Concentration and distribution of PCNs in ambient soil of a municipal solid waste incinerator

Zhenyu Tian, Haifeng Li, Huiting Xie, Chen Tang, Ying Han, Wenbin Liu *

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, P.O. Box 2871, Beijing 100085, China

HIGHLIGHT

- Impact of MSWI on PCNs in surrounding soil was studied.
- Analysis suggested that MSWI may be a direct source of PCNs in soils.
- Limited area surrounding MSWI was influenced by emissions.
- Decline of PCNs with increasing distance from the stack was quantified.

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ABSTRACT

The impact of a typical municipal solid waste incinerator (MSWI) on polychlorinated naphthalene (PCN) concentrations in surrounding soil was studied. We collected 6 stack gas samples from the MSWI and 21 soil samples from sampling sites at distances of between 300 and 1700 m from the MSWI stack. Total dl-PCN (dioxin-like PCN) concentrations in the stack gas samples ranged from 6898 and 89,032 pg m^{-3} , with a mean value of 36,241 pg m^{-3} . The total dl-PCN concentrations in the soil samples ranged from 30.35 to 280.9 pg g^{-1} , with a mean value of 87.03 and a median value of 70.32 pg g^{-1} , while the TEQ values were between 7.7 and 130.2 fg TEQ g^{-1} , with a mean value of 41.12 fg TEQ g^{-1} and a median value of 31.52 fg TEQ g^{-1} . The PCN homologue patterns and the results of Principal Component Analysis suggested that the MSWI may be a source of PCNs in the soils. A contour map, created using an ordinary Kriging interpolation technique, showed that a limited area (≤ 1000 m radius) surrounding the MSWI was influenced by the emissions from the MSWI. Furthermore, an exponential function equation was proposed to quantify the relationship between TEQs of PCNs and the distance from the stack.

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1. Introduction

Polychlorinated naphthalenes (PCNs) are a group of persistent compounds theoretically made up of 75 chlorinated naphthalenes, containing one to eight chlorine atoms. Some PCN congeners are planar in structure and have biochemical toxicity properties similar to coplanar polychlorinated biphenyls (PCBs) and 2,3,7,8-polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs) (Falandysz, 1998). Because of their toxicity, PCNs were selected to be included in the list of persistent organic pollutants (POPs) by the United Nations Economic Commission for Europe POP protocol (Lerche et al., 2002). There are two main sources of PCNs in the environment. Similar to PCBs, technical PCN mixtures are industrially produced and are used, for example, as dielectrics, lubricants, and oil additives (Falandysz, 1998; Hayward, 1998). Furthermore, PCNs are also produced inadvertently and are

released from waste incineration plants and other combustion processes (Abad et al., 1999; Oehme et al., 1987). Effluents, such as stack gas, fly ashes, and slags, are often associated with the inputs of POPs (Imagawa and Lee, 2001; Sakai et al., 2006) in the areas immediately surrounding MSWIs.

Dioxin-like toxicity of PCNs is mainly exhibited by congeners with three or four fold chlorine substitution in the 2-, 3-, 6-, and 7- positions. Studies have suggested that PCNs contribute a greater proportion of the dioxin-like activity than PCBs and PCDD/Fs in some cases (Kannan et al., 1998; Kannan et al., 2001). PCNs have bioaccumulation potential, and a number of congeners have been detected in the atmosphere, soils and sediments (Zhao et al., 2011). Studies have shown that soil acts as a long-term store for atmospherically deposited PCNs (Krauss and Wilcke, 2003; Pan et al., 2013), therefore, wide-spread PCN contamination of soil may be expected (Harrad et al., 1994; Wild and Jones, 1995). While the environmental occurrence and dynamics of PCBs and PCDD/Fs have been extensively studied for more than three decades, only a few studies have surveyed PCN levels in soil close to MSWIs. Therefore,

* Corresponding author. Tel.: +86 10 62849356, fax: +86 10 62923563.

E-mail address: liuwb@rcees.ac.cn (W. Liu).

it would be valuable to conduct further monitoring of PCN concentrations in soils that are close to MSWIs, so that the influence of PCN emissions on the surrounding environment can be assessed.

As the largest developing country in the world, China generated 221 million tons of municipal solid waste (MSW) in 2010. The lack of landfill sites means that incineration is an economic and efficient alternative way of disposing of waste. In 2010, about 21.2 million metric tons of MSW were incinerated at a daily treatment rate of 58,100 tons. This has led to increasing public concern over the impacts of incineration on the surrounding environment.

The objectives of this study were to conduct a survey of PCN occurrence in soils around a typical MSWI, to explore the impact of PCN emission on environment and to study the relationships between the concentrations and patterns of PCNs in soils and the stack gas samples of MSWI. In this study, we collected 6 stack gas samples from the MSWI and 21 soil samples from sampling sites at distances of between 300 and 1700 m from the MSWI stack. A continuous contour map of PCN contamination in soil was created using ordinary Kriging interpolation analysis. Results from this study are expected to help us estimate how much PCNs are released into the environment, and should also help to address public concerns over MSWI emissions.

2. Materials and methods

2.1. Soil sampling

Our study site was the Sunrise Municipal Solid Waste Incineration Plant located in a municipality of North China. This plant was established in October 2003, and is equipped with modern facilities and has a treatment capacity of about 1600 tons per day. The combustion system uses a grate furnace and the stack gas cleaning system contains a semi-dry scrubber, an active carbon injector and a fabric-filter. The stack is 80 m high, from which the flue gas is dispersed over a wide area, thereby minimizing the impact on the surrounding environment.

Twenty-one soil samples were collected in February 2012 from various sampling sites distributed around the MSWI (Fig. 1). Land use in the surrounding area is complex, and comprises residential and commercial areas, but no heavy industry. Sampling sites were selected according to the ambient buildings and in the pathway of the prevailing

wind, using information from the wind rose diagram, which was obtained from the local meteorological office. The three concentric circles around the MSWI stack shown in Fig. 1 represent distances of 500, 1000 and 1500 m, respectively. Eighteen soil samples were collected within 1500 m of the MSWI, while 3 samples were collected at distances of between 1500 m and 1700 m from the MSWI.

Soil samples (0–10 cm in depth) were collected using a stainless steel sampler. Five soil samples, collected over an area of 25 m², were bulked together and composited into one sample (weighing about 2 kg). The exact positions of the sampling sites were recorded using a portable GPS device (Magellan GPS, San Dimas, USA). Overlying vegetation was removed before the samples were collected. After drying to constant weight at room temperature, the samples were ground and homogenized through a 60-mesh sieve, and then refrigerated until extraction.

2.2. Stack gas sampling

Six stack gas samples were collected isokinetically from the MSWI stack using a stack gas sampling system (Isostack Basic, Tecora Corp., Milan, Italy) according to the Chinese national guidelines (HJ77.2). The sampling standard was spiked into XAD-2 resin before sampling. The particulate phase of the samples was trapped by a quartz-fiber unit, and the gaseous phase was sampled using XAD-2 resin and condensed water. The probe liners were washed with acetone after sampling. Finally, the filter, XAD-2 resin, concentrated water and washing solution were combined to form one sample and stored in the dark before analysis.

2.3. PCNs analysis

PCN analysis was performed using methods applied in previous studies (Liu et al., 2010). Briefly, the samples were spiked with a mixture of ¹³C-labeled PCN internal standards (ECN-5102, tetra-octa PCN mixture comprising ¹³C-CN-27, -42, -52, -67, -73, and -75, Cambridge Isotope Laboratories, MA, USA) before Soxhlet extraction (toluene) for stack gas samples and accelerated solvent extraction (ASE) (Hexane: Dichloromethane = 1:1, V/V) for soil samples. The extracts were then sequentially cleaned by passing them through sulfuric acid-treated

Fig. 1. Wind rose diagram and locations of the soil sampling sites.

Fig. 2. PCN homologue patterns in the stack gas and soil samples.

silica gel, multilayer silica gel and basic alumina columns. The final extracts were concentrated to 20 μ l and were spiked with ^{13}C -labeled PCN injection solutions (ECN-5260, ^{13}C -CN-64, Cambridge Isotope Laboratories). Analysis of PCNs was carried out by an HRGC coupled with a DFS HRMS (Thermo Fisher Scientific, MA, USA). The recoveries of ^{13}C -PCN internal standards relative to labeled injection standards in the samples ranged from 35 to 125%. Blank samples were analyzed to check for possible contamination.

2.4. Statistical analysis

Principal component analysis (PCA) was performed to evaluate the distribution patterns using SPSS version 13.0. The concentrations of dl-PCN (dioxin-like PCN, including eighteen PCN congeners) were normalized to their total amounts to minimize the influence of total concentration and to permit comparison of compositional similarities among samples.

A geostatistical interpolation technique based on ordinary Kriging was used to create a continuous contour map of PCN contamination in soil. The map was produced using Golden Software Surfer 8.0 with cross-validation. In addition, the relationship between the TEQs of PCNs in soil samples and distance from the MSWI stack was evaluated using an exponential function equation simulated by the Gaussian Plume Diffusion Model. When fitting the regression model, it was assumed that the relationships being modeled were uniform throughout the study area.

3. Results and discussion

3.1. PCN concentrations in stack gas samples

The PCN concentrations in 6 stack gas samples (Table S1) were examined to obtain detailed information on MSWI emissions. Eighteen PCN (dl-PCN) congeners have been frequently detected in different kinds of matrix, and they are referred to as dioxin-related compounds, which are considered equal to PCDD/Fs in toxicity (Pirard et al., 2005; Wu et al., 2011). We used the 2,3,7,8-tetrachlorodibenzo-p-dioxin relative potency factors (RPFs) of individual CN congeners to calculate the corresponding toxic equivalents (TEQs) of PCNs (Noma et al., 2004). Total dl-PCN concentrations in the 6 stack gas samples ranged from 6898 and 89,032 pg m^{-3} , with a mean value of 36,241 pg m^{-3} . PCN-48/35 and PCN-38/40 levels were relatively high in the dl-PCN congeners. The TEQs ranged from 1.59 to 26.76 pg TEQ m^{-3} , with a mean value of 11.9 pg TEQ m^{-3} . PCN-66/67 and PCN-73 were the dominant toxic congeners, contributing 43.50% and 19.77% to the total TEQ, respectively. The total PCN concentrations (from MoCNs to OCN) in the stack gas ranged from 68.04 to 1404.34 ng m^{-3} , which were significantly higher than the results (1.08–21.36 ng m^{-3}) investigated in 5 MSWIs in Spain (Abad et al., 1999).

3.2. PCN concentrations in soil samples

The concentrations of PCNs in the soil samples are presented in supporting information as Table S2. The total dl-PCN concentrations in the soil samples ranged from 30.35 to 280.9 pg g^{-1} , with a mean value of 87.03 and a median value of 70.32 pg g^{-1} , while the TEQ values were between 7.7 and 130.2 fg TEQ g^{-1} , with a mean value of 41.12 fg TEQ g^{-1} and a median value of 31.52 fg TEQ g^{-1} .

PCN-1 and PCN-5/7 were generally the dominant dl-PCN congeners by concentration in the soil samples collected near the MSWI, making up 22.75% and 28.56% of the total dl-PCN concentrations, respectively. However, similar to the stack gas samples, PCN-66/67 and PCN-73 were the main contributors to the total TEQs, with corresponding contribution rates of 31.09% and 53.49%. These congeners together contributed more than 84% to the total TEQs of PCNs.

Total PCN concentrations (from MoCNs to OCN) were between 0.89 and 5.41 ng g^{-1} in soil samples, with a median of 2.27 ng g^{-1} . To gain a perspective on the relative levels of PCNs in soils in the vicinity of MSWIs, the total concentrations were compared with those found in other studies carried out in a range of industrial and urban areas. Krauss and Wilcke (2003) determined the concentrations of 35 PCNs in 49 urban top soils from different land uses and found median values of 1.9 and 0.74 ng g^{-1} in industrial and urban areas of Bayreuth, Germany. Their reported values were lower than those from the current study, and the homologue profiles were similar. Although sampled in various positions instead of specific contaminated area, they attribute the source of PCNs to combustion. Wyrzykowska et al (2007) reported

Fig. 3. Loading plot from the PCA of soil and stack gas samples.

Fig. 4. PCN contour map (fg TEQ g^{-1}) of the soil samples. The coordinate point (0,0) represents the MSWI stack.

low PCN concentrations (from TrCNs to OCN, $0.35\text{--}1.10 \text{ ng g}^{-1}$) in soil samples in Poland, and possible sources could be urban areas as well as industrial PCN products. Also, comparing to a recent study in soil samples from South China, which featured a total PCN concentration range from 59.9 to 86.7 pg g^{-1} (Wang et al., 2012), soil samples in current study showed higher PCN concentrations. However, the total PCN concentrations in the current study were much lower than those (from TrCNs to OCN) in soil contaminated by emissions from a chlor-alkali plant ($17,900 \text{ ng g}^{-1}$) (Kannan et al., 1998).

3.3. Comparison of PCN homologue and congener profiles

The profiles of PCNs in soils can be used to trace their sources. However, the profiles may change during atmospheric transport, or they may be altered by redistribution and degradation in soil. Homologue profiles of PCNs in the stack gas and soil samples at the various sampling locations (Fig. 2) were compared to investigate their similarities. From left to right, the 21 soil samples were arranged in order of distance from the MSWI stack.

Particularly, the homologue profile of S16 was very different from other soil samples as it presented high proportion of OCN and HpCNs. From Fig. 1 it could be seen that soil sample S16 was collected from the dark green area, which represents the plow land. In the investigated region, there was no industrial plant or other stationary source for PCNs. But usually there were unregulated open burning events in the plow lands. Based on the unusual pattern and the situation of those arable lands we assumed that the open burning of biomass or agricultural garbage might be the source for PCNs in this spot. Apart from S16, The contribution of different homologue groups to the total PCNs did not vary significantly among different soil samples. The concentrations of mid-chlorinated PCNs, namely TrCN and TeCNs, were much higher than those of other homologues. The average contributions of TrCNs and TeCNs to the total PCN concentration were 32.85% and 18.10%. The profiles were very similar to the stack gas samples, in which TrCNs and TeCNs were also dominant homologues, contributing 56.72% and 27.59%, respectively. Therefore, the MSWI may be a direct source of PCNs in the soils. This common homologue pattern, according to

previous researches, was typical for the industrial thermal sources (Liu et al., 2014). The PCN homologue patterns in soil samples were different from patterns that have been reported in seafood from Guangzhou and Zhoushan, China, which were dominated by TrCNs and PeCNs (over 60% in mass) (Jiang et al., 2007). The similar research conducted by Kannan et al. (1998) in soil, sediment, and biota collected near the site of a former chlor-alkali plant in Japan also found different distribution of homologues. The PCN profiles in soil and sediment samples were dominated by HxCNs and HpCNs, contributing 70% of the total PCN concentrations. Therefore, the difference in composition of PCN homologues between different kinds of samples seems to indicate a different pattern of pollution. A homologue profile featured by less chlorinated PCNs (TrCNs and TeCNs) was usually from thermal processes, while higher chlorinated ones (PeCNs to OCNs) were dominant homologues in most chemical products, like Halowax and Aroclor (Liu et al., 2014). The homologue patterns found in the soil samples were somewhat different from the patterns of stack gas samples. On one hand, the contribution of TrCNs in the soils was significantly lower than that in the stack gas samples (from 56.72% to 32.85%). On the other hand, both higher chlorinated PCNs (PeCNs to OCN) and lower chlorinated ones

Fig. 5. Relationship between distance from the MSWI stack and TEQ of PCNs.

(MoCNs and DiCNs) got a higher proportion than that in the stack gas samples.

In addition, we used PCA to provide information on relationships between the PCN levels in the various samples and emissions. For the PCA of congener profiles, the factors were 18 dl-PCN congeners. Two principal components, which explained 56.6% and 17.8%, were extracted and used in the plot (Fig. 3). Results showed a separation of some stack gas samples from soil samples, which might suggest a change of pattern through the atmospheric transport. And S16 was still away from other samples, which was consistent with the result of homologous profile.

3.4. Spatial distribution of PCNs

To analyze spatial distribution of PCNs in the soil samples around the MSWI, a contour map of the TEQs of PCNs was created using the ordinary Kriging interpolation technique (Fig. 4) with Golden Software Surfer 8.0.

Remarkable variation of PCN concentrations in soil at different distances from the stack was observed. The highest PCN concentrations were found near the stack, but decreased as distance from the stack increased. We found notable variation and high PCN concentrations in the samples collected within about 1000 m radius of the stack, suggesting that a limited area surrounding the MSWI was influenced by PCN emissions. Also, the PCN level of S16 (grid reference (−1000, 1200)) was relatively high, which might suggest other PCN sources in that area.

Furthermore, to quantify the relationship between the PCN contamination in the soil (except S16) and the distance from the MSWI stack, an exponential function equation simulated by the Gaussian Plume Diffusion Model was proposed (Arystanbekova, 2004). The equation was given in Fig. 5, and the R^2 of the equation was 0.31. Similar to what was shown in Fig. 4, TEQs of PCNs declined with increasing distance from the stack, indicating that the incinerator is the source of PCNs to the adjacent soil.

4. Conclusion

Stack gas and soil samples were collected from a typical modern MSWI to evaluate the impact of PCN emissions from the MSWI on the surrounding environment. Total PCN concentrations and TEQs of toxically relevant congeners were evaluated in this study. PCN emissions from the MSWI and distance from the stack were the main factors influencing PCN concentrations in the surrounding soil. The contour map showed that a limited area, within a radius of ≤ 1000 m of the MSWI, was influenced by PCNs emitted from the MSWI. Therefore, advanced pollution control techniques and strict PCN emission standards should be adopted. Further, facilities such as this MSWI should be located at a safe distance from residential areas to protect human health and the environment.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2013.12.130>.

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