

Possibilities of Field Experimental Photolysis of Polychlorinated Naphthalenes

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Introduction

Polychlorinated naphthalenes (PCNs) are industrial chemicals¹ which were globally popular during the period from around 1910 until the 1970s^{2,3}. PCNs have been used mainly in numerous industrial electromagnetic equipment including capacitors, transformers, switchgear, etc. Several types of technical PCN formulations were manufactured in different parts of the world¹⁻⁴, e.g., Nibren waxes from Germany, Seekay from the UK, Clonacire from France, Woskol from Poland, Halowax in the US, etc. The Halowax series were the most recognized technical PCN formulation and were manufactured from 1914 until the 1970s^{2,3} by Koppers Co. (USA), which was the major global producer. Those chemically inert and persistent compounds were also produced experimentally in Japan⁵. Traces of PCNs occur as by-products in some synthesized organochlorine compounds. They are also produced unintentionally in thermal processes such as combustion, incineration, and others³. Leakages of technical PCN formulations from electrical equipment, coupled with releases from unintentional production, have led to PCNs being widely diffused as environmental contaminants and consequently, occurrence in food and humans has been reported worldwide^{6-8,18}. Moreover, they are registered in the Stockholm Convention on Persistent Organic Pollutants (POPs) as listed chemicals in Annex A or C⁹. PCNs can contain from one to eight chlorine atoms per naphthalene molecule and form a complex mixture of 75 PCN congeners. Among PCN congeners, predominant congeners found in technical formulations (fingerprints) have been frequently used to elucidate emission sources, and several PCNs are known to contribute to dioxin-like activity¹⁻³. Therefore, an evaluation of the profile of PCN congeners is important to perform both fingerprint and risk assessments.

On the other hand, an insight into possible atmospheric fate and some photolytic characteristics of several POPs has been obtained recently in controlled experiments performed in the high mountain environment, and from a study of real water media samples collected from the Himalayan region of the Eastern Tibetan Plateau. The experiments performed in vitro and the study of glacial samples from a region of the peak of Minya Konka (Mt. Gongga) from the Eastern Tibetan Plateau showed sunlight induced degradation by several perfluoroalkyl substances (PFASs) containing PFCAs (perfluorocarboxylic acids) and PFSA (perfluorosulfonic acids). Exposure to sunshine resulted in degradation (probably via de-alkylation) of longer chain compounds to form shorter chain compounds or complete degradation of some PFASs^{10,11}. Similarly, Halowax PCN mixtures when exposed to sunlight in a mountain environment (at the top of the Mt. Mauna Kea in Hawaii, USA)¹² or an environment of other type (campus of the Yuxi Normal University in Yuxi, Yunnan Province, China)¹³ undergo widespread photolytic degradation but some hexachlorinated naphthalenes, i.e. 1,2,3,4,6,7-HxCN/1,2,3,5,6,7-HxCN (PCN #66/67), remain unaffected.

The aim of this study was to investigate possible field photo-degradation by sunlight of highly chlorinated naphthalenes dissolved in water, such as hepta-, and octachlorinated naphthalenes (HpCNs and OCN).

Materials and methods

The sites selected for the field experiments were a campus of the National Research Center for Geoanalysis (NRCGA), Beijing, China, the Ruogai in Sichuan Province (China) and additionally, Rajasthan Province (India). The experiment in Beijing was carried out for 85 days (20 September to 14 December, 2016) at an elevation of 55 m above sea level, experiment in Sichuan Province was carried on for 416 days (August 19 to September 9, 2017) at an elevation of 3445 m, and the experiment in Rajasthan Province was carried on for 314 days (June 29 to May 9, 2017) at an elevation of 320 m. Halowax 1051 (content: 1,2,3,4,5,6,7-HpCN (PCN #73) 5 %, 1,2,3,4,5,6,8-HpCN (PCN #74) 20 %, 1,2,3,4,5,6,7,8-OCN (PCN #75) 75 %; AccuStandard, USA) was dissolved in methanol, and then diluted with Milli-Q water. Methanol amount in the test solutions was at a concentrations of around 1 %. For Chinese sites, a p,p'-DDT (Sigma-Aldrich Japan) standard was also dissolved in a mixture of methanol and acetone, and then diluted with Milli-Q water (methanol and acetone amounts in the

test solutions was around 1 % each). A 3 ml aliquot of these solutions was sealed in three Quartz tubes. One solution was randomly selected as a control and kept under darkness at $-20\text{ }^{\circ}\text{C}$ immediately after preparation. The other tubes were transported under darkness within 2 days from preparation to the sampling locations. During the solar irradiation, the test tubes were kept in a clear polyethylene container without a top cover. The initial concentration of each of the studied compounds was approximately $1\text{ }\mu\text{g mL}^{-1}$. After the photolysis experiments, the compounds were extracted with *n*-hexane and separated by capillary gas chromatography coupled to quadrupole mass spectrometry with SIM (selected ion monitoring) /Scan mode (GC/MS, Agilent Technologies 6890 GC and 5973 MS, USA)^{12,13}. Column oven temperature was programmed from $110\text{ }^{\circ}\text{C}$ (0.5 min) to $160\text{ }^{\circ}\text{C}$ at a rate of $20\text{ }^{\circ}\text{C min}^{-1}$, and to $225\text{ }^{\circ}\text{C}$ at a rate of $1\text{ }^{\circ}\text{C min}^{-1}$, with a final hold time of 42 min (total run time = 110 min). The injection was performed on-column with the inlet temperature programmed at oven track mode with constant flow. Helium was used as the carrier gas. The quadrupole mass spectrometer was scanned from *m/z* 50 to 420 using EI ionization.

After irradiation, an aliquot of the solutions was also monitored for the chlorine anion, using ion chromatography. An ion chromatograph (IC, Thermo Scientific/Dionex DX-320, USA) connected to Dionex IonPac AS12A separator column and IonPac AG12A guard column was used¹⁴. The eluent was a mixture solution of sodium carbonate (2.7 mmol) and sodium bicarbonate (0.3 mmol), at a flow rate of 1.5 mL min^{-1} . The regenerant was sulfuric acid (10 mmol). Measurement time was 15 min. A 100- μL portion of representative prepared solutions was injected in chemical suppression mode.

Results and discussion:

The extracted ion chromatograms of stock and exposed Halowax 1051 solutions showed that the abundances of octachloronaphthalene (OCN) decreased significantly after the field experiments except for the experiment in Beijing (Figure 1). This observation is similar to a photolysis study using UV ramps on OCN in hexane solutions reported by Keum¹⁵. OCN in the sunlight exposed solutions was depleted at a degradation rate of over 80 % in experiments in Sichuan Province (China) and Rajasthan Province (India). This behavior might be linked to exposure periods and geographical dependence. The number of days of exposure are Beijing 85 days; Sichuan 416 days; Rajasthan 314 days. The differences in elevations are also significant (Sichuan Province, China (3445 m) and Rajasthan Province, India (320 m)), but considerably more so, at Beijing, China (55 m). The Beijing site therefore had the lowest exposure period, as well as the lowest elevation.

As shown in Figure 2, the total concentrations of PCNs #73, #74, and #75 in exposed solutions decreased relative to the stock solution. This is comparable to previous studies in Mt. Mauna Kea and Yunnan Province using Halowax mixture, where total PCN concentrations decreased due to solar irradiation. These observations demonstrate the potential for the most highly chlorinated PCNs to undergo photolytic degradation.

Interestingly, the relative concentration of PCN #73 (relative to PCNs# 74 and 75), which shows dioxin-like toxicity, increased in exposed solutions, while the relative concentration of PCN #74 decreased. In other word, PCN #73 was more resistant to solar irradiation, compared to PCN #74. The relative increase of PCN #73 in exposed solutions could also be considered as a degradation product arising from PCN #75. This observation is comparable to that report by Keum¹⁵ where the toxic equivalents from PCNs increased tentatively after solar irradiation. .

None of the known degradation products such as naphthalene and lower chlorinated naphthalenes were found in these experiments on Halowax 1051 and it may be necessary to use more sensitive high-resolution mass spectrometry to identify other degradation products. Results from previous studies on the Hawaiian¹² and Yunnan¹³ experiments using Halowax mixture, show that some congeners (PCNs #66/67, which also contribute to dioxin-like activity) survive to a greater extent. Thus this resistance to photolytic degradation may be linked to the relationship between the energy of ultraviolet rays from sunlight in each region and the profiles of the exposed PCN congeners. This would only be confirmed from many more results obtained from similar irradiation experiments on PCN mixtures. Similar field experiments will be conducted as part of future work and additionally, the effects of accelerated weathering tests using xenon arc and/or sunshine carbon arc ramps will be investigated.

No significant detected peaks for the chlorine anion were found in the IC chromatogram of the exposed solutions. Finally, in the experiment performed in the sites at Beijing and Sichuan Province, p,p'-DDT

disappeared almost entirely from the exposed solution (data not shown). This behavior resembled the previous results in Hawaiian, Yunnan conditions¹⁶, and those reported by Chu¹⁷.

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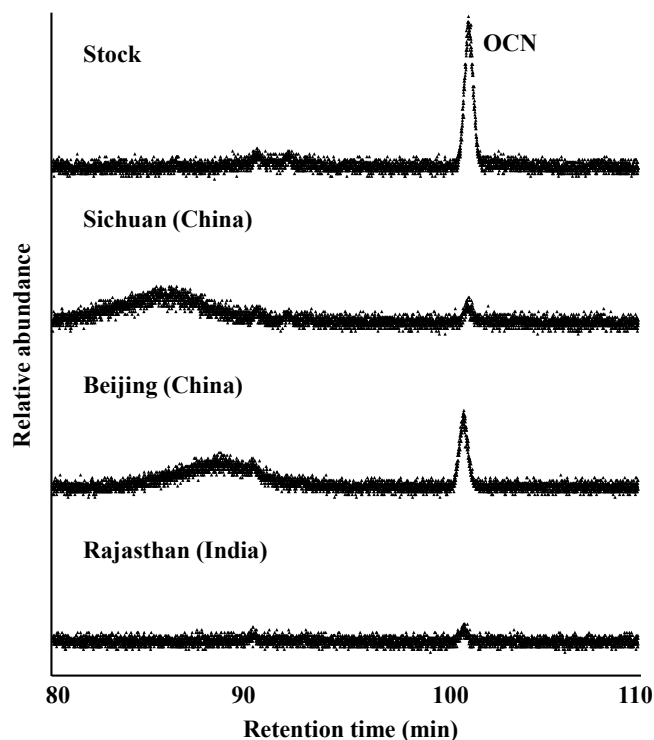


Figure 1: Extracted ion chromatograms of octachlorinated naphthalene (OCN) in stock and exposed solutions (Sichuan Province and Beijing, China and Rajasthan, India)

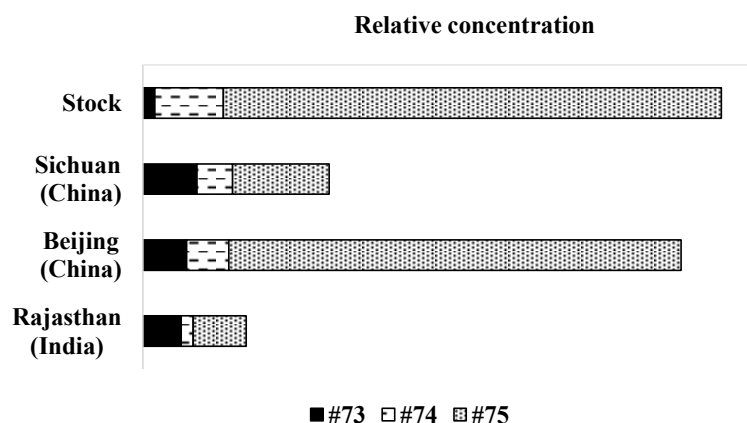


Figure 2: Relative concentrations of hepta-, and octachlorinated naphthalene (HpCN and OCN) congeners in stock and exposed solutions (Sichuan Province and Beijing, China and Rajasthan, India). PCN congeners #73, #74, and #75 represent 1,2,3,4,5,6,7-HpCN, 1,2,3,4,5,6,8-HpCN, and 1,2,3,4,5,6,7,8-OCN, respectively.