



# Isomer-Specific Analysis and Toxic Evaluation of Polychlorinated Naphthalenes in Soil, Sediment, and Biota Collected near the Site of a Former Chlor-Alkali Plant

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Concentrations and composition of polychlorinated naphthalene (PCN) congeners were determined in soil, sediments, blue crab, striped mullet, and boat-tailed grackle collected near a chlor-alkali plant to determine their congener profile, bioaccumulation properties, and toxic potential. Concentrations of total PCNs as high as 23  $\mu\text{g/g}$ , dry wt, were found in sediments collected at the marsh contaminated by disposal of wastes from the chlor-alkali process. The spatial distribution of sediment-PCN concentrations was not related with those observed for polychlorinated biphenyls (PCBs). The PCN congener profile did not resemble those of any technical mixtures. Hepta- and octa-chloronaphthalenes were the most abundant congeners accounting for greater than 50% of the total PCN concentrations in soil and sediments. A characteristic profile of PCNs in samples collected at the chlor-alkali site suggests the formation of chloronaphthalene congeners during chlor-alkali process, as has been suggested for polychlorinated dibenzofurans (PCDFs). Concentrations of total PCNs in biota were 3–5 orders of magnitude less than in sediments. The profile of PCN congeners in biota was predominated by tetra- or penta-chloronaphthalenes, while hepta- and octa-chloronaphthalenes were not detected. Affinity of more chlorinated naphthalene congeners to sediment organic carbon and steric factors that affect membrane permeability have contributed to less bioavailability. The 2,3,7,8-TCDD equivalents (TEQs) estimated for PCNs in sediments and biota were greater than those reported for PCBs, PCDDs, or PCDFs. Our results suggest that the chlor-alkali process has been an important source of PCNs due to their formation in the process. The contribution of PCNs to dioxin-like toxicity in environmental media near the chlor-alkali process may overwhelm those due to PCBs, PCDDs, or PCDFs.

## Introduction

Polychlorinated naphthalenes (PCNs) are primarily industrial chemicals consisting of two fused aromatic rings substituted with one to eight chlorine atoms. The physical and chemical properties of PCNs are similar to polychlorinated biphenyls (PCBs) with high thermal stability and inertness, which favored their application in the electrical industry as dielectric fluids in transformers and capacitors and as cable insulators. PCNs were also used as engine oil additives, wood preservatives, electroplating masking compounds, and feedstocks for dye production (1). Besides their production as technical mixtures for use in various applications, chlorinated naphthalenes are also formed during combustion processes such as municipal solid waste incineration (MSWI) (2–5) and in metallurgical processes such as copper roasting (6, 7). Formation of chloronaphthalenes (CN) from pyrolysis of chlorinated solvents such as tetrachloroethylene and polyvinylidene chloride has also been reported (8, 9). Elevated concentrations of PCNs in environmental media collected near a chlorine manufacturing facility (10) and a magnesium refinery (11) were suggestive of their inputs from these industries. In addition, PCN congeners are also released from the use of PCBs due to their presence as co-contaminants in technical PCB mixtures (10, 12).

Technical PCN mixtures with chlorine contents ranging from 22 to 70 wt %, known as Halowaxes, have been produced by Koppers Company in the United States since the 1920s. PCNs have also been manufactured in other countries as Nibren waxes (Bayer, Germany), Seekay waxes (ICI, U.K.), Clonacire waxes (Prodelec, France), and Cerifal materials (Caffaro, Italy). The exact amount of production of technical PCN mixtures is not known, but it has been estimated to be approximately 150 000 tons, which is 10% of the total global production of PCBs (13, 14). Although the industrial production of technical PCN formulations has declined in the United States since the early 1980s, products containing these formulations are still present in the environment (15). Furthermore, the secondary formation of chlorinated naphthalenes in thermal processes such as MSWI suggests sustaining environmental sources of PCNs.

Similar to PCBs, several chlorinated naphthalene congeners are persistent, lipophilic ( $\log K_{ow}$  3.9–8.4), and bioaccumulate in the food chain (16–21). Chlorinated naphthalene congeners have been measured in air (22, 23), water (15, 24), sediment (10, 25), and biota (10, 18–20, 26) including human tissues (27–29) from various locations. Several of the 75 possible PCN congeners exhibit toxic effects similar to those of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). These include induction of aryl hydrocarbon hydroxylase (AHH) and ethoxyresorufin-*O*-deethylase (EROD), chloracne, and liver damage (30–34). The relative toxicities of planar halogenated aromatic hydrocarbons (HAHs) are calculated by expressing their toxicity in relation to TCDD, the most potent compound in this class of chemicals. Toxic equivalency factors (TEFs) are fractional potencies that relate a compound's potency to that of TCDD. The TCDD equivalents (TEQs; estimated by multiplying concentrations with TEFs) of two hexachloronaphthalene congeners PCN-66 (1,2,3,4,6,7-HxCN) and PCN-67 (1,2,3,5,6,7-HxCN) in fish from Swedish lakes were 0.3–13% of the total TCDD-like toxicities from HAHs (17). Despite their bioaccumulation and toxic potential, studies describing congener-specific distribution, behavior, and fate of PCNs in the environment are scarce.

Distribution, bioaccumulation, and fate of PCBs, polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated

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