

PATTERN OF POLYCHLORINATED NAPHTHALENES IN HALOWAXES AND ON FLY ASHES

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Introduction

Polychlorinated naphthalenes, PCN ($C_{10}H_{8-x}Cl_x$ or Cl_xN , $x = 1-8$) build up a class of 75 possible congeners similar to the PCDD. Technical mixtures of PCN have mainly been used in the electrical industry e.g. as dielectric fluids and insulation materials. Furthermore they have been used as flame retardants, fungicides and pesticides - for example one of the first known chlorine-containing compounds to impregnate wood was chloronaphthalene - and also as additive in oils and plasticizers.^{1,5} Therefore, PCN are widespread and persistent industrial pollutants in the environment. In addition, they resist chemical and biological degradation and accumulate in the environment. PCN exhibit similar chemical and physical properties like polychlorinated biphenyls (PCB). Some of the isomers of PCN are known to be strongly bioaccumulating and showing dioxin-like toxic properties such as chloracne and liver damages.¹⁻⁶

The main input of PCN in the global environment is the use of technical PCN-mixtures. PCN are also found in trace amounts as by-products in technical PCB-mixtures. Other important sources are the formation of PCN during incineration processes like waste incineration (MWI) or incineration of coal in power plants and secondary processes like secondary aluminum process (SAP).^{1,3,5,7}

Methods and Materials

In our investigations we used 7 kinds of Halowaxes[®] with the labels 1000, 1001, 1013, 1014, 1031, 1051, 1099 purchased from Promochem (Wesel, Germany), fly ashes collected from electrostatic precipitators or fabric filters from municipal waste incinerators, and secondary aluminum processes. The fly ash was Soxhlet extracted with toluene after addition of ¹³C-PCB as internal standards, subjected to general clean up procedures and fractionated by liquid chromatography on alumina with hexane, dichloromethane and analyzed by GC-MS in multi-ion mode (MID).

Results and Discussion

Technical PCN-mixtures are produced by chlorination of molten naphthalene with chlorine gas in the presence of $FeCl_3$ and / or $SbCl_5$ as catalysts to desired chlorine content of the product. Depending on the Cl-content different Cl_xN homologues dominate in the technical PCN-mixtures like Halowax[®] (see Figure 1). In Halowax 1031 and 1000 with a chlorine content of 22% and 26% respectively, the isomers of Cl_1N and Cl_2N are dominant. In Halowax 1001, 1099 (50%, 52%) the Cl_3N , Cl_4N -isomers are most dominant, Cl_1N , Cl_2N , Cl_5N are less. In Halowax 1013 (56%) the Cl_3N , Cl_4N , Cl_5N are most, the Cl_1N , Cl_2N , Cl_6N are less dominant isomers. In the higher chlorinated Halowax 1014 (62%) the isomers of Cl_3N , Cl_6N are dominant while Cl_3N , Cl_4N , Cl_7N are less Cl_1N , Cl_2N , Cl_8N are only included in trace amounts. The highest chlorinated Halowax 1051 (70%) contains almost only Cl_7N and Cl_8N -isomers.

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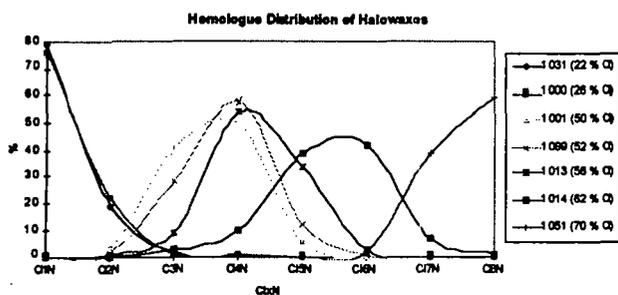


Figure 1: Cl-content of different Halowaxes and dominant grade of chlorination in Cl_xN

However the isomer distribution of Cl_xN within the homologues remains constant. According to the specific reaction mechanism of an electrophilic substitution reaction of chlorine with naphthalene and the resulting regioselectivity, all Halowaxes show the same specific pattern of Cl_xN-isomers within the series of homologues (see Figure 2).

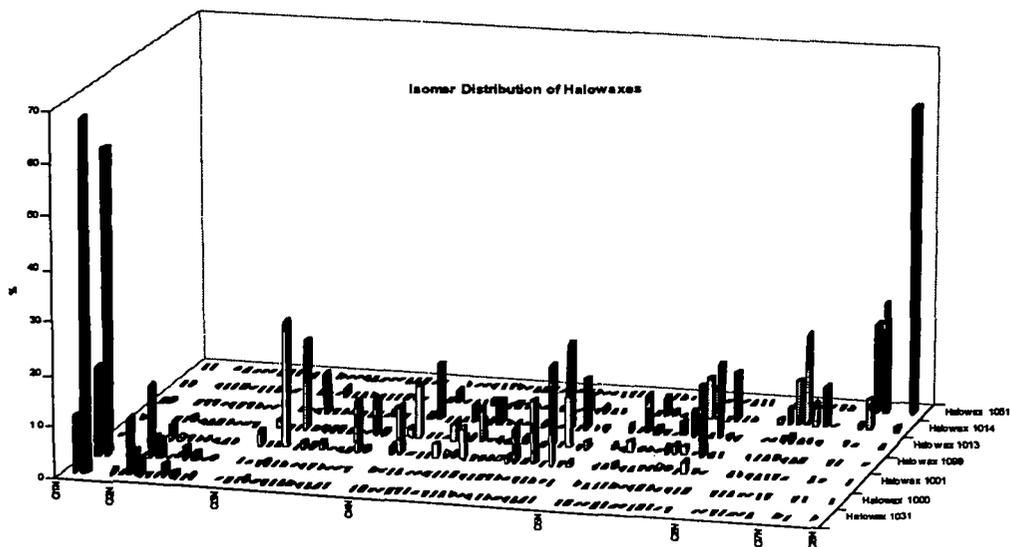


Figure 2: Isomere distribution of Cl_xN in Halowaxes

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The maximum of the homologue distribution on fly ash of MWI's is between Cl_4N and Cl_5N (see Figure 3a) and on fly ash of a secondary aluminum process is Cl_4N (see Figure 3b).

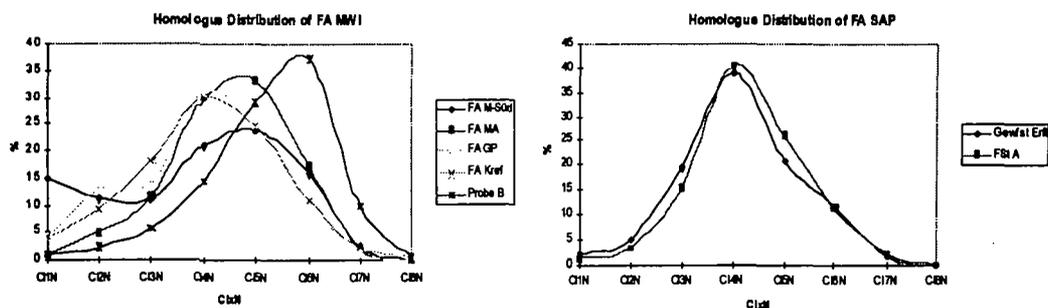


Figure 3a, b: Cl_xN homologue distribution on fly ash of a MWI and on fly ash of a SAP

The isomer pattern of chloronaphthalenes formed on fly ash in a thermal reaction shows a distinct difference compared with the pattern in technical mixtures of Halowax. On fly ash some isomers of Cl_2N , Cl_3N , Cl_4N and Cl_5N are formed preferred which are not formed in Halowax or vice versa. More striking is this difference in the isomer pattern of Cl_6N and Cl_7N where the isomer ratios were nearly inverted. This is a strong evidence/indication that there are two different formation pathways in both matrices. Cl_xN formed by incineration are possibly formed by de-novo-synthesis from the macromolecular organic carbon lattice and inorganic chlorine under the catalytic influence of transition metal ions, such as $CuCl_2$, or by C_2 -, C_4 - radicals in presence of chlorine building up an aromatic structure and precursors leading in a dechlorination reaction to the different/specific structure of chloronaphthalenes on fly ashes. There is also an evidence that the Cl_xN on fly ash are formed in a dechlorination reaction, starting with the Cl_8N leading to a nearly similar Cl_xN -pattern down to Cl_4N . The loss of similarity within the Cl_3N , Cl_2N and Cl_1N pattern seems to be the result of a superposition of the dechlorination reaction and the beginning of a chlorination reaction.

Cl_xN formed in a secondary aluminum process shows up to Cl_5N nearly the same isomer pattern like Halowax. Striking is the similarity of the Cl_3N , Cl_4N and Cl_5N pattern where nearly the same isomers were formed in same ratios. Starting with the 1,2,3,5,6- and 1,2,3,6,7- Cl_5N there is a slight shift to the fly ash pattern which is continued in the Cl_6N , especially the 1,2,3,4,6,7/1,2,3,5,6,7- Cl_6N and in the Cl_7N . This may indicate that Cl_xN formed in the secondary aluminum process are build up in a chlorination reaction out of naphthalene or low-chlorinated Cl_1N , Cl_2N (which could also be formed in a de-novo-synthesis or by precursors), similar to the electrophilic substitution of chlorine with naphthalene catalyzed by a Lewis acid in Halowax. The loss of similarity in the Cl_6N and Cl_7N pattern in comparison with the Halowax pattern, could be explained by a superposition of the chlorination reaction and a dechlorination reaction

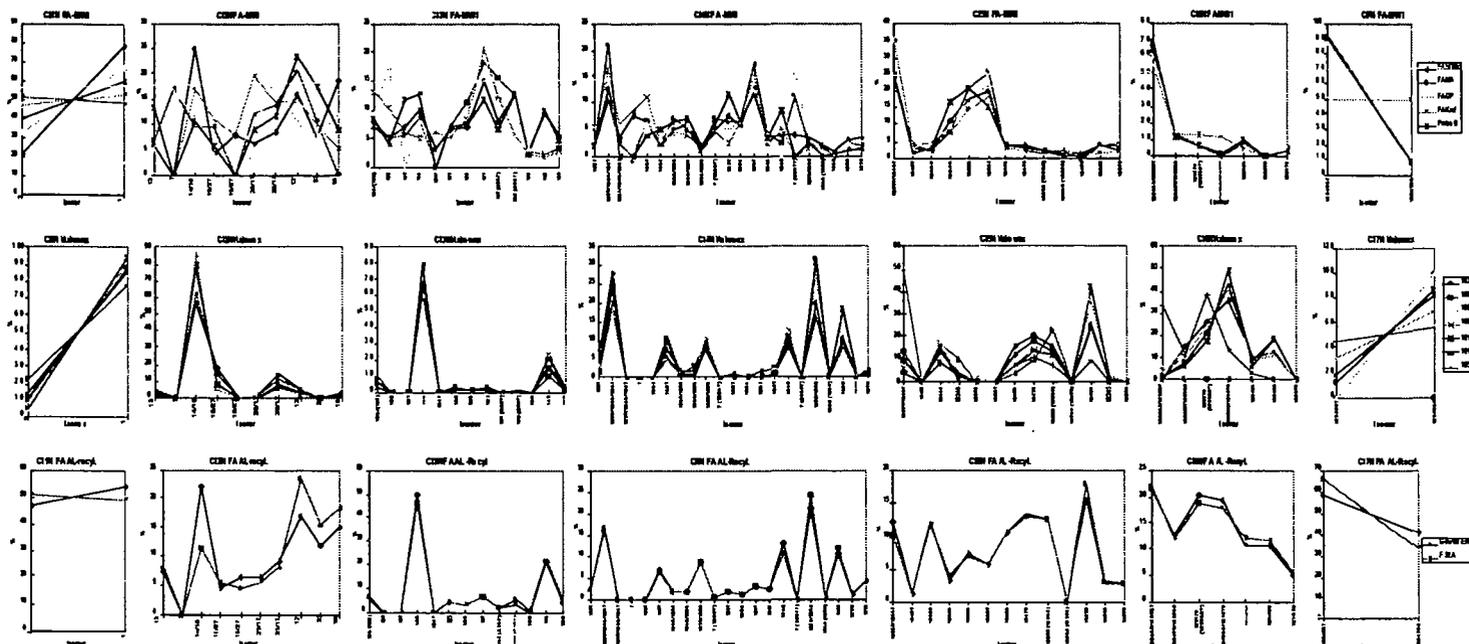


Figure 4: Isomer pattern of PCN (relative ratios of regioisomers) in FA MWI (first row), Halowax (second row) and FA SAP (third row)

References

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