

UNINTENTIONAL POPs (PCBs, PCBz, PCNs) CONTAMINATION IN ARTICLES CONTAINING CHLORINATED PARAFFINS AND RELATED IMPACTED CHLORINATED PARAFFIN PRODUCTS

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Introduction

Chlorinated paraffins (CPs) Polychlorinated n-Alkanes (C_nH_{2n+2-x}Cl_x; PCAs) are industrial products used as metal-working fluids and flame retardants for plastic materials¹. CPs are manufactured by chlorination of liquid n-paraffin or paraffin wax since the 1930s. The chlorine content is usually between 40% and 70% by weight. Short chain CPs (SCCPs, C₁₀–13) are under review by the Stockholm Convention on POPs. SCCPs have been produced in the USA, Europe, Japan, India, China and other countries². The production volumes of SCCPs were 1,500–2,500 tons in the European Union (EU) in 2006, 8,800 tons in the USA in 2005 and 502 tons in Japan in 2001^{2,3}. In Japan, since 2005 and metal-working industries voluntarily phased out the use of SCCPs by 2007. In contrast, the production of total CPs in China has continued increased the last 30 years: China began its CPs production at the end of 1950s. In 1980s, the production of CPs increased rapidly due to the high demand of CPs mainly from the plastic industry (in particular the PVC production) as plasticizers/softeners. Whereas in the early 1980s, annual production of CPs was only a few thousand tones in China, the production drastically increased to about 600,000 tones in 2007⁴. It seems that currently, China is the largest producer in the world with a total number of CP factories of more than 140 followed by India with a production volume of >150,000 tones. Although the huge production and use of CPs in China could imply potential contamination of various media, there is little information on exposure to CPs⁵⁻⁷.

We detected high levels of POPs such as PCBs, HCBz contamination in the polyurethane foam (PUF) and rubber materials which was used to prevent noise and vibration in high volume air sampler (HVS) pump. The rubber contained 2 to 6 % of CPs as flame retardant according to the Material Safety Data Sheet (MSDS), which was the main contamination source of the POPs. This report describes the investigation of this incidents of POPs contamination which can have a large implication for the formation and distribution of unintentionally produced POPs when considering the large volumes of chlorinated paraffins.

Materials and methods

All materials used for HVS were wiping tested for POPs. After detection of the contamination source, the rubber and polyurethane foam materials were analyzed in more detail based on manufactured series 2001 to 2007. The instrument analysis was basically performed with GC-HRMS (Autospec, Waters) or GC-HR-Tof-MS (GCT, Waters) with column cleanup. For PCBs a congener specific analysis was performed⁸. Technical CPs sample which used for rubber as flame retardant were analyzed also with Tof-MS as excellent screening techniques for POPs contamination and detection of non-target pollutants^{9,10}.

Results and discussion

We detected high levels of unintentionally POPs such as PCBs and HCBz contamination at ppm level in rubber and polyurethane foam materials used to prevent and reduce noise or vibration in high volume air sampler (HVS) pumps. The assessment of a time series of these (HVS) pumps revealed that the POPs levels were drastically increased after 2006 (Figure 1). The PCBs levels were 10 to 16 ppm in PUF and 4 to 5.9 ppm in rubber materials after 2006 sample. The HCBz levels were 0.22 to 0.54 ppm in PUF and 0.37 to 0.60 ppm in rubber materials after 2006 sample. Although PCBs and HCBz concentrations were higher in the PUF than rubber, total amount of PCBs and HCBz in a HVS were much higher in the rubber than the PUF.

The rubber contained 2 to 6 % of CPs as additive flame retardant from MSDS. The CPs were imported from China. The manufacturing methods of CPs were changed on 2005 according to the company's information and the change resulted in the main contamination source of unintentionally POPs. The company producing

chemicals such as chlorinated paraffin, caustic soda, hydrochloric acid, liquid chlorine, paste PVC, fumed silica, epoxy resin, lubricating oil and pesticides. The company's production capacities for chlorinated paraffin are the biggest in China.

The technical CPs information is: commercial long chain chlorinated paraffin, CP-70, carbon degree C8-30, average carbon C25.

The additions of imported CPs as flame retardant to the rubber materials were conducted in Japan. The rubbers were attached with PUF for insulating commercial products to prevent noise and vibration.

These rubber type and PUF are mainly used for heavy machinery or dot printer to prevent noise or vibration.

PCBs congener specific analysis revealed that the homologue profile were dominated by lower chlorination PCBs (Figure 2) but that the detected congener pattern was close to technical PCBs with some specific exception. This indicates that the PCBs were mainly formed by chlorination of the parent biphenyl.

GC-HR-Tof-MS screening with accurate mass spectrum acquisition identified polychlorinated naphthalenes (PCNs) and polychlorinated benzenes (PCBzs) (Figure 4 and 5) as other unintentionally POPs contaminants in the same ppm order as the PCBs (Figure 3). The exact mass spectra were close to the theoretical value and could be used for identification of the contaminants (Figure 4). The congener patterns of PCNs were close to technical PCNs (Figure 4) which indicate that these chlorinated aromatics were chlorinated in the formulation processes from the basic aromatic structure probably present as impurities of the starting material in the technical CPs production.

As mentioned above, the rubber material contained 2 to 6 % of CPs as flame retardant according to the MSDS. This additive resulted in the main contamination source of the detected POPs in HVS.

The total contamination of PCB in one of the HVS (2007) was estimated based on contamination level and amount of rubber and PUF.

Rubber weight: 1100g, PCBs levels: 4.0 to 5.9 ppm, total PCBs in the rubber material: 4.4 to 6.9 mg

PUF weight: 131g, PCBs levels: 10 to 16 ppm, total PCBs in PUF: 1.3 to 2.1 mg

Therefore a total amount of 5.7 to 8.6 mg of PCBs were contaminated in HVS materials.

The analysis of POPs in technical CPs used for this rubber revealed a contamination level of 140 to 190 ppm of PCBs and 6.8 to 8.9 ppm of HCBz in which is in the order of magnitude to explain the contamination level in the rubber. Furthermore the predominant homologue and congeners of PCBs (fingerprint) were similar to the PCB pattern in the rubber sample.

We recently reported high levels of SCCPs in dietary samples from Beijing⁶. It seems that the above mentioned high production and usage volumes result today in the contamination of food in China⁶. It has up to now not assessed to which extent the PCB, PCN and PCBz impurities in the chlorinated paraffins additionally contributes to the unintentionally POPs contamination of food but also the environment and possibly humans.

The results from this study suggested that unintentionally POPs contamination as impurities from technical chemicals such as CPs are serious problems for unintentional POPs inventories. especially for developing countries with low techniques and increasing production for CPs. The chlorinated aromatics in technical CPs are most likely formed by chlorination of aromatics impurities in the starting paraffin material. Considering that chlorinated paraffins are produced in the order of 1 million tonnes per year such a contamination could have large implications on total production and release of these unintentional POPs release from CP production and use.

After having proven the POPs contamination in the product the HVS were recalled by the providing company.

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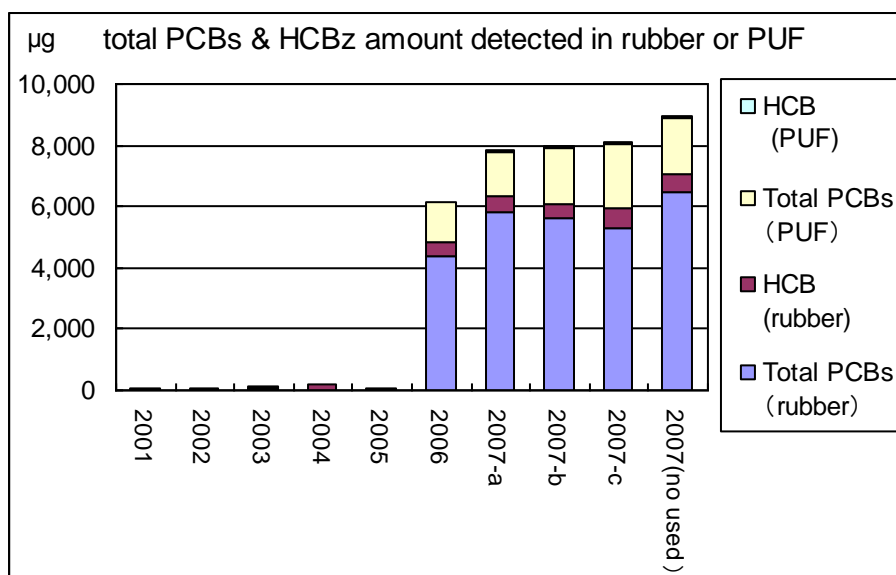


Fig.1. PCBs and HCBz amount detected in rubber & PUF materials in a time series.

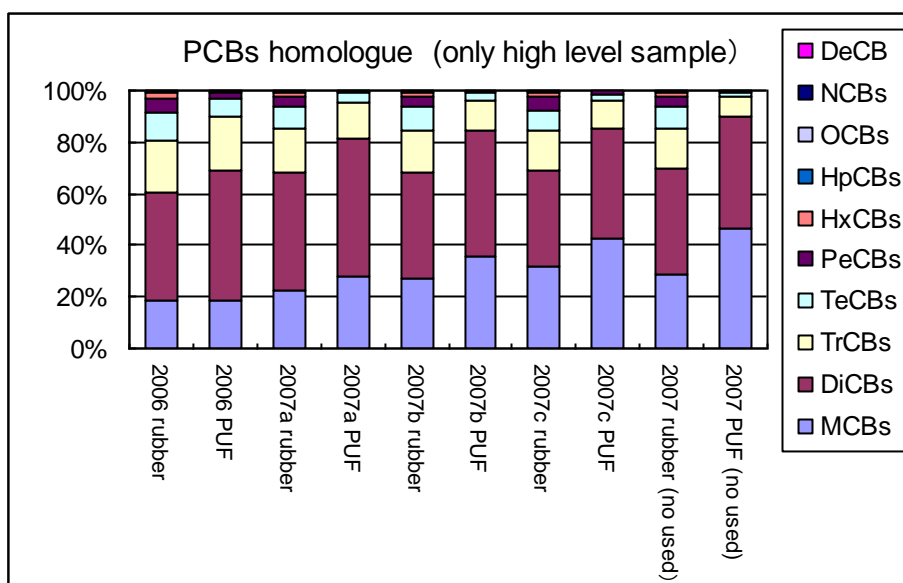


Fig.2. PCBs homologue profiles detected in rubber & PUF materials at high levels.

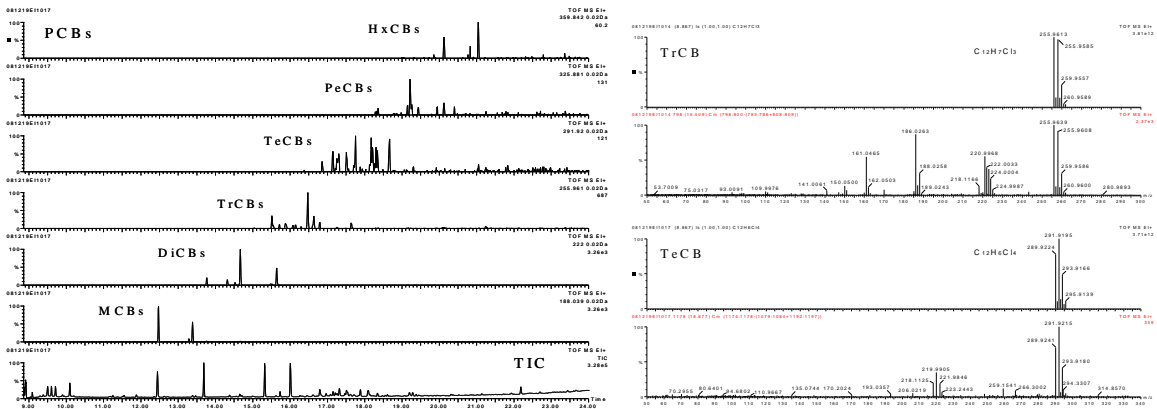


Fig.3. Exact mass chromatograms and mass spectra for PCBs detected in rubber sample including CPs additive by GC-HR-ToF-MS.

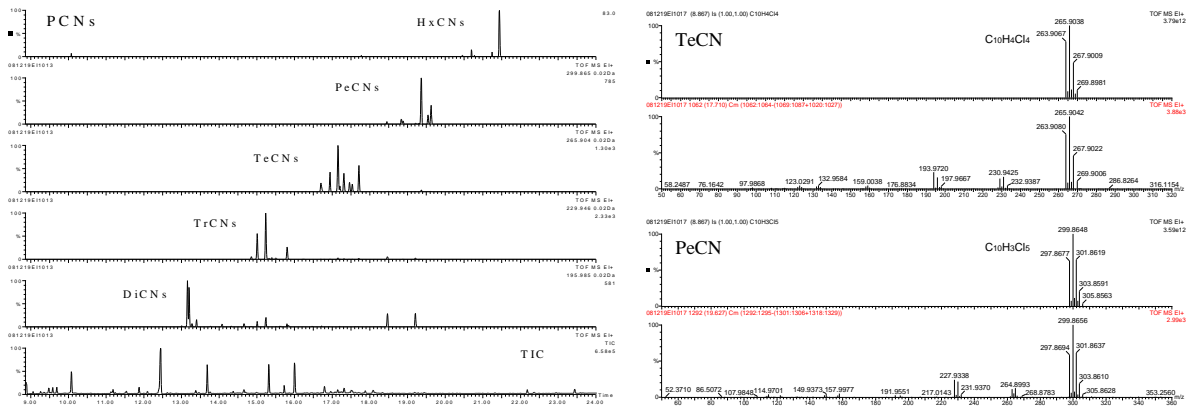


Fig.4. Exact mass chromatograms and mass spectra for PCNs detected in rubber sample including CPs additive By GC-HR-ToF-MS

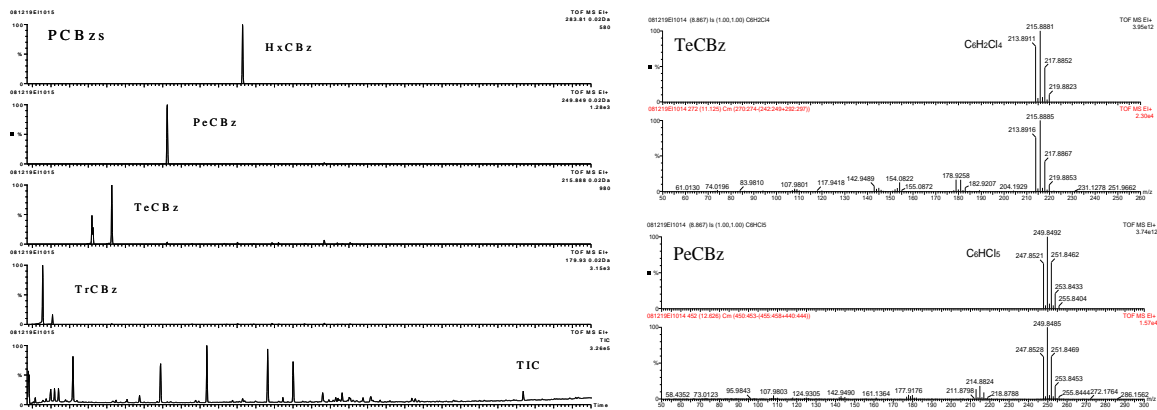


Fig.5. Exact mass chromatograms and mass spectra for PCBzs detected in rubber sample including CPs additive by GC-HR-ToF-MS.