

Source characterization and the environmental impact of urban street dusts from Egypt based on hydrocarbon distributions

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ABSTRACT

The aliphatic and aromatic fractions of the extracts of ten street dust (SD) samples collected from eight cities covering a wide geographic area of Egypt were analyzed using gas chromatography with flame ionization detector (GC-FID) and GC-MS to compare their hydrocarbon distributions. To identify their sources, the extracts of the possible source materials were also analyzed. The impact of SDs on the marine environment was investigated in a marine sediment collected from the Western Harbor of Alexandria. The GC-FID profiles of the aliphatic fractions showed considerable differences in the *n*-alkane distribution that permits the classification of the SDs into five groups. This grouping reflects the environments of the cities in which they are collected. The carbon preference index and the unresolved complex mixture relative to the total resolved peaks values revealed that automobile exhaust is the main source of the hydrocarbons in these SDs with a significant contribution from terrestrial higher plant waxes to group 1 (Nile Delta cities). The sterane and hopane profiles supported this conclusion. The total polycyclic aromatic hydrocarbon (PAH) concentrations ranged from 27 to 379 ng/g (dry wt.) and showed clear differences between the SDs. The lowest and highest concentrations were found in samples from Shebeen and Port Said, respectively. The PAH distribution patterns and the ratio of the sum of combustion specific PAHs to total PAHs in samples from Alexandria, Port Said and Cairo were similar, implying similar sources. PAH ratios indicated a mixture of pyrogenic and petrogenic sources of PAHs in all samples where asphalt and automobile fuel exhaust were the major contributors of PAHs in Alexandria, Port Said, Cairo and Sharm El Sheikh cities. These ratios also indicated the predominance of diesel-operated vehicles to the PAHs signatures of Alexandria, Port Said and Cairo while gasoline emissions influence more strongly the PAH distributions in the SDs from Shebeen, Kafr El Sheikh and Sharkea. The PAH fingerprints excluded fresh oil and tire particles as major contributors. Both SDs and petrogenic sources significantly contributed to the hydrocarbon signature of the marine sediment from the Western Harbor of Alexandria.

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1. Introduction

Urban air pollution is of major concern in Egypt and other countries as industrial wastes, traffic congestion and over-crowding in cities lead to pollutants that significantly contribute to environmental damage and health problems. Urban atmospheric environments contain many organic pollutants which are related to incomplete fuel combustion in domestic heating, industrial plants and vehicular exhausts, such as long-chain alkanes, mono- and dicarboxylic acids, polycyclic aromatic hydrocarbons (PAH) and terpenoids [1].

In the urban environment, there are many sources of *n*-alkane release into the atmosphere. The relative distribution of homologous *n*-alkanes provides insight into the likely sources that contrib-

ute to an ambient sample. Normal alkanes of higher molecular weight originate from biosynthetic processes, which produce homologues that range from C₁₂ to C₄₀ [2]. Biosynthetic *n*-alkanes exhibit a strong odd carbon number predominance.

Hopanes and steranes are among the most important hydrocarbon groups in petroleum used for chemical fingerprinting. Relative to alkanes and most aromatic compounds, they are highly resistant to degradation in the environment [3]. Therefore chemical analysis of hopanes and steranes can generate highly specific source information of great importance to environmental forensic investigations in terms of studying the fate and behavior of hydrocarbons in the environment, identifying petroleum derived contamination in the marine and aquatic environments, and indicating chronic industrial and urban releases [4–6].

Polycyclic aromatic hydrocarbons are a group of lipophilic anthropogenic chemicals that are ubiquitously distributed in the environment. They form an important class of environmental

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contaminants, because some of them exhibit a carcinogenic or mutagenic potential. PAHs have been described in all environmental compartments and their formation, sources and fate have been reviewed [7,8]. They can be emitted to the atmosphere as combustion products. Since combustion processes occur rapidly (considering a radical formation mechanism [9]), PAH formation and growth by addition of hydrocarbon radicals also occur quickly, leading to condensation of heavy PAHs on particles. After formation, PAHs disperse in the atmosphere and are distributed between the gaseous and particulate phases according to their vapor pressures. Sources of PAHs to street dust (SD) include atmospheric deposition and direct deposition (crankcase oil, for example). Atmospheric deposition of PAHs is a significant source of these contaminants in surface waters, especially coastal inland waters of industrialized areas. There is concern about PAHs in SDs since runoff can transport them into water bodies, thus contaminating sediments [10] and consequently the food chain. The PAHs are relatively stable and can serve as diagnostic source constituents of petroleum. Combustion products of petroleum in SD are directly related to urban use and in more trafficked streets they occur in higher concentrations than in less trafficked areas.

The relevance of the mentioned hydrocarbon classes in the environmental investigations has been applied in determining the sources of atmospheric pollution of different cities around the world. The fluoranthene/pyrene (FL/PY) ratio has indicated that PAH fractions of airborne particulate in Lanzhou, China were mainly from incomplete combustion [11]. Pengchai et al. [12] have reported that tire particles and pavement debris as well as vehicle exhaust are the major contributors to street dust in Tokyo. Furthermore, it has been cited that traffic emissions are the main PAH sources in the Genoan urban area [13]. The higher input of vascular plant wax components to the respirable suspended particles collected from a coastal–rural site in central Portugal has been demonstrated by the distribution pattern of *n*-alkanes homologous series [14].

The present study examines the distribution of the various classes of hydrocarbons present in SDs collected from different cities in Egypt and attempts to fingerprint the sources of these SDs. The possible source materials – including fresh and used lubricating oils, automobile exhaust, asphalt and tire particles – were analyzed. A sediment (S) sample collected from the Western Harbor of Alexandria was also analyzed to study the impact of SDs on the marine environment.

2. Materials and methods

2.1. Sample collection

In July 2005, 10 samples of SDs were taken in eight cities, covering a wide geographic area of Egypt (Fig. 1). Their environment and climatic conditions are different. Two cities are located on the Mediterranean coast (Alexandria and Port Said), while two other cities (Sharm El Sheikh and Rudies) are located on the Gulf of Suez and surrounded by desert. Rudies is one of the largest oil producing fields in Egypt and the city of Rudies was constructed to serve the oil industry. Three cities (Shebeen, Kafr El Sheikh and Sharkea) lie in the Nile Delta and are surrounded by a vast area of agricultural land. The last city is Cairo which is the capital and famous tourist city. The 10 SD samples were taken from heavily trafficked streets in Alexandria (SD1, SD5 and SD6), Port Said (SD2) and Cairo (SD7) and residential streets in Sharm El Sheikh (SD3), Shebeen (SD4), Kafr El Sheikh (SD8) and Sharkea (SD9). The SD10 is from Rudies city center. All sampling sites are paved with asphalt. Street dust was collected by using a small plastic brush and a small aluminum shovel. The samples were stored in amber glass containers and sealed with aluminum foil. They were stored in an ice-chest at 4 °C and conveyed to the laboratory in

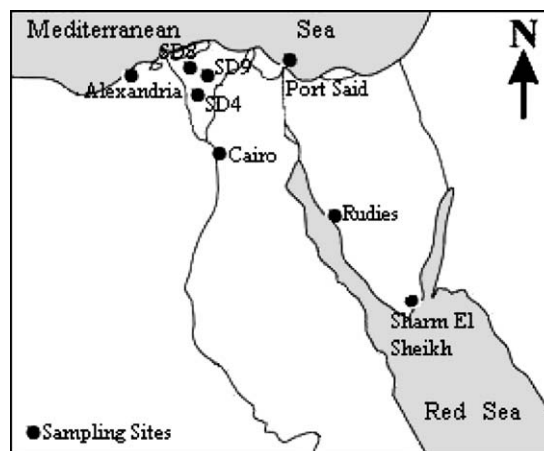


Fig. 1. Location of street dusts sampling sites in Egypt.

which the samples were freed from stones and other foreign materials. They were then air-dried to constant weight, ground with mortar and pestle and then sieved through a 200 µm mesh. Sediment sample representing the top ~20 cm was taken with an Ekman grab sampler. The sample was carefully inspected to ensure that undisturbed sediment was collected. The sample was freeze-dried and stored at 4 °C until analysis.

A fresh lubricating oil sample (Mobil) was purchased from the Egyptian market. One used oil sample was taken from storage tanks in an automotive workshop in Alexandria. The samples were collected using a pre-cleaned 10 ml glass pipette and placed in previously baked 30 ml amber vials. The samples were transported to the laboratory and stored in a freezer until further analysis.

Fresh asphalt samples were obtained from two pieces of asphalt detached from the surface of an asphalt-paved road in Alexandria city. The samples were wrapped in aluminum foil, transported to the laboratory, stored in a clean plastic zip-lock bag, and stored in a freezer until further analysis. The back sides of the broken asphalt were ground with a stainless steel file, with care taken to avoid contamination by street dust from the surfaces of the piece.

Automobile exhaust samples were taken from an automobile of Japanese make. The automobile was equipped with a spark-ignition engine (1600 cc). On sample collection, the engine was operated at ca. 3000 rpm with no load. The exhaust from the automobile was introduced into a 300 L chamber and the automobile exhaust particles were collected on prebaked glass-fiber filter for 30 min of vacuuming (15 L/min) with a vacuum cleaner.

Particles from used automobile rubber tires were obtained by abrasion of their surfaces with a stainless steel file.

2.2. Analytical procedures

The entire procedure for the extraction, purification, and fractionation is similar to that described by Short et al. [15]. Briefly, freeze-dried SDs, auto exhaust, sediment and tire particles were Soxhlet-extracted with dichloromethane (DCM). Oil and asphalt samples were dissolved in DCM. An appropriate volume of PAH surrogate internal standard mixture containing 1-fluoro-2-methylnaphthalene and 1-fluorophenanthrene [16] was added to the extracts. A 20 mg aliquot of extracted sample was transferred onto a chromatographic column (120 × 8 mm) packed with 2.5 g silica gel (Kieselgel 60, Fluka, 70–230 mesh), followed by 2.5 g alumina (Brockmann I, Fluka). Silica was activated at 200 °C for 12 h and alumina at 450 °C for 12 h, then 5% water was added to both gels which were stored at 155 °C. Cyclohexane (30 ml) was used to elute aliphatic hydrocarbons, and 40 ml of dichloromethane/cyclohexane (1:1, v:v) was used to elute aromatic components.

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