Pedosphere **26**(5): 676–686, 2016
doi:10.1016/S1002-0160(15)60076-5
ISSN 1002-0160/CN 32-1315/P

Published by Elsevier B.V. and Science Press

PEDOSPHERE
www.elsevier.com/locate/pedosphere

Soil Polycyclic Aromatic Hydrocarbons Across Urban Density Zones in Shenzhen, China: Occurrences, Source Apportionments, and Spatial Risk Assessment

ZHANG Di[1,2], WANG Junjian[3] and ZENG Hui[1,2,*]

[1] *College of Urban and Environmental Sciences, Peking University, Beijing 100871 (China)*
[2] *Shenzhen Key Laboratory of Circular Economy, Shenzhen Graduate School, Peking University, Shenzhen 518055 (China)*
[3] *The Belle W. Baruch Institute of Coastal Ecology & Forest Science, Clemson University, Georgetown SC 29442 (USA)*

(Received August 25, 2015; revised May 31, 2016)

ABSTRACT

Urbanization may cause increased exposure levels to polycyclic aromatic hydrocarbons (PAHs) and associated health risks for over half of the world's population living in cities, but little evidence has shown a direct spatial relationship between urbanization and soil PAH pollution. Based on the monitored PAH concentrations in 188 topsoil (0–5 cm) samples in Shenzhen, the most rapidly developing city in China, in recent decades, we applied geographical demarcation to determine the occurrences, source apportionments, and spatial ecological risks of soil PAHs across five zones of varying urban densities. Mean concentrations of the 16 US Environmental Protection Agency (EPA) priority PAHs (Σ_{16}PAHs) and the 7 carcinogenic PAHs (Σ_7CarPAHs) both followed the order: Zone D (60%–80% constructive land density (CLD)) > Zone E (80%–100% CLD) > Zone C (40%–60% CLD) > Zone B (20%–40% CLD) > Zone A (0%–20% CLD), suggesting that the highest PAH levels occurred in the suburban-urban center transitional zone (Zone D) rather than the urban center zone (Zone E) in Shenzhen. There were significant correlations of Σ_{16}PAHs to TOC and sampling altitude across all samples but not within highly-urbanized regions (Zones D and E), implying a considerable disturbance of urbanization to the soil PAH pool. Source apportionments suggested that soil PAHs of all zones were mainly derived from fossil fuel combustion, with Zone E showing the highest contribution from oil sources among different zones. Spatial ecological risk analysis showed that the contaminated area (467 km^2; 23.9% of total area; toxic equivalency quotients > 33 ng g^{-1}) had a higher contribution from the highly-urbanized regions (Zones D and E) than the uncontaminated area (42.3% *vs.* 18.1%). Overall, our study highlighted a strong spatial relationship between urbanization and soil PAH pollution.

Key Words: altitude, carcinogenic PAHs, soil PAH pollution, total organic C, toxic equivalency quotient, urbanization, US EPA priority PAH

Citation: Zhang D, Wang J J, Zeng H. 2016. Soil polycyclic aromatic hydrocarbons across urban density zones in Shenzhen, China: Occurrences, source apportionments, and spatial risk assessment. *Pedosphere*. **26**(5): 676–686.

INTRODUCTION

Sprawling cities around the world support over half of the earth's population (UN DESA, 2010). Understanding how urbanization potentially influences the occurrence and environmental behavior of the potentially toxic polycyclic aromatic hydrocarbons (PAHs) is one critical issue linking urban development and environmental public health (Jiang *et al.*, 2009; Peng *et al.*, 2012). Polycyclic aromatic hydrocarbons, especially the 16 US Environmental Protection Agency (EPA) priority PAHs (Σ_{16}PAHs), are ubiquitous in the environment with well-documented carcinogenic, mutagenic, and teratogenic properties (Lehr and Jerina, 1977; Wang *et al.*, 2013). They originate mainly from incomplete anthropogenic organic matter combustion and oil volatilization or leakage (Von Lau *et al.*, 2012), though some are related to natural processes such as volcanic eruptions and forest fires (Zhang *et al.*, 2004; Choi, 2014). Among various environmental matrices, surface soil is a common focus for its role as a large PAH reservoir in the terrestrial system (> 90%) (Wild and Jones, 1995) and its sensitivity to anthropogenic activities (Zheng *et al.*, 2012). Due to their lipophilicity and persistence, PAHs tend to persist in the soil (Wang *et al.*, 2013), which to varying degrees jeopardizes human health through dermal contact and/or ingestion of contaminated food (Zhang *et al.*, 2012; Bortey-Sam *et al.*, 2014). Further, as the most crucial carrier of pollutants from high-intensity anthropogenic activities, urban soil can also be a source of atmospheric PAHs through volatilization and water PAHs through surface runoff (Diblasi *et al.*, 2009), thereby increasing PAH exposure to urban residents.

---

*Corresponding author. E-mail: zenghui@pkusz.edu.cn.

PAH contamination in urban soils has been widely reported worldwide. For example, Peng *et al.* (2012) found relatively high levels of soil Σ_{16}PAH concentrations under covers of tree-shrub-herb (1 782 ng g^{-1}), greenbelt (1 117 ng g^{-1}), woodland (1 101 ng g^{-1}), and grassland (455 ng g^{-1}) in urban green spaces. Morillo *et al.* (2007) compared soil PAH concentrations from three European cities and identified climatic conditions, soil organic carbon, and pollution source as significant factors affecting soil PAH accumulation. Soil PAHs in Ulsan, Korea were investigated by Kwon and Choi (2014) and found to have mainly originated from vehicles and industrial complexes. In addition, environmental samples collected along main transportation routes show similar PAH sources, suggesting that traffic exhaust is a major cause (Zhang and Wang, 2011). However, few studies focus on the mass inventory and source apportionment of PAHs from different urban density zones, and there is limited understanding of the quantitative differentiation of soil PAH occurrence, sources, and ecological risks across the urbanization gradient. Although some studies refer to the concept of "urbanization levels", most adopted a cursory or empirical definition for urban density zoning (Zuo *et al.*, 2007; Cai *et al.*, 2012; Xie *et al.*, 2012), making it difficult to explore the in-depth correlation between urbanization levels and soil PAH occurrence.

China has undergone rapid urbanization (Lin *et al.*, 2015), with urbanization levels increasing from 19% in 1980 to 47% in 2010 (UN, 2010). It took developed countries such as UK and USA much longer to accomplish this (Ni *et al.*, 2011). As a representative city with the most rapid urbanization rate in China over the last three decades, Shenzhen developed from a rural fishing village in the 1980s (population = 0.33 million, GDP = 0.27 billion RMB) to a modern metropolis in 2010 (population = 10.37 million, GDP = 958.15 billion RMB) (Shenzhen Municipal Bureau of Statistics, 2014). However, the accompanying densely populated aggregation and constructive land sprawl, such as increasing industry and transportation, have delivered a negative impact on urban environmental quality and human health (Wang *et al.*, 2011; Sun *et al.*, 2012; Sun *et al.*, 2013). Studying the soil PAH occurrence in Shenzhen, our previous research estimated the overall potential fate of and human non-dietary exposure to soil PAHs (Cao *et al.*, 2010; Ni *et al.*, 2011). Yet little is known about the dependence of PAH occurrence, composition, and spatial ecological risks on the spatial pattern of urbanization. This study adopted geographical demarcation to separate zones with different urban densities and focused on the variations in mass inventory, sources, and ecological risk of exposure to surface soil PAHs across the urbanization gradient. The correlations of soil PAH levels with soil total organic carbon (TOC) and sampling altitude were also evaluated in different urbanization regions. The results of this study will be instrumental in coupling the change of spatial environmental quality with urban expansion.

MATERIALS AND METHODS

Study area and soil sampling

Located on the southern coast of Guangdong Province, Shenzhen is the "experimental field" of China's reform and opening-up. It has a subtropical monsoon climate. Its average annual temperature, rainfall, and hours of sunshine are 22.4 °C, 1 933.3 mm, and 2 120.5 h, respectively. A total of 188 surface soil samples (0–5 cm) were collected in winter 2007 from different types of land use according to principles of even distribution and random sampling. Specifically, a five-point sampling method was adopted, and five samples (about 500 g each) from four 10 m × 10 m square corner points and the center point were fully mixed as the local sample (Cao *et al.*, 2010). Soil samples were placed in a cool, dark room and air-dried. Then soil samples were stored in amber glass bottles at −4 °C in a refrigerator after being crushed and sieved (100 mesh) until further analysis. The spatial distribution of sampling sites is shown in Fig. 1. Soil TOC content and sampling altitude of the 188 topsoil samples are shown in Table I.

Urban density zoning

Shenzhen land-use data was obtained from the Urban Planning & Design Institute of Shenzhen, China. We chose constructive land density (CLD) as the urbanization level indicator which is closely connected with the corresponding intensity of human activities and urban population (Zeng *et al.*, 2007; Zhao *et al.*, 2013). An ArcGIS 10.0 neighborhood statistics analysis was used to divide the entire study area into five urban gradients based on CLD (including industrial, commercial, transportation, and residential land-use types) with a 20% interval (Fig. 1). Then the zones with CLD levels of 0%–20%, 20%–40%, 40%–60%, 60%–80%, and 80%–100% were defined as a rural zone (Zone A), rural-suburban transitional zone (Zone B), suburban zone (Zone C), suburban-urban center transitional zone (Zone D), and urban center zone (Zone E), respectively. These five zones, from Zone A to Zone E, covered 33.9%, 22.5%, 20.4%, 16.9%, and 6.3% of the city's gross area, respectively. Number of topsoil samples in the each zone ranged from 27 to 61.