EVALUATION OF THE POLLUTION LEVELS OF SHORT CHAIN CHLORINATED PARAFFINS IN SOIL COLLECTED FROM AN E-WASTE DISMANTLING AREA IN CHINA

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Abstract

As a group of chlorinated derivatives of *n*-alkanes including 10 and 13 carbon atoms, short chain chlorinated paraffins (SCCPs) have been listed as candidates of persistent organic pollutants to be added to the Stockholm Convention. While in China, though chlorinated paraffins are currently produced and used a lot, no work about the environment fate or distribution of SCCPs have been carried out yet. In this paper, we built an instrument method using high resolution gas chromatography-tandem mass spectrometry (HRGC/MS/MS) coupled with electron ionization source to evaluate of the pollution levels of an e-waste dismantling area in China.

Introduction

Chlorinated paraffins are chlorinated derivatives of n-alkanes. They are divided into three groups of compounds named short chain chlorinated paraffins (C10-C13), medium chain chlorinated paraffins (C14-C17), and long chain chlorinated paraffins (C18-C30) depending on the number of the carbon atoms. As one of group compounds of the list of candidates of persistent organic pollutants (POPs) of Stockholm Convention (SC), SCCPs proposal have been evaluated against the criteria of Annex D of SC by persistent organic pollutants review committee.

Since the complex compositions of SCCPs contain thousands of isomers, it is a difficult task to quantify the concentrations of these compounds in environmental metrics. In general, SCCPs are analyzed by gas chromatography with electron-capture detection (GC-ECD) or GC-mass spectrometry (GC-MS) coupled to electron ionization (EI) or electron-capture negative ionization (ECNI). The reporting results are the total concentrations of ∑(SCCPs +MCCPs+LCCPs), many interfering halogenated compounds in the samples also included. GC-MS coupled with EI can report the total concentrations of CPs excluding impurity. GC-ECNI-MS can quantify the concentrations SCCPs, MCCPs, and LCCPs separately, so it is an appropriate instrument for investigating the pollution levels in environment. But the drawback of the method is that the error for the concentrations of certain isomers in samples is big if it is not included in the standard.

The presence of CPs in various environmental matrices from different countries or regions such as air (1), water (2), sediment (3), and biota (4) has been reported. While in China, very limited work about the distribution, pollution characteristics, environmental fate of SCCPs and MCCPs have been carried out yet although the production and usage of CPs are huge.

In this paper, we built a pretreatment and instrument method for analyzing SCCPs and MCCPs and MCCPs in soil. Then we selected an e-waste dismantling area in southeast China as our target region to evaluate the pollution levels of SCCPs and MCCPs. To our knowledge, this is the first work about SCCPs and MCCPs in environment in China.

Materials and methods

Sample pretreatment

Four soil samples were collected from an e-waste dismantling area in southeast China in November 2005. Each topsoil sample (0–20 cm) was obtained by mixing at least five adjacent sub-samples from one paddy field (four corners and the centre; approximately 10 × 10 m^2). Six soil samples collected from control area, which are 10-20 kilometers from e-waste dismantling area in this study. In addition, one sample from background area was also collected.

Reference SCCP (chlorine contents of 51.5%, 55.5%, 63%) and MCCP(chlorine contents of 52.0% and 57.0%) with concentrations of 100ng μL^{-1} in cyclohexane as well as ε-hexachlorocyclohexane (ε-HCH, solution in cyclohexane, 10 ng μL^{-1}) were purchased from Ehrenstorfer GmbH (Augsburg, Germany). ^{13}C10-trans-chlordane (100 ng μL^{-1}, solution in n-nonane, purity 99%) were supplied by Cambridge Isotope Laboratories (Andover, USA). Soil samples were freeze-dried and homogenized by sieving through a stainless steel 75-mesh (0.5 mm) sieve. An aliquot of 5g of sample was mixed with 15g anhydrous Na_2SO_4, spiked with 10ng $^{13}C_{10}$-trans-chlordane and extracted by using a Dionex ASE 350 (Dionex Canada Ltd., Oakville, ON, Canada) accelerated solvent extractor (ASE) at a temperature of 100 ℃ and a pressure of 1500psi (5). A mixture of dichloromethane (DCM)/hexane (1:1) was used as the extraction solvent. The thermal equilibration time is 5 min, and the static extractions are performed within three cycles, 10 min per cycle.The cell was purged with gaseous nitrogen for 100 s. After extraction, about two gram of activated copper powder was added to the extract to remove elemental sulfur, and then filtered through approximately 5 g of anhydrous sodium sulfate. The extract was rotary-evaporated to about 2 ml and then cleaned up by passing through a multi-layered Florisil column containing, from bottom to top, 3 g of activated Florisil, 2 g of activated silica gel, 5 g of acid silica gel (30%, w/w) and 4 g anhydrous sodium sulfate. The column was pre-cleaned by passing 50 ml hexane prior to the transfer of the sample extracts. After the sample was loaded, CPs congeners were eluted with 40 ml hexane followed by 120 ml DCM and hexane (1:1). The eluant was then concentrated to 2 ml on the rotary evaporator. Its volume was further reduced with a gentle nitrogen flow and the solvent was changed to 100 μL cyclohexane in a minivial. Then, 10 ng ε-HCH was added and the vial mixed by vortexing prior to GC injection.

Instrument analysis

Gas chromatographic separations combined with 7000A triple quadrupole MS (Agilent Technologies) were performed on a 7890A (Agilent) gas chromatograph using an electron impact (EI) ion source. Exactly 1μL of concentrated extract was injected with a 7683B Series Injector (Agilent) in splitless mode into a DB-5MS (30-m length, 0.25-mm i.d., 0.25 μm film thickness) capillary column. Helium was the quench gas at a constant flow rate of 2.25 mL/min. The initial oven temperature was 100 ℃, which was held for 1 min. It was increased to 160 ℃ at 30 ℃/min, held for 5 min, then ramped to 310 ℃ at 30 ℃/min and held for 22 min. Quantifications were carried out with the MRMs m/z 91 → 53 (collision energies -10 V) and confirmed with m/z 102

→ 65 (-10 V). The precursor ion m/z 383 and the product ion m/z 276 were chosen for $^{13}C_{10}$-trans-chlordane (collision energy -21 V), while forε-HCH were 219 → 183 (-15 V). Conditions (6) for EI-MS/MS were as follows: 70eV electron energy, dwell time 300 ms, resolution of Q1 is wide and of Q3 widest, and nitrogen as collision gas at 1.5 mL/min. Quantification was carried out with the internal calibration standard method.

Quality assurance and quality control

Strict quality controls were implemented to ensure the correct identification and accurate quantification of the target compounds. Sample preparation and analysis were conducted in a clean room with double HEPA air filtration and positive ambient pressure. All glassware was thoroughly rinsed before and after use with dichloromethane. Method blank samples were included to monitor the contamination. The detector response was liner in the tested range of 0.25 and 20 ng μL^{-1}. Seven-point calibration was prepared using individual SCCPs, MCCPs and their mixtures. Linear regression confidence values $R^2 \geqq 0.999$. The analytical detection limit for the sum of CPs was 0.25 ng μL^{-1}. The signal to noise quantification ratio was set to be higher than 3. Mean recoveries of $^{13}C_{10}$-trans-chlordane was 73.9 ± 22.5 %.

Results and discussion

All concentrations reported are on a dry weight (dw) basis.

Triple quadrupole EI-MS/MS chromatograms from soil samples are shown in Figure 1. The chromatograms of the samples from different areas show apparently differences depending on the polluting characteristics.

∑(SCCPs+MCCPs) concentrations of samples from E-waste dismantling areas of the samples ranged from 1095 to 4985 ng/g, with an average value of 2909 ng/g. The pollution levels are comparable to the estimated concentrations in sewage sludge-amended soils (7, 8). The concentrations in samples from control area, which were about 10 to 20 km away from the contaminated areas, varied between 1031 and 1579 ng/g with an average value of 1210 ng/g. One sample from remote area contains 203 ng/g of ∑(SCCPs+MCCPs).

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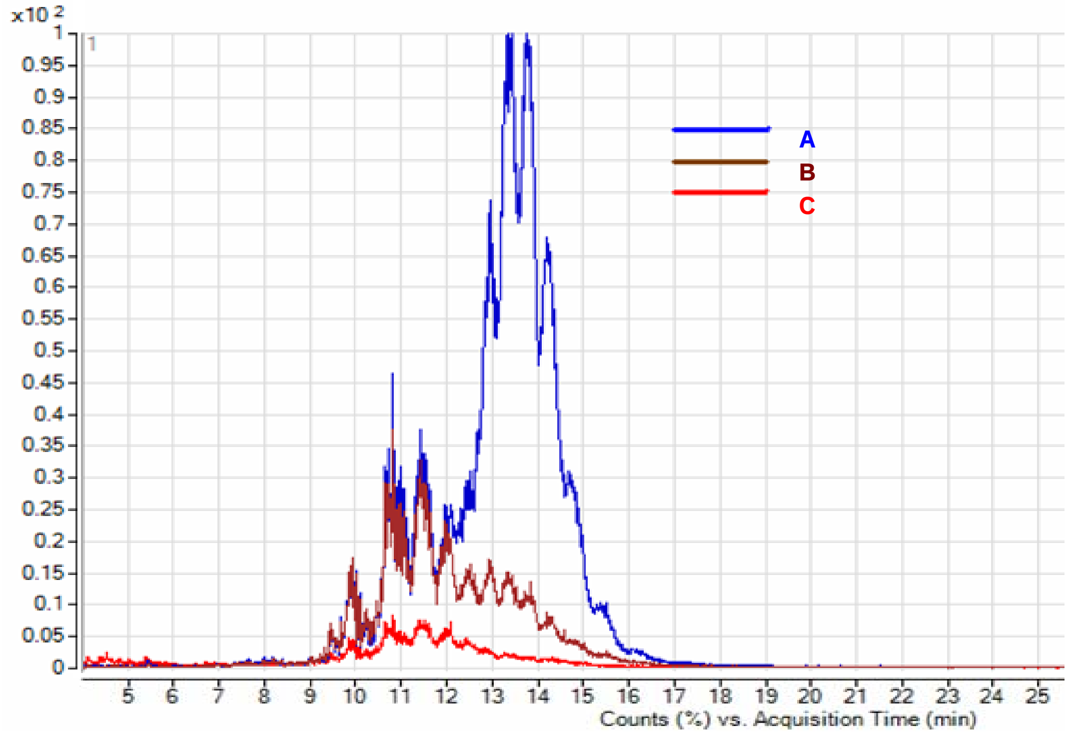

Figure 1. EI-MS/MS chromatograms of two soil samples extracts. (A) Soil sample from E-waste recycling areas; (B) Soil sample from control areas; (C) Soil sample from background area.

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