Pine needles as biomatrix of polychlorinated naphthalenes (PCNs) in ambient air from Poland

Anna Orlikowska[1], Nobuyasu Hanari[2], Barbara Wyrzykowska[1], Jerzy Falandysz[1], Ilona Bochentin[1], Nobuyoshi Yamashita

[1]University of Gdańsk

[2]National Institute of Advanced Industrial Science and Technology (AIST)

Introduction

In view of the fact that the surface wax layer of leaf poses an ability to absorb the organohalogens from the surrounding air, the pine three needles are considered as the suitable passive indicators for monitoring of persistent and lipophilic compounds in the troposphere. They can be useful for identification pollution point sources, areas with background concentrations as well as for studies concerning regional similarities and differences for the past and recent use of lipophilic compounds. Moreover evergreen character, widespread distribution of the sampling sites and easy sample collection with its low costs make themwell suited for studies of contaminant levels [1,2]. Therefore, in this work pine needles were selected as the environmental matrix to investigate the concentrations and emission sources of polychlorinated naphthalenes (PCNs) to atmospheric air in Poland.

This country with its variety of industrial, agricultural and forestry sites opens chances for identification of sources of PCNs and their patterns in the environment. Also location in the center of Europe makes Poland interesting region to observe an impact of those pollutants from surrounding countries.

Polychlorinated naphthalenes are known as widespread environmental pollutants. Many from their 75 congeners are bioaccumulated and as a member of dioxin-like chemicals group can cause Ah receptor-mediated mechanism of toxicity with combination of various toxic responses. Additionally, there are continuously released into environment from many evaporative emission sources such as technical formulations, which found numerous industrial applications of additive character but also are formed duringmunicipal solid wastes incineration or metallurgical and chloroalkali processes [2,3]. Consequently, these circumstances induce scientists to estimate risk connected with occurrence of PCNs in the environment by assessment of input to dioxin like toxicity (TEQ).

Materials and Methods

The one year old pine needle samples were collected during October 2002 at 25 locations in Poland (Fig. 1). The samples were packed in aluminium foil, put in plastic bags and kept frozen at -20 °C until analysis. Subsequently, before Soxhlet extraction, pine needle samples were spiked with internal standards containing a mix of $^{13}C_{12}$-labeled coPCBs and PCDDs/Fs. The concentrated extract was cleaned-up using a multi-layer silica gel column chromatography. Furthermore the activated basic alumina column chromatography, Hypercarb-HPLC and PYE-HPLC were performed for additional clean up and extract fractionation. Further separation as well as detection, identification and quantitation of PCNs was done using high-resolution gas chromatograph (HRGC) coupled to a high-resolution mass spectrometer (HRMS). Details of analytical procedure are given elsewhere[2].

Results and Discussion

The purpose of this work was to investigate the concentrations and emission sources of PCNs to atmospheric air in Poland using pine needles.

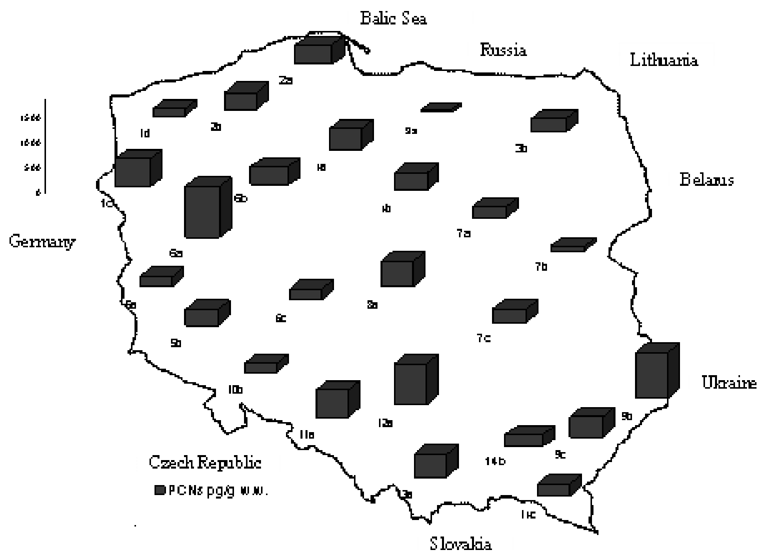

Fig. 1. Location of the sampling sites and level of PCNs of pine needles in Poland.

An elevated concentration of PCNs was noted for densely populated and industrialized region of Poland, and their total content in pine needles varied between 70 and 1100 pg/g wet weight (Fig. 1). Mono- and di-CNs were not quantified. Tri- and tetraCNs but also octaCN usually were the most dominant in CN homologue group profile (Fig. 2).

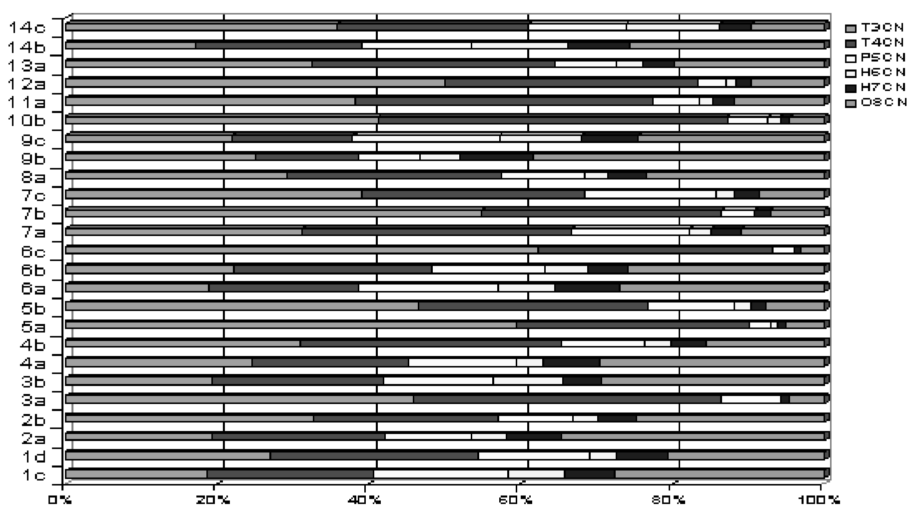

Fig. 2. PCN residues composition (%) of pine needles of Poland.

Congener sets 14/21/24 and congener IUPAC no. 38 made up the largest percentage among tri- and tetraCN homologue group. They were also the main compounds in PCN technical formulation Halowaxes[4] and were found in PCB mixtures[5]: Phenoclor DP3 and Aroclor 1016, Aroclor 1232. Among pentachlorinated naphthalens congener IUPAC no. 59 was the most dominant in all Polish pine samples and significant in Halowax 1013 and 1014 plus Aroclor 1232, Aroclor 1248 and Phenoclor DP4. Large amount of octachlorinated naphthalene detected in examined samples can also be found in technical formulations as Halowax 1051, Chlorofen, Sovol, Clophen T64, Phenoclor DP6 as well as in Aroclor 1260 and 1262.

The composition profile of CN congeners varied somehow between the sites implying existence of different pollution sources. The pine needle samples collected at the central and south-eastern regions of Poland displayed a relatively elevated concentration of chloronaphtalene congener IUPAC no. 54. Chloronaphthalene IUPAC no. 54 was absent or present only in ultra trace amount in the technical chloronaphthalene formulations of the Halowax series or as by-side impurity in many of the technical chlorobiphenyl formulations examined, but is formed during various thermal processes and relevant in fly ash[4,5,6]. Hence, a relative enrichment of pine needles in CN IUPAC no. 54 at some of the sites investigated point out combustion processes as important emission source of PCNs to ambient air in these regions. However, in Poland the main sources of studied compounds might be landfill disposal of different items containing PCNs. Moreover past use of PCN and PCB technical mixtures in diverse electrical equipment and also production of chlorine and chloroorganic compounds, which is important industry in Poland, seem to have significant impact on amount of these compounds in Polish environment[7,8].

Similarities and differences in composition pattern were further investigated using Cluster Analysis of the data set (Fig.3), giving clearer picture which sites are similar according to PCNs “fingerprinting”.

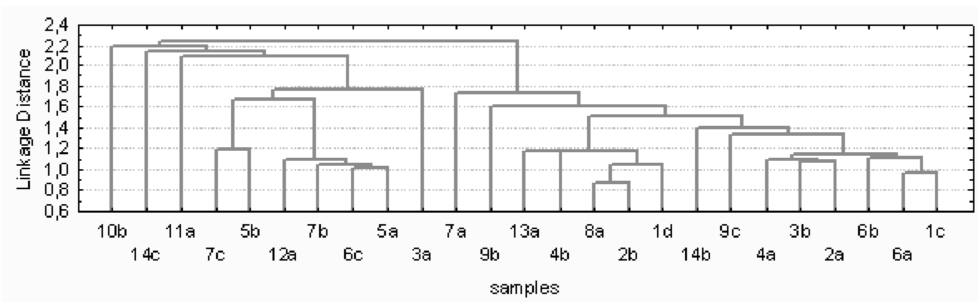

Fig. 3. Cluster analysis data of PCNs of pine needles of Poland.

Since PCNs are complex toxic environmental micropollutants, it is important to give attention to their potential ongoing sources and environmental levels not only in absolute concentration values but also when normalized in terms of dioxin toxicity equivalents (TEQs). Based on available REP values[9,10] for PCNs their content of pine needles was assessed as between 0.001 and 0.13 pgTEQ/g wet weight. Unfortunately the number of data on toxic effects generated by singular CN congeners is limited, and used REP values do not necessarily present a complete range of toxicity generated by all potentially toxic CN congeners. Thus TEQ values were also evaluated using predicted activity data of CNs for two bioassays (7-ethoxyresorufin-*O*-diethylase (EROD) and luciferase (luc))[11]. TEQs derived

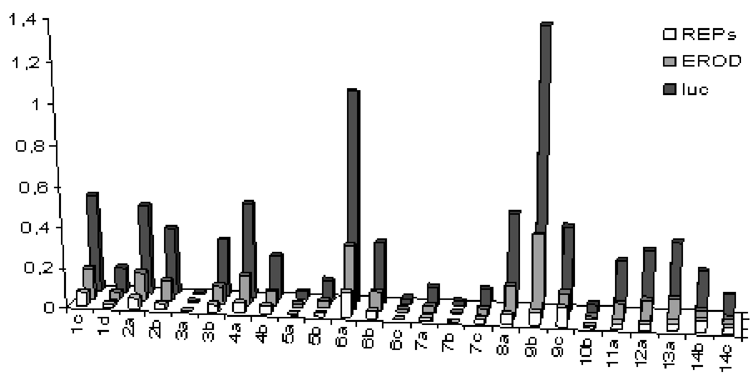

Fig. 4. PCNs concentration (pgTEQ/g wet weight) of pine needles of Poland.

from EROD and luc inducing potency ranged from 0.007 to 0.41 and from 0.01 to 1.37 pgTEQ/g wet weight, respectively (Fig. 4). The pine needles collected at the sites localized at the most industrialized and urbanized parts of the country displayed the highest toxic potential, while tenfold less where those of the largely agricultural and forestry regions.

Acknowledgments

The authors are grateful to Dyrekcja Generalna Lasów Panstwowych, Warsaw, Poland and to Dyrekcje Regionalne

Lasow Panstwowych for kind cooperation.

References

1. Jensen S., Eriksson G., Kylin H., Strachan W.M.J. (1992) *Chemosphere* 24, 229.

2. Hanari N., Horii Y., Okazawa T., Falandysz J., Bochentin I., Orlikowska A., Puzyn T., Wyrzykowska B., Yamashita N. (2004) *J. Environ. Monit.* 06, 305.

3. Jakobson, E., Asplund, L. (2000) *The Handbook of Environmental Chemistry, vol. 3, Part K. New Types of Persistent Halogenated Compounds*, edited by J. Passivirta (Berlin: Springer), 97.

4. Noma Y., Yamamoto T., Sakai S. (2004) *Environ. Sci. Technol.* 38, 1675.

5. Yamashita N., Kannan K., Imagawa T., Miyazaki A., Giesy J.P. (2000) *Environ. Sci. Technol.* 34, 4236.

6. Helm P.A., Bidleman T.F. (2003) *Environ. Sci. Technol.* 37, 1075.

7. Bogutyn W. (2003) Stockholm Convention GEF project GF/POL/01/004. Report for Institute of Environmental Protection in Poland, GF/POL/INV/R.23.

8. Kołsut W. (2002) Stockholm Convention GEF project GF/POL/01/004. Report for Institute of Environmental Protection in Poland, GF/POL/INV/R.11.

9. Blankenship A. L., Kannan K., Villalobos S. A., Villeneuve D. L., Falandysz J., Imagawa T., Jakobsson E., Giesy J. P. (2000) *Environ. Sci. Technol*. 34, 3153.

10. Villeneuve D.L., Kannan K., Khim J.S., Falandysz J., Nikiforov V.A., Blankenship A.L., Giesy J.P. (2000) *Arch. Environ. Contam. Toxicol.* 39, 273.

11. Falandysz J., Puzyn T.(2004) *J. Environ. Sci. Health. A* 39, 1505.