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Determination of Phenanthrene in Urban Runoff of Tehran, Capital of Iran

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ABSTRACT

In many big cities, surface runoff is collected by separate collection system and is then directed to receiving water bodies. Since it washes out the materials from the surface of different lands, is known as the source of pollution. Polycyclic aromatic hydrocarbons (PAHs) are one class of carcinogenic contaminants that are commonly found in storm water runoff. In this study, phenanthrene was measured in the surface runoff of south of Tehran, capital of Iran. After identifying three main drainage channels, three sampling stations were chosen, based of the fact that all urban surface runoffs completely passed through these points and taken samples were more expected as representative of all kinds of pollutants. Surface runoff flows in three main channels from north to south of Tehran. At each month two samples were taken from each station, afterwards concerning the USEPA method, 60 samples were extracted and analyzed with High Performance Liquid Chromatography device. Results show that the average concentration of PAH in the most polluted drainage was about 9.4 µg/l. The minimum and the maximum concentrations of PAH in all of the taken samples were zero and, 15.1 µg/l, respectively. In the rainy season, the concentration of phenanthrene was the highest, because the rain washed out the pollutant from the surface of the street. In addition, the concentration of phenanthrene in the middle drainage channel was more than two others, because this station received the runoff from city center whose traffic load was high.

Keywords: *PAH, Phenanthrene, Urban Runoff, Drainage, Iran*

INTRODUCTION

Polycyclic aromatic hydrocarbons PAHs released into the environment arise mainly from anthropogenic sources. They are mainly formed as by-products of incomplete combustion of organic materials. PAHs have been identified in many emission sources, such as vehicle exhausts power plants chemical, coke and oil industries as well as urban sewage. Primary natural sources of PAHs are forest fires and volcanic activity (Trapido, 1999; Burton and Pitt, 2002).

The most common organic toxicants have been from automobile usage (PAHs), combustion of wood and coal (PAHs), industrial and home use solvents (halogenated aliphatic and other volatiles), wood preservatives (PAHs, pentachlorophenol), and a variety of agricultural, municipal, and highway compounds, also pesticides (Turlough and Guerin, 1998; Howsam et al., 2000; Wong and Wang, 2001; Burton and Pitt, 2002). Automobile use contributes significantly too many of these materials. PAHs, the most commonly detected toxic organic compound

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found in urban runoff, are mostly from fossil fuel combustion. Photo-induced toxicity occurs frequently during low flow conditions and wet-weather runoff and is reduced during turbid conditions (Burton and Pitt, 2002).

The Technical University of Denmark has been involved in a series of tests to examine the effects of storm water infiltration on soil and groundwater quality. It found that heavy metals and PAHs presented little threat for groundwater contamination if surface infiltration systems were used. However, it makes concern about pesticides, which are much more mobile. Scientists presented information concerning stormwater and its potential as a source of groundwater MTBE contamination (Turlough and Guerin, 1998; Burton and Pitt, 2002). PAHs [especially benzo (a) anthracene, chrysene, anthracene, and benzo (b) fluoroanthenene] have also been found in ground waters near industrial sites (Burton and Pitt, 2002).

The PAHs are found in runoff from all areas, but they are in higher concentrations and occur more frequently in industrial areas. The types and concentrations of toxic organic compounds that are in storm waters are driven primarily by land use patterns and automobile activity in the watershed. Most non pesticide organic compounds originate as wash off from impervious areas in commercial areas having large numbers of automobile startups and/or other high levels of vehicle activities, including vehicle maintenance operations and heavily traveled roads.

The compounds of most interests are PAHs that are adsorbed in sediments. Sediment toxicant analysis includes PAHs and pesticides. The list of specific toxicants is similar to that of the sediments (copper, zinc, lead, and cadmium, plus PAHs and pesticides). Two of the PAHs (fluoranthene and phenanthrene) were found in all of the street dirt samples. Many organic priority pollutants were detected in the soil samples. The most important organics found were PAHs. The PAHs Rapid Assay can test 16 common PAHs ($1275/100 samples) and is comparable to EPA SW-846 Method #4035 and GC method 8270 or HPLC method 8310, with assay ranges in soil and water of 0.2 to 5.0 ppm and 0.9 to 66.5 ppb, respectively. Scientists describe a study in San Diego where LAB, along with PAHs and aliphatic hydrocarbons (AHs), were measured to indicate the relative pollutant contributions of wastewater from sanitary sewage, nonpoint and hydrocarbon combustion sources. They developed and tested several indicator ratios (alkyl homologue distributions and parent compound distributions) and examined the ratios of various PAHs [such as phenanthrene to anthracene, methylphenanthrene to phenanthrene, fluoranthene to pyrene, and benzo (a) anthracene to chrysene] as tools for distinguishing these sources. Toxicity may also be reduced in runoff. When turbidity increased during high flow, photo induced toxicity of PAHs was reduced *in situ,* as compared to base flow conditions (Burton and Pitt, 2002). High concentrations of many of the PAHs were more likely associated with long antecedent dry periods and large rains, than by any other storm or sampling location parameters (Sun et al., 1998; Turlough and Guerin, 1998; Howsam et al., 2000; Burton and Pitt, 2002).

Some organics such as PAHs are metabolized by many organisms, so detection in tissues may indicate recent exposures. Green coke has been shown to release more PAH during quenching than non-green coke. PAHs are a relevant group of compounds which can be concentrated in sludges. Wastewater contains high amounts of PAHs coming from industrial waste and domestic sewage, atmospheric rainfall, precipitation, airborne pollutants, runoff of road surface, etc (Qian, 1993; Miege et al., 1998; Environment Australia, 1999; Howsam et al., 2000; Wong and Wang, 2001;).

Chronic exposure to PAH can cause dermatitis and hyperkeratosis may have also possible upshot on placental endocrine and hormonal functions. It can be transformed to carcinogenic or co-carcinogenic derivatives in mammals (including humans) by the cytochrome P-450 mono- oxygenase and epoxide hydrolyses systems. Biochemical and cellular responses, measured at the cellular level, such as mixed function oxidase (MFO) activity, DNA adduct formation, and lysosomal destabilization, can provide an early warning signal of potential adverse effects that may result from PAH exposure (Qian, 1993).

MATERIALS AND METHODS

This study has been done in Tehran, capital of Iran. Three stations were selected at three main drainages channels of Sorkhe Hesar, Emad Avard and Kan (Map1); then from Nov. 2003, two samples were collected monthly from each station. Since the sampling was difficult and the analysis by the equipment was limited it was decided to have 60 samples only.
The samples were transferred to the laboratory and were prepared for analysis. Detection range for HPLC device was 0.02 to 100 µg.L^{-1}. PAH is less soluble in runoff and thus accumulates in the sediments of the drainages. Sediments related to 1 liter of runoff were separated and let to dry at rt, and then samples of different sediments were mixed with acetone and diluted up to an acetone/water ratio of 4:1 (v/v) and a solid/ liquid ratio of 1:10 g/ml. The resulting slurry was sonicated for 15 min (Retsch UR 2) and was shaken at rt for 1 h (150 rpm, Gerhardt Laboshaker, Bonn, Germany). Then the extracts were centrifuged (5 min, 13 000 g; Biofuge Pico, Heraeus Instruments, Osterode, Germany) and analyzed for PAHs by HPLC (Pump and auto sampler: Separations, H.I. Ambacht, Holland; Columns: Vydac, Hesperia, CA, USA; Detector: Gynkotek, Germering bei Munchen, Germany) (Cuypers et al., 2002). Different types of PAHs known as 1235–1245 and 1237 were separated on a reverse phase C18 column (Vydac 201TP54, 5l) with external guard column (Vydac 102GD54T, 5 l) using a mixture of acetonitrile and water as diluents. The separation was performed at a constant flow of 1 ml/min, varying the acetonitrile/water ratio from 1:1 to 99:1 (v/v) (0– 5 min, 1:1; 5–20 min, linear increase from 1:1 to 99:1; 20– 40 min, 99:1; 40–45 min, linear decrease from 99:1 to 1:1; 45–50 min, 1:1). PAHs were detected by UV absorbance at 254 (Gynkotek UVD 340S). Phenanthrene (3 ring PAHs) was measured as previously described (Sun et al., 1998; Pawluk et al., 2000; Rababah and Matsuzawa, 2001).

RESULTS

In Fig.1 to 3, the concentrations of phenanthrene in urban runoff for three drainages are presented. In each figure, the concentration of phenanthrene for each sample and each month is given.
The maximum and minimum concentrations of phenanthrene for Sorkhe Hesar, Kan and Emad Avard drainages were about 5.3 and zero µg/l, 9.8 and 6.7 µg/l, as well as 15.1 and 1.0 µg/l, respectively (Fig.1). The average concentration of those three drainages was 3.1, 8.2 and 9.4 µg.l-1, respectively (Fig. 4).

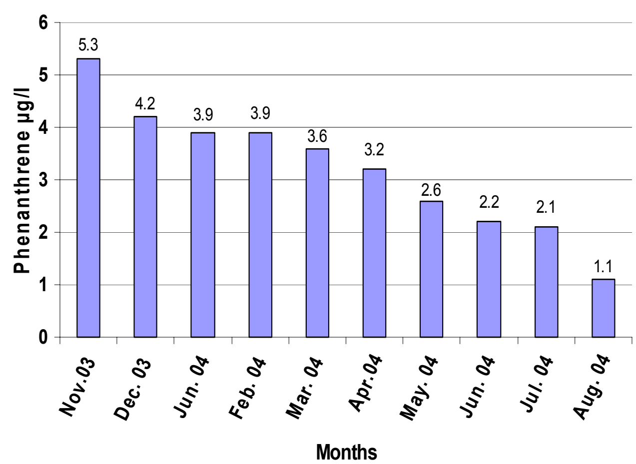
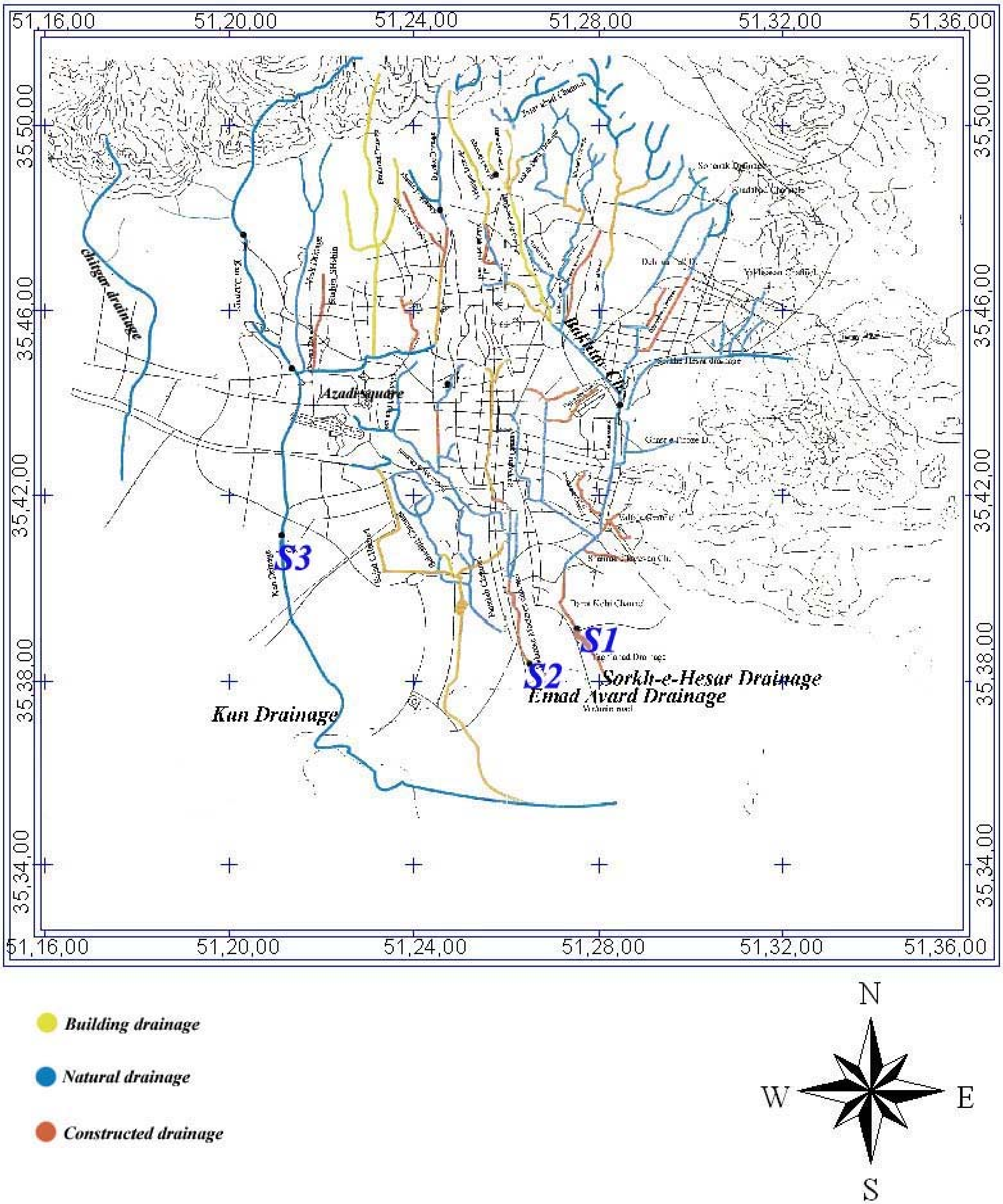


Fig.1: Phenanthrene concentration of Sorkhe Hesar Drainage



Map 1: Drainage channels of Tehran and sampling stations spots, S1= Sorkhe Hesar, S2= Emad Avard, S3= Kan

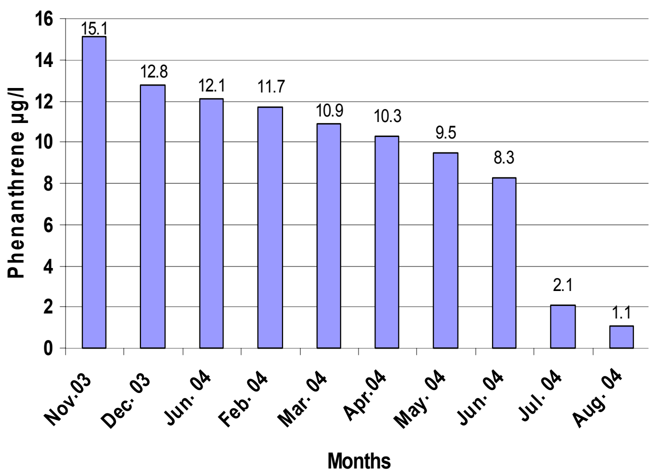


Fig. 2: Phenanthrene concentration of Emad Avard drainage

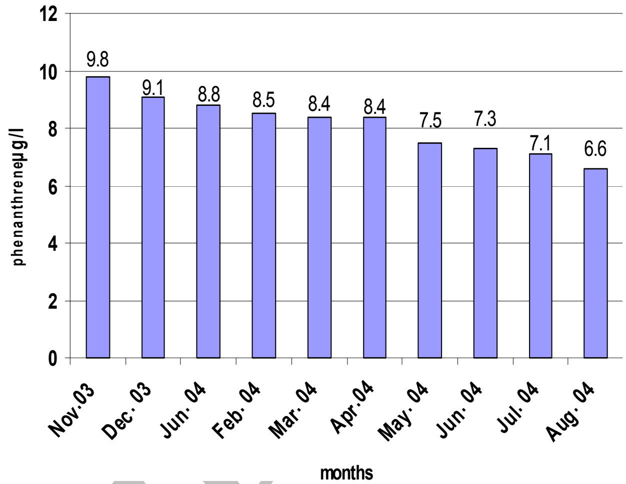


Fig. 3: Phenanthrene concentration of Kan drainage

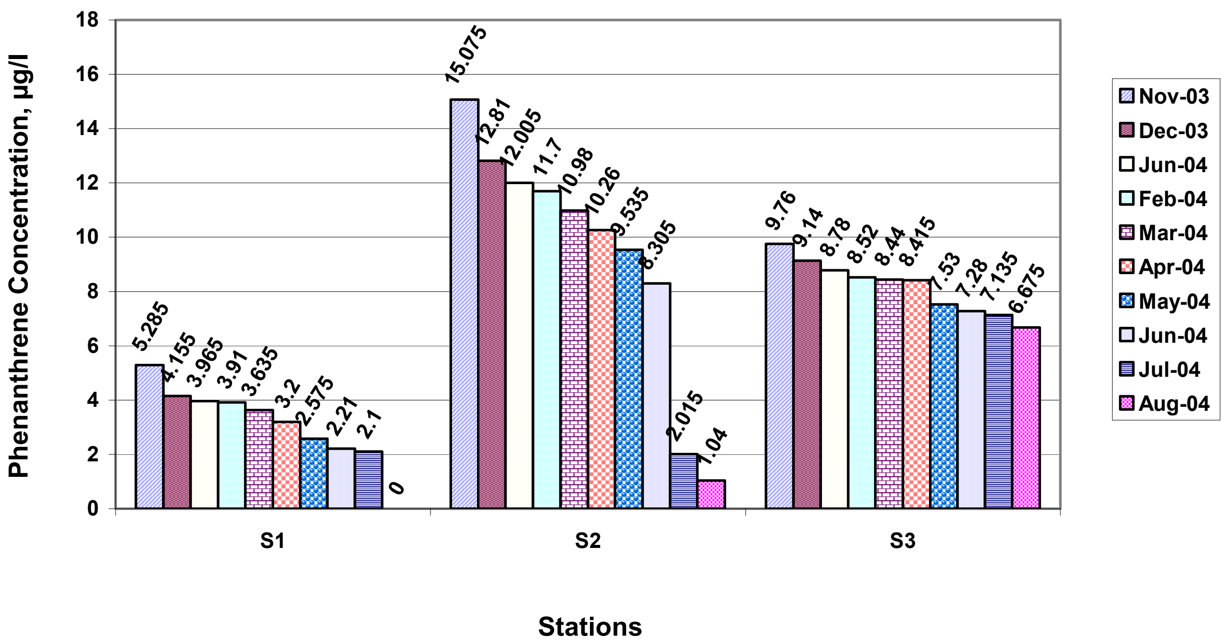


Fig. 4: Phenathrene concentration of three drainage

DISCUSSION

Levels of the sum of the 16 USEPA priority pollutant PAHs vary from below detection limits (ca. 1 $\mu g.g^{-1}$) to over 10000 $\mu g.g^{-1}$ (Sediment PAHs level of runoff) (USEPA, 2004). The concentrations of total PAHs were extremely variable, ranging from 33 $ng.g^{-1}$ dry weights in the Edisto River estuary to 9600 $ng.g^{-1}$ in Carolina sediment (Ngabe et al., 1999). PAHs in a sediment core taken from inertial flat in Yangtze Estuary in China were determined by gas chromatography–mass spectrometry; the results indicated that the total concentration of PAHs ranged from 0.08 to11.7 $\mu g.g^{-1}$ (Wong and Wang, 2001). The collected storm water run-off in urbanized areas of South Carolina was investigated for the levels and sources of polycyclic aromatic hydrocarbons PAHs. Fourteen compounds were analyzed and determined by gas chromatography mass spectrometry. The mean concentrations of total PAHs were 5590 ngr.l^{-1} in the city of Columbia and 282 ng.l^{-1} in the coastal community of Murrells Inlet. Lower concentrations were found in estuarine water at Murrells Inlet means 35 ng.l^{-1} and at undeveloped North Inlet estuary about 13 ng/l^{-1}. The PAH profiles in Columbia and Murrells Inlet runoff were similar to those of atmospheric particulate matter and unlike those in used crankcase oil (Ngabe et al., 1999). Examination of the aliphatic fraction of Columbia runoff samples by gas chromatography with flame ionization detection showed patterns that were more similar to used crankcase oil than to urban aerosols.

Phenanthrene concentrations in Sorkhe Hesar drainage exist at the range of zero to 5.3 µg.L-1. The phenanthrene concentrations obtained in this study are in accordance with other surveys conducted in Carolina and Yangtze Estuary in China (Ngabe et al., 1999; Wong and Wang, 2001). Data results showed that phenanthren concentration in November 2003 at first precipitation was high in all stations of Sorkhe Hesar, Emad Avard and ; but in August 2004 it declined to zero, 1 and 6.7 µg.L-1, respectively, for each drainage. Results showed that phenanthrene concentration in Emad Avard drainage was more than two other drainages which may be due to receiving from city center and slow traffic, fuel, exhaust stack, frequency in car stoppage, more abrasion of asphalt, abrasion of tire and spill oil from engine, industrial effluents, which lead to discharge of polycyclic aromatic hydrocarbons PAHs in runoffs. Declining of phenanthrene in Kan drainage may be attributed to the more industrial activities in this area compared to two others.

Since the maximum permissible standard of PAH concentration in drinking water is 0.2 µg/l (Ministry of Power, 2001) and the concentration of phenanthrene in the samples taken from three drainages in Tehran was much more than this, it is suggested that surface runoff should be treated prior to discharging into the ground water sources.

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