

Polychlorinated naphthalenes in groundwater samples from the Llobregat aquifer (Spain)

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Abstract

Polychlorinated naphthalenes (PCNs) have characteristics fairly similar to those of polychlorinated biphenyls and terphenyls (PCBs and PCTs) and although they have been used in numerous applications, very few reports on the occurrence of PCNs in water have been published. Both automated solid-phase extraction (SPE) and liquid–liquid extraction (LLE) procedures were evaluated to concentrate PCNs. High-resolution gas chromatography with electron-capture detection (HRGC–ECD) and mass spectrometric detection in the selected ion monitoring mode (SIM) were used to analyze PCNs in groundwater samples from the aquifer of the Llobregat river near Barcelona (NE Spain). The homologue distribution profiles of PCNs found in groundwater samples and the standard mixtures of Halowax (1099, 1013 and 1014) were compared. Quantification was achieved by HRGC–ECD. Total PCN concentrations expressed as Halowax 1099 equivalents ranged from <0.5 ng/l to 79.1 µg/l in the water samples, with tetrachloronaphthalenes (TetraPCN) as the major group of congeners. © 1997 Elsevier Science B.V.

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1. Introduction

Polychlorinated naphthalenes (PCNs) are industrial compounds produced by chlorination of naphthalene which have been manufactured in substantial amounts since the beginning of the century and which have been worldwide used until 1980 [1,2]. These compounds have been mainly used as dielectric fluids in transformers and capacitors, flame retardants, plasticizers, oil additives, fungicides, cable covering compositions, sealants and to impregnate wood paper and textiles [1,3].

PCNs have physicochemical properties essentially similar to those of polychlorinated biphenyls (PCBs)

and polychlorinated terphenyls (PCTs). PCNs are manufactured for uses analogous to those of PCBs, although their production has been estimated to be 10% that of PCBs [1]. PCNs have also been detected as byproducts of commercial PCB formulations [4,5].

The systematic numbering of all 75 possible congeners has been carried out by Wiedmann and Ballschmiter [6] although only a limited number have been detected in environmental samples. Conversely, fly ash samples from municipal solid waste incineration (MSW) have shown very complex patterns and the presence of several PCN congeners not present in commercial mixtures such as nos. 31, 39, 40, 44, 45, 48, 49, 54 and 55 [7–11]. In this context, Nakano et al. [8] reported the detailed isomeric

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pattern of PCN in Halowaxes in two capillary columns; Imagawa et al. [9,10] published the synthesis and the separation of all tetra and pentachloronaphthalenes in several capillary columns and Takasuga and Yamashita [11] developed an all congener specific analysis of PCNs in ambient air and MSW incineration samples. The complete synthesis of several penta-, hexa- and heptachloronaphthalenes has been reported by Auger et al. [12].

Extensive reports on the toxicity of PCNs [13] and cases of PCN intoxication has been published [14]. PCNs have been implicated in causing various diseases, such as chloracne, liver damage, X-disease in cattle and chicken oedema [1,15]. Some of the isomers of PCNs are known to be strongly bioaccumulating such as i.e. no 67 in liver [16] and congeners nos. 66 and 67 were found in human adipose tissue from Ontario municipalities [17]. The determination of 2,3,7,8-TCDD toxic equivalent factors for several PCN congeners using biological tests has been carried out [18]. Some PCN congeners (nos. 66 and 67) have been shown to induce enzymes such as EROD (7-ethoxy-resorufin *O*-deethylase) and AHH (aryl hydrocarbon hydroxylase) in a similar way to dioxins [18] being its toxicity in the same range than mono-*ortho*-chlorinated PCBs [19].

The presence of PCNs in environmental samples is rare especially when compared with the data available in the literature for PCBs and even PCTs. PCNs have been detected in biota [13,20–23], in human adipose tissue and mothers' milk [17,24,25], as impurities of PCBs [26], in the electronic equipment of a laboratory [27], formed during municipal waste incineration [7–11], in sediment samples from a ditch in Florida, a river in California and from the Gdańsk Basin in Poland [22,28,29] and scattered landfills several years after their disposal [30]. The presence of PCNs in water has been seldom reported in the literature with concentrations varying from the low ppb level in Florida [28] to the ppt level in Sweden [13].

The Llobregat river supplies water to Barcelona for drinking purposes. Groundwater wells from the Llobregat aquifer sometimes constitute water reservoirs when the water treatment plant is in downtime or the quality of the river water is low. Organic compounds previously detected in these groundwater samples comprise a wide range of chlorinated solvents, dicyclopentadiene and derivatives, di- to hexa-

chlorinated ethane to butane saturated and unsaturated hydrocarbons [31] and traces of gasoline. The former came probably from the poor disposal of illegal landfills closed in the early 1970s in the studied area, whereas the origin of gasoline was from an accidental pipeline spill.

The aim of this study was to assess the fate and occurrence of PCNs in this aquifer and to evaluate the extent of the pollution. Automated solid-phase extraction (SPE) followed by HRGC-ECD and high resolution gas chromatography-mass spectrometry (HRGC-MS) in selected-ion monitoring (SIM) mode were the analytical procedures used to monitor the presence of PCNs in groundwater. The homologue distribution of both commercial mixtures and PCN profiles in real samples was compared. Quantitation was performed by HRGC-ECD expressed as Halowax equivalents and sum of congeners.

2. Material and methods

2.1. Sampling

Samples were collected during 1995 and mid-1996. The 33 sampling points are shown in Fig. 1. They are located at approximately 10 km from the mouth of Llobregat river. Groundwater samples from wells (E1, E2, E3, E4, E5, E6, ETV, T1, T2) were used until several years ago for drinking water purposes in small villages and eventually when the waterworks plant of Barcelona was in downtime or the river water quality was low. At present, only E1 and occasionally E2 are still in use. Boreholes (S1, S4, S5, G3, G4, G5, E7, E8, E9 and E10) were drilled to control the quality of the groundwater during the petrol pollution event. The rest of samples (189, 178, 158, 187, 97, 186, A, 34, 36, 38, 41, B, 114 and C) are wells which are mainly used for agricultural and industrial purposes. Grab samples were collected in amber glass bottles (1 l) fitted with teflon screw caps. The unfiltered water samples were transported and stored at 4°C until their analysis, performed within 24–48 h.

2.2. Chemicals and reagents

Halowax standard mixtures 1000, 1014 and 1099, 1,4-dichloronaphthalene (no. 5) and octachloronaph-

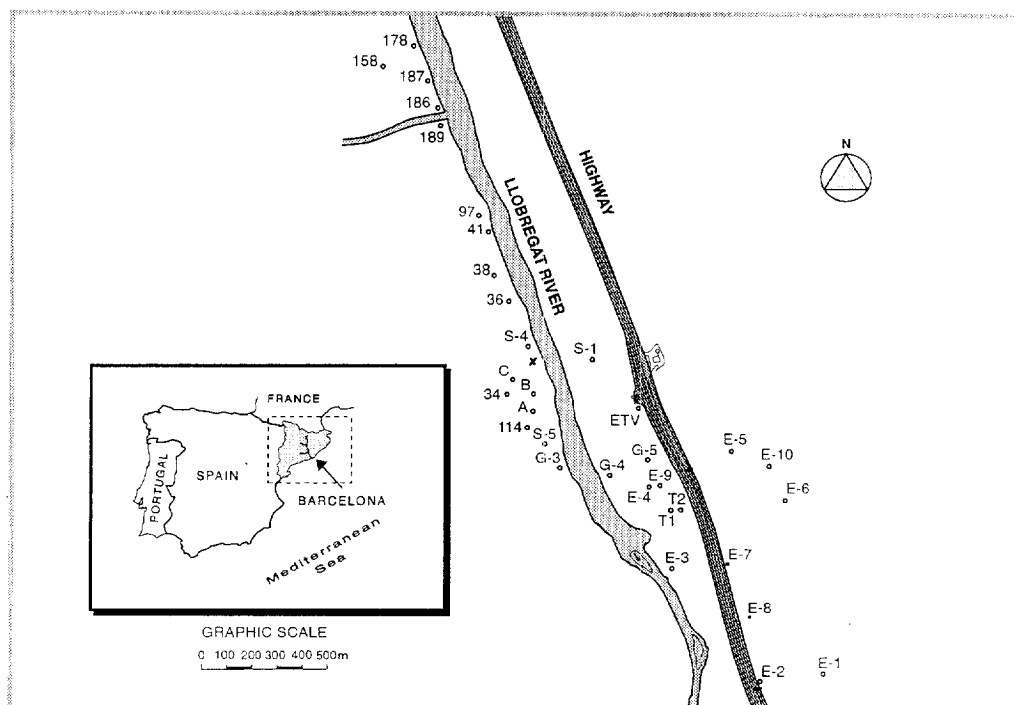


Fig. 1. Geographical situation of the analyzed samples.

thalene (no. 75) were purchased from AccuStandard Inc. (New Haven, CT, USA). The 1-chloro and 2-chloronaphthalene congeners (nos. 1 and 2) were from Aldrich (Germany) and 1,2,7-trichloronaphthalene (no. 17), 2,3,6,7-tetrachloronaphthalene (no. 48), 1,2,3,6,7-pentachloronaphthalene (no. 54), 1,2,3,5,6,7-hexachloronaphthalene (no. 67) and 1,2,3,4,5,6,7-heptachloronaphthalene (no. 73) congeners were from Promochem (Wesel, Germany).

Solid-phase extraction (SPE) was performed by using either Accubond (J&W Scientific, Folsom, CA, USA) ODS- C_{18} cartridges (500 mg/6 ml), Empore C_{18} (10 mm/6 ml) extraction disk cartridges (Varian, Harbor City, CA) or Empore C_{18} (47 mm) extraction disks (Varian).

As solvents, acetone (Carlo Erba, Milan, Italy), methanol, dichloromethane and ethyl acetate (J.T. Baker, Phillipsburg, NJ) were used and their purity checked by concentration and injection of the extract into the GC-ECD system. All glass materials were cleaned with AP-13 Extran alkaline soap (Merck, Darmstadt, Germany), rinsed with Milli-Q water, acetone and dried overnight.

2.3. Analytical procedure

Automated solid-phase extraction (SPE): Accubond C_{18} cartridges (500 mg/6 ml) were pre-washed with 10 ml each of methanol and water at a flow-rate of 10 ml/min. Samples of 1 l were allowed to flow through the cartridge at 10 ml/min. After the sample had passed, each cartridge was dried under a stream of nitrogen for 10 min to remove traces of water. PCNs were eluted by passing 2×3 ml of ethyl acetate through the cartridge at a flow-rate of 2 ml/min. The ethyl acetate eluate was evaporated to ca. 1 ml with a Zymark TurboVap LV evaporator (Varian). Then, 100 μ l of iso-octane was added to the extract before concentration in order to avoid losses of analytes and evaporated, under a gentle stream of nitrogen, to ca. 100 μ l.

Empore C_{18} extraction disks cartridges (10 mm/6 ml) were pre-washed with 2 ml each of methanol and water at a flow-rate of 5 ml/min. Samples of 100 ml were allowed to flow through the cartridge at 5 ml/min. After the sample had passed, each cartridge was dried under a stream of nitrogen for 10

min to remove traces of water. PCNs were eluted by passing 2×2 ml of ethyl acetate through the cartridge at a flow-rate of 2 ml/min. The concentration of the ethyl acetate eluate and the exchange to *i*-octane followed the same procedure as described before.

Empore C₁₈ extraction disks (47 mm) were conditioned with 10 ml each of methanol and washed twice with 10 ml of water. A 5 ml volume of methanol was added to 1 l water samples and well mixed. The water sample was added to the reservoir and, under vacuum, filtered through the disk at a flow-rate of approximately 30 ml/min. The PCNs were eluted with 2×10 ml of ethyl acetate allowing the remaining solvent to soak the disk for about 1 min and then draw remainder through under vacuum. The extract was concentrated following the same way as described before for cartridges.

Liquid-liquid extraction (LLE): 1 l water samples were extracted with dichloromethane (2×150 ml). The organic layer was dried over sodium sulphate and concentrated with a rotavapor to ca. 1 ml. Iso-octane was added to the extract and concentrated to ca. 100 µl under a gentle stream of nitrogen.

2.4. Apparatus

The automated SPE isolation step of PCNs was performed, as described before with a Zymark Autotrace Workstation (Varian) which provides full automation of cartridge conditioning, sample loading, cartridge air-drying and analyte elution. The enrichment on Empore disks was accomplished with a Millipore filtration instrument (Millipore, Bedford, USA).

Gas chromatography was carried out on a Carlo Erba (Milan, Italy) Model Mega 5300 series gas chromatograph equipped with a ⁶³Ni electron capture detector using nitrogen as make-up gas. A DB-5 fused-silica (J&W Scientific) capillary column (60 m×0.25 mm I.D.) with a 0.25 µm film thickness, was used with helium as carrier gas at a linear velocity of 30 cm/s. Cold on column injections (1 µl) were employed. The temperature was held isothermally at 60°C for 1 min, programmed to 150°C at 20°C/min, then programmed to 285°C at 4°C/min and maintained at this temperature for 10 min. The injector and detector temperatures were ambient and 300°C, respectively. The chromatographic

data were analyzed using the MiniChrom (Fisons, Manchester, UK) software.

For HRGC-MS a Fisons Model 8060 gas chromatograph coupled to a Fisons Trio 1000 mass spectrometer was used. A 60 m DB-5 (J&W Scientific) fused-silica capillary column (0.25 mm I.D., 0.25 µm film) was used. The temperature programme for GC-MS – full scan and selected ion monitoring (SIM) modes – was from 60°C (held for 1 min) to 150°C at 20°C/min, and then from 150 to 285°C (held 15 min) at 4°C/min, using the splitless mode. The HRGC-MS operating conditions were as follows: ion source and interface temperatures, 225° and 285°C, respectively; ionization energy, 70 eV (electron impact mode) and a mass range 40 and 500 *m/z* at 1 s per decade when the full-scan mode was used. In the HRGC-MS-SIM mode the ions at *m/z* 162, 164, 196, 198, 230, 232, 264, 300, 302, 334, 336, 368, 370, 402 and 404 from mono- to octachloronaphthalenes were monitored and *m/z* 207 was used as lock mass.

3. Results and discussion

3.1. Recovery studies

Recovery data of Halowax 1099 was performed by spiking Milli-Q water and river raw water at a concentration of 1 µg/l. Volumes of 100 ml were passed through the 10 mm/6 ml C₁₈ Empore extraction disk cartridges. Higher volumes (1000 ml) were used for the 500 mg/6 ml C₁₈ cartridges, the 47 mm Empore extraction disks and methylene chloride liquid-liquid extraction. The obtained results are shown in Table 1, automated SPE presented recoveries in the range 66–80% for Milli-Q water samples (*n*=7), being the best results for the extraction disks cartridges and, in addition, less time consuming. No significant variations of recovery (65%) were observed when river water was used to study matrix effects instead of Milli-Q. Several solvents were tested, where ethyl acetate was preferable to the mixture of acetone-ethyl acetate (75:25, v/v) for eluting the PCN standard (66% and 55%, respectively). Cartridges with enriched PCNs can be transported and stored for a long period of time as has been proved for other compounds [32]. Empore

Table 1
Recoveries of PCN in reagent Milli-Q water spiked with Halowax 1099 (1 µg/l)

Volume (ml)	Extraction method	Solvent elution	Recovery (mean ±S.D.) (%)
1000	SPE C ₁₈ cartridges (6 ml, 500 mg)	AcOEt (2×3 ml)	66±7
1000	SPE C ₁₈ cartridges (6 ml, 500 mg)	25% AcOEt 75% Acetone (2×3 ml)	55±6
1000 ^a	SPE C ₁₈ cartridges (6 ml, 500 mg)	AcOEt (2×3 ml)	64±10
1000	LLE Cl ₂ Me (2×150 ml)	–	100±8
100	SPE C ₁₈ disk-cartridges (6 ml, 10 mm Ø)	AcOEt (2×2 ml)	80±5
1000	SPE C ₁₈ disks (47 mm Ø)	AcOEt (2×10 ml)	84±4

^a Raw water from the Llobregat river spiked with 1 µg/l of Halowax 1099.

disks and liquid–liquid extraction procedures showed better results (84% and 100% recovery) than those reported for cartridges. Nevertheless, comparative values were obtained for both types of disks (10 mm and 47 mm) demonstrating that for the analysis of PCNs both are adequate and superior to cartridges. In addition, the disks showed lower coefficients of variation than the cartridges. Other advantages, included avoiding hazardous solvents and the fact that automated SPE is less time consuming, were also considered, although usually samples have to be analyzed immediately after enrichment with disks. The obtained results prompted us to perform the analysis of PCNs with the extraction disk cartridges instead of disks and liquid–liquid procedures since it offers the possibility of automatization.

3.2. PCNS in groundwater

Quantification of complex mixtures like PCTs or PCNs is difficult due to the lack of commercial availability of most individual congeners. PCTs and PCNs can be quantified using technical mixtures (i.e. Aroclors or Halowaxes, respectively) as standards. This analytical approach has several disadvantages; one of them is related to the different sources of standards. Thus, Wester et al. [33] discussed the

different peak pattern of PCTs in the Aroclor 5442 from the same company (Monsanto) but produced in different countries (USA and UK, respectively). Falandysz et al. [22] found that the profile of PCN congener groups in sediment samples and most of the organisms analyzed was quite different from Halowax 1014 but no comparison could be made with European PCN formulations (i.e. Nibren D130 or RN 130 from Bayer, Germany) due to the unavailability of a detailed PCN congener composition of these mixtures in the literature. It seems clear that in a first approach, quantification of PCTs or PCNs expressed as technical mixtures equivalents must consider the origin of the samples. Thus, American and European samples must be quantified with American and European standards, respectively, if they are available. Quantification of these polychlorinated mixtures can be performed either on the basis of selected ions, by using GC–MS with electron impact (EI) or negative chemical ionization (NCI) [33,34], or by comparing the total area of all relevant peaks in the total ion chromatogram (TIC) of the samples with those for the standards. A comparison of different methods of quantification for PCTs in sediments and biota has been recently published [33] and HRGC–ECD has been considered the best option for semiquantitative analysis [33,35].

Table 2
Concentration range of PCN (ng/l) in wells and boreholes from the Llobregat aquifer

	178	158	187	186	189	97	41	38	36	S4	S1	C	B	34	A	ETV ^a	
Halowax 1099	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd-20 200	55 100-79 100	nd	nd	nd	nd	8.5	
ΣDi PCN ^a	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd-1400	nd	nd	nd	nd	nd	1.0	
ΣTri PCN ^b	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd-5200	8300-17 100	nd	nd	nd	nd	2.6	
ΣTetra PCN ^c	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd-12 200	38 000-44 100	nd	nd	nd	nd	2.6	
ΣPenta PCN ^d	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd-1200	670-14500	nd	nd	nd	nd	0.5	
ΣHexa PCN ^e	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd-100	210-330	nd	nd	nd	nd	0.1	
ΣHepta PCN ^f	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	
114	S5	E5	E5	G5	G3 ^h	G4 ^h	E10	E9 ^h	E4 ^h	T1 ^h	T2	E6	E7	E3	E8	E1	E2
Halowax 1099	nd	nd-2500	165	2600	17.3	2.6	nd	8.5	6.0	2.9	nd	nd	nd	nd	nd	nd	nd
ΣDi PCN ^a	nd	nd	3.0	nd	0.8	nd	nd	0.6	0.5	0.2	nd	nd	nd	nd	nd	nd	nd
ΣTri PCN ^b	nd	nd-400	136	600	0.8	0.8	nd	3.6	2.6	1.3	nd	nd	nd	nd	nd	nd	nd
ΣTetra PCN ^c	nd	nd-1200	14.5	1800	10.1	1.2	nd	3.4	2.2	1.3	nd	nd	nd	nd	nd	nd	nd
ΣPenta PCN ^d	nd	nd-300	2.9	100	nd	0.3	nd	0.4	0.3	nd	nd	nd	nd	nd	nd	nd	nd
ΣHexa PCN ^e	nd	nd-600	nd	100	nd	0.2	nd	0.1	0.1	nd	nd	nd	nd	nd	nd	nd	nd
ΣHepta PCN ^f	nd	nd	nd	nd	nd	0.1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

Quantification method GC/ECD. nd=not detected.

^a ΣDi PCN expressed as congener (no. 5) equivalents.

^b ΣTri PCN expressed as congener (no. 17) equivalents.

^c ΣTetra PCN expressed as congener (no. 48) equivalents.

^d ΣPenta PCN expressed as congener (no. 54) equivalents.

^e ΣHexa PCN expressed as congener (no. 67) equivalents.

^f ΣHepta PCN expressed as congener (no. 73) equivalents.

^h Values from [36].

Levels of PCNs from different wells and boreholes in the studied area are displayed in Table 2. HRGC–ECD was the method of quantification chosen after univocal confirmation by GC–MS. The results are

expressed either as a congener equivalent for each group of chlorination or as Halowax 1099 equivalents, because it was impossible to obtain any commercial mixture of Spanish or other European

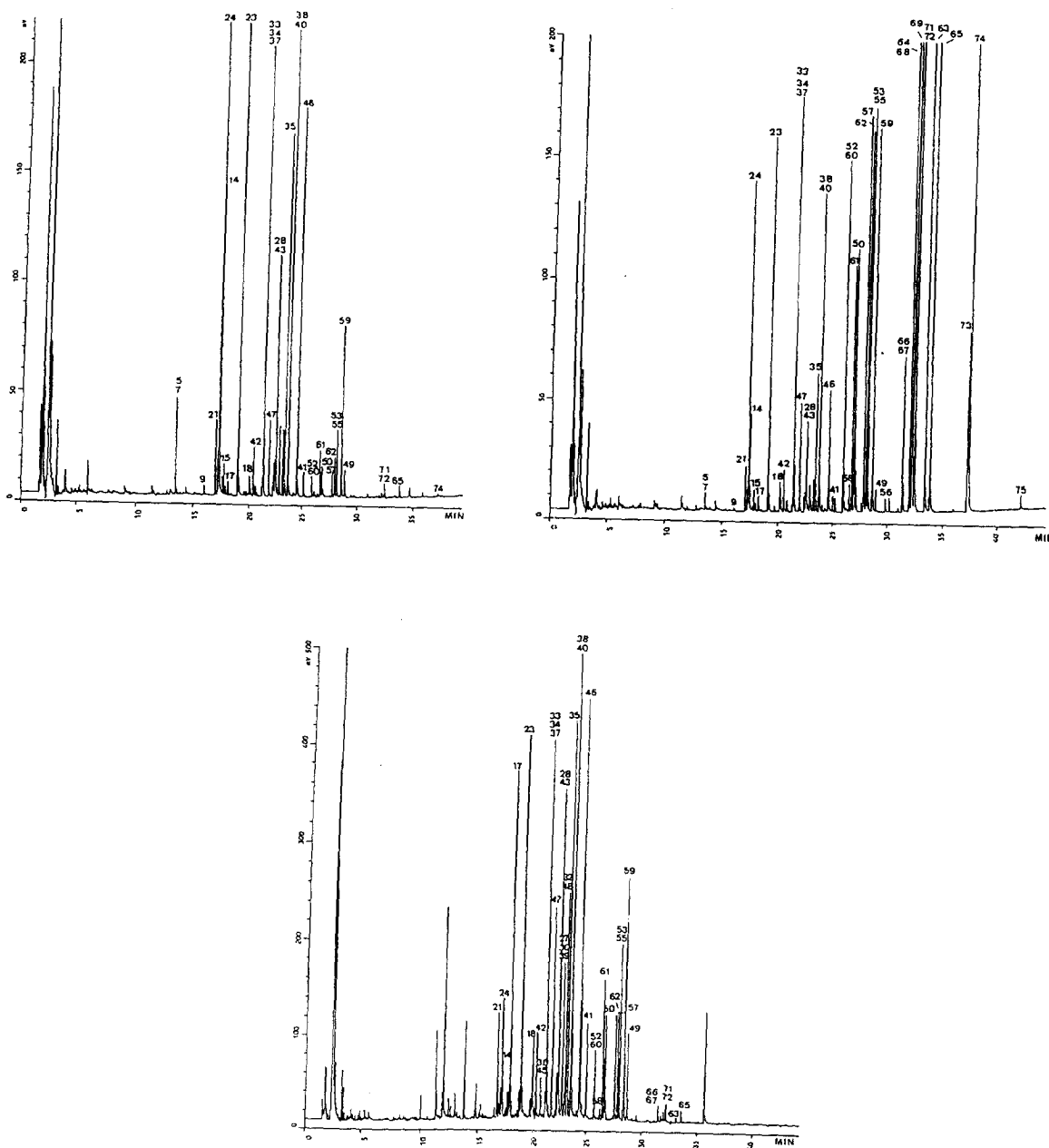


Fig. 2. ECD chromatogram of technical mixtures Halowax 1099 (top left), Halowax 1014 (top right) and the borehole S5 (bottom). Wiedman and Ballschmitter's nomenclature [6] used.

PCN formulations. Since the complete separation of all isomers is practically impossible, coelution between congeners of the same group occurs. However, no coelution between congeners of different groups is observed and this minimizes the possible errors associated with congener overlapping and variation in response. We assumed that all congeners of the same group had the same recovery and response than those available individual congener standards. Therefore, the quantification of each group of PCNs was performed by interpolating the value of the sum of all congener areas into the calibration curve of the individual congener standard.

Fig. 2 shows, as an example, a comparison of the chromatographic (HRGC–ECD) profiles of the commercial Halowax 1014, Halowax 1099 and the borehole S5. Congeners have been numbered according to Wiedmann and Ballschmiter's nomenclature [6]. The individual congener distribution observed in this chromatogram for the highest concentrated sample is in agreement with all the positive samples studied.

PCNs were found at high ppb level in four (S4, S1, S5 and G5) of the 33 samples investigated. Table 2 displays the range levels of the sum of di- to heptachloronaphthalenes in the water samples and their Halowax 1099 equivalents. The value range for

these four samples was from 2.5 $\mu\text{g/l}$ (S5) to a maximum of 79.1 $\mu\text{g/l}$ for S1. Several samples (G3, G4, E4, E9, ETV and T1) showed PCN concentrations in the ppt (ng/l) range. These low level samples were quantified by HRGC–MS in the selected-ion monitoring mode (SIM) using the two most abundant isotope peaks from the molecular ion region (M^+ and $[M+2]^+$), their isotopic ratio for confirmatory purposes and chromatographic windows for each group of PCN homologues to avoid ion contributions from $[M-2Cl]^+$ ions [36]. No PCNs were detected in any of the wells above S4 (see Fig. 1) which were primarily devoted to industrial and agricultural purposes. The three most concentrated samples were analyzed two more times when extensive pumping was done or piezometric levels could be changed significantly. The measured concentrations show great variations of the PCN levels but further research is needed in order to evaluate their leaching into the aquifer.

Fig. 3 displays, as an example, the homologue distribution of different commercial mixtures (Halowax 1099, 1013 and 1014) and the more concentrated samples (S1, S4, S5 and G5). The pattern of the groundwater samples varied from triPCN to pentaPCN congeners, being the tetraPCN the most abundants, whereas the mono, di-, hepta

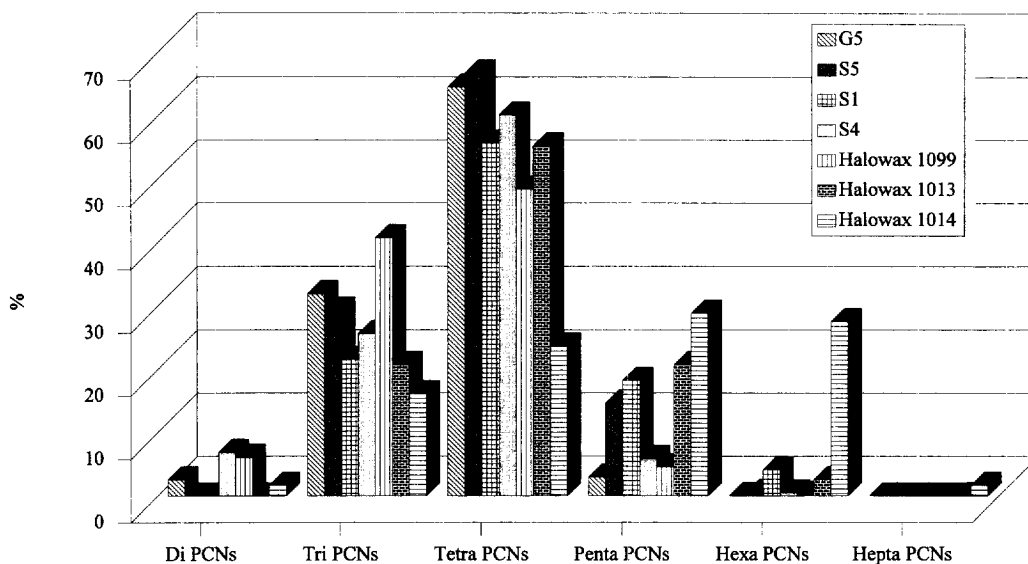


Fig. 3. Homologue distributions for Halowax 1099, Halowax 1013, Halowax 1014 and several groundwater samples.

and octa-PCNs were practically absent. Thus, the homologue distribution for PCNs of the most concentrated samples matched reasonably well, in the absence of any European standard, with those observed for Halowax 1099.

The obtained results shows a relative small area where PCNs are highly concentrated with minor spread in the neighbourhood. This site was illegally used as a landfill in the early 1970s, and probably the poor disposal of wastes is the origin of the pollution by PCNs. Chlorinated solvents, dicyclopentadiene and derivatives, gasoline and polychlorinated saturated and insaturated hydrocarbons are among the main industrial organic compounds detected in this area [31].

According to the EEC regulations concerning drinking water quality [37], PCNs can be included into the parameter no. 55, the same group of PCBs, PCTs and organochlorinated insecticides, herbicides and fungicides. The maximum admissible concentration (MAC) for these compounds set at 0.5 µg/l is exceeded in the boreholes S4, S1, S5 and G5. Although the values reported for wells (ETV, E4, E5, E9 and T1) are far below this limit, the contamination of the aquifer by the landfill is a source of concern for human health and the evolution of PCNs in these wells must be checked regularly in order to guarantee its safety to potential consumers. Further research is needed to determine the amount and spread of PCNs and other potential toxic compounds in the soil of the suspected location of the landfill to evaluate the feasibility of its removal.

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References

- [1] U.A.Th. Brinkman, H.G.M. Reymer, *J. Chromatogr.* 127 (1976) 203.
- [2] J. Falandysz, L. Strandberg, S.E. Kulp, B. Strandberg, P.A. Bergqvist, C. Rappe, *Chemosphere* 33 (1996) 51.
- [3] U.A.Th. Brinkman, A. De Kok, in: R.D. Kimbrough (Ed.), *Halogenated biphenyls, terphenyls, naphthalenes, dibenzodioxins and related products*, Elsevier/North-Holland, Amsterdam, 1980.
- [4] J.S. Vos, J.H. Koeman, H.L. van der Maas, M.C. ten Noever de Braw, R.H. de Vos, *Food Cosmet. Toxicol.* 8 (1970) 625.
- [5] G.W. Bowes, M.J. Mulvahill, B.R. Simoneit, A.L. Burlingame, R.W. Risebrough, *Nature* 256 (1975) 305.
- [6] T. Wiedmann, K. Ballschmiter, *Fresenius J. Anal. Chem.* 346 (1993) 800.
- [7] T. Wiedmann, K. Ballschmiter, *Organohalogen Compounds* 9 (1992) 331.
- [8] T. Nakano, K. Fujimori, Y. Takaishi, H. Umeda, *Rep. Hyogo Prefect. Inst. Environ. Sci.* 25 (1993) 34.
- [9] T. Imagawa, N. Yamashita, A. Miyazaki, *J. Environm. Chem* 3 (1993) 221.
- [10] T. Imagawa, N. Yamashita, A. Miyazaki, *Organohalogen Compounds* 19 (1994) 215.
- [11] T. Takasuga, T. Inoue, O. Ireland, *Organohalogen Compounds* 19 (1994) 177.
- [12] P. Auger, M. Malalyandi, R.H. Wightman, C. Bensimon, D.T. Williams, *Environ. Sci and Technol.* 27 (1993) 1673.
- [13] U. Järnberg, L. Asplund, C. de Wit, A.K. Grafström, P. Haglund, B. Jansson, K. Lexen, M. Strandell, M. Olsson, B. Jonsson, *Environ Sci. Technol.* 27 (1993) 1364.
- [14] F. Kover, *Environmental hazard assesment report: Chlorinated naphthalenes*, US EPA Report 560/8-75-001, US EPA, Washington, DC, 1975.
- [15] F.A. Beland, R.D. Geer, *J. Chromatography* 84 (1973) 59.
- [16] L. Asplund, B. Jansson, G. Sundström, I. Brandt, U.A.Th. Brinkman, *Chemosphere* 15 (1986) 619.
- [17] D.T. Williams, B. Kennedy, G. Le Bel, *Chemosphere* 27 (1993) 795.
- [18] A. Hanberg, F. Waern, L. Asplund, E. Haglund, S. Safe, *Chemosphere* 20 (1990) 1161.
- [19] M. Engwall, B. Brunström, E. Jakobsson, *Arch. Toxicol.* 68 (1994) 37.
- [20] M. Schlabach, A. Biselh, H. Gundersen, J. Knutzen, *Organohalogen Compounds* 24 (1995) 489.
- [21] B. Jansson, L. Asplung, M. Olson, *Chemosphere* 13 (1984) 33.
- [22] J. Falandysz, L. Strandberg, P.A. Bergqvist, S.E. Kulp, B. Strandberg, C. Rappe, *Environ. Sci. Technol.* 30 (1996) 3266.
- [23] J. Falandysz, C. Rappe, *Environ. Sci. Technol.* 30 (1996) 3362.
- [24] R. Takeshita, H. Yoshida, *Eisei Kagaku* 25 (1979) 24.
- [25] D.G. Hayward, J.M. Charles, C. Voss de Bettancourt, S.E. Stephens, R.D. Stephens, P.J. Papanek, L.L. Lance, C. Ward, *Chemosphere* 18 (1989) 455.
- [26] P. Haglund, E. Jacobsson, L. Asplund, M. Athanasiadou, A. Bergman, *J. Chromatogr.* 634 (1993) 79.
- [27] C. Weistrand, A. Lunden, K. Noren, *Chemosphere* 24 (1992) 1197.
- [28] H.J. Crump-Weisner, H.R. Feltz, M.L. Yates, *J. Res. US Geol. Survey.* 1 (1973) 603.

- [29] L.M. Law, D.F. Goerlitz, *Pest. Mon. J.* 8 (1974) 33.
- [30] A. De Kok, R.B. Geerdink, U.A. Th Brinkman, *Chromatogr. Biochem. Med. Environ. Res.* 1 (1983) 203.
- [31] F. Ventura, J. Romero, J. Parés, *Environ. Sci. and Technol.* (1997), in press.
- [32] S. Lacorte, N. Ehreshman, D. Barceló, *Environ. Sci. and Technol.* 29 (1995) 2834.
- [33] P.G. Wester, J. de Boer, U.A.Th. Brinkman, *Environ. Sci. and Technol.* 30 (1996) 473.
- [34] L. Canton, J.O. Grimalt, *Chemosphere* 23 (1991) 327.
- [35] A. de Kok, B. Geerdink, G. de Vries, U.A.Th. Brinkman, *Int. J. Environ. Anal. Chem.* 12 (1982) 99.
- [36] I. Espadaler, E. Eljarrat, J. Caixach, J. Rivera, I. Martí, F. Ventura, *Rapid Commun. Mass Spectrom.* 11 (1997) 410.
- [37] EEC Directive relating to the quality of water intended for human consumption; 80/778/EEC (OJL 229.30.8.80).