

# POLYCHLORINATED NAFTALENES AND DLPCBs

## POLYCHLORINATED NAPHTHALENES IN PINE NEEDLES: AN ATMOSPHERIC EVALUATION OF SELECTED LOCATIONS IN THE SOUTHEASTERN UNITED STATES

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### Introduction

Polychlorinated naphthalenes (PCNs) are a group of 75 compounds that are composed of a naphthalene ring substituted with 1 to 8 chlorine atoms<sup>1,2</sup>. PCNs were widely in industrial applications due to their good electrical insulation properties, excellent weather resistance, low flammability, and are lipophilic. Technical PCN formulations were used as capacitor dielectrics, cutting oils, engine oil additives, electroplating stop-off compounds, die casting, ship insulation, wood, paper, and fabric preservatives, and wire insulation<sup>2</sup>. They also occurred as impurities in commercial PCB fluids. Present day environmental sources of PCNs include municipal solid waste incineration, metallurgical processes like copper roasting, and chlor-alkali processes<sup>3,4</sup>. Because of their widespread use, PCNs were detected in air, sediment, fish, birds and human tissues<sup>1,5,6</sup>. PCNs have been shown to be toxic to animals and humans through the Ah-receptor mediated mechanism<sup>1</sup>.

Although PCNs were detected in air, very little is known on accumulation of PCNs in pine needles. In this study, we have measured PCN levels in pine needles, which have been demonstrated as a fixed site, regenerative, annual monitoring matrix for the evaluation of local, regional and national distribution of lipophilic air pollutants<sup>7</sup>. Pine needles were collected from the surroundings of Paducah Gaseous Diffusion Plant (PGDP) and Marshall County in westernmost Kentucky and PCB and mercury contaminated Superfund site at Brunswick, Georgia and the pine needles were analyzed using high-resolution gas chromatograph interfaced with high resolution mass spectrometer (HRGC/HRMS).

### Methods and Materials

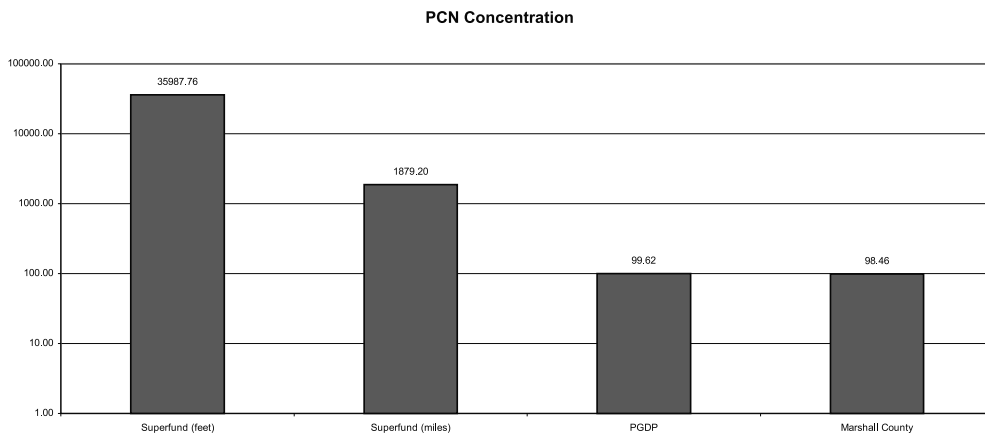
One year old pine needles were collected from the surroundings of the Paducah Gaseous Diffusion Plant (3 sites), Marshall County (3 sites) in westernmost Kentucky and a highly contaminated (PCBs and mercury) superfund site in Brunswick, GA (4 sites). Background information about the superfund site can be found elsewhere<sup>8</sup>. The pine needle samples were stored at -20 °C until analysis. The samples were Soxhlet extracted using methylene chloride and acetone (3:1 v/v). The concentrated extract was cleaned using a multi-layer column chromatography. Alumina column chromatography and HPLC-Hypercarb separation was performed to fractionate various analytes. Identification and quantitation of PCNs was done using a Hewlett-Packard 6890 series high-resolution gas chromatograph (HRGC) coupled to a JEOL JMS-700 high-resolution mass spectrometer (HRMS). The mass resolution of the spectrometer was greater than 10<sup>-4</sup> mass units. PCN congeners were separated using a DB-1 capillary column. The column oven temperature programs include an initial temperature

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of 70 °C with a hold time of 1 min. Then, from 70 to 180 °C at a rate of 15 °C/min and then to 270 °C at 2 °C/min with a final hold time of 5 min. Injector and transfer line temperatures were held at 260 and 250 °C, respectively. Helium was used as the carrier gas. The mass spectrometer was operated at an electron impact (EI) energy of 70 eV. PCN congeners were determined by selected ion monitoring (SIM) at the two most intensive ions of the molecular ion cluster. Halowaxes 1001, 1014 and 1051 containing all the tri- through octachloronaphthalenes were used as a PCN standard.

## Results and Discussion

Polychlorinated naphthalenes were detected in all pine needles analyzed. Total PCN concentrations in pine needles varied from 99 pg g<sup>-1</sup> dry wt to 18,934 pg g<sup>-1</sup> dry wt. The samples taken from the superfund site had an average concentration (18,934 pg g<sup>-1</sup> dry wt.) of PCNs that is over two orders of magnitude greater than the average concentrations (99 pg g<sup>-1</sup> dry wt.) of pine needles collected at the sites in Westernmost Kentucky (Fig.1). Also the pine needles taken within feet from the superfund site had PCN concentrations ten times greater than samples taken miles away from the Superfund site. There was little or no difference in the PCN concentrations taken from the two locations in Western Kentucky.

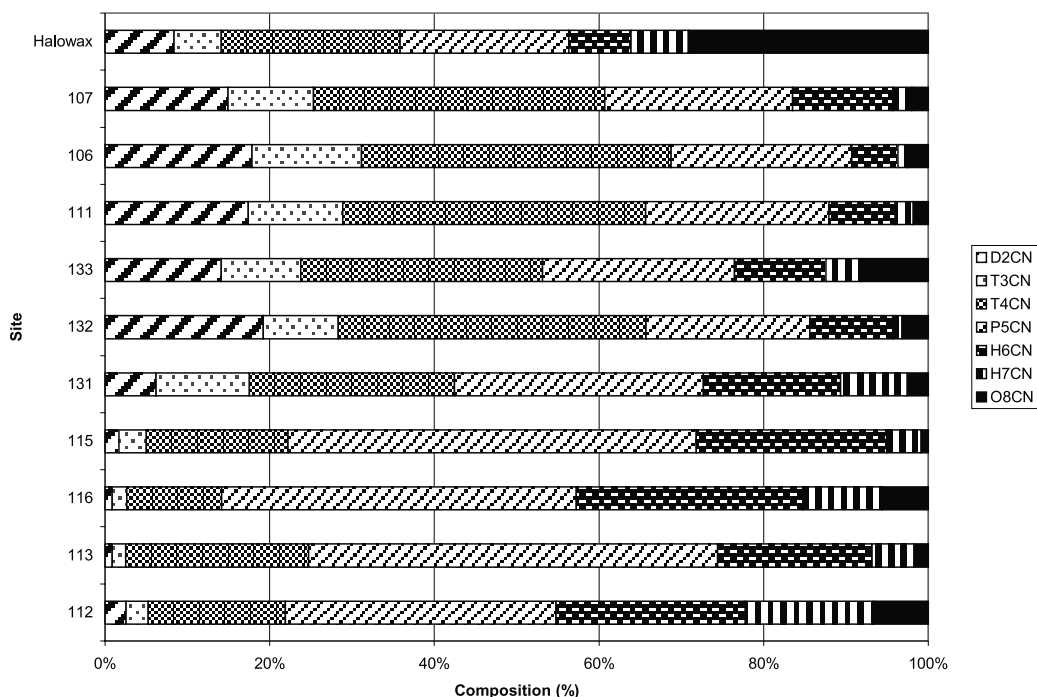


**Figure 1.** Total PCN concentrations (pg g<sup>-1</sup> dry wt) in pine needles collected from selected locations in southeastern United States.

Percent composition of PCNs was presented in Fig. 2. In general, superfund sites (#112, 113, 115 and 116) contain larger proportion of higher chlorinated (penta- hexa-, hepta-, octa) PCNs, while other sites in western Kentucky (#106, 107, 111, 131,132, 133) contain relatively higher proportion of lower chlorinated PCNs. Pentachloronaphthalenes (P5CN) accounted for >40 % (average) of the total PCN concentrations in superfund sites. P5CN accounted for less than 25 % at the locations in Western Kentucky (Fig. 2).

At the Superfund site, penta-CN congeners 52/60 accounted for an average of 26 % of the total concentration. At the PGDP locations (#131, 132 and 133) no one congener predominated at all three sites. At the Marshall County locations (106, 107), P4CN congener sets 33/34/37, 28/36/43, and 38 made up the largest percentage of the total and had approximately the same percentage within each site.

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**Figure 2.** Percent composition of PCNs in pine needles collected from several locations in southeastern United States.

Earlier studies have reported elevated concentrations of PCNs in environmental media collected near chlorine manufacturing facility and a magnesium refinery, and suggested of their inputs from these industries<sup>5,6</sup>. In addition, PCN congeners are also released from the use of PCBs due to their presence as co-contaminants in technical PCB mixtures<sup>5,6</sup>. In the present study, elevated concentrations of PCNs were recorded in pine needles collected at sites near PCB contaminated superfund site than other relatively uncontaminated sites. PCNs might have volatilized from the contaminated site and accumulated in pine needles. Higher percent contribution of lower chlorinated PCNs in pine needles collected from relatively less contaminated general locations indicate that lower chlorinated PCNs are transported long distance from the point source locations.

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