Atmospheric concentrations of saturated and aromatic hydrocarbons around a Greek oil refinery

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Abstract

Petroleum refineries are large industrial installations that are responsible for the emission of several pollutants into the atmosphere. Hydrocarbons are among the most important air pollutants that are emitted by petroleum refineries, since they are involved in almost every refinery process. The ambient air concentrations of many saturated and aromatic hydrocarbons were measured in several sites around an oil refinery, near the city of Corinth in Greece, during 1997. At the same time several meteorological parameters were also recorded. The seasonal, diurnal and spatial variations of the ambient air concentrations of these hydrocarbons were investigated and analyzed. An estimation of the contribution of the refinery to the measured atmospheric levels of hydrocarbons was also performed. The ambient air mixing ratios of the saturated and aromatic hydrocarbons in a large area outside the refinery were generally low, in ppbv range, much lower than the ambient air quality standards or the ambient air concentrations in the two largest urban centers in Greece, Athens and Thessaloniki. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Hydrocarbons, which are the main group of atmospheric volatile organic compounds, play an important role in the physicochemical processes of the troposphere (Finlayson-Pitts and Pitts, 1986; Warneck, 1988) as they largely contribute to the formation of ozone and other photochemical oxidants. Moreover, some hydrocarbons are highly toxic or carcinogenic, such as benzene, toluene and xylenes. Hydrocarbons are present in the urban and industrial atmosphere essentially as a result of human activities, arising mainly from motor vehicle exhausts and other combustion processes utilizing fossil fuels, petrol storage and distribution, solvent usage and other industrial processes. Emission from the vegetation is also an important source of some highly reactive hydrocarbon species (Finlayson-Pitts and Pitts, 1986; Warneck, 1988).

The operation of refineries, which are in general big industrial installations, is associated with the emission of various substances into the atmosphere, mainly originating from the production processes, the storage tanks, the transport pipelines and the waste area. Among the most important atmospheric pollutants, which are emitted by refinery plants are volatile organic compounds (mainly hydrocarbons), sulfur compounds, nitrogen oxides as well as particulate matter (Westaway and Brockis, 1978). These atmospheric pollutants once emitted into the atmosphere may cause a pollution problem on local scale, but are also involved in other phenomena of air pollution on regional scale, like acid rain or photochemical ozone production in the troposphere initiated by the reaction of hydrocarbons with OH radicals in the

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presence of nitrogen oxides and sunlight (Finlayson-Pitts and Pitts, 1986).

In order to control atmospheric pollution around a refinery the usual practice is to monitor the atmospheric concentrations of hydrocarbons, sulfur compounds (mainly hydrogen sulfide and mercaptans) and oxides of nitrogen. The aim of the present work is the determination of atmospheric pollution levels of two hydrocarbon families (saturated and aromatic) in the area surrounding an oil refinery in Ag. Theodori Corinthias, Greece, located about 60 km west of the city of Athens (Geographical coordinates: 37° 54′ 38″ N, 23° 05′ 00″ E). This refinery is one of the biggest refineries in Greece and produces a wide spectrum of petroleum derivatives like gasolines, LPG, jet fuels, gasoils, fuel oil, naphtha and asphalt. Its nominal capacity of crude oil processing is 4.75 million tons per year and the types of crude oil used are mainly Arabian light and Arabian medium. Due to the wide range of produced substances many process units are installed in the refinery like an atmospheric distillation unit, a thermal cracking unit, vacuum distillation units, a naphtha hydrodesulfurizer unit, a naphtha reformer unit and a catalytic cracking unit.

The existing hydrocarbon measurements in Greece, urban or industrial, usually performed by monitoring agencies, are mostly in the form of total non-methane hydrocarbons (NMHC) and only few measurements of speciated hydrocarbons in urban sites have been reported so far (Moschonas and Glavas, 1996; Hatzianestis et al., 1996; Rappenglueck et al., 1998; Vasilikiotis et al., 1998; Rappenglueck et al., 1999; Kourtidis et al., 2000). In this work speciated measurements of hydrocarbons (saturated and aromatics) around a Greek refinery are reported. The field measurements of atmospheric hydrocarbons were performed at several sites around the refinery in weekly campaigns at different seasons in 1997 (February, May, September and October). The ambient air concentrations of the following hydrocarbons were monitored: hexane, heptane, octane, benzene, toluene, ethyl-benzene, *m*-, *p*-, *o*-xylenes and 1,3,5, trimethyl-benzene. A total number of 130 hydrocarbon samples have been collected and analyzed.

2. Experimental

The hydrocarbon air samples were analyzed by passing them through special glass adsorption tubes (Chrompack) filled with Tenax-TA, where the volatile organic compounds were efficiently retained at flow rates of 100 ml min^{-1}. The sampling time was 20 min, so the total volume of air collected was 2 l. The tenax tubes after the sampling were closed with special cups to avoid contamination, transferred to the laboratory and analyzed there within three days. A filter to remove humidity was not used during the sampling as Tenax does not retain water and therefore there is no interference by humidity during the analysis. The adsorption traps were analyzed by placing them in a thermal desorption unit (Chrompack) that was adapted to a gas chromatograph (Hewlett-Packard 5890 series II) equipped with FID. The tubes were heated up to 240°C for 10 min and the desorbed compounds were transferred to a capillary cryogenic trap held at −100°C with liquid nitrogen. The cryogenic trap was consequently heated ballistically up to 200°C, and the compounds were injected to the analytical column. The analytical column was a 30 m × 0.33 mm (HP-5 column). The temperature was initially varied from 40 to 80°C at 10°C min^{-1}, then at 80°C was kept constant for 15 min, and finally was rised to 200°C at 15°C min^{-1} (Hatzianestis et al., 1996).

The calibration was performed by preparing standard solutions in methanol, containing all the measured substances in known concentrations (all the substances were provided from Supelco). One microlitre of this standard solution was injected in a clean tenax tube, the polar methanol was removed by flushing pure helium for 3 min with a rate 50 ml min^{-1} and then the tube was normally analyzed in the thermal desorption-gas chromatograph unit. In this way a four-point calibration curve was obtained. The injected amounts for each substance ranged between 5 and 40 ng. This calibration curve was confirmed daily by analyzing a standard solution. The accuracy was always below 10%, and the relative standard deviation of repeated standard injections was in all cases below 7%. The detection limit of the analytical method is 0.01 ppbv.

The meteorological measurements were performed by the means of a sonic anemometer, which was recording continuously wind direction, wind speed and air temperature. Sonic anemometer has significantly higher performances than conventional instruments. The measurement threshold for wind direction is 0.4° and for wind speed 0.05 m s^{-1}, while the measurement frequency may vary from 1/300 to 15 Hz. The meteorological measurements were recorded in the form of 10 min averages.

The air samplings have been carried out in six preselected sites around the refinery. Five of the sampling sites were at a distance of 3 km from the center of the refinery to the following directions: E, NE, N, NW and W (Fig. 1). The refinery covers an area of 2 km in radius. The sixth site was placed on the opposite coast at about 8 km to the SW direction. Samplings were performed every six hours (at 0:00, 6:00, 12:00 and 18:00 Local Time) at two neighboring sites from the above sampling sites, selected each time downwind of the refinery, and expected to be the most influenced by the refinery's plume. The continuous meteorological measurements were collected at a fixed site located at a distance of about 1 km west of the refinery.
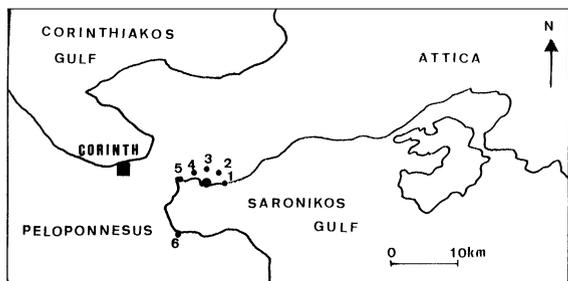
Fig. 1. Map of the refinery area. The refinery is marked with a black cycle and the numbers show the sampling sites around it.

3. Results and discussion

The saturated and aromatic hydrocarbons measurements together with the meteorological measurements for the four measuring periods in 1997 (22 February–2 March, 4–12 May, 14–21 September, 25 October–2 November) are presented in Figs. 2–5, respectively.

3.1. Meteorological conditions

Meteorological measurements were performed during three of the four measuring periods (in the May period the sonic anemometer presented technical problems right after the campaign start). A brief description of the main meteorological parameters (wind and temperature) during the weekly campaigns are as follows:

(I) 22 February–2 March, 1997: The prevailing wind direction was north-west, while during the first three days winds from the south-eastern sector were also present. The wind speed was moderate during the first 5 days of the campaign with a 4–5 m s^{-1} noon maximum. There was a sharp change in the afternoon hours of 28 February, where an important increase in the wind speed was recorded up to 13 m s^{-1}, remaining high until the end of the period. The temperature in the first five days ranged
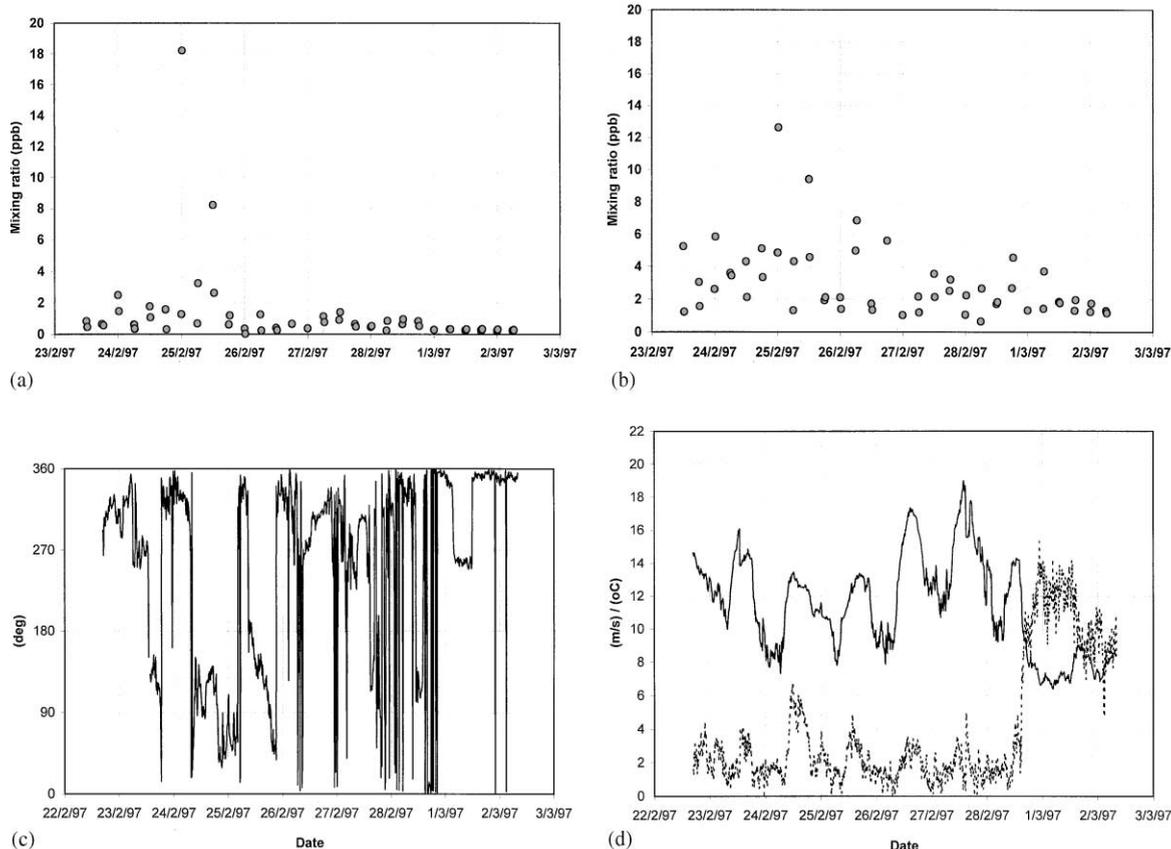

Fig. 2. (a) Atmospheric concentrations of saturated hydrocarbons in February. (b) Atmospheric concentrations of aromatic hydrocarbons in February. (c) Variation of wind direction in February. (d) Variation of wind speed (dashed line) and temperature (solid line) in February.
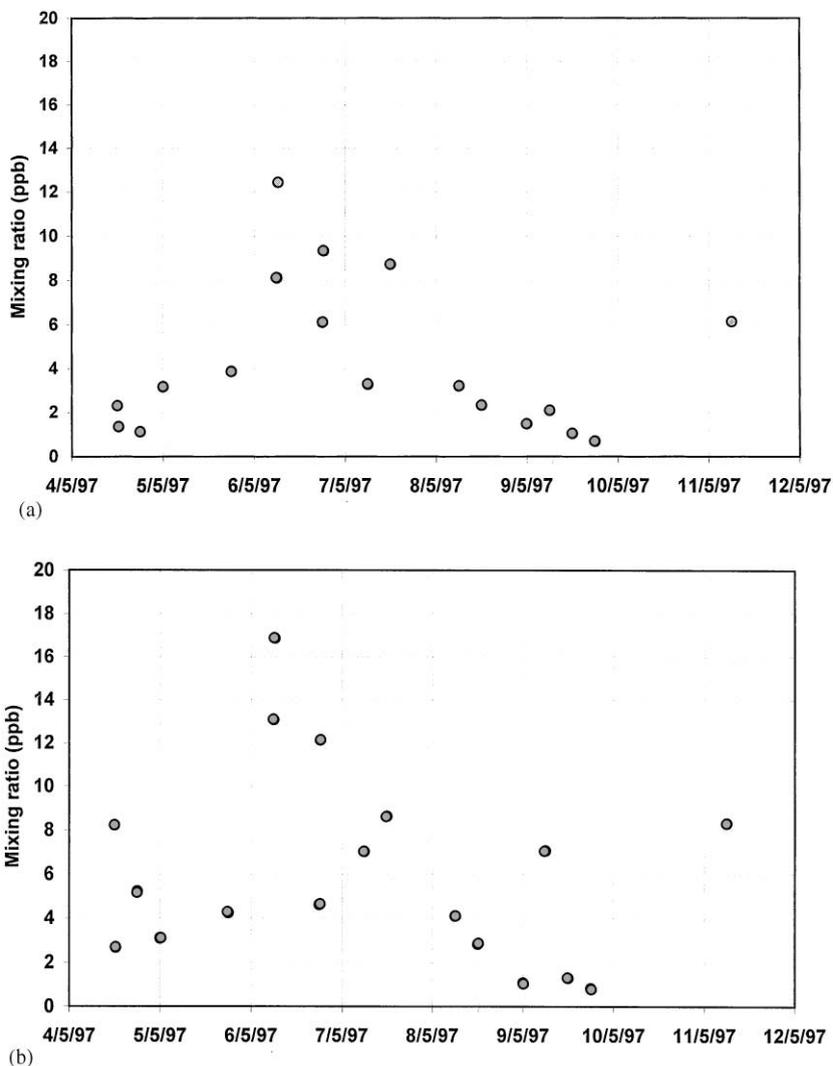
Fig. 3. (a) Atmospheric concentrations of saturated hydrocarbons in May. (b) Atmospheric concentrations of aromatic hydrocarbons in May.

from 8 to 18°C (nocturnal minimum and diurnal maximum, respectively) while an important drop occurred during the last days (7–9°C) indicating a cold front passage (Figs. 2c and d).

(II) 14–21 September, 1997: The winds were blowing mainly from the north-eastern sector, although for the half period these winds were turned to south–east during daytime, which is indicative of sea-breeze circulation (16–18 September). The intensity of the prevailing winds was moderate ranging from 4 to 7 m s^{-1} during continuous north-eastern flow and from 2 to 5 m s^{-1} during days when the south-eastern winds were also present. The recorded temperatures ranged from 11 to 22°C. From the beginning to the middle of the week, the minimum night temperatures showed a smooth decrease from 15 to 10°C, while the maximum daily temperatures showed a sharp decrease from 22 to 15°C (Figs. 4c and d).

(III) 25 October–2 November, 1997: During this measuring period the same type of anemological behavior with the September period was observed. The main wind direction was NE with changes to SE during the first half of the period. For these days the winds were varying between 2 and 5 m s^{-1}, while for the rest from 5 to 7 m s^{-1}. Temperatures were generally low for this period of the year, ranging between 4 and 9°C (Figs. 5c and d).

The rose diagrams of wind direction and wind speed recorded in our campaigns are presented in Figs. 6 and 7.
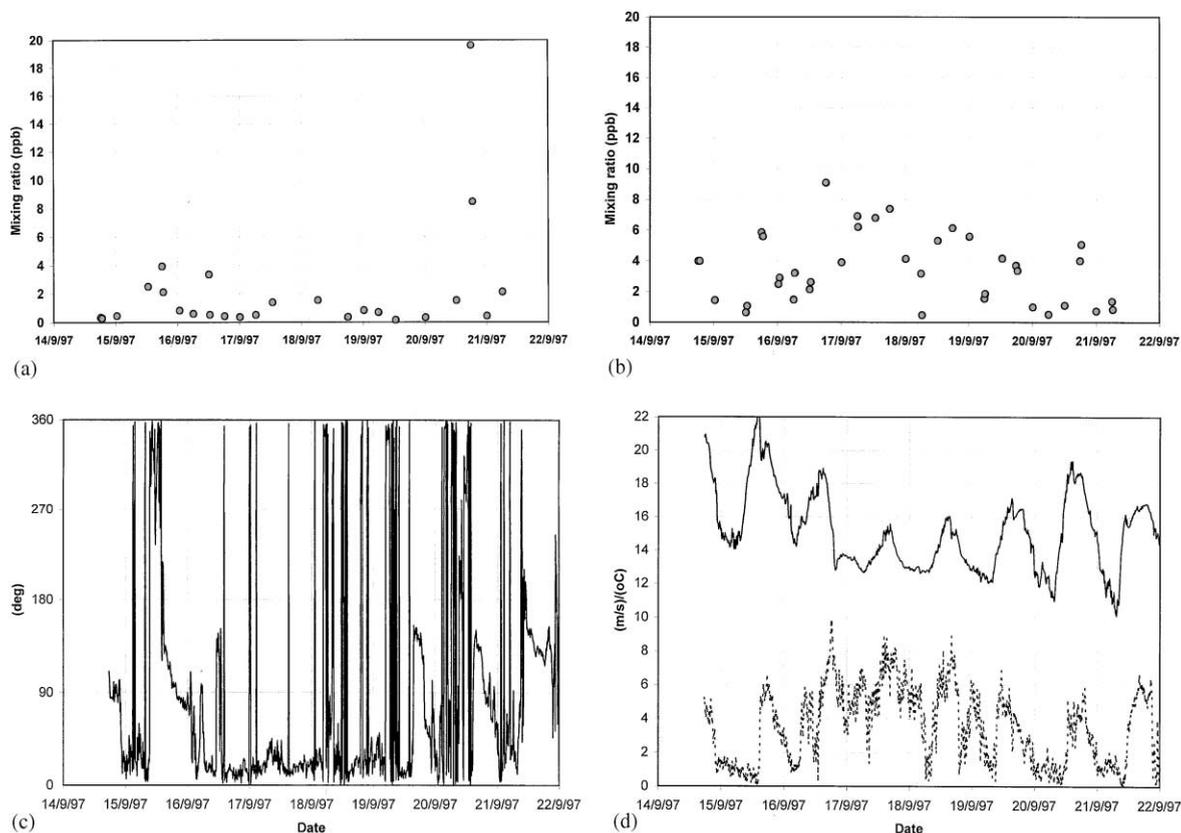
Fig. 4. (a) Atmospheric concentrations of saturated hydrocarbons in September (the extreme value of 60.8 ppb was not plotted). (b) Atmospheric concentrations of aromatic hydrocarbons in September. (c) Variation of wind direction in September. (d) Variation of wind speed (dashed line) and temperature (solid line) in September.

Fig. 6 shows that the N–NE winds prevail almost exclusively, while Fig. 7 shows that the average wind speed for the prevailing directions is relatively strong (exceeding 4 m s^{-1}).

3.2. Hydrocarbon measurements

In general, the atmospheric mixing ratios of both hydrocarbon groups are relatively low, in comparison to the concentrations monitored in polluted urban areas (Sexton and Westberg, 1984; Singh and Zimmerman, 1992; Blake et al., 1993; Moschonas and Glavas, 1996; Brocco et al., 1997; Rappenglueck et al., 1998). Hexane is the most abundant saturated hydrocarbon followed by heptane, while toluene is the most abundant aromatic (followed by benzene) but also recorded the highest values among the measured hydrocarbons as its levels are by 15% higher than hexane. The average ratio toluene/benzene is close to 2 : 1 (Table 1).

For a more comprehensive presentation, the hydrocarbons are separated into their respective families and examined as saturated hydrocarbons (hexane, heptane, octane) and aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylenes and trimethyl benzene). This can be justified by their common physico-chemical properties as well as to their different origin in the atmosphere. The aromatic hydrocarbons (BTX) are common combustion roducts of petroleum derivatives, while the saturated hydrocarbons (PAR) originate to a great extent from evaporation of oil products and organic solvents (Colbeck and Mackenzie, 1994). The aromatic hydrocarbons showed the highest values in the range 0–17 ppb, with a mean value of 3.89 ppb, while the saturated hydrocarbon values were in the range 0–61 ppb and with a mean value of 2.36 ppb (the ppb units are ppbv).

Both hydrocarbon groups showed seasonal variation of different pattern (Table 2). For saturated hydrocarbons, the average values of May and September were similar at the 4.5 ppb level, which is three times higher than the corresponding levels of February and October at about 1.5 ppb. For aromatic hydrocarbons, the average values of February, September and October were the

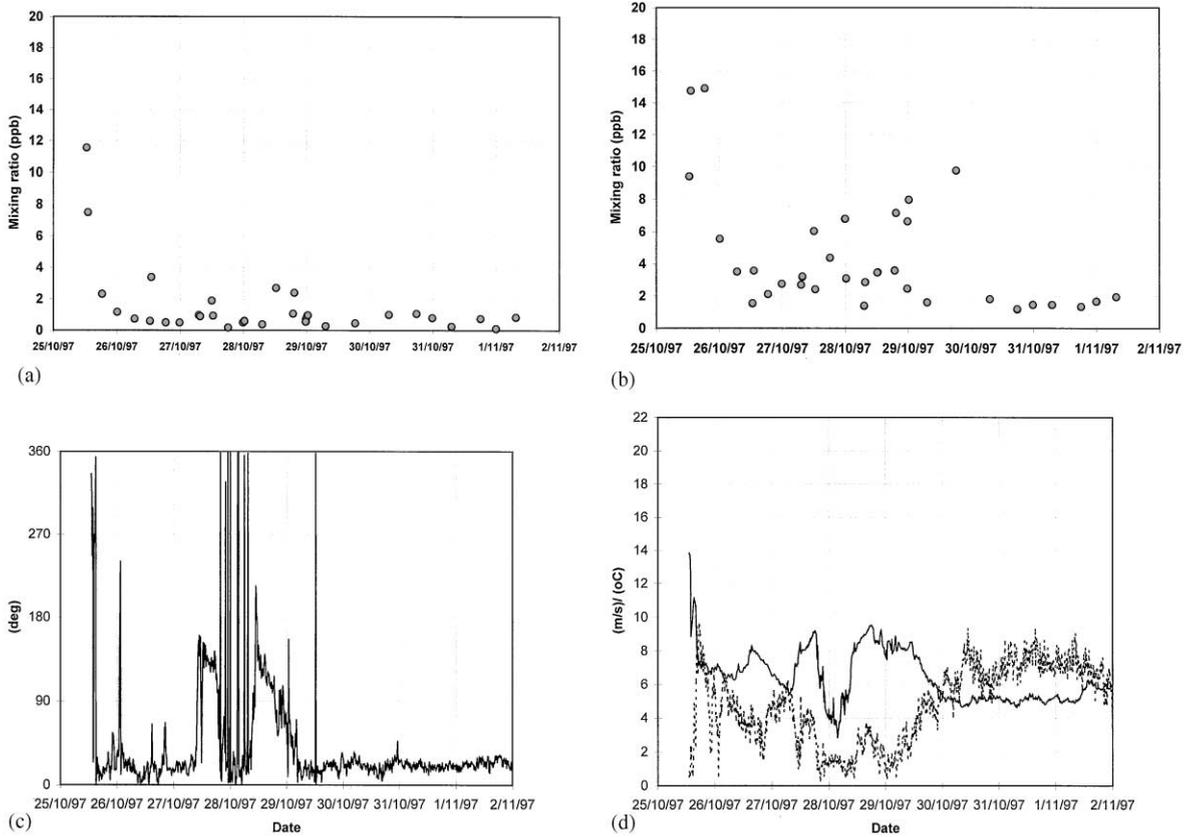Fig. 5. (a) Atmospheric concentrations of saturated hydrocarbons in October. (b) Atmospheric concentrations of aromatic hydrocarbons in October. (c) Variation of wind direction in October. (d) Variation of wind speed (dashed line) and temperature (solid line) in October.
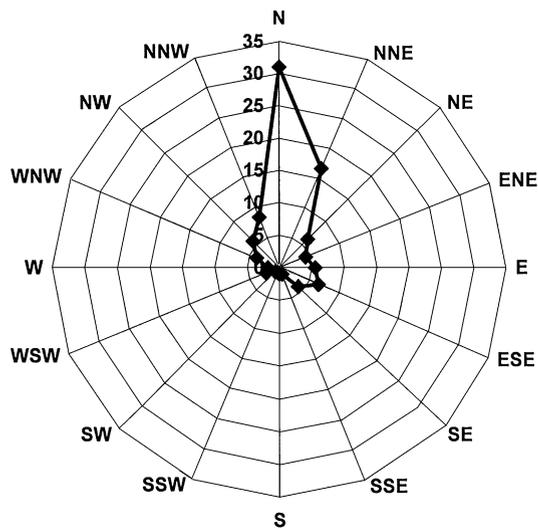

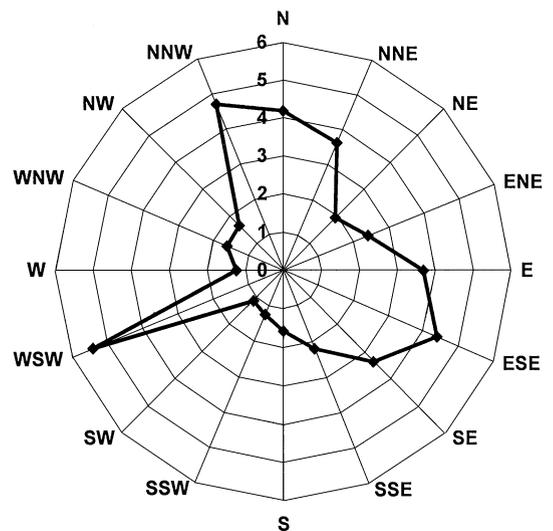Fig. 6. Rose diagram of wind direction (%) for all campaign days.

Fig. 7. Rose diagram of wind speed (m s^{-1}) for all campaign days.

Table 1
Statistics of all atmospheric measurements of saturated (PAR) and aromatic (BTX) hydrocarbons in the refinery area (in ppbv)

	Hexane	Heptane	Octane	Benzene	Toluene	Ethyl benzene	m,p-Xylenes	o-Xylene	1,3,5-Trimethylbenzene	PAR	BTX
Mean value	1.46	0.50	0.29	0.81	1.67	0.31	0.72	0.63	0.14	2.36	3.89
Median value	0.42	0.23	0.11	0.58	1.24	0.21	0.46	0.40	0.07	0.82	2.85
S. D.	4.43	1.13	0.52	0.70	1.43	0.34	0.71	0.68	0.22	6.06	3.18
Max. value	44.53	12.09	4.19	4.14	7.72	2.03	3.96	3.65	0.95	60.82	16.85
Min. value	N.D.[a]	N.D.[a]	N.D.[a]	0.02	0.21	N.D.[a]	N.D.[a]	0.05	N.D.[a]	N.D.[a]	0.49
Sample No.	129	129	111	130	130	130	128	59	18	129	130
98 percentile	9.24	2.40	1.76	3.43	6.52	1.48	3.02	2.72	0.72	14.99	13.78

[a]N.D. = not detectable.

same at 3.5 ppb, while the average value in May was higher at 6.2 ppb. Since the maximum values for all four months did not differ significantly from each other, the average value of May reflects a general increase of the values. Moreover, the median values of May for both hydrocarbon groups were significantly different from the rest of the seasons. Four times as high for PAR (3.2 ppb) and about twice as high for BTX (4.9 ppb). The maximum value for BTX was recorded in May while the corresponding value for PAR was recorded in September.

There are only slight variations in the average values of the different sites (Table 3). The highest median values were observed at sites 3 and 4 (1.5–1.8 ppb PAR, 3.5 ppb BTX). The maximum values were observed at site 1 (60.8 and 16.8 ppb for PAR and BTX, respectively).

The diurnal variation of hydrocarbons is more pronounced for the PARs, with a minimum value at midnight (1.3 ppb mean value) and a maximum value at noon (3.7 ppb mean value) as presented in Table 4. The BTX mixing ratios were about 4 ppb at all times. The maximum values of saturated hydrocarbons were recorded at noontime. Since the characteristic seasonal and diurnal variation in the concentration of saturated hydrocarbons show a good correlation with the temperature variation, it is suggested that evaporation is the main emission source of saturated hydrocarbons in the atmosphere of oil refinery plants. This argument is enhanced by the fact that if saturated hydrocarbons are examined separately, the diurnal and seasonal cycle of hexane is more important than the rest of the compounds especially for the heavier BTX, which is in agreement with the differences in their boiling point.

3.3. Estimation of the atmospheric hydrocarbon pollution due to the oil refinery

The atmospheric mixing ratios of both hydrocarbon groups were sorted according to two important dispersion parameters: (a) the wind speed and (b) the angle formed between the sampling site, the refinery and the prevailing wind direction, which is considered to be parallel with the direction of the refinery's plume during each sampling. In fact, a decrease of hydrocarbon levels is observed, in general, when each one of both parameters increases (wind speed or deviation angle).

A more quantitative analysis of the data was performed by separating the measurements on the basis of strong–weak winds and large-small deviation angles. Wind velocities higher than 6 m s^{-1} were characterized as strong, while deviation angles between the sampling site and the refinery's plume higher than 90 deg were considered as large. Therefore, the average values were calculated according to the above separation. The

Table 2
Statistics of atmospheric measurements of saturated (PAR) and aromatic (BTX) hydrocarbons in the refinery area for every measuring period (in ppbv)

	February		May		September		October	
	PAR	BTX	PAR	BTX	PAR	BTX	PAR	BTX
Average	1.23	3.00	4.27	6.18	4.41	3.52	1.51	4.38
Median	0.62	2.14	3.19	4.91	0.76	2.93	0.81	3.08
S. D.	2.67	2.21	3.43	4.44	12.17	2.44	2.30	3.61
Max	18.22	12.61	12.44	16.85	60.82	10.69	11.56	14.90
Min	0.03	0.64	0.69	0.83	0.15	0.49	0.10	1.17
No.	53	53	18	18	26	26	32	33

Table 3
Statistics of atmospheric measurements of saturated (PAR) and aromatic (BTX) hydrocarbons in the refinery area for every sampling site (in ppbv)

	Site 1		Site 2		Site 3		Site 4		Site 5		Site 6	
	PAR	BTX	PAR	BTX	PAR	BTX	PAR	BTX	PAR	BTX	PAR	BTX
Average	3.37	4.10	1.69	3.35	2.52	4.84	4.16	4.55	1.60	3.38	0.68	3.05
Median	0.69	3.16	1.14	2.24	1.89	3.48	1.52	3.48	1.01	3.06	0.47	2.04
S. D.	10.15	3.60	2.08	3.86	2.79	3.16	5.67	3.54	1.87	1.62	0.69	2.97
Max	60.82	16.85	7.50	14.77	9.34	12.13	19.63	12.61	8.48	7.97	3.39	14.90
Min	0.03	1.05	0.24	0.64	0.31	1.38	0.34	0.83	0.17	0.83	0.10	0.49
No.	37	37	11	11	9	9	20	20	18	18	40	40

Table 4
Statistics of atmospheric measurements of saturated (PAR) and aromatic (BTX) hydrocarbons in the refinery area for every hour of measurement in a day (in ppbv)

	0:00 LT		06:00 LT		12:00 LT		18:00 LT	
	PAR	BTX	PAR	BTX	PAR	BTX	PAR	BTX
Average	1.37	3.47	1.61	3.91	3.74	3.62	2.12	3.95
Median	0.51	2.61	0.72	2.89	1.22	2.53	0.65	3.05
S.D.	3.31	2.62	2.55	3.51	10.15	3.20	3.77	3.44
Max	18.22	12.61	12.44	16.85	60.82	14.77	19.63	14.90
Min	0.03	1.03	0.20	0.64	0.15	1.23	0.17	0.49
No.	29	29	35	35	36	36	35	35

separation relative to the wind speed gave the following results:

	PAR	BTX	Sample number
WS $< 6\,\mathrm{m\,s^{-1}}$	2.5 ± 7.5	3.9 ± 2.7	87
WS $> 6\,\mathrm{m\,s^{-1}}$	0.6 ± 0.5	2.4 ± 2.8	25

If the corresponding separation of hydrocarbon measurements against the deviation angle (DA) to

the plume is made, then the results are presented as follows:

	PAR	BTX	Sample number
DA $< 90°$	2.3 ± 7.1	3.7 ± 2.7	89
DA $> 90°$	1.0 ± 0.8	2.9 ± 1.7	23

For both separations about 80% of the values follow the first category of low dispersion conditions (weak winds or small deviation angles), which is expected due to

the way the campaign was performed. The values of the first category are clearly higher in both cases but also in the high-dispersion category the values are non-negligible (especially for BTX), which indicates the existence of other sources of hydrocarbons in the area.

A better estimation of the impact of the oil refinery operation to the air quality of the surrounding area may be obtained by taking into account both dispersion parameters. Therefore, the product of the wind speed and the deviation angle from the plume was calculated for every angle. The scattered plot of this parameter versus the atmospheric concentration indicates that the most appropriate separation limit is $270 \, (\mathrm{m \, s^{-1}}) \times \mathrm{deg}$, which is actually half the value of the product of the two previous separation limits ($6 \, \mathrm{m \, s^{-1}}$ and $90°$). The results of this procedure are presented below:

	PAR	BTX	Sample number
WS × DA < 270	2.4 ± 6.9	3.8 ± 2.9	94
WS × DA > 270	0.4 ± 0.2	1.9 ± 0.9	18

In this measurement sorting, the lowest values were obtained for the second category of measurements, which are not considered to be under the direct influence of the oil refinery and could be regarded as the best approach of the background levels of the area surrounding the refinery. The term "background pollution levels" denotes the pollution levels in the area caused by other sources than the refinery. This is better shown by plotting the concentration versus all three parameters separately. It is obvious from the above that the refinery is a clear hydrocarbon source, showing values at a distance of a few kilometers downwind six times higher than the estimated background levels for the saturated hydrocarbons and two times higher for the aromatics. The relatively high background value for the aromatic hydrocarbons could be attributed to the car traffic emissions from the nearby National road, linking Athens with Corinth and Patras, since BTX are regularly found in the car exhausts (Colbeck and Mackenzie, 1994; Kourtidis et al., 1999).

Therefore, the average net contribution of the refinery to the atmospheric concentrations of hydrocarbons is the difference between the two groups, which is presented below together with the relative contribution of the refinery to ambient hydrocarbon levels (average net contribution × 100/background value).

	PAR	BTX
Net contribution (ppb)	2.0	1.9
Relative contribution (%)	83	50

The above values could be considered as an upper limit of the pollution burden due to the oil refinery, since the average pollution levels from other sources were minimized as they were calculated mainly under high dispersion conditions (wind speeds higher than $6 \, \mathrm{m \, s^{-1}}$)

in contrast to the pollution of the refinery, which is related with low dispersion conditions. Therefore, it is concluded that the average hydrocarbon pollution produced by the title refinery is low of the order of 2 ppb for both examined hydrocarbon categories and is clearly below the proposed air quality standard concerning benzene (HMSO Report, 1994). However, the presence in the atmosphere of other hydrocarbon species cannot be excluded, which were not measured by our analytical system, especially the light ones, in higher values. Nevertheless, it is important to note that BTX on local scale are relatively low to the standards already proposed. In the U K the recommended air quality standard for benzene is 5 ppb as running annual average (HMSO Report, 1994). The application of the same standard in the EU is currently under discussion. The benzene share in the BTX levels around the refinery was always less than the one third.

3.4. Comparison of the oil refinery hydrocarbon levels with urban and suburban measurements in Greece

For a better assessment of hydrocarbon levels around a refinery it would be interesting to perform a comparison of the refinery measurements with similar ones obtained during recent years in the two largest urban areas in Greece, Athens and Thessaloniki. Therefore, the measurements of two campaigns (a) at two sampling sites in Athens during August and September of 1994 (MEDCAPHOT-TRACE campaign, Rappenglueck et al., 1998) and (b) at NCSR-Demokritos (10 km NE from the center of Athens) during November 1995–February 1996 (Hatzianestis et al., 1996) were examined at first. In the MEDCAPHOT-TRACE campaign one sampling site was at the suburban site of NCSR-Demokritos, at the north-eastern edge of the urban basin, while the second site was at Patission street at the permanent air pollution monitoring site in central Athens. Additionally, measurements performed at a central urban site in Thessaloniki in September 1995 will be also considered (Vasilikiotis et al., 1998). The mean values of the urban, suburban and oil refinery measurements are presented in Table 5. A comparison of these values clearly indicates that the hydrocarbon levels in the surrounding area of the title oil refinery were rather low, and especially the aromatic hydrocarbons that are of particular importance to the public health. It must be noticed that for the hydrocarbon measurements at the refinery, in the central site of Thessaloniki and the suburban site of Athens in winter the same analytical methodology and equipment has been used. It must be underlined also that the presented measurements in central Athens and Thessaloniki are taken on the side of heavy traffic roads (at 12 and 4 m high from the ground, respectively). In contrast, a measurement series performed at central Athens and at 300 m away from a major traffic street in early summer

Table 5
Comparison of mean values of saturated (PAR) and aromatic (BTX) hydrocarbons around the refinery, in the center of Athens and Thessaloniki and at an Athens suburban site (in ppbv)

	Refinery	Athens-center	Thessaloniki-center	Athens-suburban (summer)	Athens-suburban (winter)
No. of samples	129	921	44	1059	95
PAR	2.4	7.4	8.2	1.0	1.8
BTX	3.9	53.7	55.8	15.2	4.6

gives average values of saturated and aromatic hydrocarbons by 25–30% less than the street-canyon measurements (Moschonas and Glavas, 1996). Therefore, the levels of aromatic hydrocarbons in the vicinity of the examined refinery were at least an order of magnitude less than those in the center of Athens and Thessaloniki and by a factor of two lower than in the Athens suburban site of NCSR-Demokritos. It must be mentioned here that the summer measurements at NCSR-Demokritos were carried out at a site closer to a traffic road (by 200 m) than the winter ones and that also they were more influenced by the internal circulation and parking activities of the research center. However, the refinery is responsible for almost half of the measured BTX in the surrounding area, which suggests that regarding air quality there is no problem arising from the presence of hydrocarbons around this particular refinery. The saturated hydrocarbons measured close to the refinery are 2 to 3 times less than in the center of Athens and Thessaloniki and slightly higher than in NCSR-Demokritos but in general the average values remain at low levels (1 to 2 ppb). Although saturated hydrocarbons are not toxic and do not cause pollution problems on local scale, they are responsible for the production of tropospheric ozone on regional scale, which depends on hydrocarbon emissions from a wide spectrum of industrial processes as well as from automobile traffic (Finlayson-Pitts and Pitts, 1986; Colbeck and Mackenzie, 1994).

4. Conclusion

In general, the average ambient air concentrations of saturated and aromatic hydrocarbons around the refinery were relatively low, in the order of few ppb. The total aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylenes and trimethyl-benzene) were higher than the total saturated hydrocarbons (hexane, heptane, octane). The most abundant aromatic and saturated hydrocarbons were hexane and toluene, respectively.

The average values of saturated hydrocarbons for the May and September periods were three times higher than the corresponding values for the February and October periods. The average values of aromatic hydrocarbons for the February, September and October periods were almost equal, while the average value for the May period was two times higher.

The saturated hydrocarbons showed a diurnal variation with minimum at midnight and maximum at noon, but the aromatic hydrocarbons did not show any diurnal variation. It appears that evaporation is the primary emission process of saturated hydrocarbons in the atmosphere from oil refineries.

The refinery is a source of hydrocarbons in the atmosphere and is responsible for hydrocarbon concentrations at several kilometers downwind, which are six times higher than the estimated background levels for the saturated hydrocarbons and two times higher for the aromatics. The relatively high background value for the aromatic hydrocarbons could be mainly attributed to the car traffic emissions from the nearby National road since BTX retain an important share in car exhausts.

In conclusion, the levels of hydrocarbon air pollution around the title oil refinery were low for both hydrocarbon groups. This is particularly important for aromatic hydrocarbons, which are among the hazardous air pollutants (mainly benzene) and air quality standards are set for them. The average levels of benzene (less than the 1/3 of BTX) were as yearly average less than the 5 ppb air quality standard. Finally, the ambient air concentrations of BTX in the area around the title refinery were at least an order of magnitude less than in the center of Athens and Thessaloniki, and by a factor of two lower than in an Athens suburban site.

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