Petroleum contamination of soil and water, and their effects on vegetables by statistically analyzing entire data set

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HIGHLIGHTS

• The soil, water, and vegetables were contaminated in the outskirts of Xi'an.
• Inputs of herbaceous plants and floating macrophytes were differentiated.
• Pollution characteristics of Brassica and Apium were differentiated.
• Effect of petroleum contamination in soil/water on vegetables was presented.
• Correlation coefficient between multidimensional data sets was calculated.

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ABSTRACT

Aliphatic hydrocarbons have been used to assess total oil concentrations, petroleum sources, and petroleum degradation. In this study, surface soil, groundwater, surface water, and vegetables were collected from the outskirts of Xi'an, the largest city in northwestern China, and the samples were analyzed for aliphatic hydrocarbon contents. The concentrations of n-alkanes were 1.06–4.01 μg/g in the soil. The concentrations and the geochemical characteristics of n-alkanes showed that the low carbon number hydrocarbons were mainly from petroleum sources, whereas the high carbon number hydrocarbons received more hydrocarbons from herbaceous plants. The concentrations of n-alkanes were 9.20–93.44 μg/L in the groundwater and 23.74–118.27 μg/L in the surface water, respectively. The water had characteristics of petroleum and submerged/floating macrophytes and was found in concentrations that would cause chronic disruption of sensitive organisms. The concentrations and geochemical characteristics of n-alkanes in *Brassica chinensis* L. and *Apium graveolens* were different, but both were contaminated by petroleum hydrocarbons. The results from principal component analysis (PCA) indicated that the sorption of n-alkanes to soil particles could not be described by linear models. The distributions of n-alkanes in vegetables were positively correlated with those in soil, and the correlation coefficient was up to 0.9310 using the constructed vectors. Therefore, the researchers should pay close attention to the effect of soil contamination on vegetables.

1. Introduction

Aliphatic hydrocarbons are ubiquitous in soil, water, air, and biota (Adeniyi and Afolabi, 2002; Clark and Blumer, 1967; Riccardi et al., 2008; Tran et al., 1997; Wu et al., 2007). Aliphatic hydrocarbons pose risks to human health and commonly attract the attention of scientific researchers. These compounds are more likely to be sequestered in the epidermis than are aromatic hydrocarbons (Baynes et al., 2000; McDougal et al., 2000). Mineral paraffin oils or n-alkanes are responsible for pneumonia caused by inhalation of oil paraffin, folliculitis by skin contact with oil, paraffinoma or oleogranuloma by subcutaneous injection of oil, follicular lipidosis by chronic ingestion, and the accumulation of long-chain in viscera (Chou et al., 2002; Salvayre et al., 1988). Low levers (0.01%) of n-alkanes can cause inflammation in an *in vitro* model (Allen et al., 2000). Some are indigenous to a particular plant or animal and result from the decarboxylation of long chain fatty acids, while others arise as a result of contamination following a spill of mineral hydrocarbons or from the combustion of fossil fuels (Fiorini et al., 2010; Neukom et al., 2002).

Alkanes (included in aliphatic fractions) and total petroleum hydrocarbons constitute the bulk of an oil, and can be used to assess total oil

concentrations (Douglas et al., 1996). Moreover, aliphatic hydrocarbon composition analyzed by gas chromatography (GC) can provide information on petroleum sources and degradation. The ratio of low- to high-molecular-weight compounds (LMW/HMW), carbon preference index (CPI), the ratio of pristane to phytane (Pr/Ph), and the C_{16} ratio of petrogenic hydrocarbons are significantly different from those of biogenic hydrocarbons (Cincinelli et al., 2008; Guo et al., 2011; Harji et al., 2008; Tran et al., 1997). The multivariate statistical analysis can simplify the data sets by decreasing dimension, which has been used in geochemical studies and source analysis. The models statistically analyze the entire data set, so the obtained results are more robust than those from the concentration and isomer ratio methods (Liu et al., 2008). Aboul-Kassim and Simoneit (1995b) differentiated between petroleum contaminants derived from sewage and those from direct inputs using factor analysis of n-alkanes. The CANOCO 4.5 software bundled with CanoDraw for Windows can be used to perform multivariate statistical analysis, describe the structure in a single data set, and present the results in graphs. In our previous study, the variation of aliphatic hydrocarbons/polycyclic aromatic hydrocarbons between atmospheric deposition and irrigated water in a typical irrigation region was presented by PCA of CANOCO (Zhang et al., 2012, 2013).

Xi'an, located on the Guanzhong Plain at the south edge of the Loess Plateau, has an area of 1066 km^2 and a population of 5.1 million. It is the largest city in northwestern China. Xi'an, like other inland Chinese cities, has experienced slower economic development compared with the coastal cities, such as Beijing or Shanghai. However, it is expected to begin to develop rapidly in the near future. Xi'an has many vital communication lines and famous historical and cultural relics. Therefore, it is important to pay close attention to the environmental quality of the area. Organic contamination of aerosols in Xi'an has attracted attention from international researchers (Okuda et al., 2010). To date, data on petroleum contamination of soil, water, and vegetables has not been reported.

Our objective is to study petroleum contamination of the soil, groundwater, surface water, and vegetables in the outskirts of Xi'an by analyzing the concentration and geochemical characteristics of aliphatic hydrocarbons. In this study, we also aim to find the similarities and differences between the distributions of aliphatic hydrocarbons in soil, water, and vegetables by multivariate statistical modeling, to obtain the effect of contamination of aliphatic hydrocarbons in soil and water on those in vegetables.

2. Materials and methods

2.1. Sampling

In late July 2012, surface soil, vegetable, groundwater, and surface water samples were collected from vegetable fields in the outskirts of Xi'an, the capital of the province of Shanxi, China. The vegetable fields in the outskirts of Xi'an have an area of 60,000 ha with a typical warm temperate monsoon climate. The annual mean temperature is 13.6 °C, and the annual mean precipitation is 595.9–732.9 mm. Northeast is the predominant direction of the wind throughout the year. The main soil type is cinnamon soil. The main crops are leafy vegetable (Brassica chinensis L. and Apium graveolens).

Seven sampling areas in the Weiyang region (DJ, XCZ, GMN, XW, GM, JWD, and LL), four sampling areas in the Baqiao region (SJD, MLM, WJX, and CJW), and two sampling areas in the Lintong region (LZ and XN) were selected from vegetable fields in the outskirts of Xi'an (Fig. 1). According to the size of the planting area, different numbers of soil samples and corresponding vegetable samples were collected from different sampling areas. Each surface soil sample (0–20 cm depth) and each vegetable sample was homogeneously mixed with five diagonally sampled subsamples in each block. A portion of each sample was filled into a pre-cleaned aluminum box and transported to the laboratory at a temperature of 4 °C. The samples

were freeze-dried and ground to 1 mm for analysis of petroleum hydrocarbons. The other soil sample portions were used for analysis of basic soil properties. The soil samples and vegetable samples were labeled by the first letter of their name (S or V). Samples were then given the letter A or B, after the name of sampling areas (A. graveolens and B. chinensis L.). Samples were further distinguished by the numbers at the end of their names in each sampling area.

Groundwater samples were collected randomly and labeled with G as the first letter, followed by the name of the sampling area. The wells were unconfined wells, with depths to water of 15–30 m in the Weiyang region. The wells were confined wells, with depths to water of 100 m in the Baqiao region (except CJW with depths to water of 30 m). The wells were unconfined wells, with depths to water of 10 m in the Lintong region. Before sampling, each well was purged. A 1,000 mL brown glass jar was used to collect each water sample, and the jar was filled to the top so that no headspace was present. The samples were sealed with Teflon film, labeled, and then transported to the laboratory at a temperature of 4 °C. An aliquot of 10–30 mg of mercuric chloride was added to each sample to retard microbial activity (Christian and Karl, 1995; Doskey and Talbot, 2000). The samples were distinguished by the numbers at the end of their names in each sampling area. The surface water from Fenghui Canal (FHCS), the middle and lower reaches of the Zaohe River (ZHLS), the Wushui Canal (WSCS), the Chanhe River (CHS), the Weihe River (WHS), and the Xingfu Canal (XFCS) were collected (Fig. 1).

2.2. Analytical methods

For the extraction of petroleum hydrocarbons, a soil sample (ca. 30 g) or a vegetable sample (ca. 10 g) was pressurized-liquid extracted with dichloromethane using an ASE-300 (Dionex, USA). During the extraction, the cells were pressurized to 1500 psi/1.0×10^7 Pa, and heated to 100 °C for 5 min. The static extraction was held for 5 min followed by flushing (60% of the cell volume) and purging for 60 s at 150 psi/1.0×10^6 Pa (Dionex, 2007; Richter, 2000; USEPA, 2007a). The aliphatic hydrocarbons were obtained through eluting with approximately 20 ml n-hexane after purification with an alumina and silica gel chromatography column (Guo et al., 2007; Richter, 2000; Van De Weghe et al., 2006) and concentrated to 1 ml for analysis. For the extraction of petroleum hydrocarbons, an aliquot of approximately 1,000 mL of groundwater or surface water was subjected to solid-phase extraction with a C18 column (Supelco, USA). Aliphatic hydrocarbons were obtained through eluting with approximately 20 ml dichloromethane and concentrated to 1 ml for analysis.

The aliphatic hydrocarbons in the extracts of all samples were analyzed by gas chromatography–mass spectrometry [Agilent, 6890 N GC, 5975B mass spectrometric detector (MSD), USA] equipped with an DB-5MS capillary column (30 m, 0.25 mm inner diameter × 0.25 µm film thickness, Agilent, USA). The carrier gas was helium (high purity, 99.99%) at a constant flow rate of 1 ml min^{-1}. Oven temperature was initially set at 60 °C and held for 2 min, then increased to 180 °C at 8 °C/min. Afterward, the oven temperature was increased to 220 °C at 2 °C/min and held for 2 min, and finally increased to 320 °C at 8 °C/min and held for 30 min. MSD was operated in an electron impact mode at 70 eV with an ion source temperature of 300 °C. Mass spectra were recorded with a scan mode ranging from 35 to 600 amu to identify the n-alkanes. The n-alkanes (nC_{10} to nC_{40}), phytane and pristane were quantified using the external standard (Accustandard, US) method.

The analytical procedure was strictly evaluated (USEPA, 2007b). Calibration graphs were constructed by plotting the peak area against the reference material concentration every two days and a linear relationship with $r^2 > 0.999$ was always obtained. The recovery test was performed by spiking a soil sample or distilled water with the reference material. The recoveries for nC_{10} to nC_{40}, phytane and pristine