Environmental Pollution xxx (2016) 1–7

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Occurrences, sources and risk assessment of short- and medium-chain chlorinated paraffins in sediments from the middle reaches of the Yellow River, China

Lin Qiao [a, b], Dan Xia [a, b], Lirong Gao [a, b, *], Huiting Huang [a, b], Minghui Zheng [a, b]

[a] *State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China*
[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

ARTICLE INFO

Article history:
Received 24 March 2016
Received in revised form
19 May 2016
Accepted 20 May 2016
Available online xxx

Keywords:
Short-chain chlorinated paraffins
Medium-chain chlorinated paraffins
Sediments
The Yellow River
Homolog patterns

ABSTRACT

Chlorinated paraffins (CPs), one class of hydrophobic and toxic compounds, are easily adsorbed into sediments and then pose potential risks to the ecosystem and human health. However, few researches on short- and medium-chain CPs (SCCPs and MCCPs) in sediments have been performed. In order to comprehensively investigate the spatial distributions, sources, and ecological risks of CPs, sediments collected from the middle reaches of the Yellow River were analyzed by two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC × GC–TOFMS). The concentrations of SCCPs and MCCPs ranged from 11.6 to 9.76×10^3 ng/g dry weight (dw) and from 8.33 to 168 ng/g dw, respectively. No significant correlation was found between total organic carbon (TOC) and CP concentrations ($P > 0.05$). The spatial distributions showed that contamination levels of CPs were relevant to human activities. In addition, two types of sediment samples were classified by hierarchical cluster analysis (HCA) and results indicated the predominant congener groups were $C_{10}Cl_{6-7}$ for SCCPs and $C_{14}Cl_{7-8}$ for MCCPs. Principal component analysis (PCA) revealed that SCCPs and MCCPs in the sediments may have different sources, and SCCPs are likely to come from the production and use of CP-42 and CP-52. Moreover, complex environmental processes, including long-range transportation via the atmosphere and/or river, deposition and degradation of CPs, resulted in increased abundances of short chain and low chlorinated congeners in sediment samples compared with commercial mixtures, and different homolog patterns among samples. The significant negative correlation between SCCP concentrations and MCCP/SCCP ratios could be related to long-range transport of CPs. A preliminary risk assessment indicated that CPs at current levels posed no significant ecological risk.

1. Introduction

Chlorinated paraffins (CPs) are a class of complex technical mixtures, containing thousands of isomers, enantiomers, diastereomers and congeners (Bayen et al., 2006; Feo et al., 2009). According to the carbon chain length, CPs can be grouped into short-chain CPs (SCCPs, C_{10-13}), medium-chain CPs (MCCPs, C_{14-17}) and long-chain CPs (LCCPs, C_{18-30}). Owing to the potential for long-range transport (Tomy et al., 1999), persistence (Iozza et al., 2008), bioaccumulation (Fisk et al., 2000) and toxicity (Warnasuriya et al., 2010), SCCPs have been listed as persistent organic pollutants (POPs) candidate in the Stockholm Convention. The chemical and thermal stabilities of CPs have led them to be widely produced and used as plasticizers, lubricant additives, coolants and/or flame retardants, and in applications such as metal working fluids and sealants (Feo et al., 2009). CPs can be released into the environment during production, storage, transportation, use and disposal of these related manufactured products. Besides, CPs may also enter the environment through waste incineration (Feo et al., 2009), sewage treatment (Zeng et al., 2012b) and e-waste dismantling (Lu et al., 2015). Up to now, CPs have been found to be widespread in the air (Wang et al., 2013), water (Coelhan, 2010), soil (Wang et al., 2014), sediment (Zeng et al., 2013), aquatic and terrestrial wildlife (Reth et al., 2006; Zeng et al., 2015), and even in human breast milk (Thomas et al., 2006). So it's important to improve our understanding of the pollution status and potential risks posed by CPs.

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[*] Corresponding author. State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China.
E-mail address: gaolr@rcees.ac.cn (L. Gao).

http://dx.doi.org/10.1016/j.envpol.2016.05.057
0269-7491/

Please cite this article in press as: Qiao, L., et al., Occurrences, sources and risk assessment of short- and medium-chain chlorinated paraffins in sediments from the middle reaches of the Yellow River, China, Environmental Pollution (2016), http://dx.doi.org/10.1016/j.envpol.2016.05.057

China is the largest producer and consumer of CPs in the world. The annual production has been continuously and rapidly increasing, up to 6 × 10^5 tons in 2007 (De Boer et al., 2010) and 1 × 10^6 tons in 2009 (Chen et al., 2011), so that CPs are released into the environment on a large scale (Ma et al., 2014a; Wang et al., 2012, 2014; Zeng et al., 2011a; Zeng et al., 2012b). Because of their high Koc values (Fisk et al., 1998), CPs are easily adsorbed into sediments. They can be accumulated by the sediment-dwelling organisms and then pose potential risks to humans after being further accumulated through the food chain (Houde et al., 2008; Ma et al., 2014b). So the sediment can be regarded as an important sink of CPs. On the other hand, CPs in sediments can be re-released to the water and affect aquatic organisms, causing secondary pollution. It's therefore necessary to investigate CP contamination levels in sediments so as to reveal the sources and then put forward corresponding control measures.

Several previous studies have reported the concentrations and distributions of CPs in sediments from some regions. River Sediments from the Liaohe River Basin (China) and the Czech Republic were investigated, suggesting that local industrial activities were major sources of SCCPs (Gao et al., 2012; Pribylova et al., 2006). Researches about marine sediments from the East China Sea, Bohai and Yellow Seas indicated that CP concentrations increased with time, but decreased with the distance away from the coast (Zeng et al., 2012a, 2013). A study of sediment samples collected near a sewage treatment plant (STP) demonstrated that STP effluents could be important sources of SCCPs (Zeng et al., 2011b). However, there is no systematical discussion about the factors influencing CP homolog patterns, which are closely associated with the toxicity of CPs (De et al., 2010; Wyatt et al., 1993). Although the production and use of SCCPs has been restricted in some regions, MCCPs were produced as the replacement chemicals in a high level (EU, 2011). Data on MCCPs is scarcer than SCCPs due to the difficulties with analytical methods. Although toxicity of MCCPs is lower compared to SCCPs (Wyatt et al., 1993), MCCPs have also shown bio-accumulation (Houde et al., 2008) and even higher concentration levels (Chen et al., 2011) in some studies, suggesting that more attention should be paid to MCCPs than is currently the case. The Yellow River, regarded as the second longest river in China, is the main water supply for North China. With rapid industrialization and urbanization along the river, especially in the middle reaches of the river, an increasing number of electronic factories, metallurgical factories and petrochemical plants were set up. Moreover, a large volume of CP manufacturers have been established nearby, which could be potential emission sources of CPs.

In this study, two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC × GC–TOFMS) was used to analyze SCCPs and MCCPs in sediments from the middle reaches of the Yellow River. The objectives were to gain knowledge of the spatial distributions and congener group profiles of SCCPs and MCCPs in river sediments. The contamination sources, transport pathways and environmental fates of CPs were then explored and the factors influencing CP homolog patterns in sediments were revealed. Finally, ecological risks posed by SCCPs were assessed based on existing toxicology data. It is hoped that our work will be helpful to better understand current pollution status and environmental behaviors of CPs, as well as put forward some strategies for future reduction of CPs in the environment.

2. Materials and methods

2.1. Sample collection

Thirteen surface sediment samples (0–5 cm deep) were collected from the middle reaches of the Yellow River (Fig. S1, Supporting Information) using a grab sampler. At each sampling site, five separate samples were collected and then mixed together. After removing stones and roots, samples were freeze-dried, ground and then sieved via a 60 mesh sieve. Finally, all samples were sealed in amber glass bottles, labeled and stored at −20 °C until analysis.

2.2. Chemicals and materials

Three commercial SCCP standards (with chlorine contents of 51.5%, 55.5%, and 63%) and three MCCP standards (with chlorine contents of 42%, 52%, and 57%) at 100 ng/μL in cyclohexane were obtained from Dr. Ehrenstorfer (Augsburg, Germany). SCCP solutions with 53.5% and 59.2% chlorine content were prepared by mixing equal volumes of SCCP standards with chlorine contents of 51.5% and 55.5%, as well as 55.5% and 63%, respectively. Similarly, MCCPs with 47% and 54.5% chlorine content were gained by mixing MCCPs of 42% and 52%, as well as 52% and 57%. These above CP solutions with different chlorine contents were used to establish linear calibration curves between total response factors and chlorine contents. $^{13}C_{10}$-*trans*-chlordane purchased from Cambridge Isotope Laboratories (Andover, USA), and ε-hexachlorocyclohexane (ε-HCH) obtained from Dr. Ehrenstorfer were used as surrogate and internal standards, respectively. Silica gel (63–100 μm) and Florisil (60–100 mesh) were purchased from Merck (Whitehouse Station, NJ). Anhydrous sodium sulfate was purchased from Sinopharm Chemical Reagent Co (Beijing, China). Before use, silica gel was activated at 550 °C for 12 h, anhydrous sodium sulfate was baked at 660 °C for 6 h, and Florisil was baked at 140 °C overnight. Acid silica gel (30%, w/w) was prepared by mixing 100 g activated silica gel with 23.3 mL concentrated sulfuric acid.

2.3. Sample extraction and cleanup

In this study, the extraction and clean-up procedures were modified based on previous studies (Gao et al., 2011; Zeng et al., 2011a). Briefly, 5 g homogenized sediment was spiked with 2.5 ng $^{13}C_{10}$-*trans*-chlordane, and then extracted via an accelerated solvent extractor (ASE). Three static extraction cycles were performed, each using 30–40 mL *n*-hexane/dichloromethane (1:1, v/v) for 10 min at 1.03 × 10^4 kPa and 150 °C. Next, the extract was concentrated to approximately 1 mL and then passed through a gel permeation chromatography (GPC) column to remove sulfur-containing compounds. The eluent was concentrated again and then fractionated on a 1.5 cm i.d. silica-Florisil composite column containing, from the bottom to top, 3 g Florisil, 2 g neutral silica gel, 5 g 30% acid silica gel and 4 g anhydrous sodium sulfate. The column was conditioned with 50 mL *n*-hexane, and the sample was eluted with 40 mL *n*-hexane, followed by 100 mL *n*-hexane/dichloromethane (1:1). The second fraction was concentrated to near dryness under a gentle stream of N_2 and then reconstituted in 50 μL cyclohexane. Prior to analysis, 2.5 ng ε-HCH was added.

2.4. Instrumental analysis

The GC × GC − TOFMS analysis was conducted using an Agilent 7890A GC instrument (Agilent Technologies, Santa Clara, USA) equipped with a ZX2004 loop cryogenic modulator (Zoex Corporation, Houston, USA) and a high resolution time-of-flight mass spectrometry instrument (Tofwerk, Thun, Switzerland), according to our previous study (Xia et al., 2016). The first-dimension column was a DB-5MS column (30 m × 0.25 mm i.d. × 0.25 μm film thickness, Agilent Technologies, Santa Clara, USA), and the second-dimension column was a BPX-50 column (1 m × 0.1 mm i.d. × 0.1 μm film thickness, SGE, Melbourne, Australia). The carrier

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