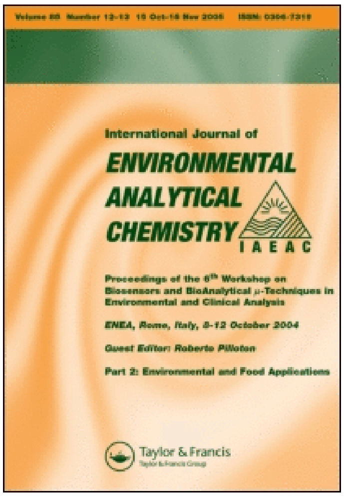

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# *N*-Alkanes in Air Particulates of the Eastern Province of Saudi Arabia

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# *N*-ALKANES IN AIR PARTICULATES OF THE EASTERN PROVINCE OF SAUDI ARABIA

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Oil hydrocarbons represent a great proportion of organic compounds in the atmosphere. Information about these compounds in the atmosphere of the Eastern Province of Saudi Arabia is lacking. In this study, *n*-alkanes and polynuclear aromatic hydrocarbons in air particulates were determined. The highest median concentration levels of *n*-alkanes in three urban areas and three areas near oil production centers were 121 ng/m$^3$ and 42.9 ng/m$^3$, respectively. Polynuclear aromatic hydrocarbons were also detected, although they are present in too low concentration for reliable quantitative measurement by GC and GC/MS techniques. A positive correlation was found between the concentration levels of *n*-alkanes in air particulates and the total suspended particulates measured at most locations. The carbon preference index (CPI) and the presence of the unresolved complex envelope suggested an anthropogenic origin for the *n*-alkanes.

KEY WORDS: Oil hydrocarbons, *n*-alkanes, air particulates, analysis, Saudi Arabia.

## INTRODUCTION

Great concern has recently been focused on the possible adverse health effects of organic pollutants present in the atmosphere. Halkiewicz *et al.*[1] reported that many organic compounds detected in the atmosphere are carcinogens or co-carcinogens. Although many organic compounds are not harmful in the form in which they were initially emitted into the atmosphere, they may be oxidized to harmful species.[2] Organic compounds exist in the atmosphere in the form of gases, particulate aerosols, or as surface films adsorbed on water droplets.[3] These compounds include organic gases and organic macromolecules derived from natural biogenic and synthetic sources. Several investigators have shown that hydrocarbons, especially *n*-alkanes and polynuclear aromatic hydrocarbons (PAHs) represent the major organic constituents of the urban atmosphere. It has been estimated that about 45 million tons of oil hydrocarbons enter the atmosphere north of the equator annually.[3] The Eastern Province of Saudi Arabia is considered a major site of oil production. In addition, it has one of the largest oil refineries in the world. Emission of oil hydrocarbons into the atmosphere in this part of the world has not yet been reported. The objectives of the present study are to determine the levels of *n*-alkanes in air particulates of major cities in the Eastern Province and in areas close to oil production centers, as well as to compare these levels with those existing in urban areas and other parts of the world.

## MATERIALS AND METHODS

### *Sampling*

Air particulate samples were collected from six different locations in the Eastern Province of Saudi Arabia from January 1981 to October 1982. A total of about 1000 samples were collected. Three of the sampling sites were located in the vicinity of oil activity centers. The other three locations were from residential areas in the cities of Dammam, Dhahran and Khobar; the sampling sites are shown in Figure 1. Air particulate samples were collected using standard high volume samplers fitted with glass fiber filters (20 cm x 25 cm). The high volume samplers used in this study were manufactured by Sierra Instruments and General Metal Works. Air samples were drawn through the filter at a controlled flow rate of 1 $m^3$/min for 24 h. Filters were weighted before and after sampling and the total suspended particulates were determined. In this study, 10% of the total number of samples were randomly selected.

### *Hydrocarbon Isolation and Analysis*

Oil hydrocarbons adsorbed on the glass fiber filter were isolated by soxhlet extraction for 3 h using high-purity, distilled-in-glass, methylene chloride as solvent (Burdick and Jackson). The extract was evaporated to 4 ml using a Kuderna–Danish concentrator. The methylene chloride was replaced with hexane by adding about 10 ml of hexane and the concentration step was continued to 4 ml. Final concentration to 1 ml was obtained using a gentle stream of nitrogen. This concentration process was found to give a recovery better than by direct concentration to 1 ml. The hexane extract residues were then passed through a chromatographic column to clean up the sample and to separate the aliphatic and aromatic fractions. The chromatographic columns (0.9 cm I.D. by 30 cm length) were filled under hexane with 4.5 g of silica to which 1.8 g of alumina were added. The column was rinsed with two bed volumes of hexane before use. At no time were the columns allowed to run dry. The residues of the filter extracts were applied to the column in small volumes, after which the aliphatic fractions were eluted with two bed volumes of hexane. The aromatic fractions were eluted with 25 ml of hexane-methylene chloride (7:3). The eluates were further concentrated to 1 ml as described above.

The concentrated fractions were analyzed using a Finnigan OWA-30 GC/MS system and a Varian GC Model 6000, equipped with a flame ionization detector (FID), and a Vista 654 data station. A fused silica capillary column (0.25 mm I.D. and 30 m long), coated with a 0.25-$\mu$m layer of SE-30, was used for analysis throughout the study. The GC oven was programmed from 50 °C to 250 °C at a rate of 5 °C per min, with an initial hold time of 4 min and a final hold time of 10 min. The mass spectrometer in electron impact mode was scanned from 45 AMU to 450 AMU in 1 sec. Helium and nitrogen were used as carrier gases in the GC/MS and GC analyses, respectively. Identification of the organic compounds was carried out using the GC/MS computer by comparing the fragmen-

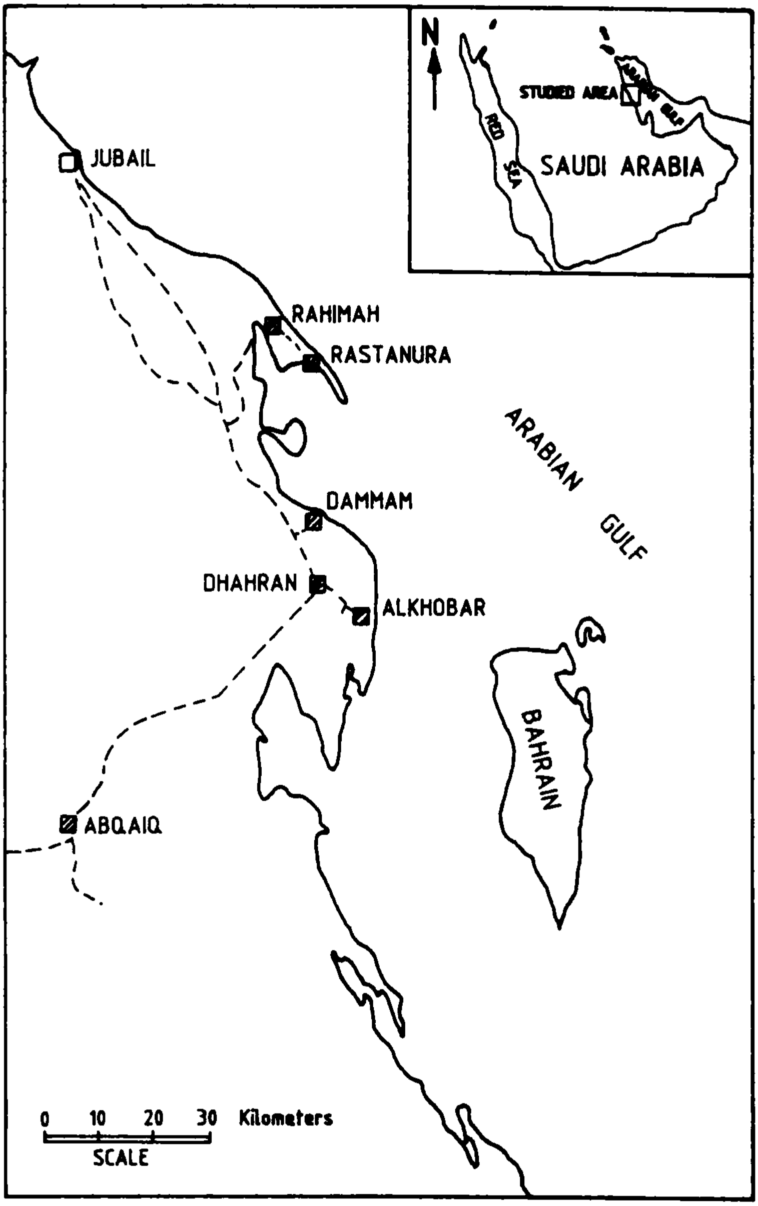

**Figure 1** Location map of the Eastern Province in Saudi Arabia showing the sampling locations ▨.

tation pattern of the unknown with those present in the computer library. Several experiments were conducted to check the performance of the analytical procedure used in this study. The efficiency of the method was evaluated by analyzing solvent blanks, procedure blanks and filter blanks, spiked with a mixture of aliphatic and aromatic hydrocarbons.

**Table 1** Recovery (%) obtained for the analysis of air filters spiked with *n*-alkanes at an average concentration of 24 μg/g each

| *Compound* | *Mean* ($n = 7$) | *S.D.*[a] |
|---|---|---|
| C-10 | 65 | 18 |
| C-12 | 62 | 12 |
| C-14 | 65 | 12 |
| C-16 | 72 | 16 |
| Pristane | 88 | 18 |
| C-18 | 80 | 15 |
| Phytane | 82 | 18 |
| C-20 | 91 | 13 |
| C-22 | 95 | 10 |
| C-24 | 93 | 10 |
| C-26 | 93 | 9 |
| C-28 | 91 | 9 |
| C-30 | 86 | 11 |
| C-32 | 88 | 8 |
| C-34 | 91 | 10 |

[a] n = number of replicates; S.D. = standard deviation.

## RESULTS AND DISCUSSION

A review of the literature indicated that there is no standard analytical procedure available for the determination of oil hydrocarbons in air particulates. In this study, an analytical method was developed and evaluated. The performance of the analytical procedure has shown that it is very reliable for the determination of *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs) in air filters. Results of the recovery study are shown in Tables 1 and 2.

It can be seen from these tables that the accuracy and precision of the procedure improve as the molecular weight of the *n*-alkanes and PAHs increase. This can be attributed to the loss of the low-molecular-weight compounds during the concentration steps, because of their relatively higher volatility. The concentrations of *n*-alkanes in various samples were determined using the external standard method. Since the odd numbered *n*-alkane standard compounds were not available to us, the detector response factors of these compounds were calculated from the average value of the response factor of the two adjacent even-numbered *n*-alkanes. Gas chromatograms obtained for representative air particulate samples are shown in Figures. 2(a) and 2(b). The homologous series of *n*-alkanes and the unresolved complex envelope are clearly observable in the chromatograms. These patterns indicate the anthropogenic origin of the hydrocarbons.

Results of the analyses by GC and GC/MS have indicated the presence of several PAHs in the samples. However, their concentrations in the extracts were too low for reliable quantitative measurements. A reconstructed ion chromatogram obtained for the aromatic fraction of a particulate extract is shown in Figure 3.

The low concentration levels of PAHs may be attributed to the decomposition

**Table 2** Recovery (%) obtained for the analysis of air filters spiked with polynuclear aromatic hydrocarbons at an average concentration of 24.4 μg/g each

| *Compound* | *Mean* (*n* = 5) | *S.D.*[a] |
|---|---|---|
| Acenaphthalene | 4.8 | 1.1 |
| Acenaphthene | 17.6 | 2.0 |
| Fluorene | 67.6 | 2.2 |
| Phenanthrene | 74.0 | 4.3 |
| Anthracene | 82.8 | 4.9 |
| Fluoranthene | 80.0 | 6.2 |
| Pyrene | 82.4 | 5.6 |
| Benzanthracene | 91.8 | 7.9 |
| Chrysene | 92.2 | 8.4 |
| Benzo(a)fluoranthene | 108.4 | 15.0 |
| Benzo(k)fluoranthene | 98.4 | 17.0 |
| Benzo(a)pyrene | 90.6 | 11.6 |
| Indeno pyrene | 103.2 | 14.7 |
| Dibenzanthyracene | 87.6 | 22.7 |
| Benzoperylene | 85.2 | 14.2 |

[a] *n* = number of replicates; S.D. = standard deviation

of these compounds on the sampling filters used, and to the loss of these compounds during the sampling process. Recently, several investigators have shown that significant losses of PAHs may occur during sampling using high volume samplers.[4,5] These losses were attributed to the chemical reactions of the PAHs while they were adsorbed on the sampling filters or to direct volatilization under the high-volume sampling conditions.

Information concerning sampling location, number of samples collected, mean and median *n*-alkane concentrations, as well as their standard deviation are depicted in Table 3.

A frequency histogram obtained for *n*-alkanes (Figure 4) indicates that the concentration levels of *n*-alkanes in most of the samples fall in the concentration range of 0.0 to 100 ng/m$^3$. These values compare favourably with those found in several parts of the world.[3,6]

It may be worth mentioning that the median value, rather than the mean, was used to compare the concentration levels of *n*-alkanes found in various locations. This is mainly because of the positive skewness of the frequency histogram as shown in Figure 4. The highest median value for *n*-alkane concentrations was found in Dammam city (Table 3). The high concentration levels found in this city may be attributed to the emission of oil hydrocarbons from heavy vehicular traffic in the city center and from the nearby industrial area, which comprises about one hundred factories.

The second highest value was measured in Dhahran at the rooftop of the Research Institute of the King Fahd University of Petroleum and Minerals (Dhahran, KFUPMRI) and at another station in the university campus about

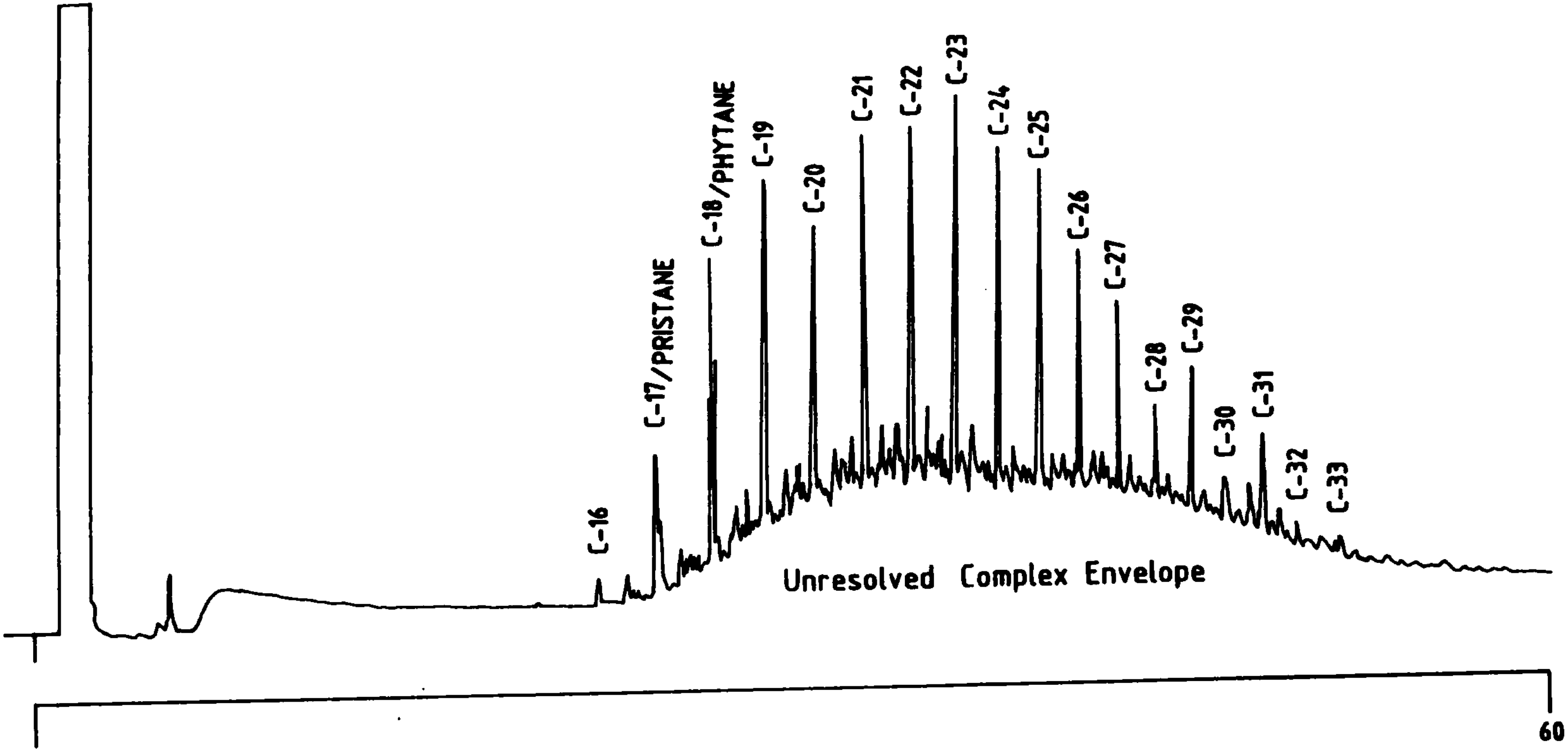

**Figure 2** (a) Gas chromatogram obtained for *n*-alkanes found in suspended particulates collected from Khobar station.

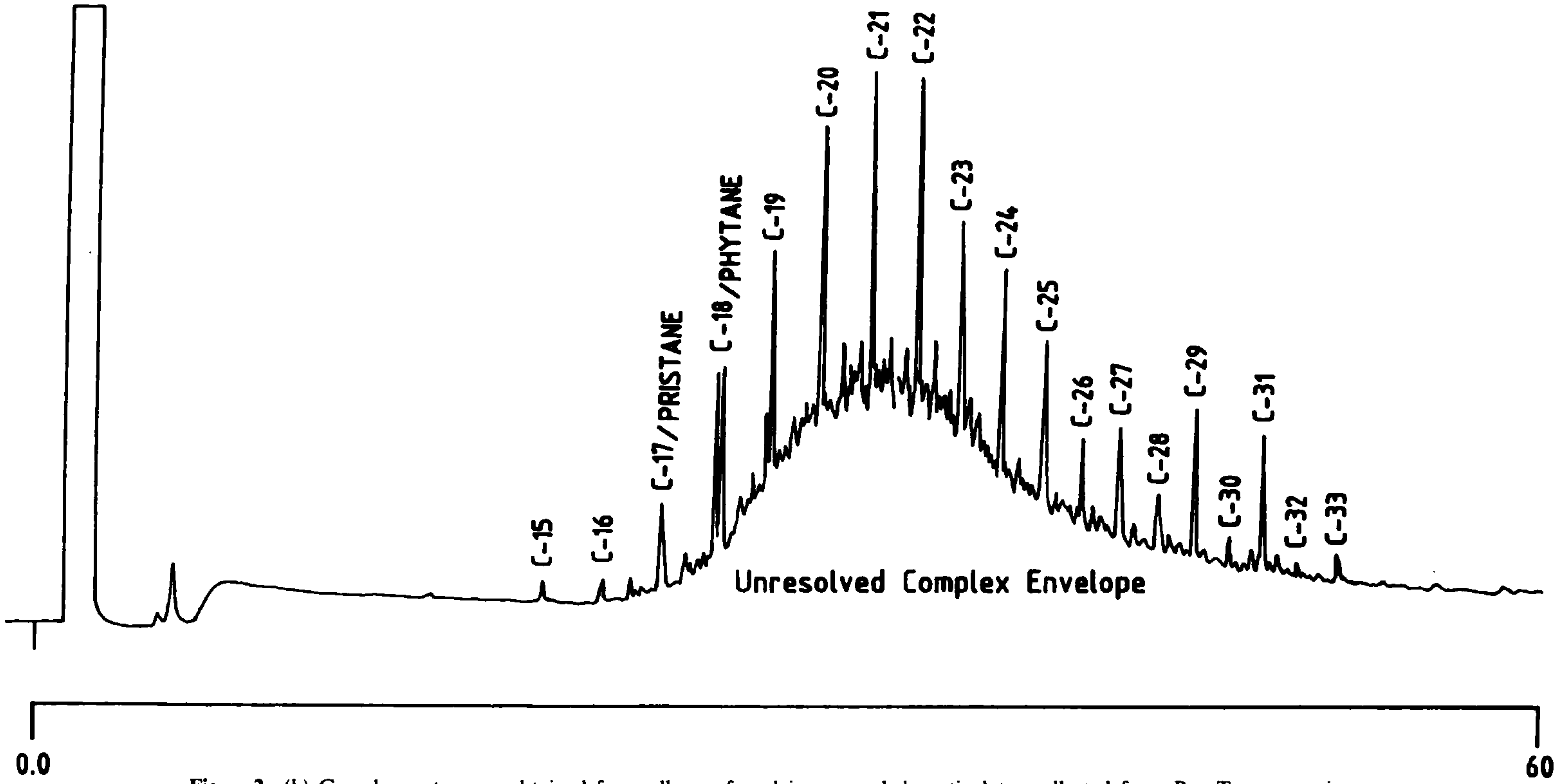

**Figure 2** (b) Gas chromatogram obtained for *n*-alkanes found in suspended particulates collected from Ras Tanura station.

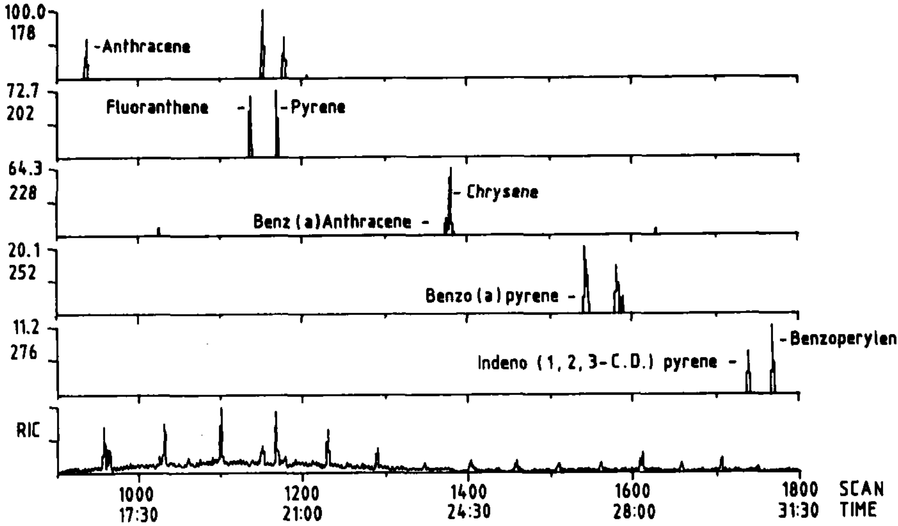

**Figure 3** Reconstructed ion chromatogram and selected ions for aromatic hydrocarbons found in air particulates collected from Dhahran.

**Table 3** Summary of results obtained for *n*-alkane concentrations (ng/m$^3$) in various samples

| *Location* | *n*[a] | *Mean* | *Median* | *S.D.* | *Minimum* | *Maximum* | *R*[b] |
|---|---|---|---|---|---|---|---|
| Dammam | 10 | 143.8 | 121.8 | 65.9 | 67.3 | 266.2 | 0.83 |
| Dhahran(lab) | 19 | 75.9 | 75.2 | 48.4 | 18.0 | 198.2 | 0.85 |
| Dhahran(KFUPMRI) | 7 | 215.1 | 70.7 | 309.9 | 10.4 | 798.7 | 0.68 |
| Khobar | 10 | 65.0 | 61.1 | 39.0 | 19.7 | 129.1 | 0.68 |
| Rahimah | 8 | 54.0 | 42.9 | 41.7 | 33.1 | 156.4 | 0.84 |
| Ras Tanura | 22 | 30.8 | 22.7 | 27.3 | 3.1 | 115.6 | 0.96 |
| Abqaiq | 26 | 53.7 | 33.6 | 53.9 | 7.0 | 240.6 | 0.76 |

[a] *n* = number of samples collected from each location.

[b] *R* = Correlation coefficient between total suspended particulates and *n*-alkanes.

2 km to the north of the KFUPMRI station. These high values may be attributed to the presence of permanent sources for oil hydrocarbon emission in the area. These sources include an international airport, a university campus desalination plant and the Saudi Arabian American Oil Company (Saudi Aramco). It is interesting to note that on two occasions, *n*-alkane concentration levels of more than 400 ng/m$^3$ were measured at the Research Institute's rooftop station. Reasons for these high values are not yet known. However, the sampling dates when these values were reported coincide with the period of the year when the Shamal wind blows in the area. Also, the values for the total suspended particulates reported on these dates were the highest. The high concentration levels of *n*-alkanes found in these cities may not only represent local emissions, but also contributions from adjacent refineries and oil production centers.

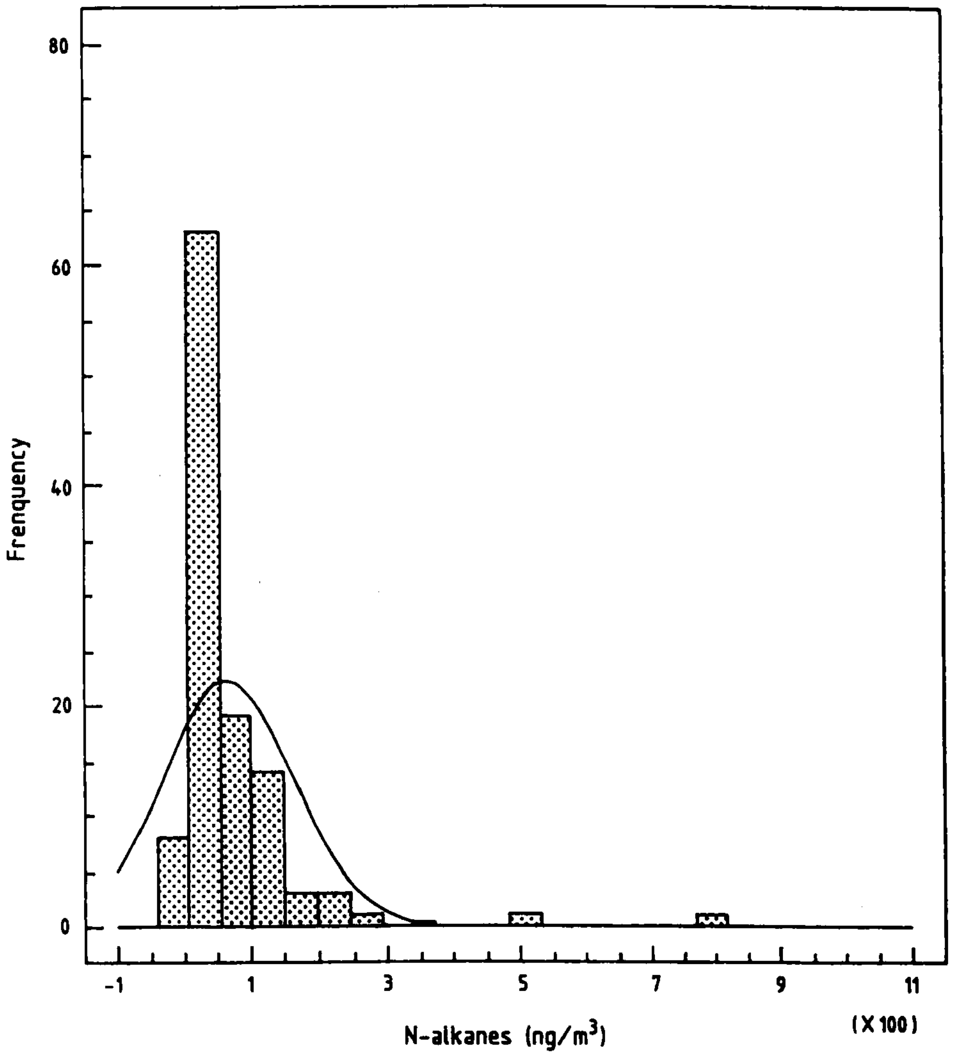

**Figure 4** Frequency histogram for *n*-alkanes found in suspended particulates at various sampling locations in the Eastern Province of Saudi Arabia.

The levels of *n*-alkanes near the oil production activity at Ras Tanura, Abqaiq and Rahimah were generally lower than those reported in the urban areas. This may be explained by the fact that the sampling stations in these areas were located away from the prevailing north to northwest wind directions. Hence, the contribution of these permanent oil emission sources to the total *n*-alkanes measured was negligible.

In order to obtain information on the relation of *n*-alkanes in the air particulates to total suspended particulates, a regression analysis was carried out between the total suspended particulates (TSP) and the concentrations of *n*-

alkanes for each station. The correlation coefficient, *R*, obtained for each station is included in Table 3. The high values of the correlation coefficients for most of the stations indicate that suspended particulates function as carriers of *n*-alkanes.

In an attempt to find out the origin of *n*-alkanes in aerosol samples, the carbon preference index or CPI (summation of odd carbon homologues over a range divided by the summation of the even carbon homologues over the same range) and the $C_{\max}$ (the carbon number maximum) for all the samples were determined. These two parameters can separately provide supportive evidences of the origin of the oil hydrocarbons present.[7] A CPI value of about 1 reflects the significant input of anthropogenic compounds, while a value of more than 3 indicates the incorporation of recent biological constituents.[6] Analytical results obtained have shown that CPI values for most of the air particulate samples are close to 1. Values for $C_{\max}$ range from *C*-21 to *C*-31. These maxima are not very conclusive for determining the origin of *n*-alkanes. Gas chromatograms of most samples have shown the presence of an unresolved complex envelope, which is normally found in gas chromatograms of petroleum. Moreover, in the absence of vegetation in the study area, hydrocarbons found in the samples are apparently of anthropogenic origin.

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