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Distribution and Sources of Polycyclic Aromatic Hydrocarbons in Soil Profiles of Tianjin Area, People's Republic of China

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Polycyclic aromatic hydrocarbons (PAHs) are of concern to the environment due to their carcinogenic properties (Neff 1979). Major activities which produce PAHs are: combustion of fuels in vehicular engines, power generation from fossil fuels, coke production, wood burning, incineration of industrial and domestic wastes, oil refinery and chemical engineering operations, etc. (Baek et al. 1991). The existence of permanent pollution sources results in the accumulation of PAH in soil, plants and water bodies (Trapido 1999).

In the last 100 years, the occurrence of PAHs in soil, especially in urban areas, has increased significantly (Jones et al. 1989). Extensive researches have been carried out (Trapido 1999; Wilcke et al. 1999). In China, however, most studies have only focused on a limited number of compounds, especially benzo[a]pyrene (He et al. 1995; Song et al. 1995).

Soil is one of the most important storage and transfer media for PAHs in the environment. In the soil, the concentrations and distributions of PAHs are subject to redistribution and transformation processes. They particularly accumulate in organic matter-rich horizons because of their persistence and affinity for soil organic matter (Wilcke et al. 1996). The further pathways of PAH dissipation in contaminated soil may be volatilization, irreversible sorption, leaching, accumulation by plants, and biodegradation (Reilley et al. 1996).

Located in the eastern part of the North China Plain, about 150 km east of Beijing, Tianjin is one of the largest industrial cities in China. In recent years, with rapid development of the economy, soil pollution is becoming more and more serious.

It is well known that the concentrations of most PAH compounds are unevenly distributed in soil profiles due to a couple of reasons. The assessment of polluted soil is essential to determine the utilization of the land for multi-purposes. In this paper, the distribution and sources of PAH compounds in soil profiles of Tianjin area are studied.

MATERIALS AND METHODS

Tianjin City contains one main urban area, four suburban areas and five counties. Five representing sites (A, B, C, D and E) were sampled (Figure 1 and Table 1) in November, 2001.

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Sampling location A locates in a rice field near Liming Village, northeastern direction of the urban area of Tianjin City. The Eastern Suburb Wastewater Treatment Plant of Tianjin City locates about 100m south of the sampling site. A wastewater ditch (Bei Tang Ditch) goes through the north edge of the sampling area. The wastewater in the ditch comes from both industrial and domestic sources of the city, and has been used for irrigation of this area at a very large scale for quite a long time.

Sampling location B locates in a vegetable field near Nanhe Village, southwestern direction of the urban area of Tianjin City. Intermittent wastewater irrigation was applied for this area during drought season using wastewater from South Ditch.

Sampling location C locates in a cultivated land growing Chinese sorghum near Yangliuqing Village, southwestern direction of the urban area of Tianjin City. Oil refineries were found in the western and southwestern directions of the sampling area. Similar to the vegetable land, intermittent wastewater irrigation was also applied for this area during drought season using wastewater from South Canal.

Sampling location D locates in a mountain area growing fruit trees near Tianchengsi Village, Ji County. No industrial sources were found in the area.

Sampling location E locates in a coastal area near Shanggulin Village, Dagang District. A very large oil field locates in this area and no cultivation activities were found there.

Soil samples were collected from eight layers. For sampling sites A, B and C, from surface downward, they are: 0-20, 20-25, 25-30, 30-40, 40-50, 50-60, 60-80 and 80-100cm respectively. For sampling sites D and E, they are: 0-1, 1-3, 3-10, 10-20, 20-30, 30-40, 40-60, and 60-100cm respectively. Each sample was mixed from soils collected from five locations in an area of about 100*100m^2 (at the four corners and the center).

Samples were air dried at room temperature and ground in an agate mortar sufficiently to pass through a 70- mesh sieve. The samples were then stored at 4°C before use. Extractions of PAHs were carried out using accelerated solvent extraction (ASE) method. The extracts were analyzed for the 16 PAHs using an Agilent 6890 GC coupled with an Agilent 5973 mass spectrometer and a 7683 autosampler (Agilent Technology). The sample extraction and analysis were carried out using a procedure (including quality control) developed by Tao and co-workers (Tao and Cui 2002). TOC, pH value and clay particle (<0.001mm) were also determined in this study. All reagents were of analytical grade or better. All glassware was cleaned in an ultrasonic cleaner.

The sixteen PAH compounds determined are: naphthalene(Nap), acenaphthylene(Any), acenaphthene(Ane), fluorene(Fle), phenanthrene(Phe), anthracene(Ant), fluoranthene(Fla), pyrene(Pyr), benzo[a]anthracene(Baa), chrysene(Chr), benzo[b]fluoranthene(Bbf), benzo[k]fluoranthene(Bkf), benzo[a]pyrene(Bap), indeno[1,2,3-cd]pyrene(I1p), dibenz[a,h]anthracene(Daa), and benzo[ghi]perylene(Bgp).

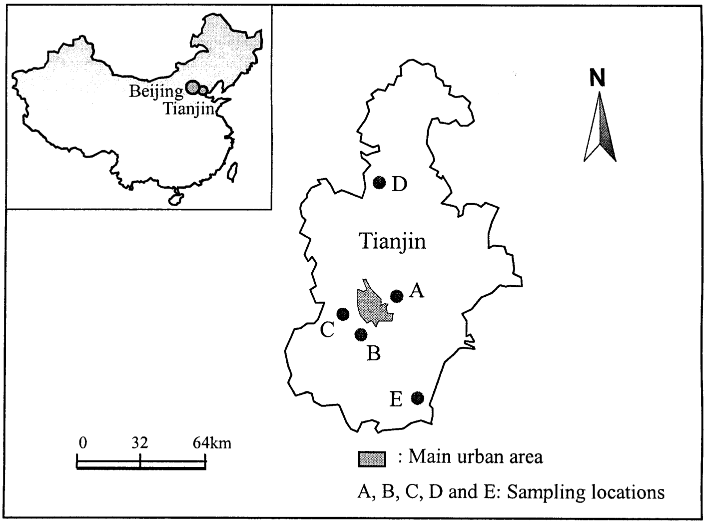

Figure 1. Map of Tianjin city and sampling locations.

Table 1. Characteristics of the sampling sites

Sampling location	Annual average temperature (℃)	Annual precipitation (mm)	Soil type	Wastewater irrigation history
A	12.8	558.4	Paddy soil	Long term and large scale
B	12.8	558.4	Alluvial brown soil	Intermittent
C	12.8	558.4	Alluvial brown soil	Intermittent
D	11.4	696.8	Leached brown soil	No
E	13.0	572.7	Seashore saline soil	No

RESULTS AND DISCUSSION

Figure 2 presents the contents of ΣPAH in the surface soil of the five sampling locations, and Figure 3 illustrates the distributions of ΣPAH and TOC in the five soil profiles. The concentrations of ΣPAH in the surface soil of sampling location A is highest among others (21015 μ g kg^{-1}). Sampling location E is the second, followed by B and C. Sampling location D is the lowest among all. It is estimated that the high concentration of PAHs in paddy soil (A) could be explained by the combined effects of precipitation and long-term and large-scale wastewater irrigation for cultivation purpose. Sampling location B and C were also irrigated with wastewater, but in much smaller scale.

Shi (2003) determined the concentrations of sixteen PAH compounds of water and suspended sediment samples collected from ditches and rivers in Tianjin area, including the ditches for which the water has been used for irrigating the land where sampling site A, B and C locate. The water and suspended sediment samples were collected in July, 2002. The water and suspended sediment sampling locations

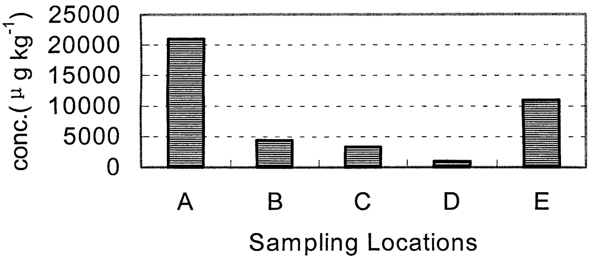

Figure 2. Concentrations of ΣPAH in the surface soils of the five sampling areas.

are not far from our soil sampling sites. Results of the determination are presented in Table 2. It can be seen that the concentrations of PAHs in water and suspended sediment are very high. This has demonstrated the contribution of wastewater irrigation for PAHs accumulation in soil.

Table 2. Average concentrations of ΣPAH in water and suspended sediments in ditches and rivers

Wastewater irrigation source	Sampling sites where the soil were irrigated with the wastewater	Concentrations in Water (ng L^{-1})	Concentrations in Suspended sediment (μ g kg^{-1})
Bei Tang Ditch	A	1059.11	46301.73
South Ditch	B	583.08	10866.37
South Canal	C	58.19	938.28

Source: Shi (2003).

Sampling location E has the second highest concentration among others. It can be explained by the combined contributions from precipitation and petroleum sources. One of the largest oil field in China is located in this area.

The sampling location D shows relatively low content of ΣPAH in the surface soil compared with location A, B, C and E. This might be attributed to the fact that this area is far from residential and industrial areas and less human disturbance were observed.

The concentration and distribution of PAHs in soil profiles subject to physical, chemical and biological processes such as biodegradation, chemical degradation, photolyzing, leaching, adsorption, volatilization, etc (Trapido 1999). TOC and clay particles play very important roles in these processes (Cousins et al. 1999). PAHs particularly accumulate in organic matter-rich horizons because of their persistence and affinity for soil organic matter. In natural soil such as forest soils, the concentrations of PAHs frequently increase from the upper partly decomposed horizon to the lower organic horizon directly overlying the uppermost mineral soil horizon, because the PAH disappearance rate which is governed by decomposition, volatilization, deposition from the atmosphere, and leaching to underlying soil horizons is slower than organic matter turnover (Krauss et al. 2000).

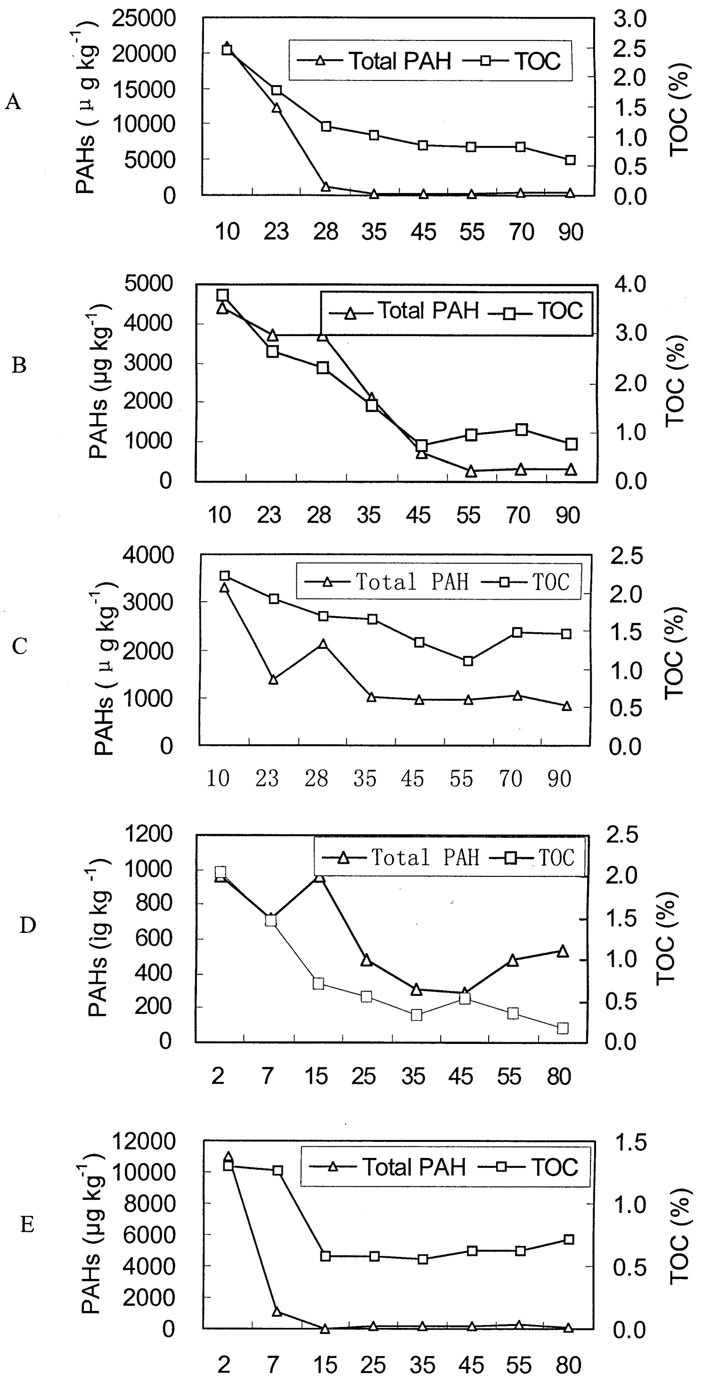

Figure 3. Vertical distribution of ΣPAH and organic matter.

Different from the natural soil described by Krauss and co-workers (Krauss et al. 2000), in the sampling area of this study, the overall trends of ΣPAH in the profiles are decreasing in concentrations with depth. As one of the major industrial cities in China, air precipitation in Tianjin City caused by combustion of fuels might be the major contributors to the accumulation of PAHs in the topsoil. Wastewater irrigation, petroleum pollution and others may serve the specific contributors in some areas.

The vertical distributions of ΣPAH in sampling locations A, B, C show similar patterns. For these sampling locations, the frequent disturbance in the plough layer caused by the cultivation activities reduces the differences of concentrations with depth in the plough layer. As a result, the concentrations of ΣPAH decrease slowly with depth in the plough layers (0-30cm), but decrease sharply below the plough layers (30-50cm) and then remain stable below 50cm in the profiles. The contents of TOC show similar distribution patterns as ΣPAH in these sites.

The contents of ΣPAH in the soil profile of sampling location D show similar pattern as A, B and C, since sampling location D is cultivated agricultural land and air precipitation may play the major contributor to the accumulation of PAHs in the soil.

Compared with A, B, C and D, sampling location E shows somewhat different patterns. The contents of PAHs in the surface layers of location E are very high and decrease sharply to the lower layers. This may attribute to the fact that sampling location E is located in an oil field in the coastal area, and is not used for agricultural purposes. Much less disturbance was observed in this area.

Naphthalene, phenanthrene and benzo[a]pyrene are selected to carry out a study on the vertical distribution of PAH compounds in soil profiles. With increasing molecular weight, PAHs are increasingly accumulated relative to soil organic matter. Studies shown that the extent of the enrichment of individual PAH, described by the concentration ratio, in different organic matter enriched horizons correlates positively with the octanol-water partition coefficient (K_{ow}) (Wikcke and Zech 1997). Therefore, $\log K_{ow}$ can be applied to represent the adsorption ability of trace organic compounds to soil (He et al. 1995; Cousins et al. 1999). Naphthalene and phenanthrene are low ring PAH and are likely to be photolyzed, biodegraded and leached in the soil. As a highly toxic substance, benzo[a]pyrene is a high ring PAH and tend to stay in soil for longer time.

Besides cultivating activities, bioturbation and leaching also result in PAH transport to the lower horizons. Low molecular weight PAHs (<four fused rings) are probably mainly transported as true solutes (Guggenberger et al. 1996), while higher molecular weight PAHs are transported in association with dissolved organic matter (Marschner 1999).

Figure 4 presents the contents of naphthalene, phenanthrene and benzo[a]pyrene in the surface soil in the five sampling locations. The vertical distributions of the three PAH compounds in the sampling areas are illustrated in Figures 5.

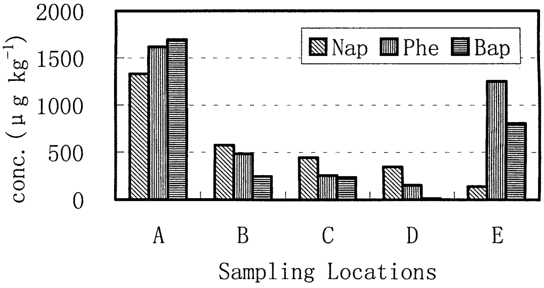

Figure 4. Concentrations of naphthalene, phenanthrene and benzo[a]pyrene in the surface soils of the five sampling sites.

From Figure 5, we can see that naphthalene, phenanthrene and benzo[a]pyrene show similar distribution patterns in the soil profiles in the cultivated areas (A, B, C and D), while sampling location E presents sharper decline of PAH compounds in the soil profile. The concentrations of benzo[a]pyrene for all profiles are below the determination limit at lower layers of the profile, while relatively high concentrations can be found for naphthalene and phenanthrene. The concentrations of naphthalene are higher than benzo[a]pyrene in the whole profiles of the sampling sites. Benzo[a]pyrene accumulated mainly in the topsoil (He et al. 1995). The adsorption of hydrophobic trace organic pollutants in soil is controlled mainly by the contents of organic matter. Compared with naphthalene and phenanthrene, the $\log K_{OW}$ for benzo[a]pyrene is much larger and thus it is more firmly absorbed to the surface soil.

It has been pointed out that, in Tianjin City, huge amount of coal are used for industrial and heating purposes each year (Wang et al. 2003).

The sources of PAHs may be identified by ratios of individual PAH compounds based on peculiarities in PAH composition and distribution pattern as a function of the emission source. Ratio values of phenanthrene/anthracene and fluoranthene/pyrene in the surface soil of the five sampling locations are calculated and presented in Figures 6 and 7. Studies show that (Colombo et al. 1989), when phenanthrene/anthracene > 15 and fluoranthene/pyrene < 1, it indicates the PAH input was mainly from crude oil sources, and when phenanthrene/anthracene < 10 and fluoranthene/pyrene > 1, it indicates that the major PAH input was from combustion. From Figure 6, we can see that the sources of PAH contamination for the surface soil in sampling location A, B, C and D might be derived from combustion sources, and E is derived from both combustion and petrogenic sources. As farming lands near the main urban area of Tianjin City, in general, coal combustion is the major contributor for PAHs in the topsoils of sampling location A, B, C and D. Transportation is another important source (Meng and Wu 1995). However, since sampling location A, B and C locate in wastewater irrigated farming lands, the introduction of PAHs by wastewater irrigation adds the pollutant accumulation, and has made the concentrations in soil profiles varied significantly among these sampling sites. Especially, the existence of extremely high concentrations of PAHs in the paddy field has demonstrated the impact of

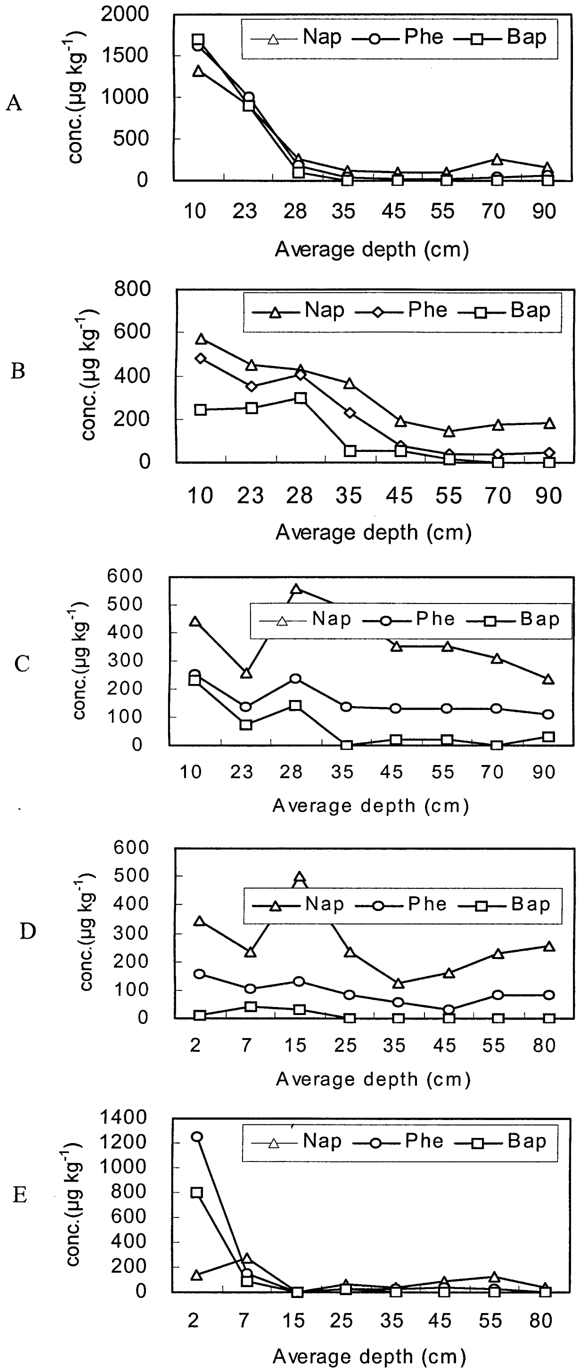

Figure 5. Vertical distribution of naphthalene, phenanthrene and benzo[a]pyrene in the five sampling sites.

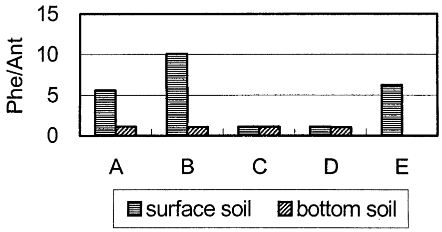

Figure 6. Phenanthren/anthracene for the surface soils of the five sampling sites.

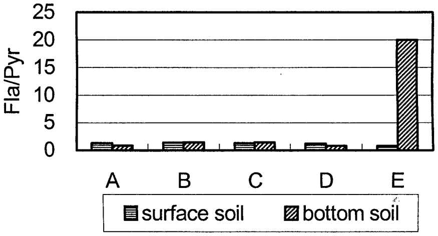

Figure 7. Fluoranthene/pyrene for the surface soils of the five sampling sites.

long-term and large-scale wastewater irrigation. Shi (2003) calculated phenanthrene/anthracene and fluoranthene/pyrene for suspended sediments in major wastewater ditches for which the water has been widely used for irrigation. Results show that phenanthren/anthracene and fluoranthene/pyrene are 4.82 and 1.49 respectively. Combustion of fuels is estimated to be major contributor of PAHs in water and suspended sediment of the ditches.

Sampling location E locates in an oil field, crude oil source may contribute to the accumulation of PAH compounds in soil. Also, since the oil field is not far from the urban area, fuel-combustion is also one of major contributors of PAHs in the soil.

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