Analysis and Seasonal/Regional Variability of Ambient Air Concentrations of Polychlorinated Naphthalenes

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INTRODUCTION

Polychlorinated naphthalenes (PCN) were manufactured as industrial chemicals. The technical PCN waxes have properties (high temperature, flame and fungus resistance) and uses similiar to those of the polychlorinated biphenyls (PCB). PCN are persistent and lipophilic substances and thus accumulate in the environment. In Germany, the production and distribution of the technical PCN waxes "Nibren" were therefore stopped in 1983. PCN were also formed as by-products in the copper ore roast leach process[1)] and in chlorine production, as well as in thermal processes like waste incineration[2-5)]. Some PCN congeners show a toxic mechanism similar to that of 2,3,7,8 tetrachlorodibenzo-p-dioxin[6)]. Thus, the occurrence of PCN in the environment is of ecological interest. Ambient air concentrations of PCN were measured from June 1992 to February 1993 at 7 stations in the city of Augsburg, Germany, and at one background station in a rural area, 18 km northwest of Augsburg. The investigations were part of a baseline assessment program around the new resource recovery facility in Augsburg, which also comprises a municipal waste incinerator.

SAMPLING AND ANALYSIS

During the monitoring period the air was sampled continuously on glass fiber filter/XAD traps and the PCN concentrations were analysed every six weeks separately for the gaseous and particulate phases. The sample, corresponding to 1100 m^3 air volume, was spiked with isotope labelled compounds as internal standards and soxhlet extracted (24 h, toluene). The clean up procedure with acid/basic silica and basic alumina column chromatography that is normally used for the PCDD/F (polychlorinated dibenzo-p-dioxins and furans) resulted in a poor recovery of some PCN congeners on the second column. The clean-up and the separation of substance classes were therefore done by column chromatography in a glass column (1 cm i.d.) packed with 5 g of activated neutral silica gel (Kieselgel 60, Merck) covered by 3 g of neutral alumina (15 % water added, ICN Biochemicals). The first eluate of 20 ml n-hexane contained the PCN, PCB and PCDD/F, the second eluate with 50 ml n-hexane/diethylether (20:1 v:v) the PAH (polycyclic aromatic hydrocarbons). The PCN fraction was evaporated to a volume of ~100µl and analysed by HRGC/HRMS on a HP 5890 series II gaschromatograph (pressure: 10psi, injector: 280°C, oven program: 100°: 1 min —[10°/min]→ 200°: 0 min —[5°/min]→ 300°: 7 min) coupled to a VG Autospec ultima mass spectrometer (resolution 10,000). A HP Ultra 2 column (25 m, 0.2 mm i.d., 0.33 µm film) was used to determine the retention times of the homologues and to achieve complete separation of the homologue groups of tri- to octachloronaphthalenes. No isotope labelled compounds of PCN for internal standardization were available, so the following substances were used to quantify the PCN: octachloro- (OCN) and 1,2,3,4 tetrachloronaphthalene (TCN, Aldrich), technical PCN mixtures of variable chlorine content (Nibren 130 and Halowax 1099) and ^{13}C labelled tri- to heptachlorinated PCB (#28, #52, #101, #153, #138,# 180) compounds. In a stepwise procedure a suitable quantitation standard was received: i) A standard of Halowax 1099, Nibren 130, TCN and OCN (5:5:1:1 by weight) was mixed. ii) The content of the PCN homologues groups in this mixed standard was determined by GC/FID. Because only pure TCN and OCN was available, the quantification of the other homologues was done using an interpolation. The molar signal response, defined as peak area/mMol, in the FID decreases with higher chlorination degree. For the tri- to heptachlorinated PCB (#28, #52, #101, #153, #138, # 180) the molar signal response in the FID was found to show a linear decline (Fig.1). The molar signal responses of 3-, 5-, 6- and 7CN were therefore interpolated linearly from the signal response of TCN and OCN (Fig.1). The content of the individual homologues groups in the mixed standard was then calculated. iii) Finally, ^{13}C labelled internal PCB standards were added to the mixed PCN standard to give the PCN quantification standard. GC/MS response factors of PCN/ ^{13}C-PCB measured in the quantification standard were used to quantify the PCN in the samples. A quantitation standard after clean up and a directly mixed quantitation standard gave the same response factors. Also the retention times of the homologue groups of PCN and PCB were matched. Thus, the ^{13}C-PCB were suitable internal standards for the PCN.

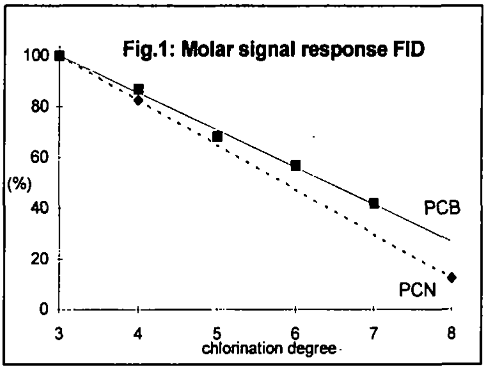
Fig.1: Molar signal response FID

RESULTS

The mean level of the sum of tri- to octachloronaphthalenes (ΣPCN) was 60 pg/m³ in the Augsburg network and 24 pg/m³ at the rural background station. The urban area showed a 2.5 higher concentration. These levels were an order of magnitude lower than levels of $\Sigma(Cl_{1-8}N)$ measured near a manufacturing site (150-1400 ng/m³) and a potential user site (10-33 ng/m³) 7). The PCN pattern (Fig.3l) was dominated by the most volatile PCN: Cl_3N- 76.5%, Cl_4N- 19.3%, Cl_5N- 2,9%, Cl_6N- 0.88%, Cl_7N- 0.35%, Cl_8N- 0.10%. This was similar to the findings near a PCN producing site: Cl_1N- 27%, Cl_2N - 31%, Cl_3N - 37%, $Cl_{4-8}N$ < 5% 7).

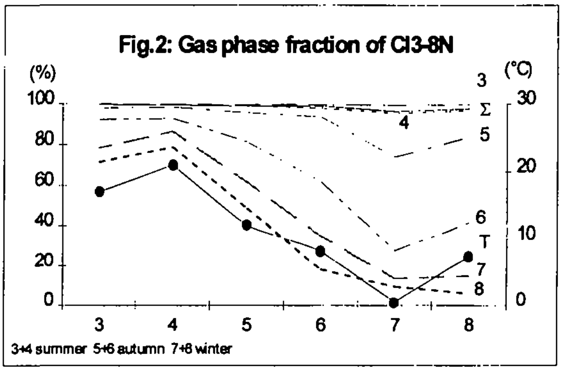
Fig.2: Gas phase fraction of Cl3-8N

98% of the ΣPCN was found in the gas phase. The mean gas phase fraction diminished with higher chlorination degree, and with lower temperature (Fig.2).

The ΣPCN concentrations reached a maximum in the summer months, fell off in autumn and were on average 5 times lower in winter (Fig.3a). Looking at the homologue groups, the lower chlorinated $Cl_{3-5}N$ showed a maximum in summer, whereas with higher chlorination degree ($Cl_{6-8}N$) a maximum in winter appeared (Fig.3i-3l). The temporal change of the ΣPCN concentration resembles the annual cycle of PCB levels$^{8-10)}$. The same explanations as discussed for the PCB are possible: PCB/PCN were introduced into the environment during or after their use. The atmospheric transport spread the PCB/PCN over a larger area. Soil and vegetation act as sinks for the PCB/PCN by adsorption of gaseous compounds or by particulate deposition. Depending on the temperature a revolatilisation of the PCB/ PCN occurs and results in the observed annual cycle.

There may also be sources currently releasing PCN into the environment. Besides waste incineration, vehicular emissions of PCN analogous to the known vehicular emissions of PCDD/F and PCB are probable. The PCN pattern from model experiments for the de-novo synthesis of organohalogen compounds in burning processes is dominated by the higher chlorinated PCN (Fig.3p)$^{4)}$. Therefore, perhaps thermal processes account for the increase of $Cl_{6-8}N$ concentrations in autumn and winter. However, in winter $\Sigma Cl_{5-8}N$ made only up to ~7% of the ΣPCN, so that the contribution of these sources to the total level is small. Apparently the ambient ΣPCN levels were mostly determined by the temperature dependent cycling of $Cl_{3-4}N$ masses between sinks and the atmosphere.

Differences in the ambient levels of the respective homologue group could be attributed to different levels of formerly released PCN in the environment or of presently emitted PCN. The distribution of the PCN ambient data at the 8 stations, as shown in the box plots (Fig.3), supported this idea. The box plots indicate the maximum, the minimum level, the median and the 25 and 75 percentil. For $Cl_{3-6}N$ (Fig.3f-3h, 3m) it is obvious that the background station H had the lowest concentrations. A rural area probably has fewer old or new pollution sources than an urban area. The distribution of ΣPCN and $Cl_{3-4}N$ (Fig.3e-3g) was very much alike for 6 of the Augsburg stations. The Augsburg stations were located within a circle of 5 km diameter, so the levels of former released $Cl_{3-4}N$ had presumably equalized. Station F was an exception which might be due to a specific emission history of this site. For $Cl_{5-8}N$ the intersite variability was higher than for $Cl_{3-4}N$. This is expected for presently emitted PCN, because the surroundings of every station concerning the distance to roads, residential and industrial areas, thus to the possible sources, was different. The intersite variability is also enhanced because the spreading of particulate ($Cl_{6-8}N$) emissions is perhaps less homogeneous than the spreading of gaseous substances ($Cl_{3-4}N$).

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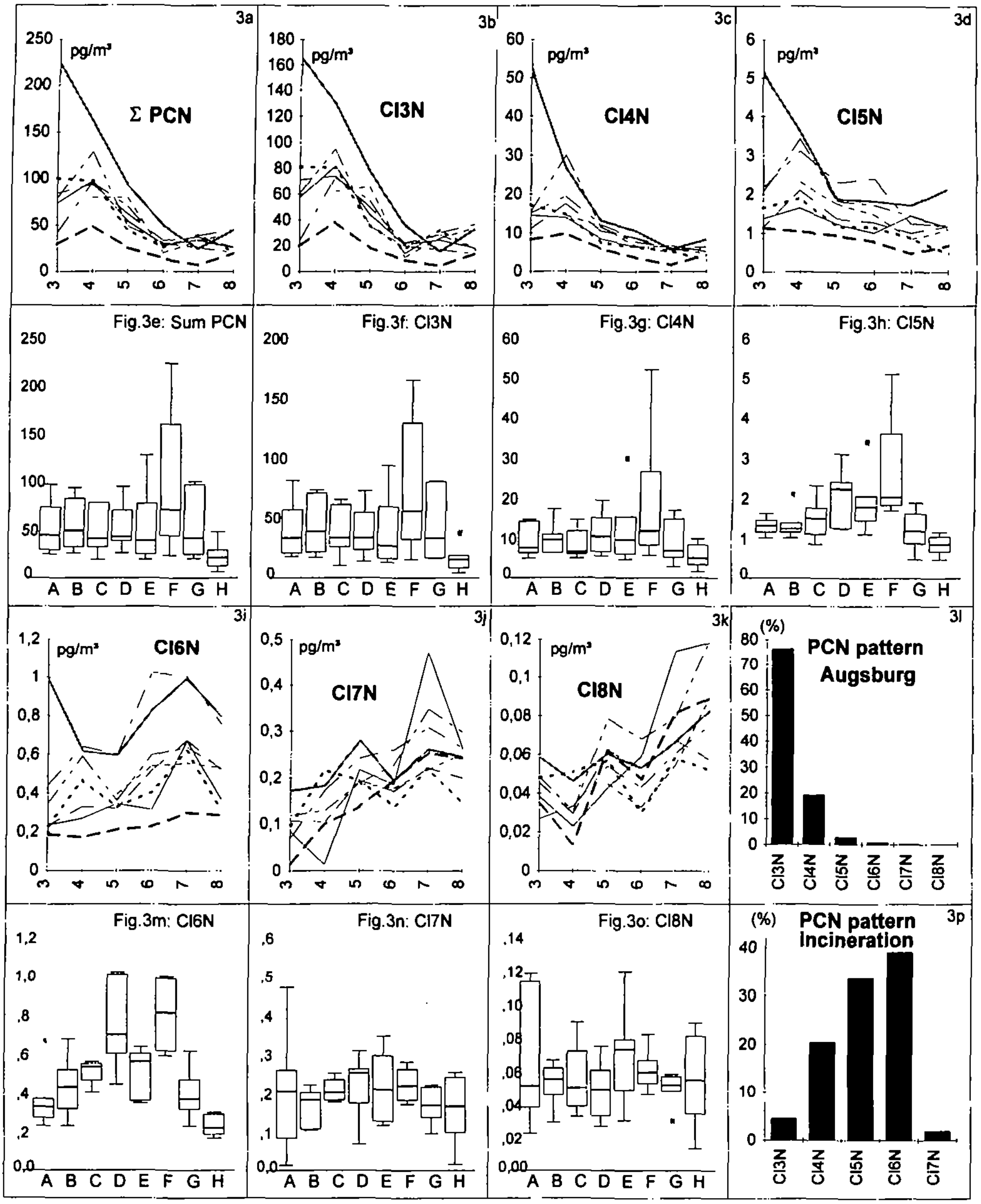

3+4 summer 5+6 autumn 7+8 winter A-G Augsburg stations H background station

Fig.3: *Seasonal variability, Boxplots and patterns of PCN*