

PRELIMINARY EVALUATION OF ENVIRONMENTAL PHOTODEGRADATION OF CHLORONAPHTHALENES BY CONGENER-SPECIFIC DETERMINATIONS WITH COMPREHENSIVE TWO-DIMENSIONAL GC/QMS

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Introduction

Chloronaphthalenes (CNs) are primary industrial chemicals¹ which became popular worldwide in 1910s–1970s^{2,3}. CNs have been mainly used in electromagnetic equipment including capacitors, transformers, and in cables. Halowax is a trade name for 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 by several companies in Europe and experimentally in Japan^{1–5}. Moreover, they are unintentionally synthesized in thermal reactions (manufacture of chlorobiphenyls, waste combustion). Because of leakages from the technical CN formulations and equipments and also due to unintentional production, the CNs became diffused globally and has been reported in food and humans worldwide^{6–8}.

Predominant congeners found among 75 possible CNs in technical formulations (fingerprints) have been frequently used to elucidate emission sources, and several CNs have been recognized as dioxin-like active. Toxicity of dioxin-like active CNs depends on their structure and they are generally less potent compared to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin^{1–3}. Therefore, evaluating profiles of CN congeners is essential to perform both fingerprints and risk assessments. However, CNs can undergo photodegradation and/or dechlorination^{9–12} by sunlight and therefore reliable evaluation of profiles can become difficult. OctaCN in *n*-hexane was degraded by UV and from tetra- to heptaCNs were formed¹⁰. Environmental data on possible photodegradation of CNs are still unknown. Moreover, independent evaluation of closely eluting CN congeners including pentaCNs (#52/#60) and hexaCNs (#66/#67) is not well understood. In this study, several Halowax products were selected to investigate their susceptibility to photodegradation by sunlight and results are described considering both the photoproducts and toxicity aspect.

Materials and methods

The location selected for the field experiments was Mt. Mauna Kea in Hawaii Island (USA). Experiment was carried out for 106 days at altitude of 4200 m, from September 10, 2010 to December 24, 2010¹³. Three technical CN formulations (Halowaxes 1000, 1014, and 1051 in methanol, Accu Standard, USA) were individually used. Each of 0.1 mL of Halowax methanol solution was diluted in 10 mL of Milli-Q water taken in polypropylene tubes. Methanol content in final test solution was approximately 1%. Test solutions were then divided into three tubes each containing 3 mL. The test tubes were made of Pyrex glass (5 mL) with butyl rubber septum cap and were tightly capped during the solar irradiation. One of the three tubes (containing each Halowax individually) was kept at –20 °C under darkness immediately after preparation (this set served as a control). The remaining two Pyrex tubes were transported to the top of Mt. Mauna Kea, under darkness, within 2 days of preparation. During the solar irradiation, test tubes were kept on a clear polyethylene container with no cover. Initial concentrations of Halowaxes in test tubes were approximately 1 µg/mL. Test solutions from the photodegradation experiments were extracted with *n*-hexane and analyzed by the comprehensive two-dimensional GC with the aid of a quadrupole mass spectrometer (GC × GC/qMS) as described elsewhere¹⁴. This enabled for congener-specific (total separation of CN compounds without co-elution) examination of Halowaxes exposed to sunlight and unexposed control material and to assess photolysis rates (reported as percentage reduction). The test solutions were also analyzed for the photoproducts. For quality assurance of GC × GC/qMS determination, relative measurement of standard deviations of CN congeners by the peak areas on repeatability of measurements were acceptable (approximately 13%) in the original solutions. Calibration curves drawn based on the peak areas of CN congeners by GC × GC/qMS were linear with values of correlation coefficient > 0.989.

Results and discussion

CNs in Halowaxes after photodegradation. The Halowax 1000 test solution originally contained from mono- to triCNs, and volume of that CN homologue classes decreased in exposed solutions down to 26%–43% of their initial content (Table). Although from tetra- to heptaCNs were compounds of original solution of Halowax 1014, only the penta- and hexaCNs were found in the sunlight exposed solutions. Moreover, volume of those CN homologue classes in exposed Halowax 1014 diminished to 0%–2% of their original concentration. In case of Halowax 1051, both octaCN and heptaCNs were constituents of original solution and apart from decreased amount of heptaCN #73 the photoproducts such as pentaCNs and hexaCNs in exposed solutions were rather abundant constituents (Figure). Furthermore, octaCN vanished in exposed Halowax 1051 and also “evaporated” heptaCN #74, while #73 survived at highly reduced volume (down to 13%). If taken into account the total CNs volume of the tested technical CN formulations, the lowest chlorinated mono- to triCNs constituents of Halowax 1000 “resisted” more favorably - to some degree, the sunlight exposition when compared to compounds of greater molecular mass and chlorine content that are major constituents contained in Halowaxes 1014 and 1051. This result can be explained based on the difference in the values of extinction coefficients of CNs⁹. And, summing up, the photodegradation/dechlorination of CNs could be observed for the technical CN formulations test solutions exposed to the sunlight at the altitude of 4200 m above sea level of Hawaiians at the Mt. Mauna Kea. This altitude is similar to the unique vast space of the World around the region of Tibet (by altitude also of Bhutan and Nepal), where in the yak meat tissues from Wolong area, the CNs from tri- to octaCN were found¹⁵.

CNs homologue classes' profiles of original and sunlighted Halowaxes. For each mono- to triCN homologue class of Halowax 1000, each volume in the test solution decreased down to 18%–44% of original content (Figure). In case of original Halowax 1014, pentaCN and hexaCN compounds were minor CN constituents, and for exposed solutions pentaCN and hexaCN homologues decreased down to 40%–65% and 18%–20%, respectively (Figure). In addition, the amount of heptaCN homologue classes in Halowax 1051 decreased in exposed solutions down to 31%. It seems that many CN congeners when sunlighted (vapor phase) could be partly degraded and individual rate of photodegradation varies depending on CN structure as CNs as the extinction coefficients⁹ of individual CNs vary. Certainly the higher chlorinated CNs if exposed to a high intensity sunlight at altitude > 4000 m above sea level are much more effectively degraded (by the direct absorption of electromagnetic energy of sun and of sunlight induced ions and radicals) compared to less chlorinated and the explanation to this phenomenon is the relatively greater extinction of a more molecular mass halogenated moieties. In a model study, hydroxyl (OH⁺) radicals were considered as the most potent destructors of CNs in atmosphere and more chlorinated congeners were considered more stable compared to less chlorinated ones¹⁶, and this is not confirmed by empirical data in this study.

Keum et al. reported that tetraCN #47, #52, #60, hexaCN #71, and hexaCN #72 were the predominant congeners formed from photodegraded octaCN (in *n*-hexane) exposed to 300 nm light¹⁰, and Jarnberg et al. reported that tetraCN #33, tetraCN #34, #52, and #60 were the predominant congeners of photodegradation by sunlight of the Halowax 1014 (in methanol)¹². For #52 and #60, our results may resemble both reported data in spite of variances in test solutions prepared with Milli-Q water.

Toxic equivalents. Toxic repercussions due to photodegradation on CNs are due to both decrease and increase of dioxin-like potency of contaminated medium. Certainly photodegradation of Halowax 1051 constituents increases the toxicity of the mixture formed due to emergence of #52, #60, #66 and #67, and which are dioxin-like active CN congeners³. And within the same time photodegradation reduced dioxin-like activity of Halowaxes 1000 and 1014

Acknowledgements

We thank the support from local team of the International Telescopes at Mt. Mauna Kea. Dr. S Taniyasu, Ms. E Yamazaki, Dr. HB Moon, and Ms. HK Lee are gratefully acknowledged for useful comments in this study. This work was supported by JSPS KAKENHI [23710030, Grant-in-Aid for Young Scientists (B)].

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Table Percentages of detected homologues after photodegradation relative to corresponding homologue in the original solutions on Halowaxes

	MonoCNs	DiCNs	TriCNs	TetraCNs	PentaCNs	HexaCNs	HeptaCNs	OctaCN
Halowax 1000	42.74	26.29	29.49					
Halowax 1014				0.00	3.69	0.71	0.00	
Halowax 1051							12.66	0.00

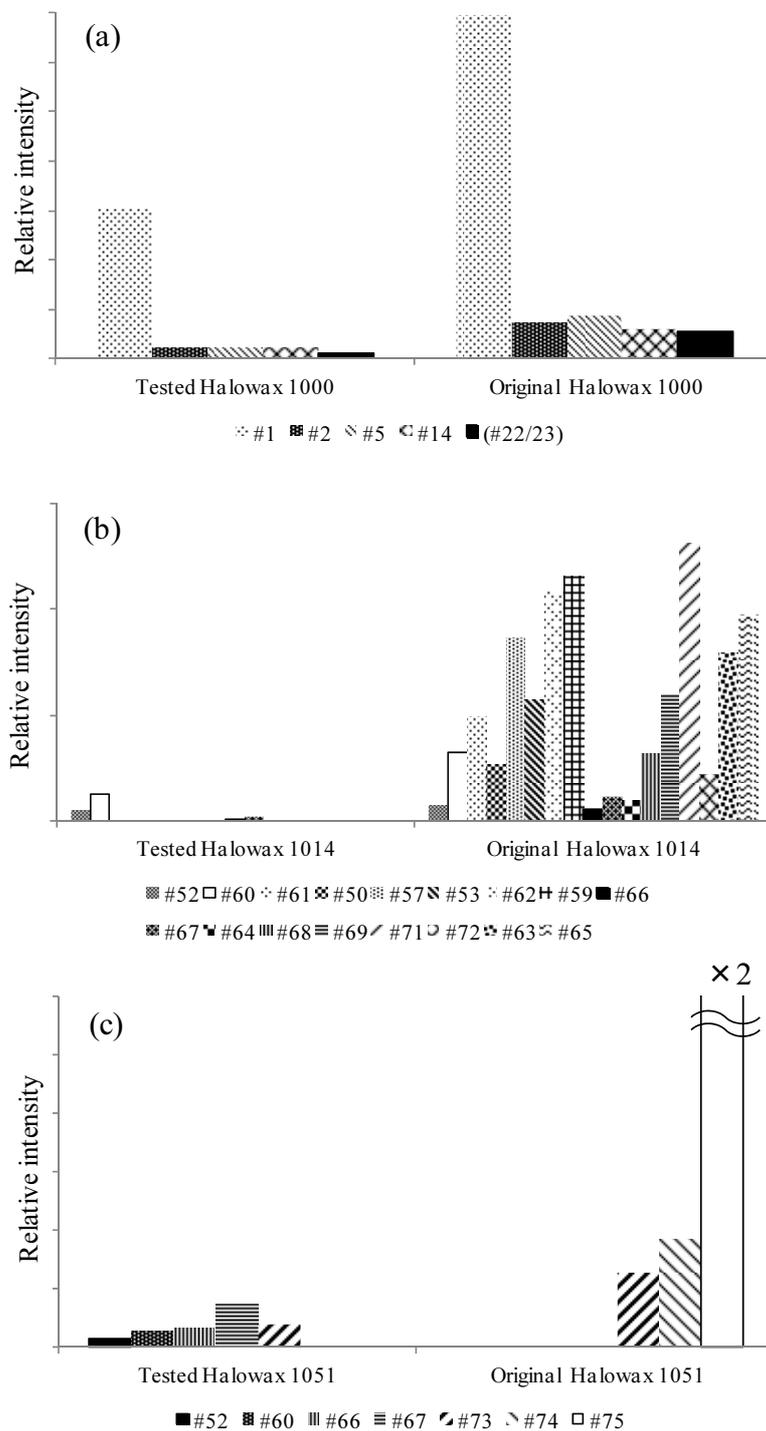


Figure Profiles of CN congeners in the original Halowaxes and in Halowaxes tested on photodegradation (a, Halowax 1000; b, Halowax 1014; c, Halowax 1051). TetraCNs and heptaCNs were not contained in profiles on Halowax 1014 because of no detection in the Halowax tested.