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FORMATION OF POLYCHLORINATED NAPHTHALENES ON FLY ASH

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Abstract

During the oxidative degradation of carbonaceous material on fly ash, besides PCDD/F, PCPh, PCBz, PCB, polychlorinated naphthalenes (PCN or Cl_XN) are formed. Thermal experiments were carried out with fly ash from a municipal waste incinerator at 300° C and reaction times of 0.5 h up to 4 h. For the study an analytical method using GC/MS was developed similar to that, used in dioxin-analysis. Isomer specific identification of chloronaphthalenes formed on fly ash was realized by comparison of Cl_XN from technical PCN-mixtures (Halowax®). For quantification of the PCN formed, ^{13}C- labelled PCB-standards were used as internal standards because no ^{13}C- labelled PCN-compounds were available.

Both, technical PCN-mixtures and PCN formed on fly ash show a characteristic pattern of Cl_XN-congeners according to their difference in formation. Cl_2N - Cl_5N were formed most and Cl_1N - Cl_3N were also found in the gas phase in high amounts. A single isomer 1,2,3,5,6,7-Cl_6N, known as a strongly bioaccumulating and toxic PCN, is formed in higher amounts together with 1,2,3,4,6,7-Cl_6N.

Introduction

Polychlorinated naphthalenes (PCN), written as $C_{10}H_{8-X}Cl_X$ or in short form Cl_XN, build up a class of 75 possible congeners similar to the PCDD. PCN exhibit similar chemical and physical properties as polychlorinated biphenyls (PCB). For example they show high thermal stability, resist chemical and biological degradation and accumulate in our environment. PCN have been used mainly as dielectric fluids, insulation materials, flame retardents, fungicides and pesticides, as addition in oils and plasticizers.[1)] Therefore PCN are widespread and persistent industrial pollutants in the environment.

Some of the isomers of PCN are known to be strongly bioaccumulating and showing dioxinlike toxical properties such as chloracne and liver damages.[1-6)]

There are three main sources of PCN: Technical mixtures of PCN, are the main input in the global environment. PCN are also found in trace amounts as by-products in technical PCB-mixtures. Another important source is the formation of PCN during incineration processes like waste incineration (e.g. MWI) or incineration of coal in power plants.[1,3,5)]

The objective of this study was to develop an isomer specific analysis of PCN in technical mixtures (Halowax) and on fly ash by GC/MS and to investigate their formation on fly ash.

Experimental

Standards and Samples

In our study Halowax mixtures (1000, 1001, 1099, 1014) and different PCN- and ^{13}C-PCB-standards were used (Promochem Wesel, Germany). By mixing Halowax 1000, 1099, 1014, Cl_7N and Cl_8N, a solution containing all possible PCN in technical mixtures was obtained.

The fly ash was collected from an electrostatic precipitator from a municipal waste incinerator (MWI). The content of organic carbon was 4.2 %. The fly ash was pulverized and homogenized and used without cleaning e.g. extraction with organic solvents to avoid formation of artefacts .(7) For the investigation of the formation and degradation of PCN on fly ash the initial PCN concentration had to be considered also and was determined by soxhlet extraction with toluene after addition of ^{13}C-PCB as internal standards.

To investigate the formation and degradation of PCN the fly ash was heated at 300° C for 0.5, 1, 2, 4 h in a vertical tube of borosilicate glass, with the fly ash on a porous glass frit. During the annealing a stream of synthetic air (50 ml/min, containing 150 mg water vapour / l air) was passed through the apparatus. Volatile PCN were trapped in two XAD-tubes in series, containing XAD-16.

After thermal treatment the fly ash was soxhlet extracted with toluene for 20 h after addition of ^{13}C-PCB-standards. The XAD was eluted with toluene and dichloromethane after addition of ^{13}C-PCB-standards. Finally extract and eluate were cleaned up and fractionated by liquid chromatography on superactive basic alumina with anhydrous Na_2SO_4 on the top. After conditioning with n-hexane two fractions were sampled - n-hexane : dichloromethane (9 : 1) as fraction 1, n-hexane : dichloromethane (1 : 1) as fraction 2. Both fractions were united before measuring.

GC/MS-Measurement

Identification and quantification was achieved by gaschromatography (GC; HP 5890) in combination with a mass selective detector (MSD; HP 5970). GC was carried out using a DB 5 (length 30 m, i.d. 0.25 mm, phase 0.25 µm) with splitless injection and He as carrier gas with the following temperature program: Isothermal at 80° C for 3 min, temperature program 10° C/min to 150° C, then with 2° C/min to 260° C, finally with 10° C/min to 300° C and held for a minute.

For identification the mass spectrometer was operated in the scan mode and for quantification in selected ion mode (SIM), using the both most intensive and characteristic ion masses from the molecular ion region for each level of chlorination of Cl_XN and ^{13}C-Cl_XB.

^{13}C-labelled compounds were used as internal standards. Since no ^{13}C-PCN were available, ^{13}C-PCB standards were found best to fulfill the needs required on an internal standard. The following ^{13}C-PCB-standards fitted best in retention time windows: 2,4,4'-Cl_3B; 2,2',5,5'-Cl_4B; 2,2',4,5,5'-Cl_5B; 2,2',4,4',5,5'-Cl_6B; 2,2',3,4,4',5,5'-Cl_7B; 2,2',3,3',4,4',5,5'-Cl_8B. Table 1 shows the time windows, the detected masses and relative intensities of PCN and ^{13}C-PCB used in GC/MS.

Table 1: Time windows and masses for detection of PCN and ^{13}C-PCB

time window	Cl_XN	m/z (rel.Int.)	m/z (rel.Int.)	Cl_XB	m/z (rel.Int.)	m/z (rel.Int.)
1	Cl_1N	162 (100 %)	164 (33,2%)			
	Cl_2N	196 (100 %)	198 (65,8%)			
2	Cl_3N	230 (100 %)	232 (98,4%)	Cl_3B	268 (100 %)	270 (98,7%)
	Cl_4N	266 (100 %)	264 (76,4%)	Cl_4B	304 (100 %)	302 (76,2%)
3	Cl_5N	300 (100 %)	302 (65,5%)	Cl_5B	338 (100 %)	336 (61,0%)
	Cl_6N	334 (100 %)	336 (81,8%)	Cl_6B	372 (100 %)	370 (50,9%)
4	Cl_7N	368 (100 %)	370 (98,1%)	Cl_7B	406 (100 %)	404 (43,6%)
	Cl_8N	404 (100 %)	402 (87,4%)	Cl_8B	442 (100 %)	438 (33,3%)

Results and Discussion

Qualitative Analysis

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, till a desired chlorine content is reached. Depending on the Cl-content different degrees of chlorination dominate in the technical PCN-mixtures, such as Halowax, as shown in table 2.[1,2)]

Table 2: Cl-content in Halowaxes and dominant degree of chlorination in Cl_XN

Halowax	Cl-content	chlorination degree Cl_XN
1000	26 %	x = 1,2
1001	50 %	x = (1,2) 3,4 (5)
1099	52 %	x = (1,2) 3,4 (5)
1014	62 %	x = (3) 4,5,6 (7)

All Halowaxes show the same specific pattern of Cl_XN-isomers, according, to the mechanism of an electrophilic substitution. In figure 1 the typical pattern is presented for Halowax 1000, 1001, 1099, 1014.

On fly ash collected in the electrostatic precipitator of a MWI, the isomers of Cl_2N, Cl_3N, Cl_4N, Cl_5N and Cl_6N are mainly found. According to the physico-chemical properties the low chlorinated Cl_1N evaporate easily and the high chlorinated Cl_7N, Cl_8N degrade under thermal conditions found in incineration processes of MWI.

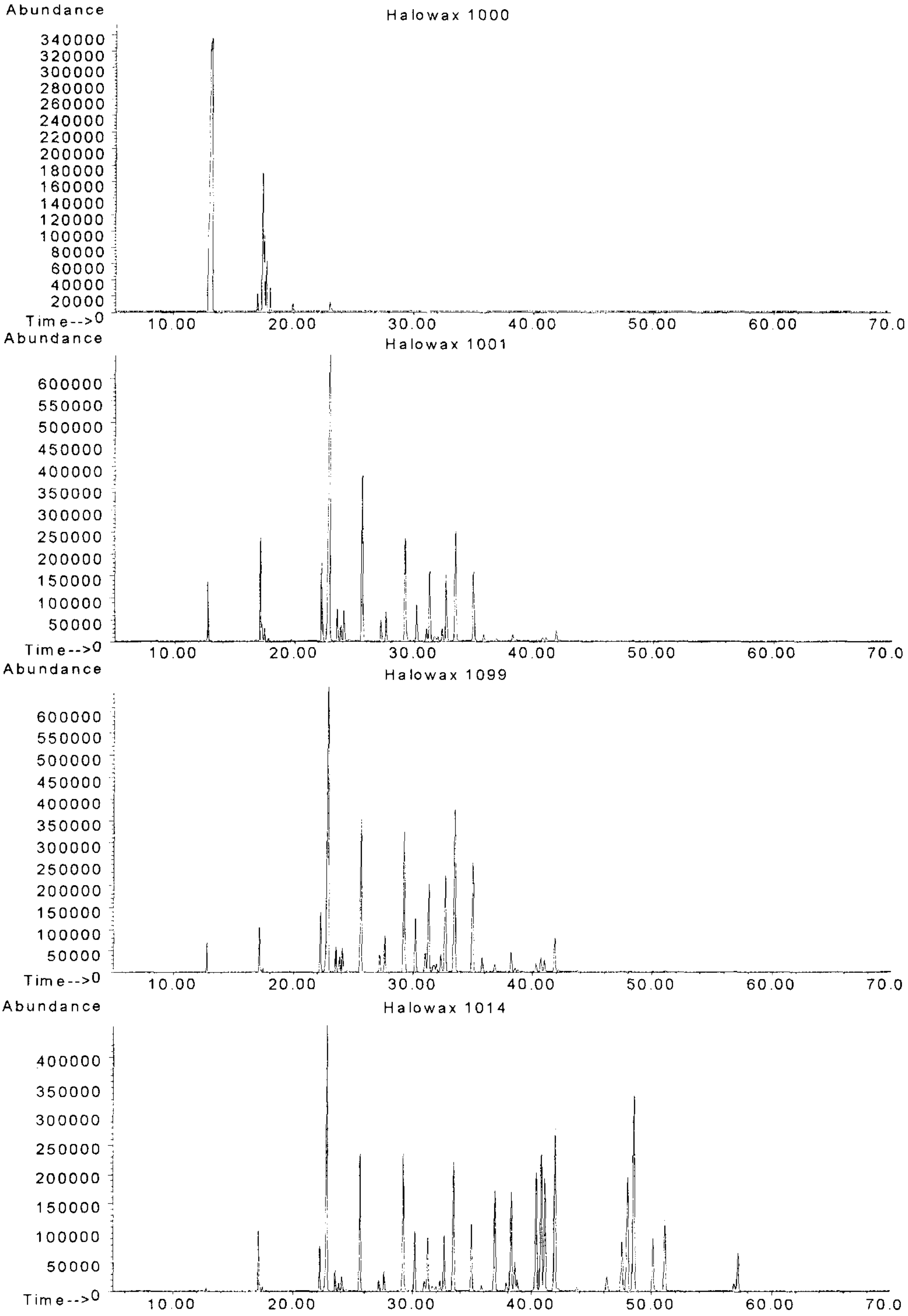


Figure 1: Chromatograms of Halowax 1000, 1001, 1099, 1014

The chloronaphthalenes formed during thermal treatment of fly ash at 300° C are shown in figure 2. Mainly Cl_1N - Cl_6N are formed in higher amounts. Due to their higher volatility the mono- to trichlorocompounds evaporate partly and therefore are found adsorbed at the XAD trap.

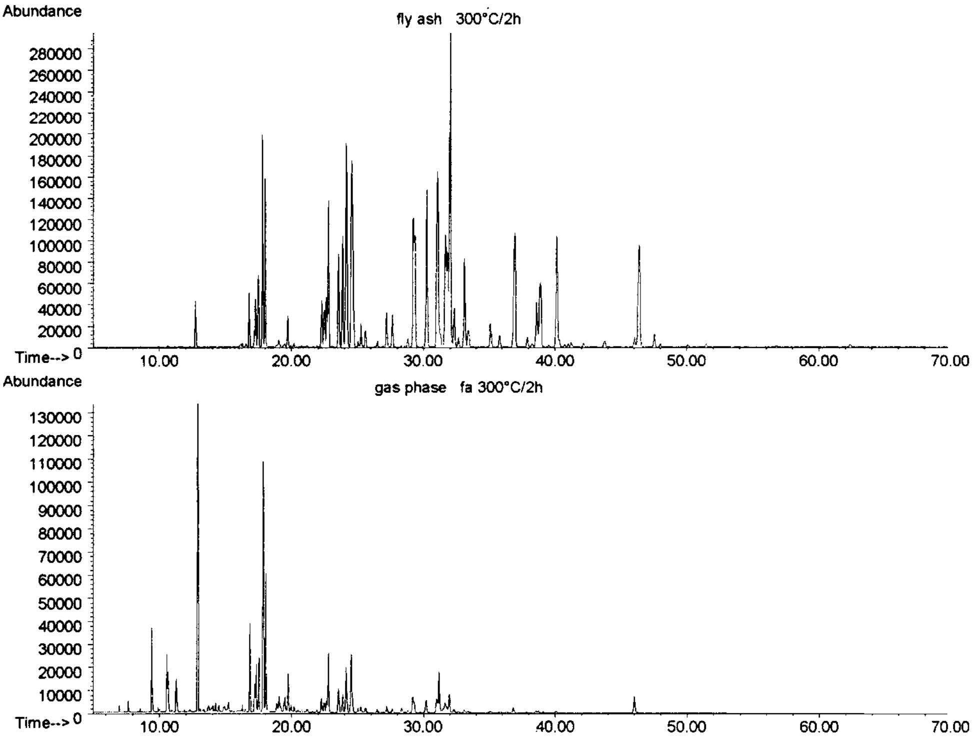


Figure 2: Chromatograms of fly ash and volatiles of the gas phase after 2h annealing at 300° C

The isomer pattern of chloronaphthalenes formed on fly ash in a thermal reaction shows a distinct difference compared with the pattern found in technical mixtures of Halowax. In figure 3 the total ion chromatograms for PCN in Halowax and in annealed fly ash are compared. In figure 4 a - d the various chloronaphthalene isomers in Halowax mixtures and formed on fly ash are presented in detail.

The qualitative differences are obvious: With the monochloronaphthalenes the 1-chloro isomer dominates in Halowax, whereas on fly ash both isomers are present. Also with the dichlorocompounds the isomer ratio is different. In stead of the 1,4/1,6-Cl_2N, as present in Halowax, the 1,2- and 2,3 Cl_2N isomers are the major isomers formed on fly ash. Further distinct differences are the preferred synthesis of 1,2,5-, 1,2,6-, 1,2,7- 1,6,7- and 2,3,6- trichloronapthalenes, of 1,3,6,7-, 1,3,6,8/1,2,5,6- ,1,2,6,7- and 1,2,5,8/2,3,6,7- tetrachloro species. Additional significant differences are in the formation of 1,2,3,5,6- and 1,2,3,6,7-pentachloronaphthalene, of 1,2,3,4,6,7/1,2,3,5,6,7- hexachloronapthalene and of 1,2,3,4,5,6,7 heptachloro isomer, wich is formed in an inverted ratio than in Halowax.

Noteworthy is especially the high formation of 1,2,3,4,6,7/1,2,3,5,6,7-Cl_6N, since 1,2,3,5,6,7-Cl_6N is known as a strongly bioaccumulating compound and shows dioxinlike toxical properties.[4,6)]

The most prominent isomers present in the two matrices are shown in table 3.[8)]

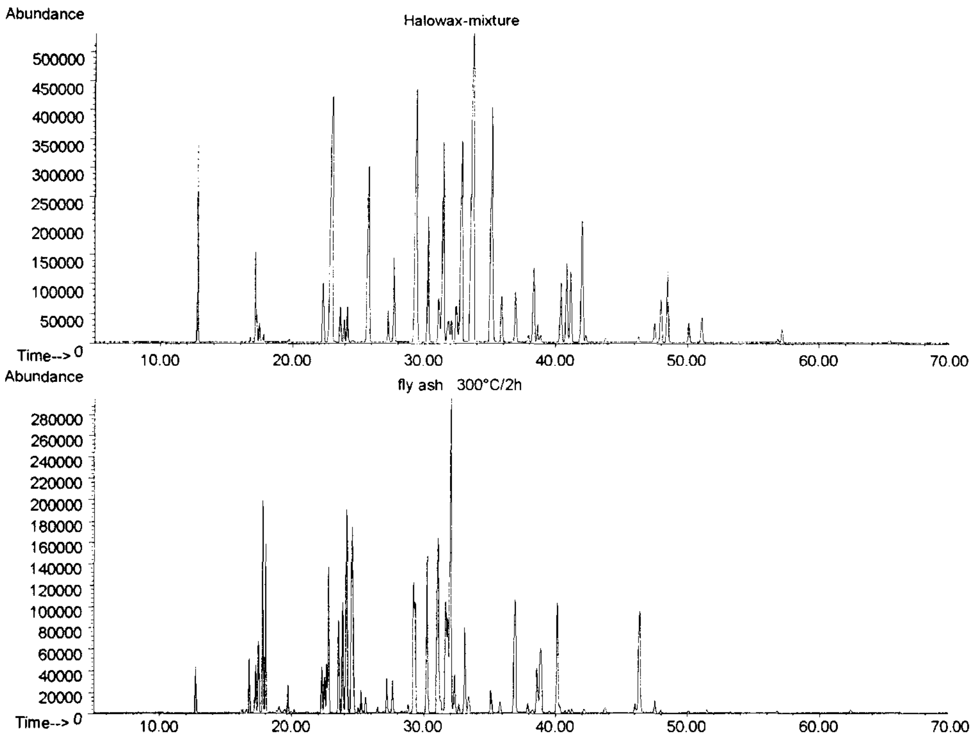


Figure 3: Chromatograms of a mixture of different Halowaxes, Cl_7N- and Cl_8N-isomers in comparison with a fly ash after 2h annealing at 300° C

Table 3: Relevant Cl_XN-isomers in Halowax and fly ash (most dominant **isomers** are in bold letters, less dominant isomers are in brackets, most toxic isomers are underlined)

Cl_XN	Halowax	fly ash
Cl_1N	1	1, **2**
Cl_2N	**14/16**	13, **12**, **23**, (18)
Cl_3N	136, **146**, **145**	135, 137, 146, 125, 126, **127**, **167/236**, (138)
Cl_4N	**1257/1246/1247**, 1467, 1235/1358, 1248, **1268**, 1458	1367, **1368/1256**, 1237, 1234, **1267**, 1258/2367, (1238)
Cl_5N	**12468**, 12456, 12478, 12358, **12458**	**12357/12467**, 12356, **12367**, (12368)
Cl_6N	123578/(123568), **124568/124578**, 123456, 123458	**123467/123567**, (123678)
Cl_7N	1234568	1234567

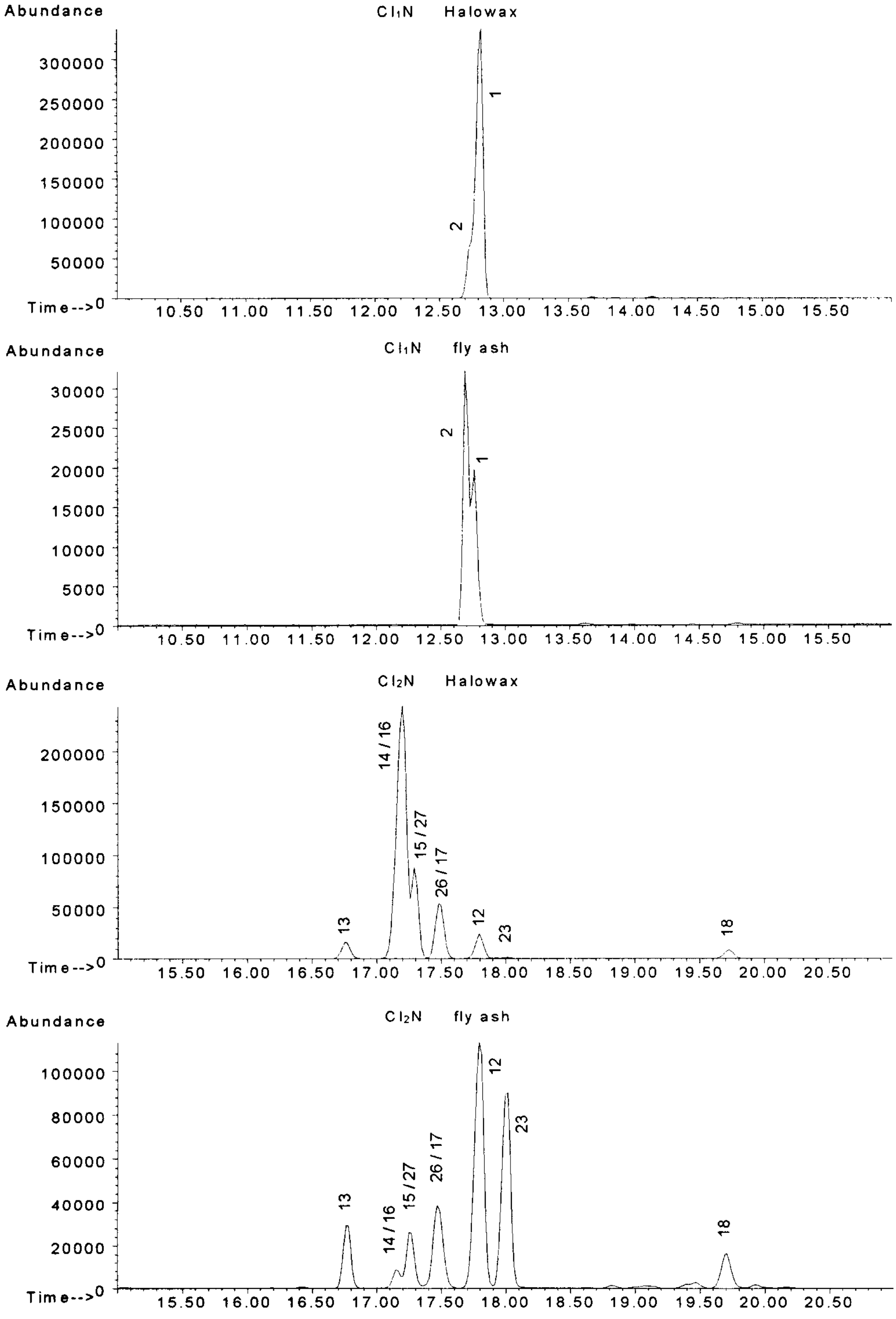


Figure 4a: Cl_XN in Halowax in comparison with Cl_XN on fly ash

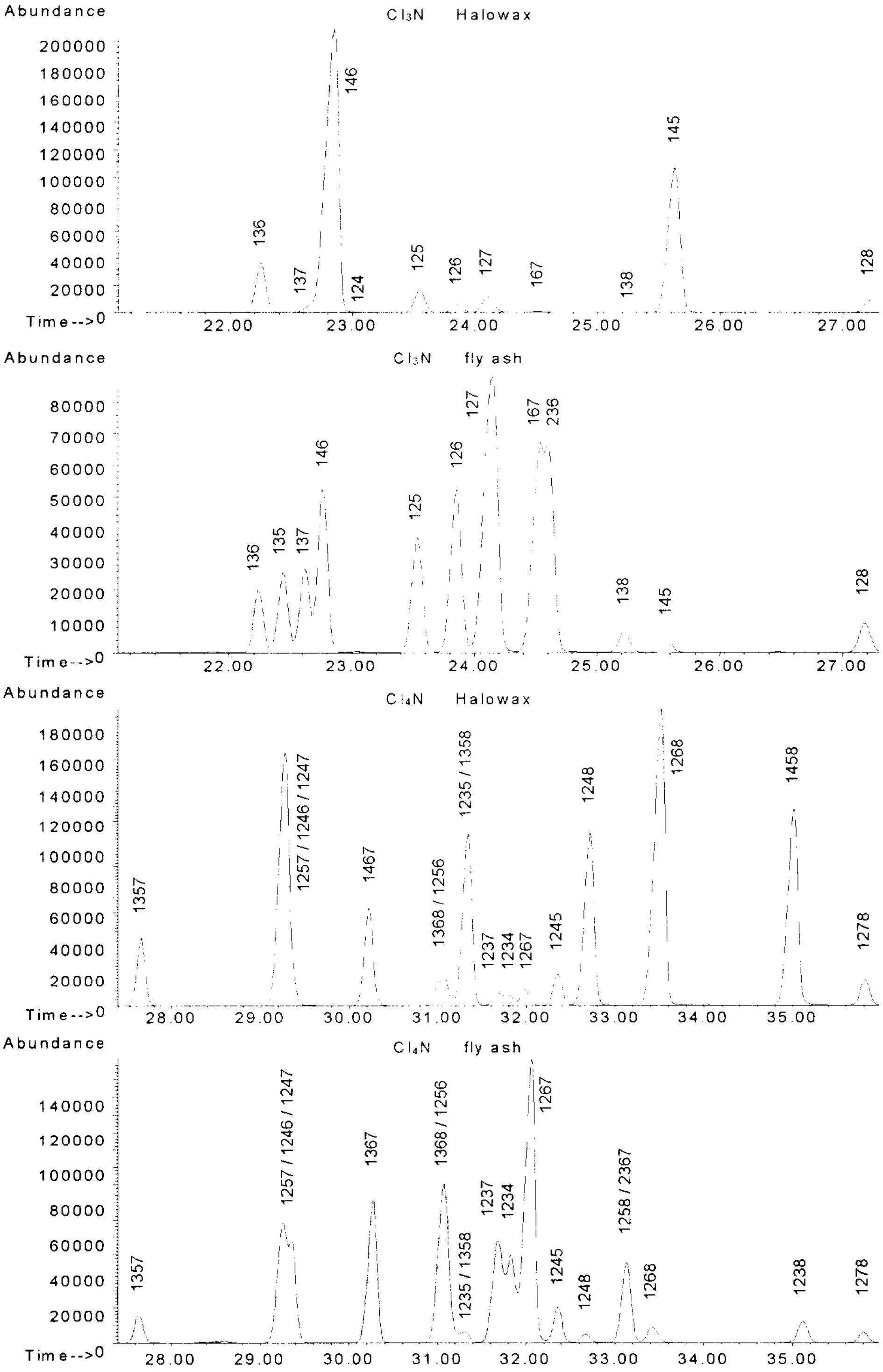
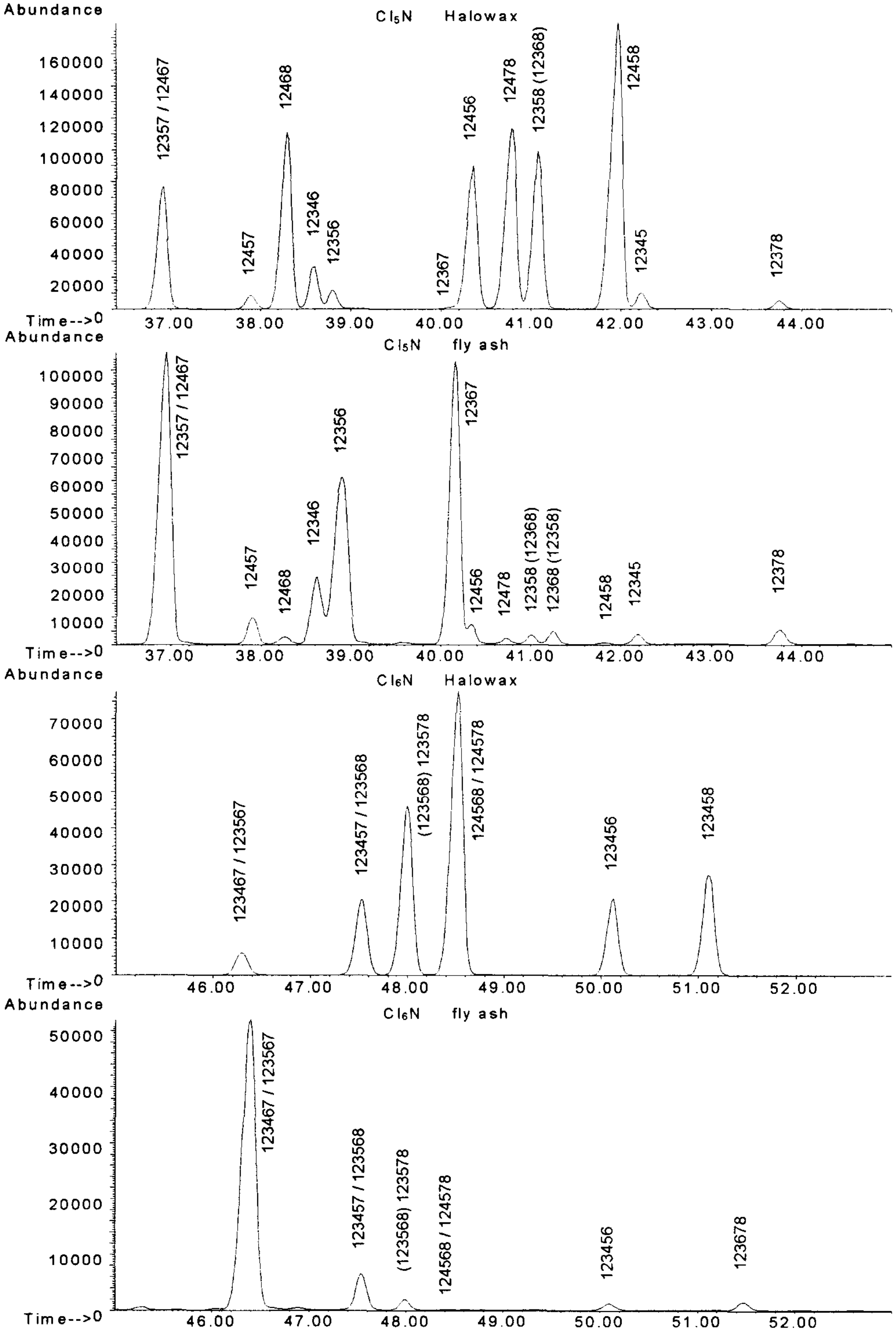


Figure 4b: Cl_XN in Halowax in comparison with Cl_XN on fly ash



Cl_5N Halowax

Cl_5N fly ash

Cl_6N Halowax

Cl_6N fly ash

Figure 4c: Cl_XN in Halowax in comparison with Cl_XN on fly ash

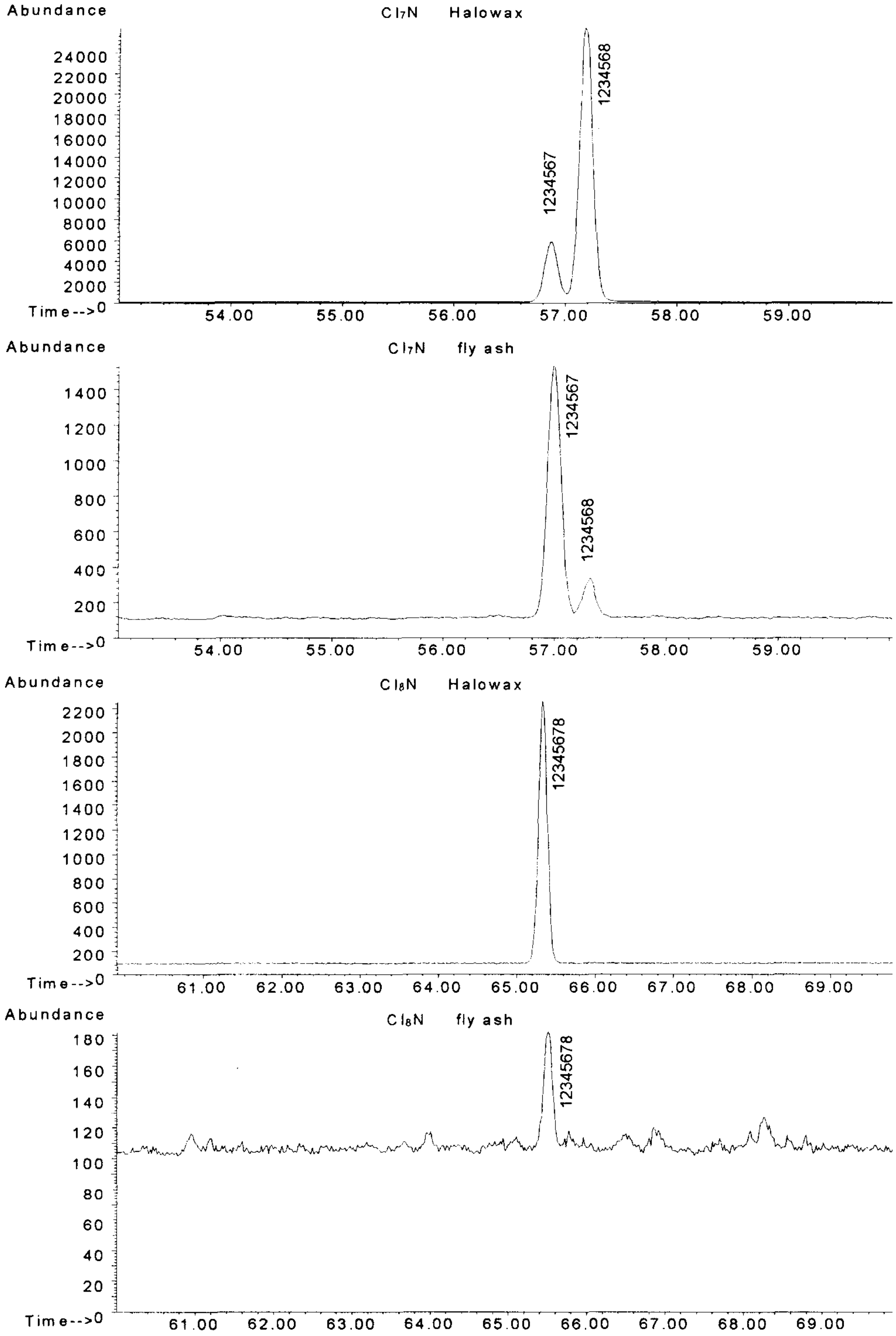


Figure 4d: Cl_XN in Halowax in comparison with Cl_XN on fly ash

Quantification

In the genuine fly ash from incineration, chloronaphthalenes are found in concentrations below 100 ng/g. Relevant homologs are Cl_5N (87 ng/g), Cl_4N (84 ng/g) and Cl_3N (60 ng/g). The 1,2,3,4,6,7-/ 1,2,3,5,6,7-Cl_6N (21 ng/g) is the most prominent species with the hexachloro congeners (32 ng/g).
The concentrations of the congener groups and the individual isomers on fly ash prior to thermal treatment are given in table 4.

On thermal treatment of the fly ash the carbonaceous material is degraded, leading among others to the formation and release of chloronaphthalenes. The data are shown in table 4. The concentrations given are the sum of the compounds in the annealed residue and those released into the gas phase and adsorbed on XAD. Also included are the initial concentrations on fly ash. From the data the net formation may be calculated as difference of the corresponding values.

Formation and degradation:
The kinetics of formation is presented in figure 5 for Cl_1N to Cl_8N as net concentrations, i.e as difference of the total concentration and the initial concentration. The concentrations of Cl_7N and Cl_8N (formed) are below 5 ng/g and negligible.
After 2 h annealing time most of the Cl_XN reached the maximum of formation. Cl_4N (1603 ng/g) and Cl_5N (1355 ng/g), Cl_3N (1074 ng/g) and Cl_2N (818 ng/g) are the species formed with the highest yields. In comparison Cl_6N (287 ng/g) were formed less, but noteworthy is the high formation of 1,2,3,4,6,7-/ 1,2,3,5,6,7-Cl_6N (251 ng/g) to be seen clearly in table 4. Cl_7N are formed in very low concentrations.
Generally formation and degradation processes occur simultaneously on the fly ash, both processes being overlapped by evaporation of more volatile compounds.

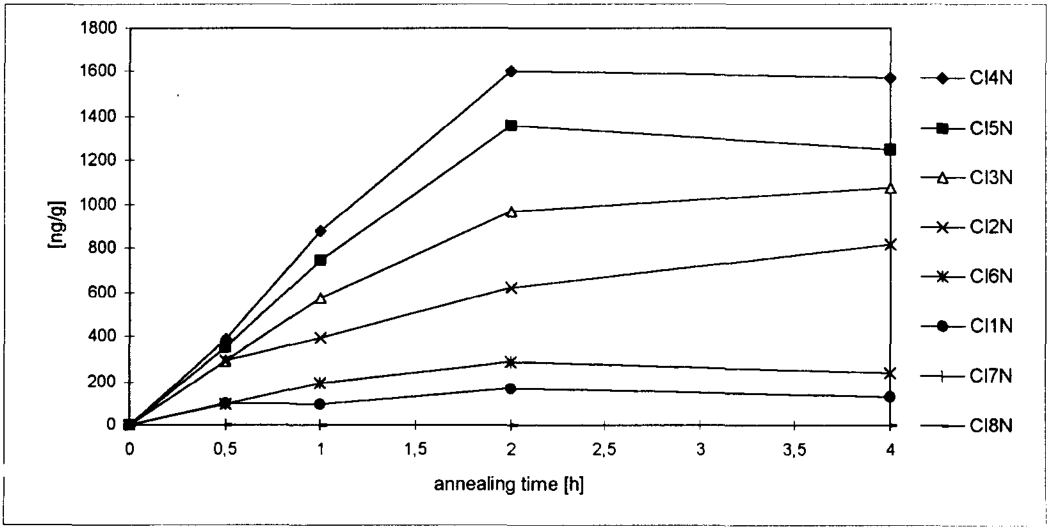


Figure 5: Kinetics of formation of Cl_XN by annealing fly ash at 300° C

Table 4: Isomer specific initial concentration and concentration on fly ash after 2h annealing at 300° C

Cl_xN isomer/s	initial conc. [ng/g]	conc. after annealing [ng/g]
Monochloronaphthalene		
2	6,8	95,6
1	12,4	94,0
sum	19,1	189,6
Dichloronaphthalene		
13	2,8	59,3
14/16	3,5	19,4
15/27	6,7	46,9
26/17	9,3	77,8
12	7,2	250,1
23	5,8	166,5
18	0,8	38,4
sum	36,0	658,4
Trichloronaphthalene		
136	2,8	36,3
135	3,2	34,7
137	3,9	39,3
146	10,2	131,6
125	3,4	86,7
126	6,2	99,0
127	11,0	242,4
167/236	15,1	286,9
138	1,3	21,4
145	0,9	15,7
128	2,0	33,1
sum	60,1	1027,2
Tetrachloronaphthalene		
1357	2,9	36,7
1257/1246/1247	12,0	181,3
1257/1246/1247	4,3	96,4
1367/(1467)	9,7	189,1
1368/1256	10,5	255,5
1235/1358	0,8	12,5
1237	10,3	172,2
1234	5,2	103,8
1267	12,7	406,6
1245	3,0	44,9
1248	2,4	11,6
1258/2367	3,8	108,0
1268	3,0	23,4
1238	2,2	31,6
1278	1,3	14,2
sum	84,2	1687,8

Cl_xN isomer/s	initial conc. [ng/g]	conc. after annealing [ng/g]
Pentachloronaphthalene		
12357/12467	23,8	486,5
12457	2,8	37,1
12468	1,8	11,9
12346	9,8	101,6
12356	15,2	310,7
12367	19,0	395,8
12456	2,6	19,6
12478	2,3	8,4
12358/12368	1,5	12,1
12368/12358	1,6	17,8
12458	0,4	2,4
12345	2,7	14,5
12378	3,3	23,7
sum	87,0	1442,0
Hexachloronaphthalene		
123467/123567	20,8	271,6
123457/123568	4,5	27,1
(123568)/123578	2,3	7,2
124568/124578	0,4	0,6
123456	2,7	5,5
123678	1,6	7,2
sum	32,4	319,3
Heptachloronaphthalene		
1234567	4,5	4,9
1234568	0,7	< 0,1
sum	5,1	4,9
Octachloronaphthalene		
12345678	0,4	< 0,1

concentrations are given as ng Cl_xN per g fly ash

Formation Pathways:

The following kinetics of formation show the main reaction pathways in the formation of Cl_2N and Cl_3N.

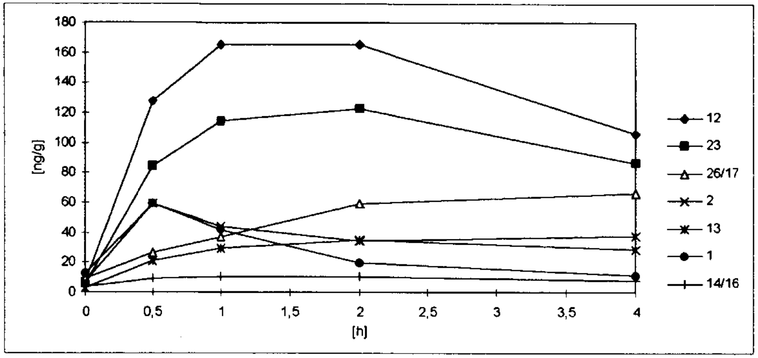


Figure 6a: Formation of $1\text{-}Cl_1N$ and $2\text{-}Cl_1N$ and further reactions
$1\text{-}Cl_1N \rightarrow 1,2\text{-}Cl_2N$, $1,3\text{-}Cl_2N$, $1,4/1,6\text{-}Cl_2N$, $17/26\text{-}Cl_2N$
$2\text{-}Cl_2N \rightarrow 1,2\text{-}Cl_2N$, $2,3\text{-}Cl_2N$

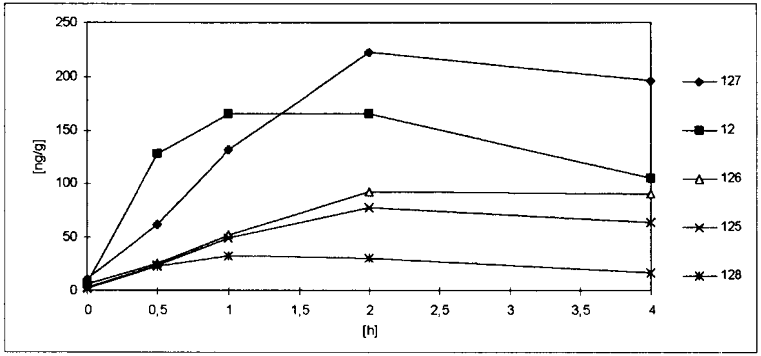


Figure 6b: Formation of $1,2\text{-}Cl_2N$ and further reactions
$1,2\text{-}Cl_2N \rightarrow 1,2,7\text{-}Cl_3N$, $1,2,6\text{-}Cl_3N$, $1,2,5\text{-}Cl_3N$, $1,2,8\text{-}Cl_3N$

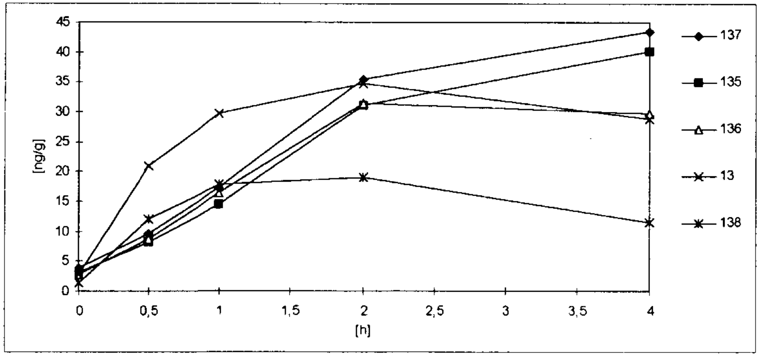


Figure 6c: Formation of $1,3\text{-}Cl_2N$ and further reactions
$1,3\text{-}Cl_2N \rightarrow 1,3,5\text{-}Cl_3N$, $1,3,6\text{-}Cl_3N$, $1,3,7\text{-}Cl_3N$, $1,3,8\text{-}Cl_3N$

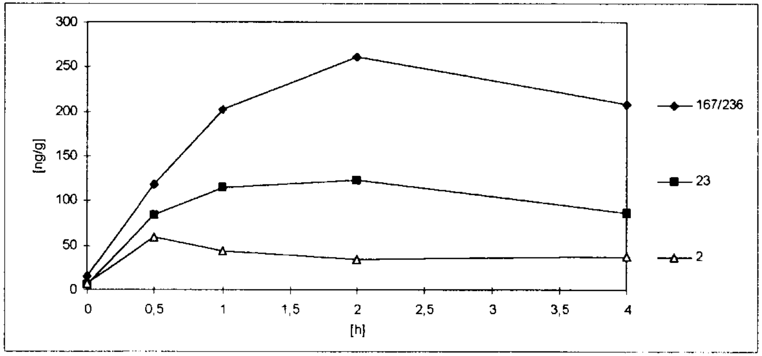
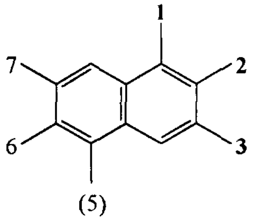


Figure 6d: Formation of $2\text{-}Cl_1N$ and reaction to $1,6,7/2,3,6\text{-}Cl_3N$
$2\text{-}Cl_2N \rightarrow 2,3\text{-}Cl_2N \rightarrow 1,6,7/2,3,6\text{-}Cl_3N$

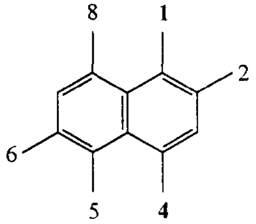
The kinetic data indicate different formation pathways between the electrophilic substitution with chlorine in presence of $FeCl_3$ and the formation of chloronaphthalenes on fly ash in a de-novo-synthesis .[1,2,9-13]
Referring to the mechanism of an electrophilic aromatic substitution with chlorine in the presence of $FeCl_3$ or other Lewis acids, the entering chlorine will be directed in para (or ortho) position to a chlorine already present in the aromatic system.[1,2] In contrast is the formation of Cl_XN from macromolecular organic carbon and inorganic chlorine under the catalytic influence of $CuCl_2$ in a de-novo-synthesis.[9-13] Structures of the macromolecular carbonaceous material, formed at high temperatures, depend on kinetic, thermodynamic and steric effects.
An unambiguous interpretation of the reaction pathways is difficult. Most of the chloronaphthalenes (Cl_XN) could be formed from different educts ($Cl_{X-1}N$) and could also react to form several products ($Cl_{X-1}N$). Never the less it is possible to interprete the dominant reaction pathways from the kinetik data and the ratio of the isomers formed. The data are presented in figure 6a - 6d.
One important difference to technical products is the formation of monochloronaphthalene in the first step. On fly ash 1-Cl_1N and 2-Cl_1N are formed with yields from 1:1 up to 1:3, i.e. the chlorination occurs in the positions α and β in the beginning with equal probabilities and is shifted to the thermodynamic stabilized 2-Cl_1N with increasing reaction time (figure 6a).
In the formation of the dichloronaphthalene another difference between the formation of Cl_XN in technical mixtures and on fly ash is noted. The formation of 1,2-Cl_2N from 1-Cl_1N (α directs in the ortho position) or from 2-Cl_1N (β directs in the 1 position) and the formation of 1,3-Cl_2N from 1-Cl_1N (α directs in the meta position) (figure 6a) is in contrast to the Halowax process. The formation of 1,2-substituted trichloro congeners mainly formed from 1,2-Cl_2N, as indicated in figure 6b and the formation of 1,3-substituted trichloro congeners from 1,3-Cl_2N is a reaction pathway not to be found in technical products (figure 6c).
The formation of 2,3-Cl_2N and subsequent 167/236-Cl_3N from 2-Cl_2N (figure 6d), is also an important difference to Halowax where these compounds are not found. 2-Cl_1N is formed on fly ash with yields between 50 and 70 % and 2,3-Cl_2N (β directs in the 3 position) is formed with high yields exclusively from 2-Cl_1N besides 1,2-Cl_2N (figure 6a). Chlorination of 2,3-Cl_2N leads only to 167/236-Cl_3N not found in Halowax also.
1,4,6-Cl_3N is formed in technical mixtures as well as on fly ash from the 14/16-Cl_2N exclusively. But in difference to the Halowax process the only possible way to form 1,4,6-Cl_3N on fly ash in higher yields leads over the 14/16-Cl_2N preformed on the macromolecular carbon lattice in a fast reaction.
The different formation of low chlorinated Cl_XN in the beginning leads to the 1,2,3,4,5,6,7-Cl_7N on fly ash and the 1,2,3,4,5,6,8-Cl_7N in Halowax at the end of the reaction pathways.
For that reason there is a closer look at one of the main reaction pathways leading to 1,2,3,4,5,6,7-Cl_7N on fly ash. This reaction pathway is based on the main isomers of each level of chlorination.
Starting with the different formation of lower chlorinated naphthalenes, the 1,2,6,7-Cl_4N is formed from 1,2,6-, 1,2,7-, 1,6,7- and 2,3,6-Cl_3N. 1,2,6,7-Cl_4N is able to form 1,2,4,6,7-, 1,2,3,5,6-, 1,2,3,6,7-Cl_5N.
All of these three Cl_5N-isomers form the main product of Cl_6N the both 1,2,3,4,6,7-/1,2,3,5,6,7-Cl_6N and react in a further chlorination to 1,2,3,4,5,6,7-Cl_7N.

Generally a comparison between the Cl_XN-isomers formed in the two matrices shows the following differences:



On fly ash the positions 1, 2, 3 (lateral β-positions) are preferred, leading to 1,2,3,4,5,6,7-Cl_7N.

Position: 1, 2, 3: mainly attacked
7, 6: very often
5: often



In the halowax process the positions 1, 4 (apical α-positions) are preferred, leading to 1,2,3,4,5,6,8-Cl_7N.

Position: 1, 4: mainly attacked
2, 5, 6, 8: very often

Conclusions:

The experiments have confirmed that chloronaphthalenes are formed in considerable yields from carbonaceous material of the fly ash in a de-novo-reaction, similar to the PCDD and PCDF.

Cl_4N (1603 ng/g) and Cl_5N (1355 ng/g), Cl_3N (1074 ng/g) and Cl_2N (818 ng/g) are the species formed with the highest yields. In comparison Cl_6N (287 ng/g) were formed less, but noteworthy is the high formation of 1,2,3,4,6,7-/ 1,2,3,5,6,7-Cl_6N (251 ng/g) known as a strongly bioaccumulating and toxic compound.

Generally formation and degradation processes occur simultaneously on the fly ash, being overlapped by evaporation of more volatile compounds - mainly Cl_1N, Cl_2N and Cl_3N.

The isomer specific identification shows significant differences between the isomer pattern of chloronaphthalenes formed on fly ash and chloronaphthalenes found in Halowaxes. In both matrices a specific Cl_XN pattern is formed according to the different conditions of formation. While Cl_XN in Halowaxes are produced in a chlorination with molten naphthalene and chlorine gas in presence of e.g. $FeCl_3$, Cl_XN on fly ash are de-novo-formed from the macromolecular organic carbon and inorganic chlorine under the catalytic influence of transition metal ions, such as $CuCl_2$.

The kinetic data indicate that the chlorination of the carbon lattice starts in positions α or β to give 1- and 2-Cl_2N. This is evident because these positions are best attacked on the carbon surface. Further chlorination leads to 1,2- and 2,3-Cl_2N and as a final result of the sequence 1,2,3,4,5,6,7-Cl_7N is formed. In contrast the catalytic chlorination of naphthalene produces nearly exclusively 1-Cl_1N and 1,4-Cl_2N resulting in the formation of 1,2,3,4,5,6,8-Cl_7N. The formation of Cl_XN-isomers on fly ash which are not found in Halowax proves that there are two different formation pathways in both matrices. The first step is the formation of a new chlorine-carbon bond on the macromolecular carbon structur followed by an oxidative degradation and release of chloronaphthalenes.

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