



Polychlorinated naphthalenes (PCNs) in Chinese forest soil: Will combustion become a major source?



Yue Xu ^{a, b}, Jun Li ^a, Qian Zheng ^a, Suhong Pan ^c, Chunling Luo ^a, Haolin Zhu ^a, Luca Nizzetto ^{d, e}, Gan Zhang ^{a, *}

^a State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

^b State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

^c Guangdong Institute of Eco-Environment and Soil Sciences, Guangzhou 510650, China

^d Masaryk University, Research Centre for Toxic Compounds in The Environment, Brno, Czech Republic

^e Norwegian Institute for Water Research, Oslo, Norway

ARTICLE INFO

Article history:

Received 9 February 2015

Received in revised form

21 April 2015

Accepted 22 April 2015

Available online 14 May 2015

Keywords:

Chinese forest soil

Combustion-related sources

Ecotone

PCNs

SOC

ABSTRACT

We collected O- and A-horizon soil samples in 26 Chinese mountainous forests to investigate the content, spatial pattern, and potential sources of polychlorinated naphthalenes (PCNs). Spatial patterns were influenced mainly by the approximation to sources and soil organic contents. High concentrations often occurred close to populated or industrialized areas. Combustion-related activities contributed to PCN pollution. Relatively high proportions of CN-73 in northern China may be attributed to coke consumption, while CN-51 could be an indicator of biomass burning in Southwest China. There are evidences that PCNs may largely derived from unintentional production. If uncontrolled, UP-PCN (unintentionally produced PCNs) emissions could increase with industrial development. The abnormally high concentrations at Gongga and Changbai Mountains appear to be associated with the high efficient of forest filter of atmospheric contaminants at these densely forested sites. We question whether this is caused by ecotones between forests, and raise additional questions for future analyses.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

It has been suggested that forests play an important role in the global fate and distribution of POPs (persistent organic pollutants). The primary effect of forests is an increase in the net atmospheric deposition to the terrestrial environment, reducing atmospheric concentrations in forest areas and thus possibly affecting depositions in other areas (Wania and McLachlan, 2001). As a consequence, the temperature-driven geochemical circulation of POPs can be altered due to the reduction in long-range atmospheric transport (LRAT) and enhancement of vapor-pressure-dependent fractionation caused by the “forest filter effect”. The reduction of POPs in the air is achieved however at the expense of soil pollution. With canopy enhanced deposition, forest soils can act as reservoir for POPs due to their strong affinity to soil organic matter; this is especially true for high-molecular-weight POPs. Chinese forests cover more than 197,290,000 ha or approximately 21.2% of the total

national land area (FAO, 2005), reserving 22.56% of the national terrestrial soil organic carbon stock (Li, 2008). Because the Chinese forests are widely distributed in mountainous areas, local geographical and meteorological conditions are favorable for trapping POPs due to multiple factors, such as low temperature, high precipitation, vegetation enhanced deposition, considerable absorption capacity, and barrier effects.

PCNs (polychlorinated naphthalenes) are candidate persistent organic pollutants (POPs) under review by the Stockholm Convention, due to their potential of persistence, dioxin-like toxicity, bioaccumulation, and long-range atmospheric transport potential (Wang et al., 2012). They are ubiquitous contaminants occurring mainly in specific commercial mixtures or as by-products of industrial processes (including, in the past, the manufacturing of polychlorinated biphenyls (PCBs)) or other thermal processes (Hanari et al., 2013). There is historical evidence of industrial applications of PCN formulations in China (Hogarh et al., 2012), but the increase in the combustion indicator CNs in the top layers of the sediment core inside Jiaozhou Bay indicates that the contributions of thermal sources of CNs have increased in recent years (Pan et al.,

* Corresponding author.

E-mail address: zhanggan@gig.ac.cn (G. Zhang).

2012). According to regional observations, the atmospheric PCN concentrations in China were higher than those in surrounding countries or some heavily polluted areas (Hogarh et al., 2012; Lin et al., 2013). Since pronounced filtering by the forests may influence POPs with $\log K_{OA}$ between 7 and 11 and $\log K_{AW} > -6$ (McLachlan, 1999), it is logical to expect that will be also accumulated effectively in forest soil. Regional research on PCN accumulation in soil remains scarce. There are currently relatively few emission studies (Ba et al., 2010; Liu et al., 2010), atmospheric observations (Hogarh et al., 2012; Lin et al., 2013) and studies on soil and sediment exposure (Pan et al., 2012; Wang et al., 2012) on a local scale.

In the present study, Organic (O-horizon) and upper mineral layer (A-horizon) soil samples were collected in Chinese forests classified based meteorological, geographical, and ecological parameters. Forests were selected in locations relatively far from anthropogenic activities to provide information on background contamination, therefore reflecting the regional pollution status. The top two soil layers together account for the majority of POP storage in the forest soil (Wenzel et al., 2002; Moeckel et al., 2008), and pose a contamination risk for soil-dwelling animals and upriver aquatic systems. This is the first study to elucidate the soil contamination levels and spatial trends of PCNs in the major areas of Chinese forests. Our objective is to provide a primary outline of PCN content in Chinese mountainous forest soils, to explore whether the exposure pattern is influenced by emissions rather than environmental factors, to identify potential PCN sources, and to assess the resulting environmental risk on a national scale.

2. Methods

2.1. Sampling

The study was carried out in 26 Chinese mountain forests widely distributed over the whole country, with the exception of the Northwest area, from July 2012 to March 2013 (Figure S1). For each mountain forest, the average temperature and precipitation generally exhibited a negative and positive relationship with altitude, respectively. One to four forest soil samples were collected at different altitudes from each mountain. Sampling sites were located at areas distant from human activity (i.e., roads, villages or tourism) in nature reserves or national forest parks, differing in altitude and therefore in climate and ecosystem type. Soil samples were collected at each site using a pre-cleaned steel tool according to the vertical structure of soil layers. The O-horizon samples generally comprised five subsamples. Five pits were dug to collect the A-horizon samples. Living plant material, large roots, and any large non-organic material were removed. All soil samples were stored in polyethylene zip-bags and immediately transported in cold conditions to the laboratory. They were subsequently freeze-dried, sieved through a steel mesh, ground with agate mortar, and stored at $-18\text{ }^{\circ}\text{C}$ until further analyses. Further details of sample treatment and TOC analysis can be found elsewhere (Zheng et al., 2014).

2.2. Sample extraction and analysis

Approximately 20 g of prepared soil sample were spiked with ^{13}C -*trans*-chlordane (10 ng) as surrogate, and Soxhlet extracted with dichloromethane (DCM) for 48 h. Activated copper was added to the extract to remove sulfur. The extract was then concentrated by a rotary evaporator and solvent-exchanged into hexane. The cleanup step was conducted using a multi-layer column containing anhydrous Na_2SO_4 , neutral silica gel (3% deactivated) and neutral

alumina (3% deactivated) from top to bottom, followed by a column containing 50% (w/w) sulfuric acid silica gel, florisil (2% deactivated) and neutral alumina, and finally a 6 g Biobead (SX-3) column. After concentrating to approximately 25 μL , ^{13}C -PCB141 was added as the internal standard prior to instrumental analysis, which was performed using an Agilent 7890A gas chromatography electron capture negative-ion mass spectrometer (GC-ECNI-MS) in the selected ion monitoring (SIM) mode. A DB-5MS column (30 m \times 0.25-mm i.d. \times 0.25- μm film thickness) was installed to separate compounds, as described elsewhere (Wang et al., 2012). The following PCN congeners (tri-CNs: CN -19, -24, -14, -15, -16, -17/25, -23; tetra-CNs: CN -42, -33/34/37, -47, -36/45, -28/43, -27/30, -39, -32, -35, -38/40, -46; penta-CNs: CN -52/60, -58, -61, -50, -51, -54, -57, -62, -53, -59, -49, -56; hexa-CNs: CN -66/67, -64/68, -69, -71/72, -63, -65; hepta-CNs: CN -73, -74; octa-CN: CN-75) were assessed in the soil samples. Of these, CN-15, -23, -28/43, -32/48, -35, -46, -58, -61, -57, -62, -53, -59, -56, -69, -71/72, -63, -65, -75 were infrequently found above the limits of detection (LODs) in <60% of samples.

2.3. QA/QC

In total, 10 procedural blanks and 19-pair repeated samples were evaluated to assess contamination and stability. The LODs were calculated as a mean blank + three times the standard deviation (SD) of the target compound. CN-42, -33/34/37, -36/45, -28/43, -27/30, -51 and -49 were detected in blanks, averagely accounting for <7% of the detected values in field samples. LODs of CNs not detected in blanks were determined as the concentrations where the signal to noise ratio was equal to 3. Individual LOD values can be found in the Supporting Information (Table S1). If the quantified concentration of a compound was below the LOD (BDL), a value half of the LOD was used in the statistical treatment of the data. The surrogate recoveries for ^{13}C -*trans*-chlordane in all samples were $85.6 \pm 13.1\%$. The reported results were corrected according to the blanks but not the surrogate recovery values.

3. Results and discussion

3.1. Soil PCN composition and concentrations

The concentrations of individual PCNs are shown in Table S1. The ΣPCN concentrations ranged from 4.5 to 140 $\mu\text{g/g}$ dw (dry weight), with an average of $26 \pm 18\text{ } \mu\text{g/g}$ dw in the A-horizon. These values are lower than those reported in surface soil from the Eastern PRD (Pearl River Delta) and comparable to those from Wolong Mountain, Southwest China (Pan et al., 2013). In the O-horizon, ΣPCNs concentrations ranged from 11 to 190 $\mu\text{g/g}$ dw, with an arithmetic mean of $78 \pm 48\text{ } \mu\text{g/g}$ dw. These values were significantly higher than those from the A-horizon (paired sample t-test, $p < 0.01$). Although enrichment of organic contents in the O-horizon leads to accumulation of PCNs, the differences between the two soil layers in high-molecular-weight congeners remained when the results were expressed as μg per gram organic carbon. At approximately half of the sampling sites, the TOC-based concentrations of tri-CNs in the A-horizon were higher than those in the O-horizon. Moeckel et al. (2008) reported that less volatile POPs are stable in the O-horizon and credited the highest tri- and tetra-CBs in deeper soil layers with the preferential transport of lower-molecular-weight POPs in truly dissolved form. This could also explain the vertical distribution of PCNs in our results given the similar physicochemical properties of PCNs and PCBs.

The major contributors to ΣPCN concentrations were tri-CNs (~53%), followed by tetra- (~15%), penta- (~14%), hexa- (~10%), and hepta-CNs (~6%). CN-24 was the most abundant congener, with an

Download English Version:

<https://daneshyari.com/en/article/6317198>

Download Persian Version:

<https://daneshyari.com/article/6317198>

[Daneshyari.com](https://daneshyari.com)