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Occurrence of polychlorinated naphthalenes, polychlorinated biphenyls and short-chain chlorinated paraffins in marine sediments from Barcelona (Spain)

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Abstract

Polychlorinated naphthalenes (PCNs), short-chain chlorinated paraffins (SCCPs) and polychlorinated biphenyls (PCBs) were analysed in marine sediment samples collected from the coastal area of Barcelona (Spain) and near of a submarine emissary coming from a waste water treatment plant located at the mouth of the Besòs River (Barcelona). An integrated sample treatment based on Soxhlet extraction followed by a simple clean-up with Florisil and graphitized carbon cartridge was employed. Gas chromatography coupled to ion-trap tandem mass spectrometry (GC–MS/MS) and gas chromatography–mass spectrometry in electron capture negative ionization mode, were used for PCN and SCCP determinations, respectively, while for PCB analysis gas chromatography with electron capture detection (GC-ECD) was used. The method developed provided low limits of detection (0.001–0.003 ng g^{-1} dry weight (dw) for PCNs, 1.8 ng g^{-1} for SCCPs and 0.006–0.014 ng g^{-1} dw for PCBs) and good run-to-run precisions (lower than RSD 8%) for the analysis of sediment samples. Concentration levels ranging from 0.17 to 3.27 ng g^{-1} dw for PCNs, between 0.21 and 1.17 μg g^{-1} dw for SCCPs, and from 2.33 to 44.00 ng g^{-1} (dw) for PCBs, were found in the coastal sediments, while for samples collected near to the submarine emissary higher levels (from 2.02 to 6.56 ng g^{-1} dw for PCNs, between 1.25 and 2.09 μg g^{-1} dw for SCCPs and from 22.34 to 37.74 ng g^{-1} dw for PCBs) were obtained. The results obtained provide new data about the occurrence of PCN and SCCP in the coastal area of Barcelona.

Keywords: Sediments; Environmental analysis; Mass spectrometry; Polychlorinated naphthalenes; Polychlorinated biphenyls; Chlorinated paraffins

1. Introduction

Persistent organohalogen compounds such as polychlorinated naphthalenes (PCNs), chlorinated paraffins (CPs) and polychlorinated biphenyls (PCBs) are well-known environmental contaminants. These three classes of compounds are ubiquitous global pollutants which can be often found in different environmental compartments, although their use and production has been restricted (CPs) or banned (PCBs and PCNs). Since physical properties and chemical structures of PCNs and PCBs are similar they have been used in similar applications, such as dielectric fluids, insulators, additives and preservatives. Chlorinated paraffins (CPs) are complex mixtures containing a very large number of individual isomers (Tomy et al., 1997; Shojania, 1999) which are particularly good PCN and PCB substitutes in a wide variety of industrial applications. In fact, world production of short-chain CPs (C_{10}–C_{13} CPs, SCCPs) has increased after the banning of PCNs and PCBs. As recognised persistent organic pollutants (POPs), these compounds are frequently detected in a wide variety of environmental matrices such as sediments, soils, water, biota and air, in both industrial and non-industrial areas (Coelhan, 1999; Eljarrat et al., 1999; Tomy et al.,

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1999a,b; Yamashita et al., 2000a,b; Nicholls et al., 2001; Castells et al., 2003; Harner et al., 2006; Manodori et al., 2006), although SCCPs are not found in air because of their low vapour pressures (Peters et al., 2000). Generally, PCNs, PCBs and SCCPs have been mainly released into the environment due improper use and disposal after intended production, although PCNs can also be released from municipal solid waste incinerators (MSWIs) and some other industrial processes (Abad et al., 1999).

Toxicity of PCNs and PCBs has been extensively reported in the literature (Falandysz, 1998, 2003; Hayward, 1998; Villeneuve et al., 2000; Brack et al., 2003; Persson et al., 2005; Yusà et al., 2006; Sprovieri et al., 2007). All PCN congeners and also non-*ortho* and mono-*ortho*-PCBs are more or less planar compounds, and carcinogenic risk derived from the exposure to such kind of pollutants is also well-known. Non-*ortho* and mono-*ortho*-PCBs exhibit dioxin-like toxicity, and several hexachlorinated naphthalenes (such as 1,2,3,4,6,7-hexaCN and 1,2,3,5,6,7-hexaCN) and 1,2,3,4,5,6,7-heptaCN have a toxic equivalency factor similar to mono-*ortho*-PCBs (Engwall et al., 1994; Falandysz and Puzyn, 2004), which is 0.001 relative to 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD). More recently, and despite their different structures and toxicity mechanisms, SCCPs with an average carbon chain length of C_{12} and 60% of chlorine content have also been included by the International Agency for Research on Cancer (IARC, 1990) in Group 2B as being *possibly carcinogenic to humans*. Therefore, several international organisations have listed SCCPs as substances requiring priority action and regulation as for PCBs and PCNs (EPA, 1991; CEPA, 1993; OSPAR, 1999).

Analysis of SCCPs, PCBs and PCNs is currently performed by gas chromatography (GC) coupled to high or low resolution mass spectrometry (MS) and electron ionisation (EI) is commonly used for the congener-specific determination of PCNs and PCBs (Kannan et al., 1998; Lunden and Noren, 1998; Yamashita et al., 2000a,b; Lundgren et al., 2002; Falandysz, 2003; Wang et al., 2005, 2007; Manodori et al., 2006; Pan et al., 2007). However, under EI conditions SCCPs, which are much more labile compounds, have shown a high degree of fragmentation (Castells et al., 2004a,b), and for this reason a softer ionisation technique such as electron capture negative ionisation (ECNI) in both high and low resolution MS is currently used (Coelhan, 1999; Tomy et al., 1999b; Nicholls et al., 2001; Nilsson et al., 2001; Zencak et al., 2004; Braune et al., 2005; Hüttig and Oehme, 2005; Iino et al., 2005; Reth et al., 2005; Stejnarová et al., 2005; Hüttig and Oehme, 2006). PCNs have also been successfully determined using GC–ECNI-MS (Meijer et al., 2001; Egeback et al., 2004; Carrizo and Grimalt, 2006) but, unfortunately, for CPs no congener-specific determination can be accomplished due to the huge number of isomers present in these mixtures. Nevertheless, quantification of the different homologue groups of CPs is possible mainly by monitoring their corresponding $[M-Cl]^-$ ions, although the use of $[HCl_2]^-$ and $[Cl_2]^{-\bullet}$ ions has also been reported for SCCP determination (Nicholls et al., 2001; Castells et al., 2004a,b).

GC–ion-trap tandem mass spectrometry (GC–IT-MS/MS) has been also proposed for the analysis of these compounds in several matrices. For instance, PCBs in atmospheric particulate samples (Mandalakis et al., 2001), PCNs in biological tissues (Wang et al., 2005, 2007) and sediments (Yusà et al., 2006), and the screening of SCCPs in biological marine samples (Zencak et al., 2004) have been performed using this technique providing good selectivity and sensitivity at a lower cost than HRMS.

This paper is mainly focused on the determination of the above mentioned organochlorine compounds (PCNs and SCCPs) in marine sediment samples from a coastal area of Barcelona (Spain) with the aim of assessing PCN and SCCPs contamination in this area. For this purpose, a GC–IT-MS/MS method was developed for PCN determination while SCCPs were analysed by a GC–ECNI-MS method previously developed (Castells et al., 2004b). In addition, PCB congeners were also determined in the sediments with the aim of comparing the results with those obtained for PCNs and SCCPs and to provide information about their presence on this area.

2. Materials and methods

2.1. Standards and reagents

A stock standard solution mixture of eight PCN congeners (PCN-MXA) in nonane was obtained from Wellington Laboratories Inc. (Guelph, Ontario, Canada). This mixture contained the following PCN congeners at a concentration of 5.0 μg ml^{-1}: 2-monoCN (PCN-2), 1,5-diCN (PCN-6), 1,2,3-triCN (PCN-13), 1,2,3,5-tetraCN (PCN-28), 1,2,3,5,7-pentaCN (PCN-52), 1,2,3,4,6,7-hexaCN (PCN-66), 1,2,3,4,5,6,7-heptaCN (PCN-73) and octachloronaphthalene (PCN-75). Each PCN congener was representative of one homologue group. PCN calibration standard solutions at concentrations between 0.2 and 300 ng ml^{-1} were prepared by dilution of the stock standard solution in isooctane. Halowax 1014 and Halowax 1051 at a concentration of 10 μg ml^{-1} in cyclohexane were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

A stock standard solution of short-chain chlorinated paraffin (SCCP C_{10}–C_{13}, 63% Cl) in cyclohexane of 100 μg ml^{-1} was obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Individual analytical-reagent grade PCB congeners, 28, 52, 101, 105, 118, 128, 138, 149, 153, 156, 170 and 180, at purity higher than 99%, were supplied by Promochem GmbH (Wesel, Germany). A stock standard solution mixture of the 12 PCB congeners at 300 ng ml^{-1} was prepared by weight in isooctane from the individual standard solutions. Five calibration standard solutions of SCCPs (between 1 and 80 μg ml^{-1}) and PCBs (from 0.5 to 200 ng g^{-1}) were prepared by dilution of the primary standard solutions in isooctane for