Available online at www.sciencedirect.com
SCIENCE DIRECT®
Atmospheric Environment 39 (2005) 7420–7432
ATMOSPHERIC ENVIRONMENT
www.elsevier.com/locate/atmosenv

Distribution of particle-phase hydrocarbons, PAHs and OCPs in Tianjin, China

Shui-Ping Wu, Shu Tao*, Zhi-Huan Zhang, Tian Lan, Qian Zuo

Laboratory for Earth Surface Processes, College of Environmental Sciences, Peking University, Beijing 100871, PR China

Received 14 May 2005; received in revised form 25 August 2005; accepted 25 August 2005

Abstract

Aliphatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs) were determined in the total suspended particles (TSP) collected from 13 different locations in Tianjin, China, where intensive coal burning for domestic heating in winter takes place and a large quantity of pesticides had been produced and applied. Carbon preference index (CPI), carbon number maximum (C_{max}) of *n*-alkane and plant wax index (%wax C_n) indicate that *n*-alkanes come from both biogenic and petrogenic sources, and biogenic source contributes more *n*-alkanes in autumn than in winter. Petroleum biomarkers as indicators of petrogenic source such as hopanes and steranes were also detected in both seasons' samples. The sum of 16 PAH concentrations ($\sum PAH_{16}$) ranged from 69.3 to 2170 ng m^{-3} in winter and from 7.01 to 40.0 ng m^{-3} in autumn. Seasonal variations were mainly attributed to the difference in coal combustion emission and meteorological conditions. The results of a source diagnostic analysis suggest that PAHs in TSP mainly come from coal combustion. Seven OCPs (four hexachlorohexanes (HCHs) and three dichlorodipheny-trichloroethane and metabolites (DDTs)) were detected in most samples. Concentrations of the sum of α-, β-, δ- and γ-HCH ($\sum$HCH) and the sum of *p*,*p*′-DDT, *p*,*p*′-DDD and *p*,*p*′-DDE ($\sum$DDT) in autumn varied in the ranges of 0.002–0.9 ng m^{-3} and 0.025–2.21 ng m^{-3} with the average ± standard deviation values of 0.127 ± 0.241 ng m^{-3} and 0.239 ± 0.546 ng m^{-3}, respectively. In winter, $\sum$HCH and $\sum$DDT in TSP ranged from 0.071 to 5.35 ng m^{-3} and from 0.416 to 3.14 ng m^{-3} with the average ± standard deviation values 1.05 ± 1.88 ng m^{-3} and 0.839 ± 0.713 ng m^{-3}, respectively. Both of the illegal application of technical HCH and DDT and the volatilization from topsoil contributed to the particle-phase contents of HCHs and DDTs in the atmosphere.

Keywords: Aliphatic hydrocarbons; PAHs; HCHs; DDTs; Seasonal variation

1. Introduction

Suspended particles contain a significant fraction of toxic organic compounds and have adverse effect on human health (Simoneit, 1984; Didyk et al., 2000). Many of the organic compounds in airborne particles have been indicated to be mutagenic or carcinogenic (IARC, 1991; US EPA, 1992), and are generated from anthropogenic activities. Airborne particles are rather complex matrixes, and the sources apportionment is very difficult due to the complexation in sources and meteorological conditions. In spite of these difficulties, many efforts have been made in this field. Measurements of aliphatic hydrocarbons (*n*-alkanes, isoprenoid, terpanes and

*Corresponding author. Tel./fax: +86 10 6275 1938.
E-mail address: taos@urban.pku.edu.cn (S. Tao).

1352-2310/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2005.08.031

steranes) and polycyclic aromatic hydrocarbons (PAHs) in airborne particles have been conducted in rural and urban air (Simoneit, 1984; Harrison et al., 1996; Didyk et al., 2000; Bi et al., 2003).

Rogge et al. (1993) reported that *n*-alkanes in fine particles in Los Angeles atmosphere mainly came from incomplete combustion of fuels and from lubricant oil. The ratio of the concentrations of odd- to even-number *n*-alkanes, commonly referred as the carbon preference index (CPI), is usually greater than 10 for biogenic detritus (Didyk et al., 2000) and approximately one for petroleum residues (Simoneit, 1984). CPI values of *n*-alkanes have been used to characterize their sources by many researchers (Azevedo et al., 1999; Zheng et al., 2000; Kalaitzoglou et al., 2004). The petroleum biomarkers, hopanes and steranes, were also used to identify pollution sources (Azevedo et al., 1999; Didyk et al., 2000; Kalaitzoglou et al., 2004).

The quantitative compositions of PAHs in airborne particles have been widely reported and the major emission sources are fossil fuel combustion and biomass burning (waste incineration, firewood and straw) (Venkataraman and Friedlander, 1994; Harrison et al., 1996). Atmospheric PAH concentrations in urban atmosphere are often higher than those in rural area because of the emission from motor vehicle and domestic fuel combustion (Caricchia et al., 1999; Schnelle-Kreis et al., 2001).

In comparison with aliphatic hydrocarbons and PAHs, few measurements of organochlorine pesticides (OCPs) in suspended particles have been reported due to their very low particulate-phase concentration (Sanusi et al., 1999; Yeo et al., 2004). Garmouma and Poissant (2004) observed that the particle-phase α- and γ-hexachlorohexanes (HCHs) were less than 0.1% of the atmospheric concentrations in St. Lawrence River in Québec, Canada. Particle-phase pesticides in ambient air came from field application, surface-to-air transfer, wind erosion (soil, vegetation, formulation powders) and long-range transport (Seiber and Woodrow, 1995; Bidleman, 1999).

The exposures to airborne particles include direct breath and indirect intake of deposited-particles contaminated vegetables and grains (Menzie et al., 1992; Smith et al., 1995). The deposited pollutants to soil, water and vegetables may bioaccumulate through the food chain. Moreover, particle-bound constituents can be carried through the atmosphere to remote regions (Muir et al., 1992; Savinov et al., 2003).

Tianjin, located on the west of Bohai Sea, with an area of 11,919 km^2 and a population over 9.5 million, is one of the largest industrial cities of northern China (Fig. 1). A large amount of fossil fuels is consumed each year for both industrial and domestic utilization. As a result, PAHs in urban atmosphere may impose severe impact on human health. Emissions of PAHs in rural and suburban areas are mainly from numerous low-efficiency boilers and stoves and open-air biomass burning (Wu et al., 2005a). The distributions of aliphatic hydrocarbons (*n*-alkanes and fossil fuel markers) can be used to distinguish the emission from biogenic detritus and petroleum hydrocarbons (coal, oil and gas) (Schauer et al, 1996; Didyk et al., 2000).

Although the use of HCH and dichlorodiphenyltrichloroethane (DDT) had been banned in China in early 1980's (technical HCH) and early 1990's

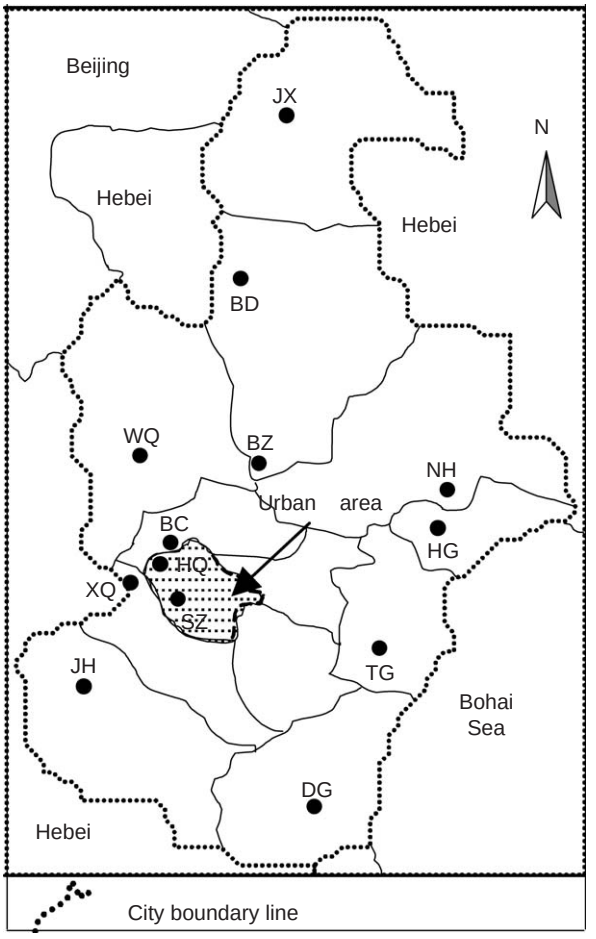

Fig. 1. Location of the sampling sites. Dimension of the block is 120 km × 180 km.