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Determination of total petroleum hydrocarbons (TPH) in agricultural soils near a petrochemical complex in Guangzhou, China

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Abstract The total petroleum hydrocarbons (TPH) pollution in regional agricultural soils was investigated. Seventy soil samples collected from surface layers (0–20 cm) and horizons of five selected pedons in the vicinity of a petrochemical complex in Guangzhou, China were analyzed, and the vertical variation and spatial variability of TPH were evaluated. The TPH concentration in top soils around the petrochemical complex ranged from 1,179.3 to 6,354.9 mg kg^{-1}, with the average of 2,676.6 mg kg^{-1}. Furthermore, significant differences between land-use types showed that the TPH concentration in top soils was strongly influenced by accidental spills. Both the TPH trends in pedons and the identified hot-spot areas also showed that the accidental explosions or burning accidents were mainly responsible for the pollution. The results reported here suggest that the regular monitoring and inspection shall be conducted for safety and to avoid or minimize the accidents, and the effective measures should be taken to remediate the contaminated areas and to assure that the important industrialization of Guangzhou area would not mean human health risks near the petrochemical complex.

Keywords Agricultural soils · Guangzhou · Petrochemical complex · Spatial distribution · TPH

Introduction

Petrochemical industries have been identified as important emission sources of organic pollutants (Nadal et al. 2007). Significant amounts of organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), especially total petroleum hydrocarbons (TPH), have been detected in surroundings near oil refineries (Cetin et al. 2003; Iturbe et al. 2007; Nadal et al. 2004, 2007). An excess cancer risk was observed among the communities adjacent to the petroleum refinery plant (Lin et al. 2001; Yang et al. 2000a, b, 2004). In addition, studies have also shown that the residential petrochemical air pollution can affect the outcome of pregnancies,

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such as sex ratios at birth (Yang et al. 2000b), the excess risk of delivering low-birth weight babies at term (Lin et al. 2001), and the higher prevalence of delivering preterm birth infants (Yang et al. 2004).

Since 1978, one of the largest petrochemical complexes in China has been located in Huangpu District (Guangzhou City, China), with the petroleum refinery together with the petrochemical industry within in the area. The refinery has the capacity to process up to 13 million tons of crude oil and produce 200,000 tons of ethylene per year. Therefore, any emissions from the oil refineries may directly affect residents living in the area. Petrochemical refineries produce a wide variety of petroleum and chemical products such as fuels, lubricant oils, natural gas, petroleum coke, and asphalt, and numerous pollutants are discharged into the surroundings (Li et al. 2009). The residential area is downwind from the petrochemical complex, increasing the potential health risks. In recent years, public concern over possible adverse health effects for the population living near this industrial complex has increased, especially toward the accidents. The most recent accidental explosion occurred on March 18, 2010. There have been about 10 accidents since operation began in 1978. In response to the concern of the local population to these facilities, a wide survey has recently been initiated, focused on determining the current levels of TPH, establishing the health risks for the population living in the neighborhood of the petrochemical complex, elaborating the spatial distribution maps of TPH in agricultural soils within the petrochemical area, as well as identifying the pollution sources.

Materials and methods

Study area

The study area is located immediately south of the Pearl River and near a petrochemical complex in Guangzhou (latitude, 22°26′ to 23°56′N; longitude, 112°57′ to 114°03′E), the capital city of Guangdong Province in southern China (Fig. 1). The area shows a typical subtropical monsoonal climate, with the annual average temperature of 21.4–21.8°C and the average rainfall of 1,689.3–1,876.5 mm (Lu et al. 2007), which is very suitable for the growth of most subtropical fruits and vegetables. The prevailing wind direction in the study area, as measured by the Guangzhou Meteorological Bureau, shows that winds predominantly originate from the north in winter and east to southeast in summer (Fig. 2). Two canals, serving as the main irrigation water sources of the arable land, flow through the study area and become the recipients of municipal sewage and

Fig. 1 Location map of the study area

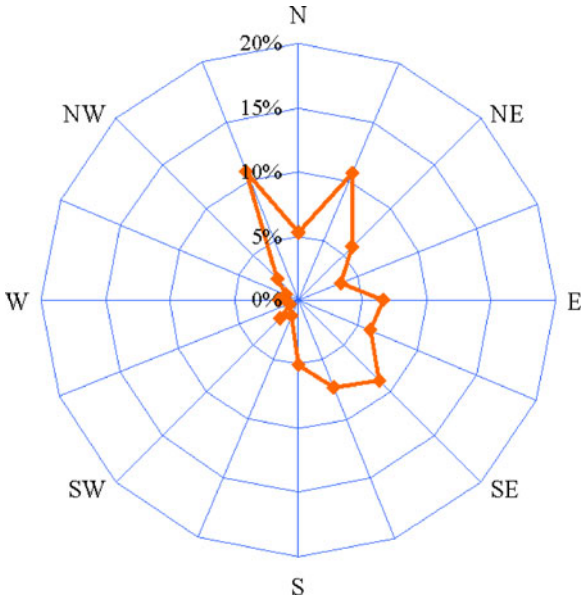

Fig. 2 Wind frequency in directions to Guangzhou

industrial waste water, directly discharged into the Pearl River afterward. The study area is located on surrounding uplands with a granitic soil parent material and the soil of the study area is classified as Plinthosols and Anthrosols (Li et al. 2009). The agricultural activity is centered on vegetables and fruits.

Sampling

A total of 70 soil samples was collected from 50 different sites in the vicinity of the petrochemical complex in January, 2007 (Fig. 3). The sites were chosen primarily to reflect both the increasing distances (100, 500, 900, and 1,300 m) from the petrochemical complex and different land-use types, including vegetable field, orchard, and woodland. The composite top soil samples were obtained by mixing five random sub-samples within 25 m^2 in each sampling site. Five pedons, i.e., P1, P2, P3, P4, and P5, located at the sampling point No. 48, 10, 8, 32, and 19, respectively, were dug and soil samples were collected at 0–10, 10–20, 20–40, 40–60, and 60–80 cm depth individually. All soil samples were collected using a hand auger and then stored in polyethylene bags.

Chemicals

The TPH stock solution was prepared using the 1:1 ratio (v/v) of unleaded gasoline (purity, 99%) and diesel (purity, 99%) purchased from the Caltex Company in Macau SAR, China. Dichloromethane (purity, 99%) and acetone (purity, 99%) were purchased from the International Laboratory (USA).

Analytical methods

The pretreatment of soil samples and the determination methods for basic soil physico-chemical properties, including soil clay content, pH, electrical conductivity (EC), cation exchange capacity (CEC), and organic matter (OM), along with soil metal (Zn, Cu, Pb, Cd, Hg, and As) concentrations, are found elsewhere (Li et al. 2009, 2010). The total contents of Cd, Cu, Pb, and Zn in soils were determined by digesting about 0.2 g soil sample (dry wt) with a mixture of HNO_3, HF, and $HClO_4$ in a polyvinyl-fluoride crucible and then using elemental analysis. Cu and Zn concentrations were analyzed using a flame atomic absorption spectrophotometer (Hitachi Z-5000), and Pb and Cd concentrations were analyzed using a graphite furnace atomic absorption spectrophotometer (GFAAS-AA800, PerkinElmer Inc.). Soil Hg was measured by cold vapor atomic absorption (F732-V, Shanghai) after soil sample was digested with a mixture of H_2SO_4, HNO_3, and $KMnO_4$. Soil As was measured by hydride generation atomic fluorescence spectrometry (HG-AFS 230, Beijing) after digested with HCl and HNO_3. Quality assurance and quality control of metal analyses were assessed using duplicates, reagent blanks and standard reference material (ESS-3, GSBZ50013–88, from National Environmental Monitoring Center of China). The recoveries of analyzed metals in standard reference material were within ±10% of recommended values, and the relative standard deviation of duplicate measurements was less than 10%.

The accelerated solvent extraction (ASE) was applied for the quantitative extraction of TPH from soil, and the GC-FID-based TPH-determination method was used to analyze the extracts. TPH (4,000 mg kg^{-1}) as the internal standard was

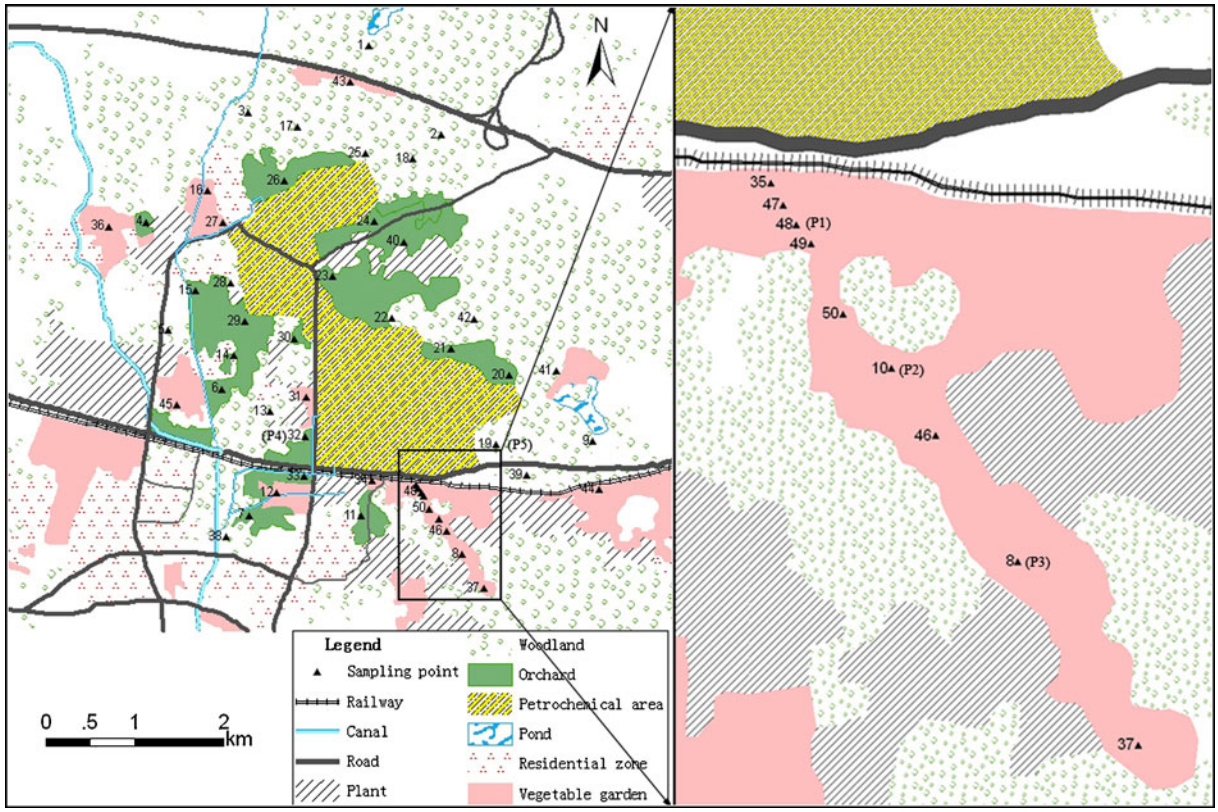

Fig. 3 Soil sampling points in the study area

added to the sample vials to determine the recovery efficiency (96-102%). All extractions were performed using the Dionex (Sunnyvale, CA, USA) ASE 200 system. For the extraction, 5 g soil (<2 mm fraction) mixed (5:1) with the ASE Prep DE (diatomaceous earth) was weighted out into the extraction cell (11-mL stainless steel cells). Glass fiber filters (Restek, Bellefonte, PA, USA) were placed at the outlet of each cell prior to loading with samples. The optimized condition (Richter 2000; Dionex 2004) was employed for the extraction, at 175°C with dichloromethane-acetone (1:1, v/v) with 8 min heat-up time and 5 min static time with the pressure of 1,500 psi nitrogen gas for all samples (1 psi = 56,894.76 Pa). The flush volume was 70% of the extraction cell volume and the purge time was 60 s with 150 psi. The extracts were collected in pre-cleaned 40-mL glass vials (I-Chem, New Castle, DE, USA).

Quantification of the extracts was performed on a gas chromatograph (Agilent, 6890N, Agilent Technologies Co., Ltd, China) equipped with a flame ionization detector (FID) and a capillary column (Agilent HP-5; 30 m × 0.53 μm I.D. with a stationary-phase film thickness of 0.88 μm). One microliter of the liquid sample was injected by the autosampler injector (7638 Series, Agilent Technologies Co., Ltd, China) equipped with a tapered microsyringe (Hamilton 5181-1267, Hamilton Company, USA). Injector and detector temperatures were 230°C and 280°C, respectively. The temperature program for column was with the initial temperature 40°C (hold for 2 min) and incrementally increased (12°C/min) to 280°C (hold for 20 min).

Statistical analysis and GIS mapping

The descriptive analysis was made with the SPSS V13.0 for Windows. Principal Component Analysis (PCA), based on the correlation matrix, was performed with the XLStat-Pro 7.5.2 software,

used as a Microsoft Excel plug-in. A probability level of $p < 0.05$ was considered significant. The map of spatial distribution of TPH concentrations was generated by kriging interpolating data from 50 surface soils by using the ArcGIS V9.0.

Results and discussion

Results for TPH concentrations in the agricultural top soils in the proximity of the petrochemical complex indicated that the TPH concentration ranged from 1,179.3 to 6,354.9 mg kg^{-1}, with the average of 2,676.6 mg kg^{-1}. And the TPH levels were higher compared to other petrochemical areas (Adeniyi and Afolabi 2002; Adeniyi and Owoade 2009; Iturbe et al. 2004; Soukup et al. 2007). Results also indicated that the soil TPH concentrations varied among three land-use types (Table 1). The average TPH concentration in top soils was in the order of woodland > orchard > vegetable field, which was in the reverse order toward soil concentrations of Zn, Pb, Cd, Hg, and As (Li et al. 2009). The soil TPH concentrations for woodland and orchard were significantly higher than for vegetable field, implying a possible result from petroleum air emissions, storage tank and pipeline leakage, accidental spills, and improper waste disposal practices.

The vertical variation of TPH concentrations in five soil profiles (Fig. 4) showed that the TPH content had a systematical increasing tendency with the increase of depth. The TPH concentrations in the vegetable field (P1, P2, and P3) were the lowest and showed little variation with the depth increase, compared to woodland pedon (P5) and orchard (P4). For the vegetable field, the TPH concentrations in pedons 1 and 2 increased with depth, while for pedon 3, initially increased with depth and then decreased. Similar to pedons 1 and 2 in the vegetable field, the TPH concentrations in pedon 4 (orchard) and pedon 5 (woodland) showed increasing trend with depth. The TPH compounds showed a great tendency to leach and migrate into the subsurface soil or groundwater, potentially impacting groundwater.

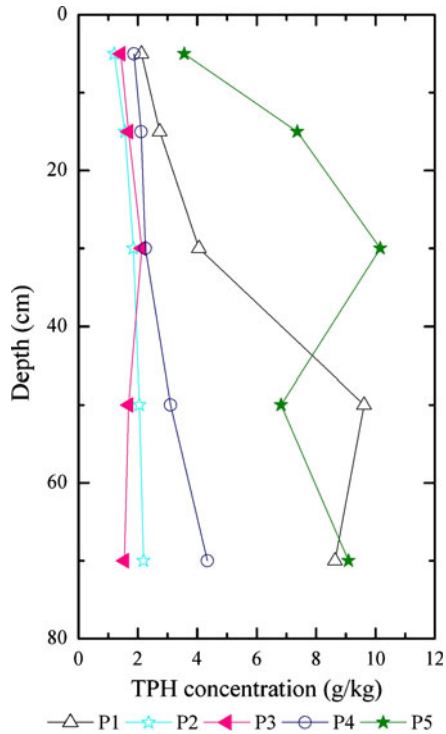

Fig. 4 Vertical variation of TPH concentrations in soil profiles

The spatial distribution of contaminant concentrations is a useful visual aid to assess the possible sources of enrichment and to identify hotspots of

Table 1 Comparison of TPH concentrations (mg kg^{-1}) in top soils of three land-use types

	Vegetable field	Orchard	Woodland	Total
n	20	14	16	50
Range	1,179.3–2,904.0	1,511.2–6,354.9	1,539.4–5,735.0	1,179.3–6,354.9
Mean	1,934.3b	2,886.6a	3,420.8a	2,676.6
SD	596.2	1,251.3	1,181.9	1,182.9

Results are presented as arithmetic means. Means within a row for a certain land-use type followed by different letters are significantly different at the 0.05 level
n is the number of samples

contamination within the plot (Lee et al. 2008). The spatial distribution map of TPH contamination in top soils is shown in Fig. 5, with TPH showing a relatively high spatial variability. As shown, the spatial distribution pattern for TPH was totally different, compared to metals Zn, Cu, Pb, Cd, Hg, and As (Li et al. 2009). Two different hotspot areas for TPH were identified, i.e., in the south-eastern and north-western areas of the petrochemical complex. The elevated concentrations might be due to the anthropogenic influences, particularly related to the accidental spills. There have been about 10 accidental explosions or burning accidents since the operation of the petrochemical complex in 1973, including the pipeline leakages in 2004 (July and August), the heavy oil spills in 2005 (August), and the oil-containing waste water leakage caused by the explosion of sewage recycling cans in 2007 (January), which seriously contaminated the area. The wind direction frequency (Fig. 2) did not answer for the hotspot areas, while the air emission of petroleum might also be responsible for the high concentration areas.

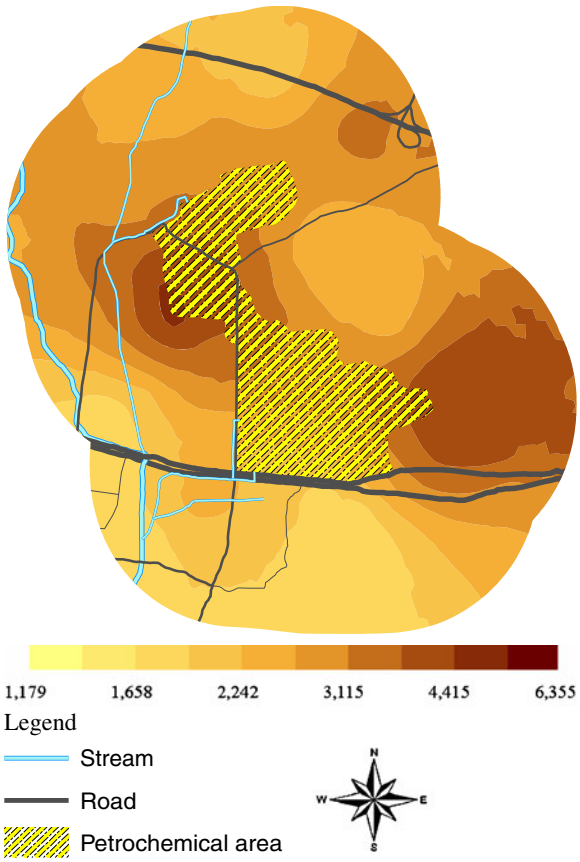

Fig. 5 Spatial distribution of TPH concentrations (mg kg^{-1}) in top soils

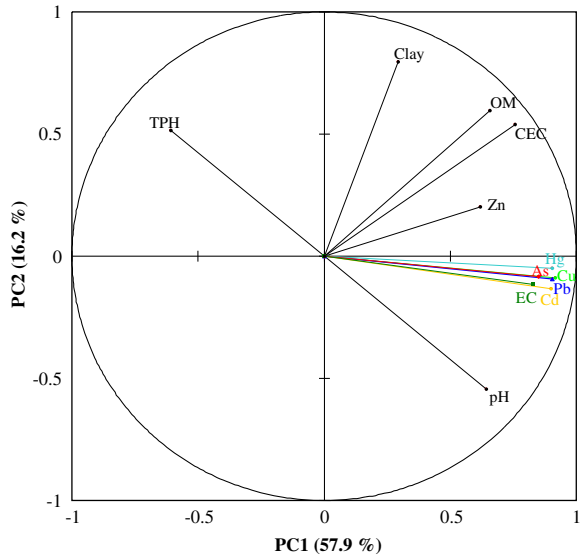

Fig. 6 Plot of the first two principal components obtained from the PCA of soil TPH, soil metals, and selected soil parameters

The principal component analysis (PCA) is a way of identifying patterns in data and expressing the data in such a way as to highlight their similarities and differences, and is a powerful tool for analyzing data. The PCA (Fig. 6) was performed with the TPH concentration, the total concentrations of each metal, and the selected soil properties, in order to analyze the relationships among these indices. The first principal component, with a relative inertia of 57.9%, was positively determined by metals and EC but negatively determined by TPH. The second principal component, with a relative inertia of 16.2%, was positively determined by clay, OM, and CEC but negatively determined by pH. The TPH concentration was shown almost in a straight line toward pH, indicating a negatively significant correlation between them, which is different from the correlation between metals and pH (Li et al. 2009). The presence of TPH may result in the decrease of soil pH. The TPH present in the surface soil might be biodegraded

by the indigenous microorganisms, and the activity of microorganisms may have produced organic acids and this resulted in the decrease of pH. In addition, the TPH concentration was negatively correlated with each metal, but poorly related to CEC, OM, and clay. Since such human activities as waste water irrigation and intensive application of sewage sludge and various agricultural chemicals are the main reasons for heavy metal elevation in soils (Li et al. 2009) and the source of TPH is different from the metals, it was considered that the oil leakage was possibly the main source of TPH accumulated in soil.

Conclusion

The soil in the vicinity of a petrochemical complex in Guangzhou was polluted by TPH, especially for woodland and orchard. The spatial distribution of TPH along with the PCA showed that the accidental explosions or burning mainly accounted for the TPH pollution.

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