# Polychlorinated naphthalenes in pine needles from Poland

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## Introduction

Polychlorinated naphthalenes (PCNs) are a group of 75 compounds, which have been commercially produced and used in a wide range of industrial applications for the sake of their specific chemical properties. They are recognized as good electrical insulators and also as water and flame resistant materials. Technical PCNs formulations were mainly used as capacitor dielectrics, engine oil additives, electroplating stop-off compounds, in wire insulations and as paper, wood and fabric preservatives. Moreover, they have been formed during production of PCBs formulations. Although recently most countries have stopped synthesis of PCNs, they still are widely distributed in the environment. Nowadays the principal sources of these compounds are municipal solid wastes incineration, metallurgical and chloro-alkali processes[1,2].

In last years PCNs concentrations in the environment have posed the cynosure of big group of scientists in the whole world. They relatively high concentrations are regarded as an environmental problem. Because they are persistent, toxic and lipophilic they might be bioaccumulated in living organisms and generate the danger for animals and humans[2,3]. It is essentially to monitor their levels in air, regional transport, as well as estimate specific sources. It is possible by using as a biomonitors pine tree needles. These trees are considered as the very suitable passive indicators for monitoring of PCNs concentrations in the troposphere. This is because the surface wax layer of the needles poses an ability to absorb these lipophilic compounds from the surrounding air[4,5,6]. In the current study pine needles were employed as biomonitors of PCNs concentrations in the ambient air of Poland. This country with its past history of production and use of different applications including these compounds, as well as with its location in the centre of Europe, presents the interesting region to these researches.

## Materials and Methods

The one year old pine needle samples were collected during October 2002 at eleven sites in Poland (Fig. 1). At each sampling point needles were taken from several *Pinus silvestris* trees at height of 1,5-2 m above the ground in distant at least 200 m from the nearest road. The samples

immediately after collection were packed in aluminium foil and put in plastic bags. They were frozen and stored at -20°C until analysis.

The samples were spiked with a $^{13}$C-labeled PCBs and PCDDs/Fs recovery standard and further Soxhlet extracted using toluene and 50% methanol in dichloromethane. Chlorophyll was removed by silica gel. The concentrated extract was cleaned using a multi-layer silica gel column chromatography. In the next step the activated basic alumina column chromatography was performed for fractionation. Fraction 1 was eluted by hexane, fraction 2 by 0.5 % dichloromethane in hexane and fraction 3 by 50 % dichloromethane in hexane.

Hypercarb-HPLC and PYE-HPLC separation were performed for farther fractionation. The Hypercarb-HPLC column was forward eluted using 50 % dichloromethane in hexane (Fr. 2-1 or 3-1) and back flushed using toluene (Fr. 2-2 or 3-2). The effluent from Hypercarb-HPLC column was micro concentrated to 100 µl and further subjected for additional sub-fractionation step using a pyrenyl silica column. The analyte from the PYE-HPLC column was collected each into four sub-fractions using, respectively, 10 % dichloromethane in *n*-hexane and dichloromethane – Fr. 2-2-1, 3-2-1, 2-2-2, 3-2-2, 2-2-3, 3-2-3, 2-2-4 and 3-2-4. Each sub-fraction was micro concentrated to 100 µl under gentle stream of nitrogen. Identification and quantitation of PCNs were done using high-resolution gas chromatograph (HRGC) coupled to a high-resolution mass spectrometer (HRMS). Details of analitical procedure are given elsewhere[6].

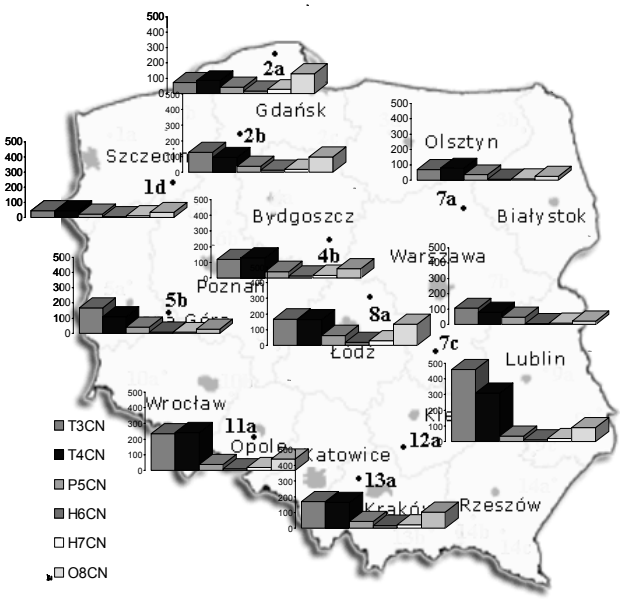


Fig. 1. Location of the sampling sites and concentrations of PCNs homologue groups in pine needles from Poland.

**Results and Discussion**

In this study the pine needles samples were analyzed to estimate 63 PCNs congeners concentrations in troposphere of Poland. The results of the study are given in the table 1.

Total PCNs concentration ranged from 165 to 925 pg/g wet weight. The highest concentrations of these compounds were found in the samples from the densely populated and industrialized region of Poland ( 8a, 11a, 12a, 13a).

Table 1. Concentrations (pg/g w.w.) of PCNs in pine needles from Poland.

| | **1d** | **5b** | **7a** | **7c** | **2a** | **2b** | **4b** | **8a** | **11a** | **12a** | **13a** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **T3CN** | 44,44 | 168,55 | 68,86 | 106,06 | 71,89 | 125,94 | 117,26 | 167,81 | 234,00 | 460,79 | 168,19 |
| **T4CN** | 45,25 | 110,04 | 78,66 | 79,99 | 84,32 | 93,92 | 129,86 | 163,93 | 241,02 | 309,17 | 164,84 |
| **P5CN** | 23,94 | 41,81 | 34,67 | 47,15 | 42,05 | 37,99 | 41,63 | 62,89 | 37,74 | 34,65 | 42,26 |
| **H6CN** | 5,96 | 7,68 | 6,38 | 6,78 | 17,33 | 12,95 | 13,03 | 17,52 | 9,72 | 11,65 | 17,16 |
| **H7CN** | 11,17 | 6,98 | 8,45 | 8,83 | 26,40 | 19,27 | 17,13 | 29,45 | 17,70 | 19,15 | 22,08 |
| **O8CN** | 33,84 | 27,72 | 24,25 | 23,16 | 128,41 | 95,65 | 59,04 | 135,18 | 72,76 | 88,52 | 101,29 |
| **Total** | **164,60** | **362,78** | **221,28** | **271,97** | **370,40** | **385,72** | **377,95** | **576,79** | **612,95** | **923,93** | **515,82** |

The most dominant homologues in the majority of samples were tri- and tetrachlorinated naphthalenes. T3CN congener sets 14/21/24 and 22/23 made up the largest percentage among this homologue group. Congener 38 was dominant T4CN in almost all samples, only in samples 11a and 12a congener set 33/34/37 made up the largest percentage of T4CN. Also T3CN and T4CN were the most dominant homologue groups in PCNs technical formulation Halowaxes: 1000, 1001, 1013, 1031, 1099., where dominant congeners among T3CN were 21/24, 14 and 23. Tetrachlorinated naphtalenes numbers 38/40, 33/34/37 and 46 were significant in those Halowax mixtures[7]. It can suggest those technical preparations as one of sources of these compounds in environmental samples. PCNs can be found in PCBs mixtures as their impurities. High content of T3CN, especially congeners 22/23 and 14/24, are found in Aroclor 1016, Aroclor 1032 and Phenoclor DP3. Tetra congeners which were dominant in Polish pine needle samples, were also main components in Aroclor 1016, Aroclor 1032, Pchenoclor DP3, Phenoclor DP4, Clophen A40 and Kanechlor 300[8].

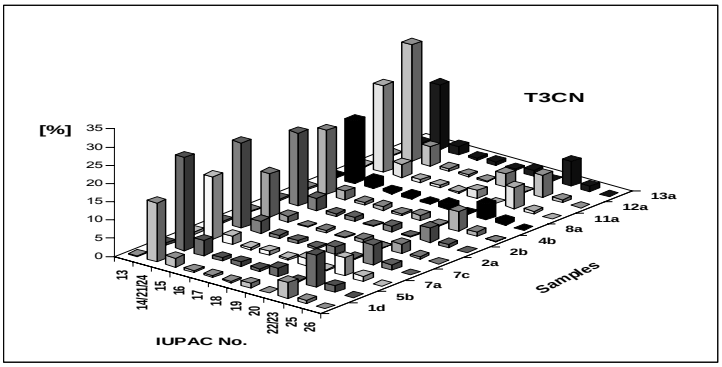


Fig. 2. Composition (%) of individual T3CN congeners in Polish pine needle samples.

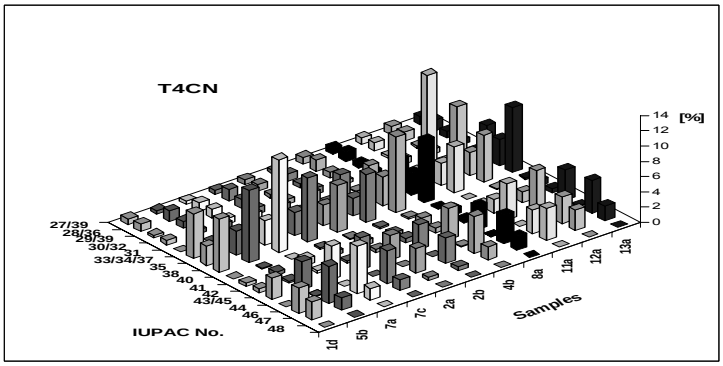


Fig. 3. Composition (%) of individual T4CN congeners in Polish pine needle samples.

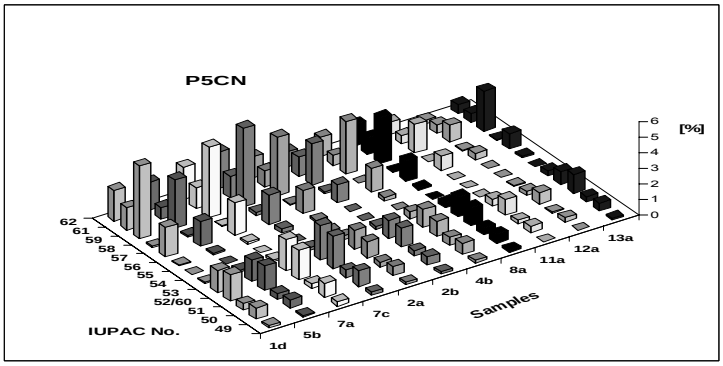


Fig. 4. Composition (%) of individual P5CN congeners in Polish pine needle samples.

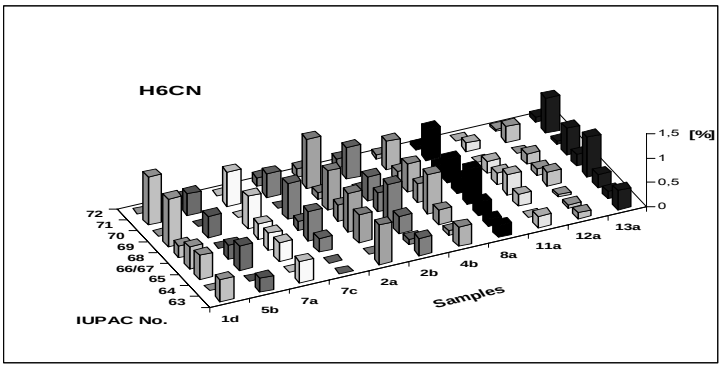


Fig. 5. Composition (%) of individual H6CN congeners in Polish pine needle samples.

Among P5CN congener 59 is the most dominant in all samples, also congener sets 52/60, 53, 57, 61 and 62 had significant share in P5CN concentration. In each sample H6CN and H7CN were the minor homologue groups.

Octachlorinated congeners had significant contribution among PCNs homologue group pattern of pine needles. Especially in sample 2a concentration of O8CN was over 34% of the total. Large amount of octachlorinated naphthalene can be found in Halowax 1051, Chlorofen, Kanechlor 600, Aroclor 1260 and 1262. It should be noticed that PCBs technical preparation Chlorofen, where O8CN presents 98% of total PCNs content, was produced and used in Poland.

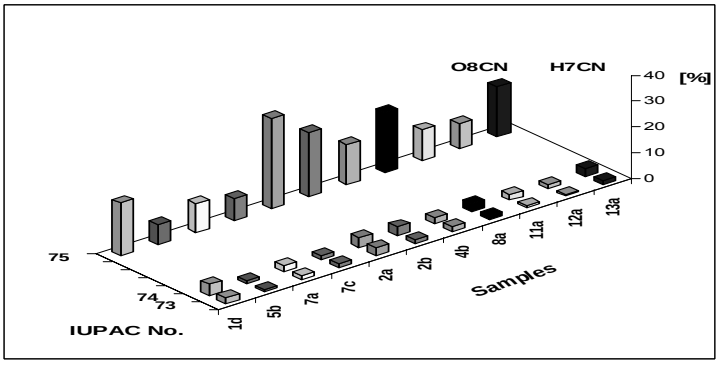


Fig. 6. Composition (%) of individual H7CN and O8CN congeners in Polish pine needle samples.

Similar pattern of PCNs congeners composition in Polish pine needles may suggest related origin of these pollutants. The most important sources of these compounds might be landfill disposal of different items containing PCNs, from which they infiltrate to surrounding soil.

Their presence in the environment could be also connected with places of production and use of their and PCBs technical formulations. Because PCNs and PCBs technical preparations have found

the application in diverse electrical equipment, especially concentrated in industrial area, it can be the reason why their higher levels are present in the ambient air of these regions.

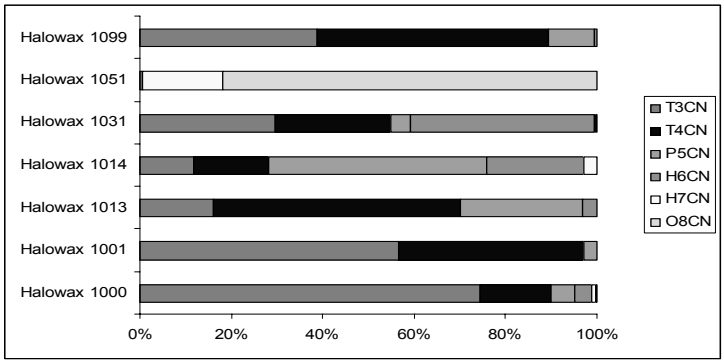


Fig. 7. Composition (%) of chloronaphtalen homologues in Halowax mixtures, data were taken from Noma et al. (2004)[7].

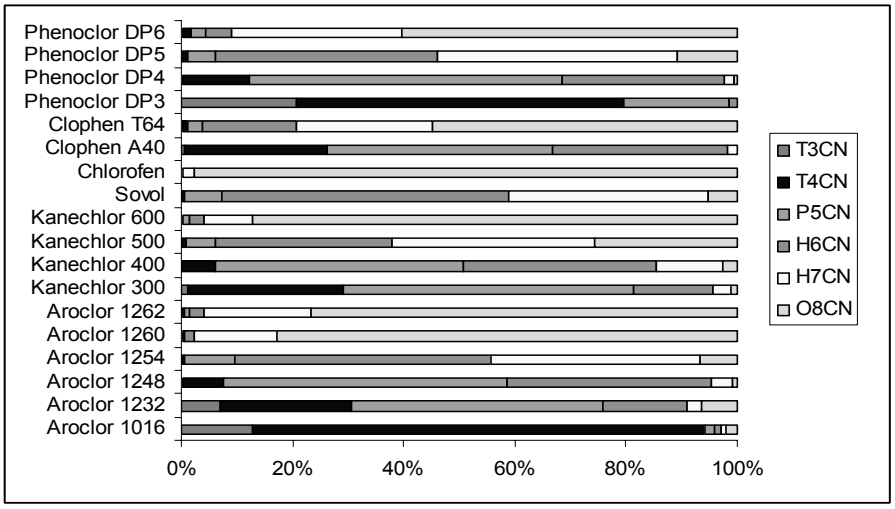


Fig. 8. Composition (%) of chloronaphtalen homologues in technical PCB mixtures, data were taken from Yamashita et al. (2004)[8].

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