

POLYCHLORINATED NAPHTHALENES

POLYCHLORINATED NAPHTHALENES FROM A SWEDISH PERSPECTIVE

Ulf Järnberg

Institute of Applied Environmental Research
Laboratory for Analytical Environmental Chemistry
Stockholm University
SE -106 91 Stockholm, Sweden. e-mail: ulf.jarberg@itm.su.se

PCNs from inventory to environmental problem

Polychlorinated naphthalenes or PCNs were first described in 1833 by Laurent¹. He provided a remarkably thorough description of their properties and composition. A couple of more works were published during that century that further described the composition of PCNs but it wasn't until World War One that PCNs became industrially produced for various applications. The reason was probably the timing of a sufficient supply of electrical power to produce elementary chlorine. Production and use increased rapidly and it was recognised that PCNs are excellent for several purposes; weather resistant impregnant for textiles and dielectric and sealant wax in electrical applications. In 1930 awareness rose of the acute toxicological properties of PCNs through a series of fatal intoxication of both workers occupied in electrical industries and cattle, which were accidentally exposed^{2,3}.

Sweden never produced any large quantities of PCN. Actually there is no record of PCN production although several companies had the facilities for chlorination. This provided us with a situation where studies on various environmental compartments could be performed on the assumption of no large scale source. The first findings of PCNs in biota from an unpolluted area was reported in 1984 by Prof. Jansson and coworkers⁴.

Congener specific approach - chromatographic aspects

A comprehensive investigation on liquid chromatographic properties of a number of individual PCN congeners was performed by Prof. Brinkmann and co-workers in the 1970:s⁵. During the 1980:s these studies were followed up by investigations of the gas chromatographic properties of PCNs on different types of stationary phases in an effort to approach a congener specific determination⁶. Recently, the separation of all penta- and hexachlorinated PCN congeners on a chiral cyclodextrin modified GC column was demonstrated⁷. Today the situation is still such that a complete congener separation requires the use of several stationary phases in combination. A divergence in the identity of some of the tetrachloronaphthalenes is still seen in the literature and this problem is likely to be overcome when more commercial standards are being available and chromatographed on similar columns. Results are today mostly obtained on 5%-phenyl modified stationary phases (DB5 equivalent) and the elution order differs from that of cyanopropyl modified phases (OV1701 equivalent). A chromatogram of tetrachloronaphthalenes on a 50% phenyl modified capillary column is shown in Fig 1. The elution order on this column is similar to that of

POLYCHLORINATED NAPHTHALENES

DB5 but an increased separation is obtained.

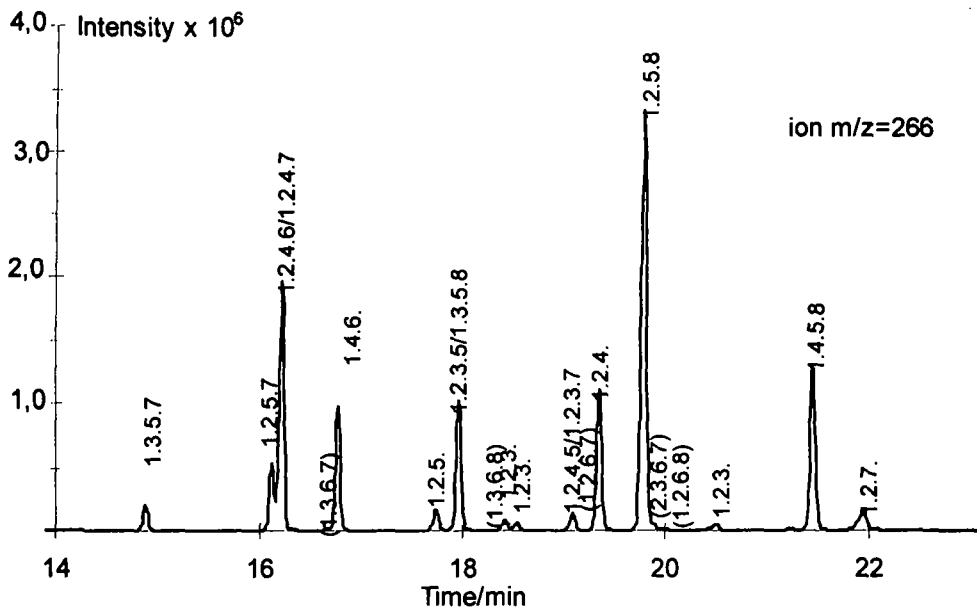


Figure 1. Selected ion chromatogram of tetrachloronaphthalenes in technical Halowax 1014 on a 50% phenyl-dimethylsilylated silica capillary column. The position of minor congeners are indicated within brackets.

Approaching the environmental fate of PCNs

In the 1970:s PCNs a Dutch team studied the photochemical properties of individual PCNs and these studies formed a basis for later studies on photochemical alteration of PCN products at our laboratory^{8,9}. In an effort to explain the differences in congener concentration distributions found between technical PCN products and distributions found in environmental samples two degradation studies were performed; aerobic microbiological degradation utilising a standard activated sludge degradation assay and photochemical degradation using sunlight in methanol solution. These preliminary results indicated that sunlight photodegradation may be one explanation for the differences encountered while the biodegradation assay showed no change over a 28 day period. These results do not exclude the possibility of biodegradation of PCNs but only indicate that PCNs are slowly degraded in municipal sewage water treatment plants and that this route may be of less importance. These results provided insight into the differences between congener compositions of technical PCNs and the profiles that are now encountered in the environment. Selective degradation of some congeners can occur through photolysis and this is thought to explain some of the differences found. A second possibility can be the influence of other sources, i.e. municipal waste incineration, which produces a significantly different congener concentration distribution^{10,11}.

Summary of available PCN data and identification of major analytical needs.

ORGANOHALOGEN COMPOUNDS

Vol. 47 (2000)

POLYCHLORINATED NAPHTHALENES

The behaviour of PCNs in biota has been investigated to some extent and bioconcentration and biomagnification data has been reported indicating that several PCN congeners bioconcentrate and biomagnify^{12,13}. The general exposure situation of the human population to PCNs is however largely unknown due to limited data on concentrations of PCNs in food and human blood and adipose tissue¹⁴. To date, PCN data exist on samples from both urban and background air and also limited data on background sediment, indicating that PCNs are widely distributed on a global scale and that the congener concentration distributions are similar to each other with a prevalence for early eluting congeners in each homologue group^{15,16,17,18}. On the following assumptions; a 300.000 ton of cumulative PCN world production, an estimated average composition of technical PCNs (Table 1a), estimated equilibrium distributions (Table 1b) and an approximate amount of available surface sediment for distribution using a simplified model adopted from Ballschmiter (1992) our lowest background sediment data suggests that around 25% of the estimated total cumulative world production may have reached the environment²⁰.

Table 1a Estimated average composition of technical PCN

TetraCNs	25%
PentaCNs	17%
HexaCNs	7%
HeptaCNs	2%

Table 1b Estimated equilibrium distribution for selected PCNs on sediment¹⁹

1,3,5,7-tetraCN	17.4%
1,2,3,5,7-pentaCN	94.7%
1,2,3,4,5,7-hexaCN	85.1%
1,2,3,4,5,6,8-heptaCN	96.1%

Table 2. Comparison of model estimates of PCNs in sediment and measured values

	<i>Model estimate soil/sediment</i>	<i>found, background sediment</i>
TetraCNs	0.094 ng/g	0.038 - 0.11 ng/g
PentaCNs	0.36 ng/g	0.066 - 0.64 ng/g
HexaCNs	0.13 ng/g	0.031 - 0.28 ng/g
HeptaCNs	0.043 ng/g	0.0069 - 0.28 ng/g
sum tetra-heptaCNs	0.63 ng/g	0.14 - 1.31 ng/g

This figure could be compared to the estimated value of 30% of the total cumulative world production of PCBs that has reached the environment. These calculations are based on a limited data set both regarding environmental concentrations and production figures. Thus, there is a need for extended analyses of background media such as sediment, water and air to be able to provide data for more elaborate modelling of the distribution of PCNs into and within the environment.

References

- 1) Laurent, M.A. (1833) Sur les chlorures de Naphtaline. Ann. Chim. Phys. 52, 275-285
- 2) Greenburg, L., Mayers, M.R. and Smith, A.R. (1939) The systemic effects resulting from exposure to certain chlorinated hydrocarbons. J. Ind. Hyg. Toxicol. 21, 29-38.
- 3) Kover, F.D. (1975) Environmental hazard assessment report: chlorinated naphthalenes.

POLYCHLORINATED NAPHTHALENES

USEPA report 560/8-75-001, NTIS publication PB-248834, National Technical Information Service, Springfield, V.A., USA.

- 4) Jansson, B., Asplund, L. and Olsson, M. (1984) Analysis of polychlorinated naphthalenes in environmental samples. *Chemosphere* 13, 33-41.
- 5) Brinkman, U.A.Th. and Reymer, H.G.M. (1976) Polychlorinated naphthalenes. *J. Chromatogr.* 127, 203-243.
- 6) Järnberg, U., Asplund, L., Jakobsson, E., (1994) Gas chromatographic retention behaviour of polychlorinated naphthalenes on non-polar, polarizable, polar and smectic capillary columns. *J. Chromatogr.* 683, 385-396.
- 7) Helm, P.A., Jantunen, L.M.M., Bidleman, T.F., Dorman, F.L. (1999) Complete separation of isomeric penta- and hexachloronaphthalenes by capillary gas chromatography. *J.High. Resol. Chrom.* 22, 639-643.
- 8) Ruzo, L.O., Bunce, N.J. and Safe, S.H. (1975) Photoreactions of simple halonaphthalenes in solution. *Can. J. Chem.* 53, 688-693.
- 9) Järnberg, U., Asplund, L., Egebäck, A-L., Jansson, B., Wideqvist, U., Unger, M. (1999) Polychlorinated naphthalene congener profiles in background sediment samples in relation to a degraded Halowax 1014 mixture. *Environ. Sci.Technol.* 33, 1-6.
- 10) Imagawa, T. and Yamashita, N. (1994) Isomer specific analysis of polychlorinated naphthalenes in Halowax and fly ash. *Organohalogen Compd.* 19, 215-218
- 11) Schneider, M., Stieglitz, L., Will, R., Zwick, G. (1998) Formation of polychlorinated naphthalenes on fly ash. *Chemosphere* 37, 2055-2070.
- 12) Järnberg, U., Asplund, L., Grafström, A.K., Haglund, P., Jansson, B., Lexén, K., de Wit, C., Strandell, S., Olsson, M., Jonsson, B., (1993) Polychlorinated biphenyls and polychlorinated naphthalenes in Swedish sediment and biota. Levels, patterns and time trends. *Environ. Sci. Technol.* , 27, 1364-1374.
- 13) Falandysz, J. and Rappe, C. (1996) Spatial distribution in plankton and bioaccumulation features of polychlorinated naphthalenes in a pelagic food chain in southern part of the Baltic Proper. *Environ. Sci. Technol.* 30, 3362-3370.
- 14) Asplund, L., Svensson, B-G., Nilsson, A., Eriksson, U., Jansson, B., Wideqvist, U., Skerfving, S. Levels of polychlorinated naphthalenes(PCN) in human blood plasma with reference to fish intake.
- 15) Järnberg, U., Asplund, L., de Wit, C., Jakobsson, E. (1997) Distribution of polychlorinated naphthalene congeners in environmental and source related samples. *Arch. Environ. Contam. Toxicol.* 32, 232-245
- 16) Gevao, B., Harner, T., Jones, K.C. (2000) Sedimentary record of polychlorinated naphthalene concentrations and deposition fluxes in a dated lake core. *Environ. Sci. Technol.* 34, 33-38.
- 17) Harner, T. Kylin, H., Bidleman, T. F., Halsall, C., Strachan, W.M.J., Barrie, L.A., Fellin, P. (1998) Polychlorinated naphthalenes and coplanar polychlorinated biphenyls in arctic air. *Environ. Sci. Technol.* 32, 3257-3265.
- 18) Wideqvist, U., Egebäck, A-L., Järnberg, U., Asplund, L. Polychlorinated naphthalenes in background air from two Swedish locations. Manuscript.
- 19) Crookes, M.J. and Howe, P.D. (1993) *Environmental hazard assessment: Halogenated naphthalenes.*, 13th edn. Building Research Establishment, Garston, Watford, U.K.
- 20) Ballschmiter, K. (1992) Transport and fate of organic compounds in the global environment. *Angewandte Chemie* 31, 487-515.

ORGANOHALOGEN COMPOUNDS