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PRE-FEASIBILITY STUDY ON ENVIRONMENTAL PHOTOLYSIS OF CHLORONAPHTHALENES

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Introduction

Chloronaphthalenes (CNs) are primary industrial chemicals¹ which were globally popular during the period from around 1910 until the 1970s^{2,3}. CNs have been mainly used in numerous industrial applications such as the electromagnetic equipment including capacitors, transformers, cables, insulating materials etc. The Halowax series are the most famous technical CN formulations manufactured in the past by Koppers Co. (USA), which was the major global producer. Those chemically inert and persistent compounds were also manufactured in Europe and experimentally in Japan^{1–5}. Moreover, they are unintentionally synthesized in thermal reactions. Because of leakages from the technical CN formulations and the equipment, and also due to unintentional formation, the CNs were widely diffused as environmental contaminants and has been reported in foods and humans worldwide^{6–8}. Recently, CNs are registered in the Stockholm Convention on Persistent Organic Pollutants (POPs) as listed chemicals in Annex B9.

CNs can contain from one to eight chlorine atoms per naphthalene molecule and form a complex mixture of 75 CN congeners. Among the CN congeners, predominant compounds found in technical formulations (fingerprints) have been frequently used to elucidate emission sources, and several CNs have contributed as dioxin-like active^{1–3}. Therefore, evaluation of CN congener profiles is important to perform both fingerprints and risk assessments. On the other hand, CNs can undergo photolysis and/or dechlorination^{10–13} by sunlight, thus, reliable evaluation become difficult. OctaCN was degraded by UV and from Tetra- to HpCNs were formed¹¹. In our previous report¹⁴, environmental photolysis of CNs was confirmed, though environmental data on possible photolysis of CNs are still unknown. Moreover, independent evaluation of many closely eluting CN congeners and such as PeCNs (#52/#60; 1,2,3,5,7-PeCN/1,2,4,6,7-PeCN) and HxCNs (#66/#67; 1,2,3,4,6,7-HxCN/1,2,3,5,6,7-HxCN) is not well understood. In this study a mixture of the Halowax 1000, 1001, 1014 and 1051 formulations (1:1:1:1) dissolved in methanol was diluted with water and exposed to sunlight.

Materials and methods

The locations selected for the field experiments were such as the campus of the Yuxi Normal University, Yuxi, Yunnan (China) and Mt. Mauna Kea in Hawaii Island (USA). The experiments were carried out for 149 days (June–November 2015) at altitude of 1700 m in Yunnan and for 106 days (September–December 2010) at altitude of 4200 m in Hawaii¹⁵. Four technical CN formulations (Halowaxes 1000, 1001, 1014, and 1051 in methanol, AccuStandard, USA) were mixed and used for the Yunnan location. Details on preparation of the samples exposed in the Hawaiian location were described in previous report¹⁴. Aliquots of each of the Halowax sample solutions (4 x 0.1 mL) were combined and diluted with Milli-Q water (ca 10 mL) in polypropylene tubes. Methanol content of the Halowax mixture prepared was approximately 4 %. Test solutions were then divided into three tubes each containing 3 mL. The Pyrex and quartz glasses (5 mL) with butyl rubber septum caps were used. Tubes were tightly capped. One of the three tubes (containing Halowax mixture) was kept at –20 °C under darkness immediately after preparation (this set served as a control). The remaining two Pyrex and quartz glass tubes were transported to the Yuxi, under darkness, within 2 days of preparation. During the solar irradiation, the test tubes were kept on a clear polyethylene container without cover. Initial concentrations of the Halowaxes in test tubes were approximately 1 µg/mL. Test solutions from the photolysis experiments were extracted with n-hexane and analyzed using gas chromatograph (GC) interfaced with a quadrupole mass spectrometer (GC-MS, Agilent Technologies 6890 GC and 5973 MS, USA). A GC column used was Rt-β DEXcst (30 m x 0.25 mm i.d., 0.25 µm film thickness, Restek, USA). Hence, a closely eluting CN congeners together with PeCNs (#52/#60) and HxCNs (#66/#67) could be satisfactory separated¹⁶. Column oven temperature was programmed from 110 °C (0.5 min) to 160 °C at a rate of 20 °C/min, and to 225 °C at a rate of 1 °C/min, with a final hold time of 42 min, and total run time was 110 min. Injection was performed by on-column injection mode, and inlet temperature was programmed at oven

track mode with constant flow. Helium was used as the carrier gas. Quadrupole MS was operated in SIM mode using EI ionization. Peak identification was supported by referring to published data^{4,6,7,16}.

Results and discussion

Homologues

At first, the total ion chromatograms of an intact and exposed Halowax mixture samples prepared in Pyrex or quartz glass were compared (Fig. 1). CNs in the exposed Halowax mixture samples disappeared almost entirely after the photolysis experiments. For CN homologue profiles, our intact Halowax mixture sample originally contained all the CN homologues (1.0 % MoCNs, 0.4 % DiCNs, 16 % TriCNs, 29 % TetraCNs, 21 % PeCNs, 18 % HxCNs, 3.6 % HpCNs, and 11 % OctaCN at basis of a peak area percentages of CNs relative to the total peak area). Many of CNs diminished in the test mixtures because of solar irradiation. Detected in irradiated mixture were CN homologues such as MoCNs, HxCNs, and HpCNs. A cause for decomposition of some CNs and generation of other CNs might be because formation of the naphthalene radical anion, derived from the reduction of the initial dechlorination product (naphthalene), as a mediator¹⁷. These residual abundances were respectively between 0.30 and 0.48 for MoCNs, 0.06 and 0.22 for HxCNs, and 0.06 and 0.10 for HpCNs based on the total peak area for each homologue. This circumstance was because direct exposure to UV11 on the field experiments. Similarly to the Hawaiian samples prepared in Pyrex glass tube¹⁴, many CN homologues disappeared due to solar irradiation. Residual abundances of CNs in quartz glass were greater than that in Pyrex glass (e.g. in the case of HxCNs was 0.20 to 0.22 for quartz glass and 0.06 to 0.14 for Pyrex glass). A vice versa tendency was noted in an experiment with perfluorinated compounds¹⁵.

Isomers

The residual CN isomers (retention times around 55 min and 75 min on Fig. 1) detected in the Halowax mixture after the sunlight exposure were identified properly. Interestingly, in products of solar irradiation identified were HxCNs #66/#67 and HpCN #73 (1,2,3,4,5,6,7-HpCN), which are dioxin-like active¹⁻³. In previous solar experiment, the results were similar as observed in this study. The solar irradiation of a highly chlorinated Halowax 1051 (composed mainly of HpCNs and OctaCN) produced HxCNs #66/#67 due to photodegradation of HpCNs and OctaCN¹⁴. An intact Halowax 1051 has no HxCNs #66/#67 in principle. On the other hand, HpCN #73 survived in both studies despite of a disappearance of HpCN #74 (1,2,3,4,5,6,8-HpCN). The residual abundances of HxCNs #66/#67 when assessed from the total peak area increased from 2.1 to 8.0-fold. Residual abundance was greater for HxCN #66 than HxCN #67 both in the Pyrex and quartz glasses experiments (HxCN #66: 2.6 to 6.8 for Pyrex glass and 9.8 to 11 for quartz glass; HxCN #67: 1.8 to 4.2 for Pyrex glass and 5.9 to 6.7 for quartz glass). Obviously, there was certain relationship between structure of the CN isomers and solar permeability of the glass materials, which is still unclear. In near future, a variability of residual abundances over time will be studied.

Fig. 1. Total ion chromatograms of intact and exposure Halowax mixture samples prepared in Pyrex and quartz glasses.

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