CHLOROBIPHENYLS IN CHLORONAPHTHALENE HALOWAX FORMULATIONS

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Introduction

Chloronaphthalenes (CNs) and chlorobiphenyls (CBs) are an example of man-made chemicals manufactured in the 20_{th} century in large quantities which somewhat exceeded, respectively, 150 and 1500 thousand tons [1-3]. These compounds for decades of years become popular industrial chemicals and further ubiquitous and persistent environmental contaminants, which accumulate and biomagnify in human and wildlife food-chain [3,4]. Technical CN and CB formulations contain many biologically highly active constituents, which are responsible also for dioxin-like effects [5-10]. Technical chlorobiphenyl formulations such as the Aroclor, Kanechlor or Delor series and other CB mixtures are known as contaminated with by-side CNs. They were also identified as next to original CN mixtures source of environmental diffusion of dioxin-like CNs [11-14]. Nevertheless, nothing is known if technical CN formulations can contain by-side CBs and could contribute to environmental diffusion of those compounds. Data on concentration and composition of by-side CBs in the Halowax chloronaphthalene formulations manufactured in the USA and including all 209 congeners are presented in this report.

Materials and methods

All 209 chlorobiphenyl congeners in Halowax mixtures were identified and quantified in technical Halowax 1000, 1001, 1013, 1014, 1031, 1051 and 1099 formulations manufactured by the Foxboro. MA, USA, using a set of CB standard solutions (OIL-CVS-B; PCB-CVS-A10-Set 3), isotopically labeled $^{13}C_{12}$ chlorobiphenyl clean-up spike solution (MBP-MXP and PCB-LCS-A200), and syringe spike solution (PCB-IS-B100), which all originated from the Wellington Labs. Inc., Ontario, Canada. All solvents and reagents used were of dioxin analysis grade and purchased by the Kanto Chemicals (Tokyo, Japan).

Three trials with different strategies of the Halowax sample preparation, clean-up and sample extract enrichment were performed to determine separately and precisely the bulk of CBs, 197 congeners other than twelve planar non- and mono-*ortho* CBs, non-ortho CBs and mono-*ortho* CBs. In each case the CNs sample matrix was spiked with clean-up standard

solution containing isotopically labeled $^{13}C_{12}$ congeners of CB and also with syringe spike standard solution, adequately, before or after being subjected to separation and quantification step using HRGC/HRMS the samples were cleaned-up and fractionated, respectively, using concentrated sulfuric acid, silica gel, alumina and/or a porous graphitic carbon column (Hypercarb, Hypersil, USA). The details of the procedures drawn and also the HRGC-HRMS separation, detection, identification and quantification are presented elsewhere [15].

Results and Discussion

202 chlorobiphenyls with 109 single-resolved and 93 co-eluting congeners, which represented from mono- to deca-CB were quantified as by-side impurities in all seven Halowax formulations examined. PCB IUPAC Nos. 104, 145, 159, 169, 184, 186 and 188 were undetected (< 0.05 - < 0.7 ng/g). A degree of chlorination of the CN formulations examined was 27, 35, 49, 51, 54, 59 and 70 %, respectively, for the Halowax 1031, 1000, 1001, 1099, 1013, 1014 and 1051, while their CBs content was 640000, 460000, 220, 450, 1200, 3200 and 2700 ng/g. In term of absolute concentration values lower chlorinated CN formulas, Halowax 1031 and 1000 were more contaminated with CBs when compared to the Halowaxes chlorinated at 49 % level or higher. Accordingly, Halowax 1031 and 1000 were quantitatively also richest in a particular CB homologue groups when compared to more chlorinated mixtures and, in descending order, their homologue group composition followed from mono- through di-, tri-, tetra-, penta-, hexa-, > hepta-, octa- > nona- to deca-CB (Fig. 1). The profile of CB homologue groups of the Halowaxes varied and followed somehow a degree of chlorination of the parent CN mixture. For Halowax 1031 and 1000, a decreasing trend in proportion from mono- to deca-CB was evident, while for Halowax 1001, 1099, 1013, 1014 and 1051 the relative proportions between the CB homologue groups varied somehow. Evidently, content of lower chlorinated mono- and di-CBs highly decreased while in parallel steadily increased of tri- to octa-CBs, which become increasingly dominating homologue groups for higher chlorinated mixtures, respectively.

All differences and similarities in quantitative and qualitative composition of by-side CBs in seven types of Halowax formulations are well reflected in their compositional profiles presented at Fig.2. The number of chlorobiphenyl congeners quantified in the Halowax formulations in this study is greater, and especially in Halowax 1031 and Halowax 1000, when compared to their abundance in some chemicals of other type and including original CB formulations like the Aroclors, Clophens, Kanechlors, Delors, Sovol or Chlorofen.

Amongst of non-*ortho* substituted chlorobiphenyls only 3,3', 4,4'-TeCB (No. 77) was found in all the Halowax formulations, while 3,4,4', 5-TeCB (No. 81) was quantified only in lower chlorinated Halowaxes 1031 and 1000, and next also relatively rarely occurring was 3,3', 4,4', 5-PeCB (No. 126), while 3,3', 4,4', 5,5'-HxCB (No. 169) was absent at amount greater than the method limit of quantification of 0.05 ng/g. The Halowaxes 1000 and 1014 contained all eight mono-*ortho* substituted chlorobiphenyls and next most abundant in those constituents were Halowax 1031 and 1013 with lacking 2,3,3', 4,4', 5,5'-HpCB (< 0.9 ng/g; No. 189) and Halowax 1051 with lacking 2,3,4,4', 5,5'-PeCB (< 0.6 ng/g; No. 114). TEQ values of copalanar PCBs was 0.23ng-TEQ/g (Halowax 1031), 0.67ng-TEQ/g (Halowax 1000), 1.3ng-TEQ/g (Halowax 1001), 0.050ng-TEQ/g (Halowax 1013), 0.0086ng-TEQ/g

(Halowax 1099), 0.13ng-TEQ/g (Halowax 1014), and 0.021ng-TEQ/g (Halowax 1051), respsctively.

It can be assumed, that a specific composition of by-side CBs found in Halowaxes when compared to an original CB formulations is due to presence of biphenyl as impurity in technical naphthalene used as well as differences in temperature regime applied during manufacture of both groups of chemicals.

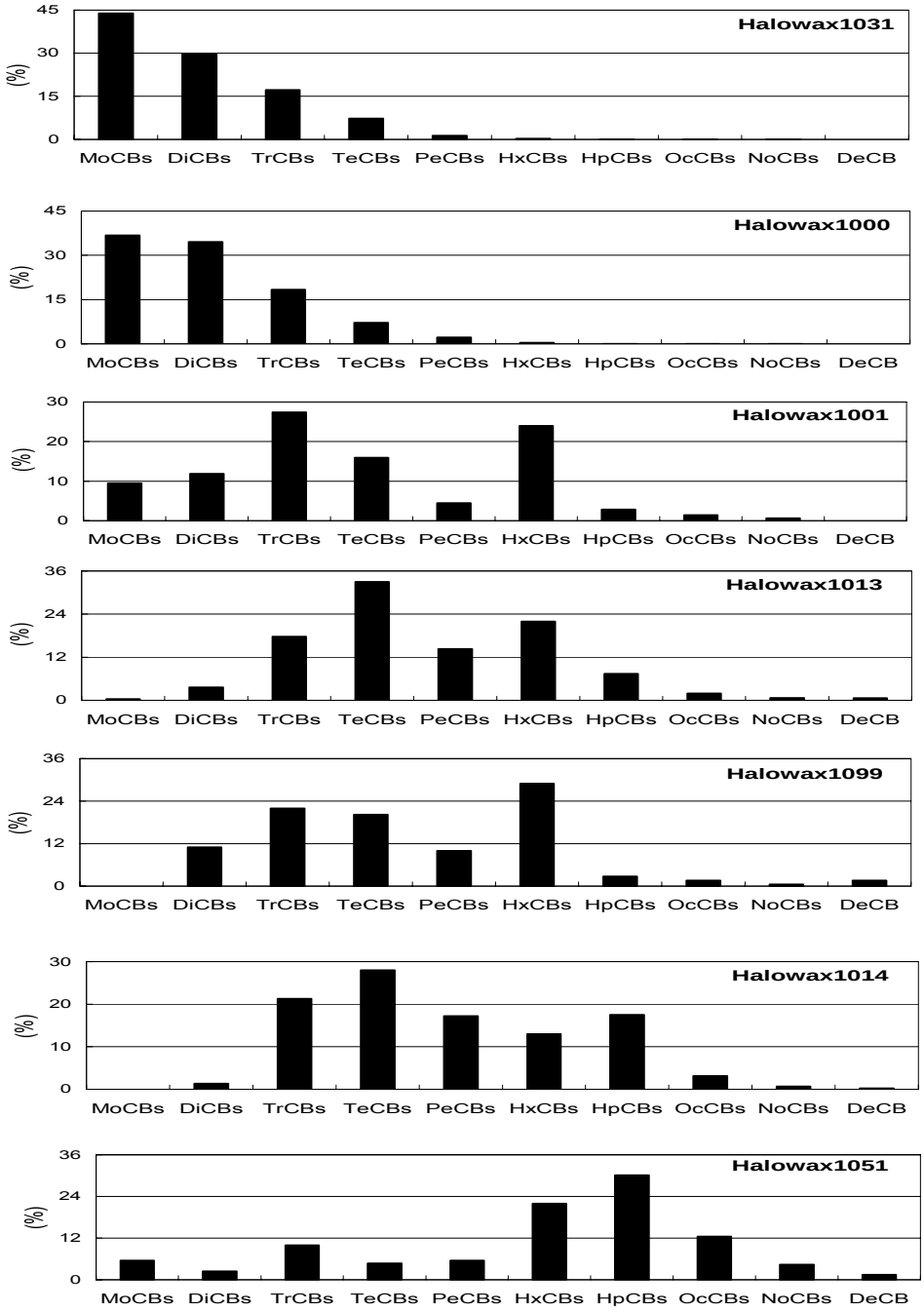

Figure 1 Chlorobiphenyl homologue group profiles (%) of the Halowax formulations.

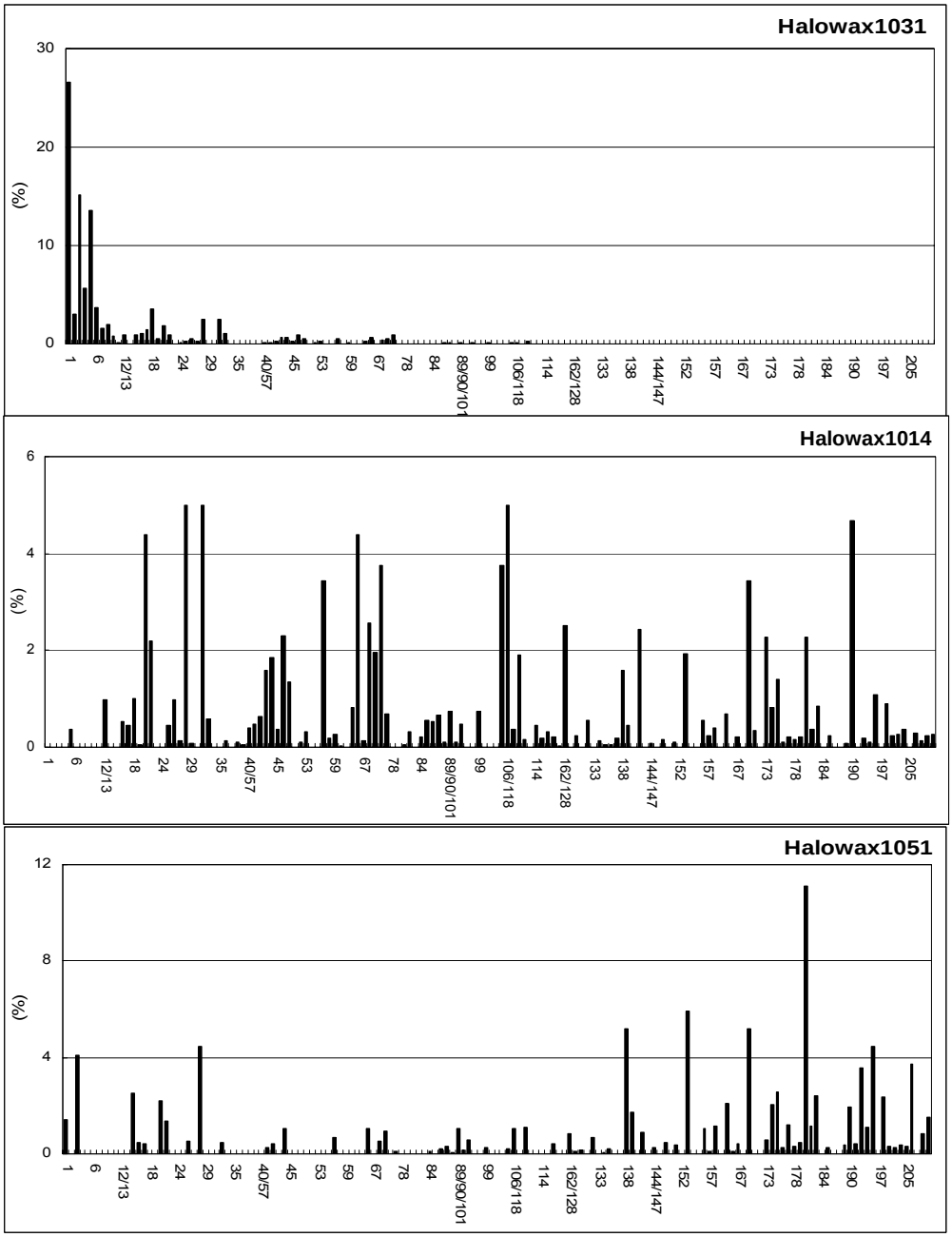

Fig.2. Chlorobiphenyl congener profiles (%) of the Halowax 1031, 1014 and 1051.

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