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Investigation of seasonal variations and sources of atmospheric polychlorinated naphthalenes (PCNs) in an urban area

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ABSTRACT

Atmospheric concentrations of 32 polychlorinated naphthalene (PCN) congeners were determined at four sites (i.e., Suburban, Urban 1, Urban 2, and Industrial) in Izmir, Turkey and their possible sources were investigated. Total PCN (Σ_{32} PCN) concentrations ranged between 5.2 (Suburban 1) to 162 pg m⁻³ (Urban 1) in summer, while in winter, they ranged from 3.7 (Suburban) to 229 pg m⁻³ (Urban 1). PCN–24/14 was the dominant congener at all sites (contributing 12–27% to Σ_{32} PCNs), followed by PCN–33/34/37, PCN–28/43, PCN–17/25, PCN–23 and PCN–19. Investigation of possible sources indicated that the combustion processes also contribute substantially to atmospheric PCN concentrations in addition to emissions from sources related to historical use of technical mixtures.

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1. Introduction

Polychlorinated naphthalenes (PCNs) have past uses and physical-chemical properties similar to polychlorinated biphenyls (PCBs), and they are also produced by combustion and thermal processes (Helm and Bidleman, 2003). PCNs were manufactured commercially as technical mixtures with the trade names Halowax (United States), Seekay (UK), and Nibren (Germany). They were mainly used in applications requiring high thermal stability such as dielectric fluids in transformers and capacitors (Falandysz, 1998), and as wood preservatives, pesticides, plasticizers, and oil additives. They are also found as trace contaminants in PCB mixtures (Falandysz, 1998; Lee et al., 2007). Current environmental PCN levels are believed to be affected by emissions from sources related to historical use of technical mixtures and from combustion sources such as waste incineration, metal refining, and iron-steel production (Helm and Bidleman, 2003; Odabasi et al., 2010). Emissions originating from the latter are enriched in "combustionrelated marker" congeners relative to technical PCN mixtures. Combustion-related congeners include PCN-20, -17/25, -26, -13, -18, -44, -36/45, -29, -27/30, -39, -35, -52/60, -50, -51, -54, -66/67, and -73 (Helm et al., 2006). Also, elevated levels of PCN-24 and -50 in air have been attributed to coal and wood combustion (Lee et al., 2005). However, information on regional or global use of PCNs, emissions from technical mixtures and combustion is limited (Bidleman et al., 2010).

Due to their potential for toxicity, bioaccumulation, persistence, and long–range atmospheric transport, PCNs have been targeted by Stockholm Convention on persistent organic

pollutants (POPs). They are currently reviewed for listing under the Convention (Stockholm Convention, 2012). Unlike the other toxic organic chemicals, studies on atmospheric PCN concentrations are relatively scarce. Only recently, air concentrations of polychlorinated naphthalenes (PCNs) were measured as part of the Global Atmospheric Passive Sampling (GAPS) study to assess their spatial distribution on a worldwide basis (Lee et al., 2007). Results from more than 40 sites on seven continents indicated that PCNs are widespread, and highest levels were detected in urban/industrial locations consistent with other air sampling studies (Lee et al., 2007).

Recent studies conducted in the study area of the present work (Izmir, Turkey) have investigated and reported environmental levels of several organic pollutants, i.e., polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls organochlorine pesticides (OCPs), and polybrominated diphenyl ethers (PBDEs) (Sofuoglu et al., 2004; Cetin and Odabasi, 2007a; Cetin and Odabasi, 2007b; Cetin et al., 2007; Bozlaker et al., 2008a; Cetin and Odabasi 2008; Odabasi et al., 2008; Bozlaker et al., 2008b; Odabasi et al., 2009; Bozlaker et al., 2009; Cetin and Odabasi, 2011; Demircioglu et al., 2011a; Demircioglu et al., 2011b). However, data on atmospheric levels of PCNs in the study area depends only on a limited number of measurements conducted during the GAPS study (Lee et al., 2007). The main objective of the present tudy is thus aimed at understanding the spatial and temporal distribution of several PCN congeners in air for the area surrounding Izmir, Turkey, with an emphasis of identifying potential sources within the study area.

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2. Materials and Methods

2.1. Sampling program and collection

Izmir is a metropolitan city, with a population of \sim 3.3 million people, and is the center of a highly industrialized area by the Aegean Sea shoreline of Turkey. Ambient air samples were collected at four sampling sites including a suburban, an industrial and two urban sites in Izmir (Figure 1).

The suburban samples were collected on a 4 m—high platform located on the Kaynaklar campus of the Dokuz Eylul University, 10 km southeast of Izmir's center. It is relatively far from any settlement zones or industrial facilities. There are residential areas located approximately 2 km southwest and a highway 0.5 km south of the sampling site. Nearby land cover is a young coniferous forest. Urban samples were collected from Yesildere (Urban 1) located near a main street with heavy traffic and residential areas.

The other urban site (Urban 2) is located in Aliaga county, ~50 km north of Izmir. There are many industrial plants (i.e., a petrochemical complex, a petroleum refinery, and LPG storage plants) within a few kilometers. Finally, samples were collected at Horozgedigi village (Industrial) located ~5 km south of Aliaga county. Nearby, there are several steel plants with electric arc furnaces, a natural gas—fired power plant (1 500 MW), a fertilizer factory, and a few small industrial facilities.

In total, 60 air samples were collected during the sampling at four sites during the winter and summer periods. Detailed information on sampling is presented in Table 1. Meteorological data for Suburban and Urban 1 sites were obtained from a 10 m high tower located at the suburban sampling site. For the Urban 2 and Industrial samples, meteorological data was obtained from the air quality monitoring and weather station operated by the power plant, located in Horozgedigi village (Industrial site) (Table 1).

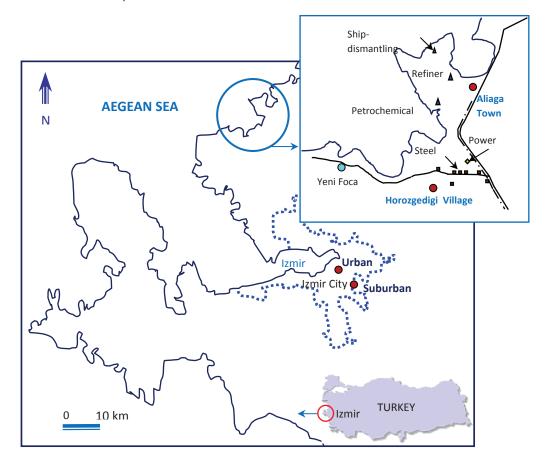


Figure 1. Locations of the sampling sites.

Table 1. Summary of sampling information (average±SD)

| Site | Date | n | Temperature (°C) | Wind speed (m s ⁻¹) | Prevailing WD | RH (%) | C (TSP) (µg m ⁻³) |
|------------|-----------------------------|---|---------------------|------------------------------------|------------------|-----------|----------------------------------|
| Suburban | 09/07-14/2004 (Summer) | 8 | 19.2±2.0 | 5.8±2.2 | N | 47±6 | 51±10 |
| | 02/04-13/2005 (Winter) | 9 | 1.8±1.4 | 7.4±2.3 | N | 58±8 | 50±28 |
| Urban 1 | 09/15-24/2004 (Summer) | 9 | 22.1±1.2 | 4.0±2.3 | N | 59±9 | 95±20 |
| | 03/03-19/2005 (Winter) | 8 | 16.4±7.4 | 3.0±1.1 | NW | 63±10 | 133±40 |
| Urban 2 | 06/13-19/2005 (Summer) | 7 | 22.4±2.0 | 3.5±1.1 | NW | 64±4 | 36±14 |
| | 03/28 - 04/07/2005 (Winter) | 6 | 10.0±2.5 | 3.8±3.2 | NW | 67±8 | 71±23 |
| Industrial | 06/13-19/2005 (Summer) | 7 | 22.4±2.0 | 3.5±1.1 | NW | 64±4 | 101±39 |
| | 03/28-04/07/2005 (Winter) | 6 | 10.0±2.5 | 3.8±3.2 | NW | 67±8 | 98±36 |

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