POLYCHLORINATED NAPHTHALENE (PCN) EMISSIONS FROM ELECTRIC-ARC FURNACES FOR STEEL-MAKING

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Introduction
Due to their potential for toxicity, bioaccumulation, persistence, and long-range atmospheric transport, polychlorinated naphthalenes (PCNs) have been targeted by Stockholm Convention on persistent organic pollutants (POPs). They are currently under review for listing under the Convention[1]. Unlike the other toxic organic chemicals, studies on atmospheric PCN concentrations and especially on their emissions are relatively scarce.

PCNs were manufactured as commercial 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[2], and as wood preservatives, pesticides, plasticizers, and oil additives. They are also found as trace contaminants in polychlorinated biphenyl (PCB) mixtures[2,3]. PCNs were produced as early as 1910 and their production and use was stopped around mid 1980s. Current environmental PCN levels are 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[4,5]. However, information on regional or global use of PCNs, emissions from technical mixtures and combustion is limited[6].

Recent studies have shown that the ferrous scrap processing steel plants with electric arc furnaces (EAFs) are important sources for several POPs[7,8]. Turkey, 29.14 million tons of steel was produced in 2010, making the country 10th biggest producer in the world. Most of the ferrous scrap (66%) used in EAFs was imported[9]. Iron-steel production processes emit particles, gas-phase inorganic pollutants and several POPs[7,10,11,12]. As indicated by recent studies PCNs are also emitted[13,14]. PCNs may be present in the scrap and are evaporated during production processes or they may form by de novo synthesis in thermal processes[10].

There is a limited number of studies in the literature on EAF source characterization and emission factor generation for PCNs[13,14,15]. The objectives of this study were (1) the measurement of emissions and generating emission factors for PCNs from ferrous scrap processing steel plants with EAFs and (2) measurement of ambient air and soil PCN levels near these industries in Aliaga industrial region in Turkey.

Materials and methods
Ambient air, stack-gas, and soil sampling
The study area is located at the Aliaga industrial region, ~45 km north of the metropolitan city of Izmir, Turkey. The area contains several pollutant sources including a large petroleum refinery and a petrochemical complex, scrap processing iron-steel plants with EAFs, scrap storage and classification sites, steel rolling mills, a natural gas-fired power plant, a very dense transportation activity of ferrous scrap trucks, heavy road traffic, a ship breaking area, and busy ports with scrap iron dockyards.

Daily ambient air samples (n=11) were collected at a site near the iron-steel plants between April 26 and May 7, 2007. Meteorological data were obtained from a meteorological station located southwest of the industrial region. There were both northerly and southerly winds during the sampling program. The location of the sampling site relative to the steel plants and these wind directions indicate that the sampling site is affected from the steel plant emissions.

Stack-gas samples were collected from the five scrap processing iron-steel plants with EAFs located near the air sampling site. The production capacities, stack-gas flow rates, and number of the electric arc furnaces of the plants range between 94-163 ton h^{-1}, 640000-1227000 Nm^3 h^{-1} (at 1 atm and 273 K), and 1-2, respectively.

Air samples were collected using a modified high-volume sampler. Particle-phase POPs were collected on 10.5-cm diameter quartz filters and the gas-phase compounds were collected in a modified cartridge containing XAD-2 resin placed between layers of polyurethane foam (PUF). Stack-gas samples were collected isokinetically using a sampling train consisting of a heated sampling probe, a filter cartridge, a condenser, a water-cooled resin (XAD-2) cartridge, a vacuum pump with flow controller and a gas-meter. Stack-gas particle-phase POPs were collected on glass-fiber thimble filters and the gas-phase compounds were collected in the XAD-2 resin cartridge. Average sampling duration was ~24 h for ambient air while it was 2.5 h for stack-gases (covering at least three production cycles). Soil samples were collected manually at 0-5 cm depth from the surface. Equal amounts of 10 sub-samples were collected over a ~100 m^2 area and were homogenized before analysis. Large particles and organic debris were removed using a 1.0 mm mesh sieve. The samples were sealed with an aluminum foil and stored at 4°C.

Sample preparation and analysis

Prior to extraction, all samples were spiked with a surrogate standard (PBDE-77). Ambient air PUFs were Soxhlet extracted for 24 hours with 1:1 acetone:hexane. The remaining samples (soil samples, ambient air filters, stack-gas thimble filters, and XAD-2 resin cartridges) were soaked in 1:1 acetone:hexane mixture overnight and then they were ultrasonically extracted. For the stack samples, the sampling probe was rinsed with acetone:hexane (1:1) and the solution was combined with stack-filter extract (particle-phase). The sampling line between the filter and resin cartridge was also rinsed with acetone:hexane. The condensate from the condenser before the resin cartridge was liquid-liquid extracted with dichloromethane and hexane. The extracts from the sampling line and condensate were combined with the extract from the resin cartridge (gas-phase). The extract volumes were reduced and were transferred into hexane using a rotary evaporator and a high purity N_2 stream. After concentrating to 2 mL, samples were cleaned up and fractionated on an alumina-silicic acid column. All the samples were analyzed for PCNs with an Agilent 6890N gas chromatograph (GC) equipped with a mass selective detector (Agilent 5973 inert MSD) working at electron capture negative chemical ionization (ECNI) mode. The capillary column used was HP5-MS. Samples were quantified for 32 tri- to octachloronaphthalenes against a technical PCN mixture (Halowax 1014, Accustandard) containing target compounds.

Results and discussion
Emissions

Measured stack-gas Σ_{32}PCNs concentrations for the four steel plants without scrap preheating ranged between 30 and 402 ng Nm^{-3} (189±157 ng Nm^{-3}, average±SD) while the concentration from the plant with scrap preheating was substantially higher (1262 ng Nm^{-3}). One of the sampled plants is equipped with a system for preheating the scrap, by the off gas for energy recovery. Scrap preheating may result in higher emissions of organohalogen compounds and other incomplete combustion products from scrap contaminated with paints, plastics, lubricants or other organic compounds[10]. Stack-gas concentrations for the plant with pre-heating were significantly higher (1.3-16.9 times for different congeners, 6.7 times for Σ_{32}PCNs) compared to the plants without pre-heating. This may be due to desorption of PCNs in the scrap when they are heated.

Emission factors for PCNs were calculated using the stack-gas concentrations, stack-gas flow rates, and steel production amounts. Similar to the stack gas concentrations, emission factors for the plant with scrap preheating was substantially higher (11.9 mg ton^{-1}) compared to those without scrap preheating (1.30±0.98 mg ton^{-1}). Liu et al.[14] have reported that the emission factors of PCNs from EAFs were 1.97-4.48 mg ton^{-1}. However, emission factors of PCNs from cupola furnaces using scrap were relatively lower (0.27-1.47 mg ton^{-1})[15]. Emission factor determined in the present study for EAFs without pre-heating was more than 2 times higher than the upper-bound literature value.

Ambient air concentrations

Total PCN (Σ_{32}PCN) concentrations ranged from 642 to 3204 pg m^{-3} (1620±800 pg m^{-3}, average±SD). Recently, air concentrations of PCNs were measured to assess their global spatial distribution[3]. ΣPCNs ranged from below detection limit to 32 pg m^{-3} and highest levels were detected in urban/industrial locations[3]. Recently reported ambient air Σ_{32}PCN concentrations in the Izmir region ranged between 5.2 and 162 pg m^{-3} in summer, while they ranged from 3.7 to 229 pg m^{-3} in winter[16]. In general, the concentrations measured in the present study were substantially higher than those measured in the Izmir area and around the world further confirming that the steel plants with EAFs are important sources for PCNs.

Soil concentrations and their spatial distribution

The soil Σ_{32}PCN concentrations (n=40) measured in the study area were highly variable, and they ranged between 0.003 and 10.02 µg kg^{-1} (dry wt) (0.70±1.75 µg kg^{-1}, average±SD) (Figure 1). The lowest PCN levels were measured in sites away from specific local sources while the highest concentrations were observed in industrial area at sites close to the local sources. Spatial distribution of soil concentrations indicated that major PCN sources in the region were industrial activities, especially the iron-steel plants.
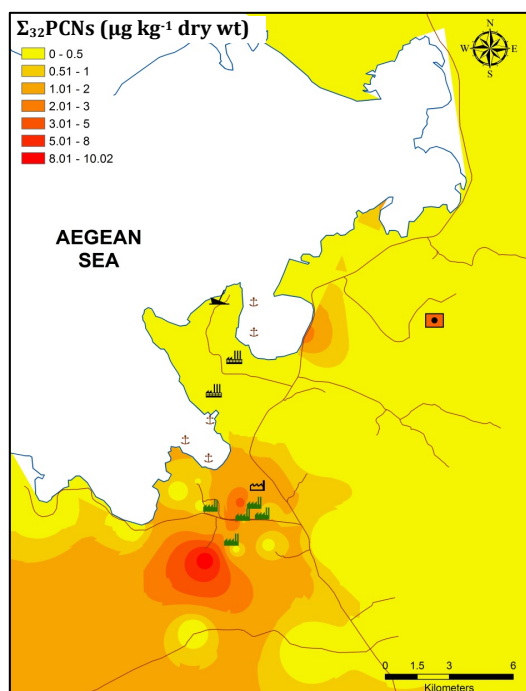

Figure 1. Spatial variation of soil Σ_{32}PCN concentrations (µg kg^{-1} dry wt).

Contribution of technical mixtures and combustion processes to measured PCN concentrations

Comparison of congener and homologue profiles for the various PCN sources and environmental samples may qualitatively indicate the sources possibly contributing to the environmental PCN levels[3](Figure 2).
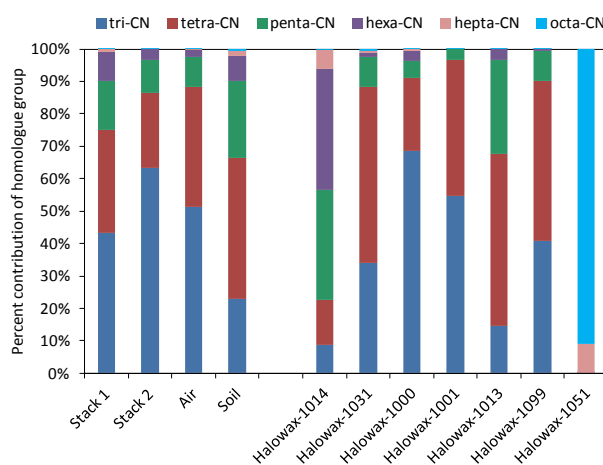

Figure 2. Percent contributions of homologue groups to stack gas, ambient air and soil Σ_{32}PCN concentrations and to Halowax mixtures (Stack 1: no preheating, Satck 2: with preheating).

Most of the Halowax mixtures (1000, 1001, 1013, 1031, and 1099) are dominated by tri-, tetra- and penta-CNs. However, Halowax 1051 is dominated by octa-CN while Halowax 1014 is dominated by penta- and hexa-CNs [17,18]. PCN profiles observed in the present study were generally similar to each other and to technical mixtures but they were quite different than those of Halowax 1014 and especially 1051 (Figure 2). In terms of homologue groups, tri-CN was the leading group for stack and air samples and for some Halowaxes (1000, 1001) followed by tetra-CN (soil samples, Halowax 1013, 1031, and 1099) and penta-CN (stack, air, soil samples and most of the Halowaxes). These observations suggest that measured PCN concentrations were affected by evaporative emissions from past use of different technical mixtures.

In addition to sources related to historical use of technical mixtures, current environmental levels of PCNs are influenced also by emissions from combustion sources[4,5,19]. Emissions originating from combustion processes are enriched in "combustion-related marker" congeners relative to technical PCN mixtures. Combustion-related congeners include PCN-17/25, -36/45, -35, -52/60, -50, -66/67, and -73 [20]. In Halowaxes, combustion-related congeners PCN-17/25, -36/45, -35, -52/60, -50, and -66/67 are generally minor components within their respective homologue groups (except PCN-73, 33.6±20.7%). However, in all types of the samples of the present study combustion-related congeners PCN-17/25, -36/45, -35, -52/60, -50, -66/67, and -73 were enriched within their respective homologue groups, relative to Halowax mixtures suggesting that the measured PCNs in the samples were influenced by combustion related processes.

References
1. Stockholm Convention, 2015.
http://chm.pops.int/Convention/ThePOPs/ChemicalsProposedforListing/tabid/2510/Default.aspx.
2. Falandysz, J. (1998) *Environ Pollut* 101, 77-90.
3. Lee, S.C., Harner, T., Pozo, K., Shoeib, M., Wania, F., Muir, D.C.G., Barrie, L.A., Jones, K.C. (2007) *Environ Sci Technol* 41, 2680-2687.
4. Helm, P.A., Bidleman, T.F. (2003) *Environ Sci Technol* 37, 1075-1082.
5. Odabasi, M., Bayram, A., Elbir, T., Seyfioglu, R., Dumanoglu, Y., Ornektekin, S. (2010) *Water, Air Soil Pollut* 213, 375-388.
6. Bidleman, T.F., Helm, P.A., Braune, B.M., Gabrielsen, G.W. (2010) *Sci Total Environ* 408, 2919-2935.
7. Odabasi, M., Bayram, A., Elbir, T., Seyfioglu, R., Dumanoglu, Y., Bozlaker, A., Demircioglu, H., Altiok, H, Yatkin, S., Cetin, B. (2009) *Environ Sci Technol* 43, 5205-5211.
8. Odabasi, M., Ozgunerge Falay, E., Tuna, G., Altiok, H., Kara, M., Dumanoglu, Y., Bayram, A., Tolunay, D., Elbir, T. (2015) *Environ Sci Technol* 49: 2105−2114.
9. World Steel Association (2011) Steel Statistical Yearbook 2011. Available at: http://www.worldsteel.org/
10. IPPC, European Commission (2010) Integrated Pollution Prevention and Control (IPPC), Best Available Techniques Reference Document for Production of Iron and Steel.
11. Alcock, R.E., Sweetman, A.J., Prevedouros, K., Jones, K.C. (2003) *Environ Int* 29, 691-698.
12. U.S. EPA. AP 42 (2008) Fifth Edition, Compilation of Air Pollutant Emission Factors, Volume 1: Stationary Point and Area Sources. Available at: http://www.epa.gov/ttn/chief/ap42/index.html
13. Liu, G., Zheng, M., Du, B., Liu, W., Zhang, B., Xiao, K. (2010) *Geophysical Research Abstracts* 12, art. no. EGU2010-2019-4
14. Liu, G., Zheng, M., Du, B., Nie, Z., Zhang, B., Hu, J., Xiao, K. (2012) *Environ Sci Pollut Res* 19, 3645-3650.
15. Liu, G., Lv, P., Jiang, X., Nie, Z., Zheng, M. (2014) *Environ Sci Technol* 48, 13165-13172.
16. Odabasi, M., Bayram, A., Elbir, T., Dumanoglu, Y., Kara, M., Altiok, H., Cetin, B. (2012) *Atmos Pollut Res* 3, 477-484.
17. Falandysz, J., Nose, K., Ishikawa, Y., Lukaszewicz, E., Yamashita, N., Noma, Y. (2006) *J Environ Sci Health, Part A* 41, 2237–2255.
18. Falandysz, J., Nose, K., Ishikawa, Y., Lukaszewicz, E., Yamashita, N., Noma, Y. (2006) *J Environ Sci Health, Part A* 41, 291-301.
19. Lee, R.G.M., Coleman, P., Jones, J.L., Jones, K.C., Lohmann, R. (2005) *Environ Sci Technol* 39, 1436-1447.
20. Helm, P.A., Kannan, K., Bidleman, T.F. (2006) *Handbook of Environmental Chemistry* (Hites, R., Ed.) Springer-Verlag: Berlin, Vol. 5.