1260 μg/L for SCCPs, 0.029–14 μg/L for MCCPs, and $1.6 \times 10^{-6}$–0.086 μg/L for LCCPs [5].

The Cl substitution pattern also significantly affected water solubility, and, in contrast with known trends for chlorinated aromatic compounds, water solubility increased with the degree of chlorination for up to five chlorines [6].

Estimated vapour pressures of individual congeners were reported in the range $2.8 \times 10^{-7}$–0.066 Pa for SCCPs, $1.7 \times 10^{-8}$–$2.5 \times 10^{-4}$ Pa for MCCPs, and $6.3 \times 10^{-15}$–$7.9 \times 10^{-7}$ Pa for LCCPs [5]. Log $K_{OW}$ were reported in the range 5.06–8.12 for SCCPs, 6.83–8.96 for MCCPs, and 8.70–12.68 for LCCPs [5].

Toxicity of PCAs appears to be inversely related to carbon-chain length and because of that much attention has been given to SCCPs. Although PCAs have generally shown low toxicity to mammals, SCCPs have carcinogenic potential in rats and mice [7]. However, no evidence of carcinogenicity was found for MCCPs and LCCPs. In addition, dose-response studies have shown that oral intake of SCCPs by mice results in an increase in liver weight. Moreover, in some studies, $C_{10}$–$C_{12}$ CPs with 58% chlorine content caused growth inhibition and reproductive effects.

Bioconcentration factors are high, reaching values of nearly $1.4 \times 10^5$ in mussels with polychlorinated dodecane with 69% chlorine content [8]. Greater bioconcentration factors were found for SCCPs, probably due to their greater water solubility. Moreover, highly chlorinated SCCPs are predicted to have the greatest bioconcentration factors because they are more hydrophobic and resistant to biotransformation than lower chlorinated PCAs, and their accumulation is not hindered by a large molecular size or extremely high $K_{OW}$, as observed for MCCPs and LCCPs [9].

PCAs have been found in biotic and abiotic samples from around the world, and, in many cases, have the highest concentration of any of the organochlorine compounds measured. For example, a survey of UK sewage sludges reported total concentrations of SCCPs and MCCPs in the range 7–200 mg/kg and 30–9700 mg/kg, respectively, whereas PCB concentrations were 110–400 μg/kg [10].

In spite of the extensive use of PCAs, information about their metabolism, bioaccumulation, and ecological toxicity is insufficient, because there is no routine analytical method available to correlate their effects with their molecular structures. The main problem in identifying and quantifying PCAs is the complexity of their mixtures, the various homologues and isomers being difficult to separate from each other.

PCA mixtures are the most complex of all halogenated mixtures of contaminants. Because of their complexity, their analysis is extremely difficult. This is certainly one reason why they have so seldom been determined.

In the USA, SCCPs have been placed on the Environmental Protection Agency (EPA) Toxic Release Inventory and, in Canada, they are classified as Priority Toxic Substances under the Canadian Environmental Protection Act. SCCPs have also been included in the list of Priority Dangerous Substances of the European Water Framework Directive [11]. Inclusion in this list means that there is a need for routine methods for SCCPs in the near future in many environmental laboratories in Europe. SCCPs are of particular interest due to the high amounts released into the environment, and due to them having the highest toxicity of all CP products [12]. Consequently, environmental levels of PCAs, especially SCCPs, should be monitored more extensively in the near future, and that will require reliable analytical methods.

This article reviews published analytical methods for the determination of PCAs in environmental and biological samples, including sample-preparation techniques as well as instrumental approaches. We survey the current state-of-the-art and outline perspectives.

## 2. Sample preparation

An analytical protocol to determine PCAs includes the following steps. PCAs are extracted from the sample, and the extract is then purified, fractionated and concentrated before final analysis.

We first present a review of sample-preparation techniques applied to PCA analyses in environmental samples. In general, the methods applied for determination of persistent organochlorines are also suitable for the analysis of PCAs. Moreover, extraction and purification procedures allow the simultaneous determination of SCCPs and MCCPs.

### *2.1. Extraction techniques*

Liquid-liquid extraction (LLE) or solid-phase extraction (SPE) are the most common techniques for preconcentration of PCAs from aqueous samples, although solid-phase microextraction (SPME) has also been reported [13]. The use of SPME has increased dramatically, as it allows efficient extraction, reduces solvent consumption and analysis time, and is easily automated.

Castells et al. [14] compared the capabilities of SPE and SPME for determination of PCAs in water. They