MONITORING AND ANALYSIS OF VOLATILE ORGANIC COMPOUNDS AROUND AN OIL REFINERY

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Abstract. Valle Galeria, a location in the outskirts of Rome, was selected as a case study to assess the pollution release from the industrial facilities operating in this area. For this purpose, an intensive field campaign was conducted during summer, where volatile organic compounds VOC (including benzene, toluene and xylenes) were sampled and analyzed at two different sites. A strong modulation of VOC concentrations was observed between daytime and nighttime, and alkane fraction was found to be the most abundant group, indicating the oil refinery as the major source of atmospheric hydrocarbons. Surface turbulence and upper air SODAR data were processed to investigate the relationships between meteorology and VOC levels and patterns. Atmospheric turbulence was found to be responsible for the daily modulation of VOC. In particular, the highest BTX pollution episode observed during nighttime was found to be correlated with a very strong atmospheric stability and a surface based inversion layer. The analysis of BTX ratios resulted effective in recognizing the relationship between the pollutants and their co-variance, as well as the dispersion and reaction patterns occurring during the transport across the two sites.

Keywords: atmospheric turbulence, BTX, petroleum refinery, SODAR, volatile organic compounds

1. Introduction

Since the knowledge of harmful effects of byproducts and exhausts dispersed into the environment by human activities was consolidated, both the scientific community and Public Health Authorities have been involved in controlling the environmental quality of industrial areas. Polluted air coming from both industrial and traffic emissions are responsible for episodes of acute irritation symptoms, respiratory diseases and cancer (Yang *et al.*, 1997). Industrialized areas set up very adverse conditions to population living on the outskirts, and especially children and any "weak portion" of population suffer direct and indirect health effects. Studies on long-term monitoring of toxic exhausts from industrial facilities confirm a significant exposure for inhabitants of these areas (Suleimanov, 1997).

Among atmospheric pollutants emitted by industry, volatile organic compounds (VOC) may achieve particular relevance for specific sources, such as petroleum

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refineries and petrochemical plants. In particular, benzene is one of the most toxic pollutants with a proven carcinogenic effect associated with the inhalation of benzene-contaminated air (Ott *et al.*, 1978). An attempt to evaluate the exposure to VOC compounds from an industrial complex was reported by Park *et al.* (2004). They monitored higher toluene, $m + p$-xylene and o-xylene "personal air" concentrations for children attending a school very close to the industrial complex, with respect to another group living far away. In general, a main problem in linking the environmental pollution to health effects is the current lack of data about the actual exposure to hazardous pollutants. In many cases the available VOC measurements are given as total non-methane hydrocarbons (NMHC), whilst lesser concern is given to their speciation. By contrast, it is necessary to draw attention on the relative importance of individual VOC, to detect compounds acting as tracers for specific industrial processes, and finally to assess the relative contributions of emission sources to pollution by means of source apportionment techniques (Watson *et al.*, 2001).

The application of remote sensing techniques, such as SODAR, to investigate the state of the Planetary Boundary Layer (PBL), was demonstrated as a suitable approach to improve the investigations concerning the effects induced by meteorology onto air pollutant concentrations and behaviour (Reitebuch *et al.*, 2000). Therefore, measurements of the standard meteorological parameters (including wind velocity and direction, ambient temperature, relative humidity and pressure) become more and more frequently integrated with data provided by these new techniques.

The aim of the present work was the determination of exposure levels of volatile organic compounds in an industrialized area (Valle Galeria) located in central Italy, approximately 30 km far from Rome centre and 15 km inland from the coast of the Mediterranean sea. In order to discriminate the effects on VOC concentrations induced by both industrial emissions and local meteorology, the data collected were critically evaluated and analyzed.

2. Materials and Methods

2.1. SITE DESCRIPTION

The Valle Galeria area is characterized by both extensive agricultural activities and some industrial plants. In particular, a petroleum refinery, a municipal landfill, a municipal incinerator and quarries facilities are installed and running in a close range each other. A sketch of Valle Galeria area and its geographical location is shown in Figure 1.

The petroleum refinery has 4 Mtons/y of production capacity and extends for 97 hectares. Production units, storage tanks, transport pipelines and a waste area were identified as its main emission sources, releasing mostly volatile organic compounds, sulphur compounds, nitrogen oxides and particulate matter.

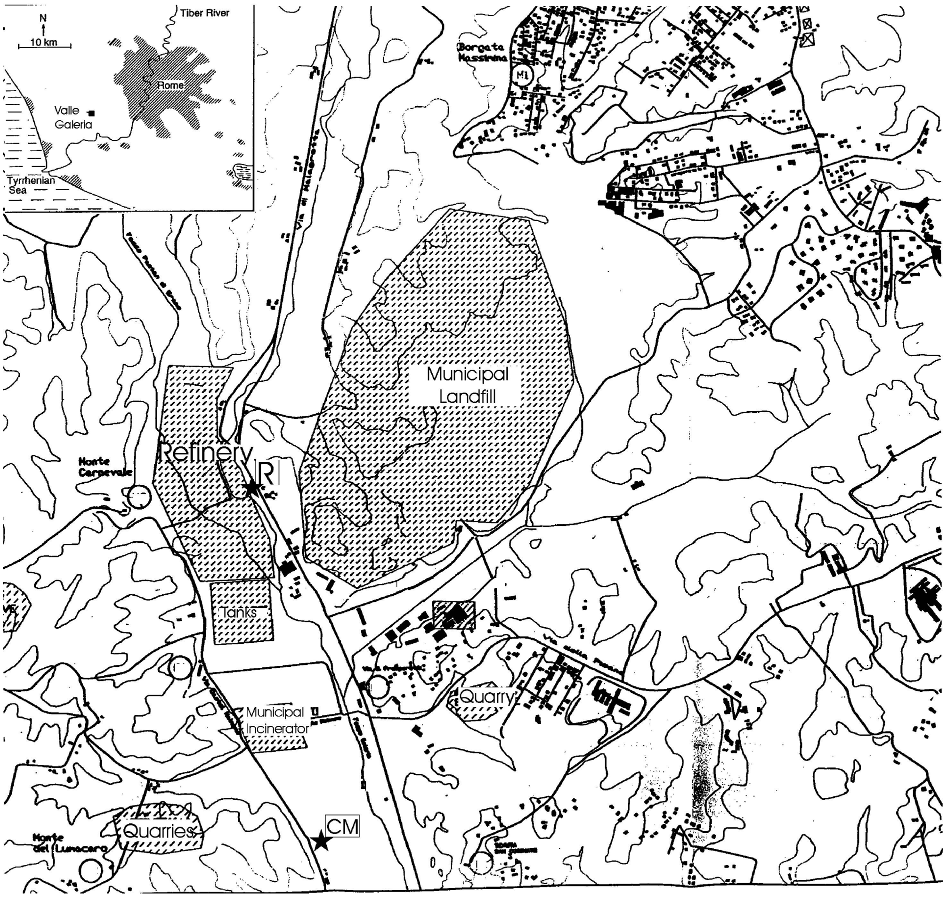

Figure 1. Sketch of the Valle Galeria area and its geographical location. Symbol ★ shows the location of Refinery (R) and Castel Malnome (CM) sampling points.

The municipal landfill exploits a capacity of 5 Ktons/day. It is the main solid waste disposal facility of Rome and one of the biggest in Europe. It is an important source of both methane and carbon dioxide.

A hospital municipal incinerator with up to 60 tons/day capacity is located about 2 Km south of the refinery. It processes organic wastes produced by hospitals, infirmaries and pharmacies all around the region. Particulate matter, acid gases, traces of metals and organics are emitted from the main stack.

Services, stuffs and goods suppliers and delivery of final products introduce vehicle emissions along roads crossing the area. It has been estimated that about 40,000 vehicles per day circulate on the local roads.

Although the area is exposed to air pollution, a monitoring network does not exist. Due to this loss of knowledge on the state of local air quality and its possible effects on human health, inhabitants complain about the industrial emissions and their impact on the environment. In the past a few field campaigns have been conducted in the Valle Galeria area (AMNU, 1990) to get information on the state of the local air quality. Results showed the absence of concentration values of criteria pollutants above law limits, although high values of total hydrocarbons were observed for short periods. Mortality studies were conducted both on population living around the Valle Galeria industrial area (Michelozzi *et al.*, 1998) and on employees of the petroleum refinery (Lo Presti *et al.*, 2001). Results on population showed no association between proximity to the industrial sites and mortality, although mortality from laryngeal cancer declined with distance from the sources of pollution. The mortality study on the oil refinery employees exhibited an excess risk from cancer of the lung and bladder in blue collar workers probably related to the exposure at PAHs compound and other hydrocarbons.

2.2. Field campaign description

In order to assess the relative amount of pollutants emitted by the above sources, a preliminary evaluation was conducted, based on both onsite measurements and estimations (API, 1989; Ntziachristos and Samaras, 2000). Refinery was found to be mainly responsible for the industrial emissions of VOC, accounting for as much as 438 Kg/day. About the same amount (484 Kg/day) was estimated for VOC emissions from vehicles running on the local main roads. These results provided indications on both the selection of the monitoring sites and choice of related VOC compounds. Since harmful effects caused by the above activities are expected and, on the other hand, any monitoring station for pollutants was never installed before, in-field measurements were conducted at two locations. An intensive campaign was carried out on July 19th–25th 2003, when, concurrently with regulated pollutants, also PAH, VOC, heavy metals and $PM_{2.5}$ were determined. Besides the acquisition of concentration levels of pollutants, an assessment of influence of meteorology was attempted.

Ambient air samples were collected at two stations located respectively north and south of the hospital waste incinerator, along the direction of predominant winds in the study period. The first station, i.e. *Refinery* (R), was located between the border of the petroleum refinery plant and the main road crossing the area, about 2 Km from both the centre of municipal landfill (east) and the municipal incinerator stack (south). The second station, i.e. *Castel Malnome* (CM), was located inside a farm, 1.5 Km south of the municipal incinerator stack and 3 Km south of both the petroleum refinery and the municipal landfill. Further details concerning the field campaign are given below.

2.2.1. *Sampling and Analysis of VOC*

VOC were sampled by aspirating air by means of a *Deluxe* SK224-PCEX8 low volume pump (SKC, ltd, Eighty Four, PA) through *Anasorb* CSC Sorbent Sample

Tubes (SKC) located at 1.5 m height respect to the ground level. A constant flow rate of 0.7 L/min was selected, while samplings were performed twice a day, corresponding to day and night times (08:00–18:00 and 20:00–06:00, respectively). After collection, cartridges were extracted with CS_2 (2 mL) and spiked with odd linear C_3 to C_9 alcohols, which were used as internal standards. Chemical analyses were performed by using a HP6890 gas chromatograph (GC) coupled with a FID. The chromatographic column was a VOCOL^{TM} (0.32 mm i.d. ×60 m, 1.8 μm film thickness, SUPELCO, Bellefonte, PA). Operating parameters were set as follows: injector temperature $= 270\,^{\circ}$C (split mode), split ratio 60:1, and carrier gas flow (helium) through the column equal to 2.3 mL/min (constant); detector temperature $= 250\,^{\circ}$C. He make up flow = 45 mL/min, H_2 detector flow = 40 mL/min, air flow at 450 mL/min. Oven temperature program started from 35 °C (held for 4 min), then +4 °C/min up to 210 °C (held for 12.25 min).

Benzene, toluene and $m + p$-xylene compounds (BTX) were also monitored in semi-continuos mode by means of a Syntech Spectras BTX Analyzer GC855 (Syntech Spectras, Groningen, Nederland) equipped with a photo ionization detector FID (LOQ $< 0.04\ \mu g/m^3$), which released BTX concentrations with 15 min time resolution.

2.2.2. *Meteorological Measurements*

A meteorological mobile laboratory (MML) was located close to the petroleum refinery to evaluate the meteorological effects on the monitored air pollutants. By means of a sonic anemometer, located at 10 m height respect to the ground level, the MML provided the standard meteorological (10 min average) as well as turbulence parameters, such as turbulence kinetic energy (TKE), friction velocity (u_*), vertical wind component (w) and its standard deviation (σ_w).

Upper air measurements of wind and turbulence were collected by means of a METEK DSDPA.90 phased array miniSODAR, which was located close to the MML station. Both wind components and turbulence were measured by the system along each beam axis over an interval 40–400 m a.g.l., with a vertical resolution of 20 m.

3. Results

3.1. AIR CONCENTRATIONS OF TARGET POLLUTANTS AND TIME SERIES ANALYSIS

VOC were grouped on the basis of chemical properties and prevailing sources in ambient air. Aromatic hydrocarbons have been associated mainly to combustion processes, while saturated hydrocarbons are known to evaporate from oil products and organic solvents (Colbeck and Mackenzie, 1994). Thus, the above two groups of VOC were analyzed and kept apart.

3.1.1. *BTX Compounds*

The time series of BTX concentrations collected at R and CM stations by means of the automatic analyzer are shown in Figure 2. A strong time modulation was observed for all BTX components. Peak values were recorded during night time, when the atmosphere is expected to be stable, with two evident exceptions, corresponding to the nights of 20th and 24th. Conversely, minimum concentrations were found during daytime when boundary layer is likely to be well mixed. A progressive increase of BTX concentrations was observed on nights starting from July 21st, with maxima occurring on July 23rd, when 321 μg/m^3 were reached by toluene and 73 μg/m^3 by benzene at the R station. Table I shows both the daily averages and maxima observed at the two monitored stations. Air concentrations at R site were up to three times higher than at CM. Looking at hydrocarbon profile, high concentrations recorded at site R were recognized to be caused by fresh emission, while dispersion and photo-induced reactions, developing during the transport from the emission source to CM, determine the decreasing of site concentrations. A comparison of VOC measured both in industrial areas of different countries and in the city of Rome is summarized in Table II. The overall average concentration of benzene was equal to 1 ppb, in agreement with data provided by Kalabokas *et al.* (2001) for a Greek oil refinery (0.8 ppb), whilst toluene was about twice than the values previously reported. Our findings are also in good agreement with Na *et al.* (2001), which measured 2.1 and 3.9 ppb, respectively, for benzene and toluene in a Korean industrial area. By contrast, Lin *et al.* (2004) observed much higher levels of BTX (110 and 118 ppb, respectively for benzene and toluene) inside and around a petrochemical plant in Taiwan. Higher benzene concentrations (6.8 ppb) were also measured by Chang *et al.* (2005) around a Taiwan petroleum refinery. Even higher

TABLE I

Daily average and maximum ground concentrations (μg/m^3) of BTX at Refinery and Castel Malnome monitoring stations

	Benzene				Toluene				$m + p$ Xylene			
	Refinery (R)		Castel malnome (CM)		Refinery (R)		Castel malnome (CM)		Refinery (R)		Castel malnome (CM)	
	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max
19/7/2003	2.5	26.9	1.5	11.0	8.5	89.2	5.5	43.5	2.6	20.1	1.5	13.0
20/7/2003	0.9	5.9	0.2	0.6	1.8	14.1	0.5	3.0	0.9	6.2	0.1	0.6
21/7/2003	2.2	21.0	1.5	7.6	7.6	69.8	5.9	29.0	3.2	18.3	2.0	11.3
22/7/2003	5.5	54.2	2.7	14.9	21.2	204.2	10.9	66.7	5.2	45.9	2.7	14.3
23/7/2003	6.8	72.7	1.3	16.0	28.4	321.4	4.5	58.3	7.5	91.4	1.2	16.5
24/7/2003	1.5	8.9	0.2	0.9	3.0	27.7	0.6	4.0	1.1	7.5	0.1	1.1
25/7/2003	3.8	25.0	1.9	31.0	14.1	108.0	6.4	88.7	4.6	27.4	1.7	18.8

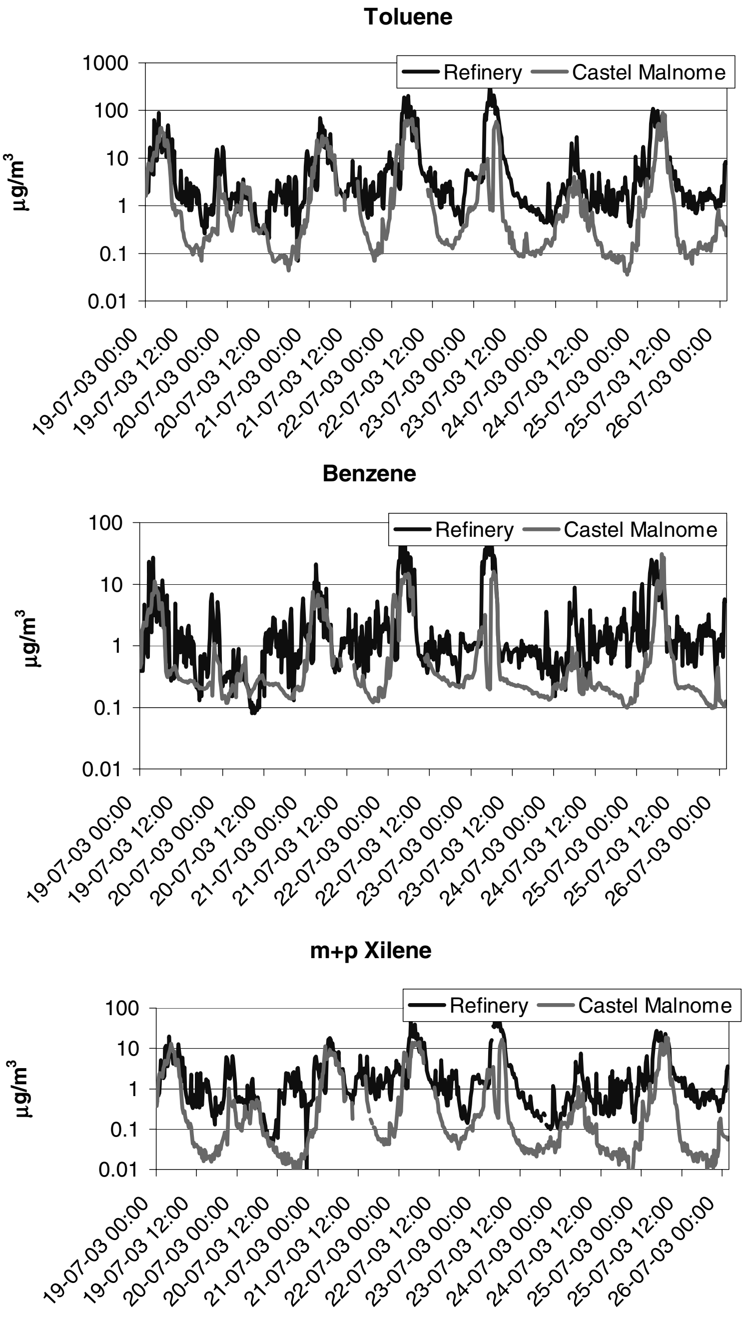

Figure 2. Time series of ground concentrations of Toluene, Benzene and $m + p$-Xylene at Refinery and Castel Malnome monitoring stations.

TABLE II

Comparison of mean values of VOC in industrial areas of different countries and in the city of Rome.

	This study		Greek oil refinery (Kalabokas *et al.*, 2001)[b]	Korean industrial area (Na *et al.*, 2001)[c]	Taiwan petrol refinery		Downtown Rome			Rome urban background station, June (Perrino *et al.*, (2001)[a]	Rome rural area (Ciccioli *et al.*, 1993)[g]	UK municipal incinerator waste centre and sewage plant (Leach *et al.*, 1999)[f]	Canadian industrial area (Cheng *et al.*, 1997)[e]
	R site	CM site			(Lin *et al.*, 2004)[c]	(Chang *et al.*, 2005)[h]	(Brocco *et al.*, 1997)[b]	(Mabilia *et al.*, 2001)[d]	(Ciccioli *et al.*, 1992)[g]				
Benzene	1.0[a]	0.4[a]	0.8	2.1	110.0	6.8	11.0	0.74	12.9	0.6	0.9	12.7	0.8
Toluene	3.1[a]	1.3[a]	1.7	3.9	118.0	5.4	25.9	2.26	25.2		1.0	17.0	1.2
BTX	2.5[D,b] 7.6[N,b]	1.[D,b] 3.[N,b]	3.8	8.7	248.0	13.2	55.2	5.2	57.2		2.5		2.6
C_6–C_8	10.[D,b] 16.[N,b]	4.[D,b] 10.[N,b]	2.5				7.5		7.7		0.3		
Aromatics	9.5[D,b] 31.0[N,b]	4.0[D,b] 12.[N,b]			266[B,D]	21.1[D,B]			236[D]		10.2[D]		
	20.2[P,b]	8.2[P,b]		92.2[B]			232.5	24.0				157	10
Alkanes	330.[D,b] 645.[N,b]	47.[D,b] 300.[N,b]				25.7[D,B]			133[D]		13.2[D]		
	488.[P,b]	173.[P,b]		210.7[B]			322.1						171
Alkenes	43 197	12 100				80.[D,B]			67[D]		0.8[D]	117[AA]	
	120	56		131.8[B]			104.9						7
VOC	383[D,b] 873[N,b]	62[D,b] 411[N,b]			582-2506[B]	127[D,B,V]			436[D,V]		24[D,V]		
	628[P,b]	237[P,b]		434[B,V]			659.5[V]					275[V]	219

BTX and C_6–C_8 values in ppb. Aromatics, alkanes, alkenes and VOC in $\mu g/m^3$ except for [B] in ppb.

[D] Average diurnal concentration.

[N] Average nocturnal concentration.

[P] Average period concentration.

[V] VOC as sum of aromatic, alkanes and alkenes to be compared with this study.

[AA] As sum of C4–C18 Alkanes+Alkenes.

[a] Automatic analyser.

[b] Adsorbent trap sampling method and GC-FID analysis.

[c] Stainless steel container sampling method and GC-FID analysis.

[d] Adsorbent diffusive trap sampling and GC-FID analysis. June data.

[e] Canisters sampling method and GC-FID analysis.

[f] Passive sampling method and GC-FID analysis, average of SS1–SS9 sampling points pre-incinerator shutdown.

[g] Adsorbent trap sampling method and GC-MS analysis. Noon data.

[h] Canisters sampling method and GC-FID or MSD analysis. Average of petroleum refinery boundary (2–4 sampling points, June 2000).

concentrations of benzene (130 ppb) have been observed by Chiu *et al.* (2005) in a Taiwan petroleum refinery. The BTX measured in Valle Galeria were much lower than those reported by Brocco *et al.* (1997) for downtown Rome and in agreement with data measured in the urban background station of the same city, reported by Perrino *et al.* (2001).

Based upon GC-FID determinations, the average daytime BTX content in air (2.5 ppb or 9.5 μg/m^3 in total) at R site was in agreement with Kalabokas *et al.* (2001), while the same author found C_6–C_8 n-alkane concentrations twice lower than our findings ($\sim$10 ppb). Lin *et al.* (2004) and Chang *et al.* (2005) in a Taiwan petroleum refinery as well as Mabilia *et al.* (2001) in downtown Rome, measured concentrations of aromatic hydrocarbons (266 ppbv, 21 ppbv and 24 μg/m^3 respectively) higher than in Valle Galeria. Daily BTX concentrations at CM were even lower (1 ppb) than at another rural site in the outskirts of Rome (2.5 ppb; see Ciccioli *et al.*, 1993).

3.1.2. *Aliphatic Compounds*

The daytime and nighttime VOC concentrations obtained by GC analysis of cartridges are shown in Table IIIa/b, respectively for R and CM sites. Total VOC reached 383 and 873 μg/m^3 on an average, respectively during day and night at R site, while at CM site they accounted for 62 and 411 μg/m^3. Lower VOC loads were reported for an industrial site in Edmonton, Canada (Cheng *et al.*, 1997) and for a municipal incinerator and sewage treatment plant (Leach *et al.*, 1999). By contrast, Lin *et al.* (2004) measured much higher concentrations in a petroleum refinery in Taiwan (total VOC ranging from 582 to 2506 ppbv among 26 sampling points in and around the plant), while Chang *et al.* (2005) found lower daily values of total VOC (127 ppb) in the boundary of a Taiwan refinery. Ciccioli *et al.* (1992) measured very high daytime levels of total C_4–C_{14} hydrocarbons (910 μg/m^3) in downtown Rome, but the sum of alkanes, alkenes and aromatics (436 μg/m^3) was comparable with the average daytime value measured at R site. Conversely their findings in a rural area of the same countryside were similar to the value measured at CM site (237 μg/m^3) only if the total VOC are considered (172 μg/m^3), but lower if the sum of aromatics, alkanes and alkenes is concerned (24 μg/m^3) (see Ciccioli *et al.*, 1993).

Light alkanes (C_4 and C_5) were the most abundant compounds measured, in agreement with literature (Mohan Rao *et al.*, 1997; Cheng *et al.*, 1997). *Iso*- and *n*-pentane, *n*-butane, or *n*-hexane, were the most abundant VOC at R and CM sites, accounting for $\sim$70% of C_4–C_{10} hydrocarbons. By contrast, Na *et al.* (2001) identified oxygenated hydrocarbons (methanol, ethanol and acetone) and C_3 components (propane, ethylene and propylene) as predominant species, although the authors remarked that the results were heavily affected by working conditions. Furthermore both Lin *et al.* (2004) and Chang *et al.* (2005) found to be ethylene and toluene the most abundant VOC compounds in a Taiwan petroleum refinery. Among the alkenes compounds trans-2-pentene, 2-methyl-1,3-butadiene, 2-methyl-1-butene

TABLE III

Daytime and nighttimes VOC compound concentrations (μg/m^3) measured at Refinery (a) and at Castel Malnome (b) sites

	19/7/03		20/7/03		21/7/03		22/7/03		23/7/03		24/7/03		25/7/03		Avg.	Avg.
	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night
(a)																
Alkanes																
n-butane	11.6	23.2	12.9	32.4	14.9	22.9	4.2	53.5	211.	9.6	197.	7.4	89.0	58.3	77.3	29.6
iso-pentane	13.1	88.4	26.2	195.	29.8	157.	20.6	1335.	186.	49.9	161.	61.5	95.8	256.	76.2	306.
n-pentane	12.0	54.0	30.9	65.2	29.5	111.	31.0	608.	199.	90.0	165.	64.0	69.0	149.	76.7	163.
n-hexane	3.4	22.7	21.7	15.7	23.3	40.6	20.2	69.0	43.5	48.8	32.1	27.1	26.0	90.0	24.3	44.8
i-butane	2.6	5.4	1.7	3.6	1.9	3.1	0.5	6.3	30.2	1.4	42.9	0.8	51.1	15.2	18.7	5.1
n-heptane	1.6	12.9	13.4	2.9	11.4	19.9	8.2	50.6	12.7	12.1	11.2	14.5	11.5	18.8	10.0	18.8
3,3-dimethylpentane	1.0	7.4	4.1	2.6	4.6	12.5	4.4	39.0	9.6	5.8	8.3	6.3	7.3	12.1	5.6	12.2
2-methylhexane	0.7	7.4	4.0	2.9	4.7	12.5	3.2	51.9	6.3	6.4	6.1	8.1	5.7	11.6	4.4	14.4
3-methylhexane	0.5	7.6	4.1	2.2	4.0	10.7	4.0	63.7	4.8	6.0	5.3	8.6	5.6	14.0	4.0	16.1
2,2-dimethylbutane	0.5	1.3	2.9	4.5	4.4	3.2	1.8	4.4	5.2	9.2	2.2	1.5	2.3	9.0	2.8	4.7
2-methylheptane	0.7	6.2	6.0	0.7	6.3	7.6	4.1	8.4	5.0	4.2	4.9	5.5	4.9	9.9	4.6	6.1
3-methylheptane	0.3	5.8	3.9	0.7	4.5	5.7	2.5	12.7	2.7	2.0	2.6	4.8	2.2	3.5	2.7	5.0
n-octane	0.7	5.4	11.0	0.7	9.4	6.4	4.9	5.4	3.5	3.3	4.1	5.9	5.8	4.3	5.6	4.5
n-nonane	1.0	7.8	14.0	0.4	14.5	12.2	9.6	4.1	3.3	2.9	5.4	5.2	7.3	7.8	7.9	5.8
n-decane	1.3	7.5	4.8	1.9	7.1	9.5	6.7	2.9	2.7	3.9	4.8	5.5	6.5	17.7	4.9	7.0
n-undecane	0.3	1.2	2.7	0.0	4.9	2.8	3.7	1.7	0.2	0.1	0.9	0.4	2.3	2.0	2.2	1.2
Total alkanes	51.3	264.3	167.7	332.4	181.9	438.5	134.5	2317.2	727.0	255.6	654.5	227.2	393.5	680.8	330	645
Aromatics																
Toluene	0.7	7.9	5.1	2.9	5.0	12.1	3.9	54.3	3.9	6.0	2.8	9.4	3.8	12.6	3.6	15.0
Benzene	0.5	3.2	2.9	1.2	2.9	6.6	1.8	14.7	1.8	3.0	2.7	4.5	4.3	8.9	2.4	6.0
Ethylbenzene	0.1	1.3	0.6	0.4	1.0	1.9	0.8	6.3	0.3	0.7	0.4	1.2	0.8	1.0	0.6	1.8
$m + p$-xylene	0.4	4.4	2.8	1.1	4.0	7.0	2.5	21.2	1.0	2.0	1.2	3.8	2.4	2.3	2.0	6.0
o-xylene	0.1	1.6	1.7	0.4	1.6	2.8	1.1	7.1	0.3	0.6	0.5	1.4	0.8	0.9	0.9	2.1
Total aromatics	1.9	18.4	13.2	6.0	14.6	30.4	10.0	103.6	7.2	12.3	7.5	20.3	12.1	25.7	9.5	31.0

(*Continued on next page*)

TABLE III

(*Continued*)

	19/7/03		20/7/03		21/7/03		22/7/03		23/7/03		24/7/03		25/7/03		Avg.	Avg.
	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night
Alkenes																
3-methyl-1-butene	0.0	0.6	1.1	2.7	0.0	2.4	0.7	5.6	0.8	1.9	0.4	1.9	1.1	4.4	0.6	2.8
1-pentene	0.0	0.0	2.7	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.1	0.0	0.0	10.1	0.4	1.5
2-methyl-1-butene	0.0	4.3	0.0	14.7	3.2	11.7	0.6	78.8	1.7	2.4	0.1	0.0	4.0	24.1	1.4	19.4
2-methyl-1,3butadiene	0.0	13.8	3.2	53.8	0.0	31.5	1.7	290.2	3.2	10.2	0.1	12.9	7.2	0.0	2.2	58.9
trans-2-pentene	1.6	10.8	2.1	40.2	4.2	17.0	1.9	269.5	5.0	6.4	0.0	7.2	12.1	38.1	3.8	55.6
cis-2-pentene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	12.9	0.0	1.8
trans-2-hexene	0.0	0.5	0.0	1.8	0.0	3.2	0.0	9.8	1.2	0.0	1.8	2.6	0.6	16.6	0.5	4.9
2-methyl-2-pentene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
cis-2-hexene	0.0	3.4	1.4	3.0	1.1	5.4	0.0	25.2	2.2	2.9	1.8	3.3	3.2	9.5	1.4	7.5
1-heptene	1.0	7.9	2.7	1.8	6.0	9.2	6.5	30.7	9.5	7.9	4.2	10.1	11.4	27.3	5.9	13.5
trans-3-heptene	0.0	0.0	0.8	0.7	0.0	1.3	0.0	2.0	0.0	0.0	0.0	0.8	1.5	2.9	0.3	1.1
trans-2-heptene	0.0	1.3	0.9	0.0	0.6	0.0	0.7	3.5	1.0	0.0	1.1	2.6	1.1	3.9	0.8	1.6
cis-2-heptene	0.3	3.3	2.2	1.6	1.6	4.8	0.0	10.7	1.5	0.0	0.0	3.5	1.4	0.0	1.0	3.4
1-octene	0.0	14.1	14.4	1.7	16.8	12.7	10.1	13.8	9.2	8.8	10.8	16.3	13.6	0.0	10.7	9.6
cis-3-octene	0.0	0.0	2.8	0.0	1.6	3.3	1.7	1.5	0.0	0.0	0.0	0.0	3.3	0.0	1.4	0.7
trans-2-octene	0.0	0.0	4.5	0.0	5.4	3.2	0.0	0.0	1.2	0.0	0.0	5.2	0.0	0.0	1.6	1.2
cis-2-octene	0.0	0.0	4.8	0.0	5.2	0.0	3.1	3.5	1.8	2.5	2.6	4.2	3.0	0.0	2.9	1.4
1-nonene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2
trans-3-nonene	0.0	0.0	0.0	0.0	0.0	0.0	1.4	0.0	1.5	0.0	2.2	0.0	1.9	0.0	1.0	0.0
cis-3-nonene	0.0	2.8	0.0	0.0	5.4	6.6	2.3	1.8	0.9	0.0	0.0	4.7	2.0	0.0	1.5	2.3
trans-2-nonene	0.6	6.7	8.1	0.0	13.6	13.5	5.2	5.0	0.0	4.7	5.6	6.3	4.3	16.0	5.3	7.5
cis-2-nonene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	11.4	0.0	1.6
1-decene	0.0	0.0	0.0	0.0	0.0	0.0	1.4	1.1	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2
Total Alkenes	3.5	69.4	51.9	122.0	64.7	126.0	37.5	753.8	40.7	47.7	30.8	81.7	71.9	177.3	43	197
Total VOC	56.7	352.1	232.8	460.4	261.1	594.8	182.0	3174.5	774.9	315.6	692.9	329.2	477.5	883.8	383	873

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TABLE III
(*Continued*)

	19/7/03		20/7/03		21/7/03		22/7/03		23/7/03		24/7/03		25/7/03		Avg.	Avg.
	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night
								(b)								
Alkanes																
n-pentane	3.3	30.8	4.2	92.3	3.3	208.2	3.4	94.4	53.5	13.5	12.7	27.5	6.7	11.8	12.5	68.3
n-hexane	5.7	26.5	7.2	25.2	11.4	41.6	6.8	11.7	15.3	25.2	23.4	38.7	4.3	11.9	10.6	25.8
iso-pentane	4.3	33.1	5.1	163.5	3.2	391.1	4.6	339.7	18.6	14.9	14.4	32.5	15.3	15.6	9.4	141.5
2,2-dimethylbutane	2.8	4.3	2.9	5.5	1.7	5.6	2.3	3.3	17.4	8.2	6.9	12.0	1.0	1.8	5.0	5.8
n-butane	0.8	4.8	1.0	18.0	0.4	22.8	0.6	67.8	6.2	1.4	1.5	6.0	4.0	1.7	2.1	17.5
2-methylhexane	0.5	6.0	0.7	5.9	1.4	16.2	0.8	3.6	2.7	2.0	2.2	3.4	1.0	2.1	1.3	5.6
3,3-dimethylpentane	0.4	4.3	0.3	7.5	1.4	13.4	0.4	4.5	4.1	1.6	1.8	1.8	0.3	1.2	1.3	4.9
iso-butane	0.3			2.2		2.3		5.9	2.9				0.8		1.3	3.5
n-heptane	0.5	4.5	0.6	12.7	1.3	22.2	0.7	4.4	3.2	2.6	1.7	3.4	0.8	2.3	1.2	7.5
3-methylhexane	2.7	3.0	0.4	6.1	0.9	19.5	0.5	4.0	1.2	2.2	1.1	2.4	0.3	1.6	1.0	5.6
2-methylheptane	0.0	0.0	0.0	5.4	0.0	7.5	0.0	1.2	0.0	0.0	0.3	1.2	0.0	0.6	0.0	2.3
3-methylheptane	0.0	0.0	0.0	4.3	0.0	6.6	0.0	1.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.8
n-octane	0.0	7.7	9.8	5.4	0.0	7.0	0.0	1.4	0.0	0.0	0.5	1.5	0.5	22.4	1.6	6.5
n-nonane	0.0	0.0	0.0	5.5	0.0	7.8	0.0	1.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.1
n-decane	1.5	0.0	0.0	3.0	0.0	3.5	0.0	1.5	0.0	0.0	0.0	3.5	0.0	0.0	0.2	1.7
n-undecane	0.0	0.0	0.0	0.8	0.0	1.2	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3
Total alkanes	22.8	125.0	32.2	363.2	25.0	778.4	20.1	547.4	125.1	71.6	66.5	133.9	35.1	73.0	47	300
Aromatics																
toluene	0.7	8.7	1.1	7.3	2.3	16.1	0.8	3.7	8.4	3.3	2.1	4.8	1.1	1.4	2.4	6.5
benzene	0.4	3.4	0.4	2.5	0.9	5.6	0.5	1.5	5.7	1.4	1.4	2.1	0.5	1.4	1.4	2.6
ethylbenzene	0.0	0.0	0.0	1.0	0.1	1.9	0.1	0.6	0.0	0.3	0.0	0.4	0.1	0.0	0.0	0.6
$m + p$-xylene	0.1	1.8	0.0	3.2	0.3	6.7	0.2	1.8	0.2	0.4	0.3	1.2	0.1	0.4	0.2	2.2
o-xylene	0.0	0.0	0.0	1.5	0.0	2.5	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.6
Total aromatics	1.2	13.9	1.5	15.6	3.7	32.8	1.6	8.2	14.3	5.2	3.8	8.5	1.8	3.2	4.0	12

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TABLE III
(*Continued*)

	19/7/03		20/7/03		21/7/03		22/7/03		23/7/03		24/7/03		25/7/03		Avg.	Avg.
	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night
Alkanes																
3-methyl-1-butene	0.4	4.1	0.6	2.4	1.5	2.3	0.7	4.7	0.2	2.4	2.7	1.3	0.4	1.0	0.9	2.6
1-pentene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.0	0.1	0.0	0.0
2-methyl-1-butene	0.7	14.7	0.3	19.5	0.0	15.1	0.5	31.7	1.8	8.3	2.7	2.9	0.0	1.7	0.8	13.4
2methyl-1,3butadiene	0.2	26.5	1.4	49.9	6.8	77.3	2.3	56.6	3.9	0.1	9.2	5.1	2.4	4.5	3.7	31.4
trans-2-pentene	0.5	11.7	0.0	39.9	1.6	51.0	0.9	54.8	3.2	4.8	4.8	6.4	0.6	7.6	1.7	25.2
cis-2-pentene	0.0	0.1	0.0	0.0	0.0	0.0	0.0	1.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2
trans-2-hexene	0.1	6.0	0.2	1.8	0.8	2.8	0.9	1.6	0.0	0.7	0.0	1.2	0.5	1.8	0.4	2.3
cis-2-hexene	0.0	0.0	0.0	3.5	0.5	7.8	0.5	3.4	0.0	0.9	0.0	0.0	0.3	0.5	0.2	2.3
1-heptene	0.0	10.9	1.2	10.4	1.2	12.1	0.7	4.1	2.3	2.8	0.1	2.8	1.5	2.9	1.0	6.6
trans-3-heptene	0.0	3.8	0.0	0.6	0.0	1.4	0.0	0.5	1.0	1.1	0.8	0.7	0.0	0.0	0.3	1.2
cis-3-heptene	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.1	0.0
trans-2-heptene	0.1	0.0	0.6	1.0	0.3	1.3	0.0	0.7	0.9	0.0	0.0	0.7	0.1	0.7	0.3	0.6
cis-2-heptene	0.0	0.0	0.0	2.4	0.0	2.4	0.3	1.6	1.7	0.0	0.9	1.2	1.2	2.1	0.6	1.4
1-octene	0.0	0.0	0.0	11.7	0.0	14.9	0.0	3.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.3
cis-3-octene	0.0	0.0	0.0	1.5	0.0	1.9	0.0	0.5	0.0	0.0	0.0	2.7	0.0	0.0	0.0	1.0
trans-2-octene	0.0	0.0	0.0	0.0	0.0	2.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4
cis-2-octene	0.0	0.0	0.0	2.9	1.2	0.0	0.0	1.1	0.0	3.1	0.0	0.0	0.0	0.0	0.2	1.0
trans-3-nonene	0.0	0.0	0.0	0.0	0.0	4.3	0.0	0.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7
cis-3-nonene	0.7	0.0	0.0	0.0	0.0	0.0	0.5	0.5	1.9	0.0	0.0	0.7	0.4	0.0	0.5	0.2
trans-2-nonene	0.0	0.0	1.6	6.0	0.6	6.1	1.1	1.1	1.2	2.5	0.0	3.6	0.6	3.3	0.7	3.2
cis-2-nonene	0.0	0.0	0.7	0.0	0.8	0.0	0.0	0.0	1.2	1.7	0.0	6.4	0.4	2.4	0.4	1.5
1-decene	0.0	0.0	0.0	0.0	0.0	1.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3
Total Alkenes	2.7	77.8	6.5	153.5	15.3	205.1	8.7	168.3	19.3	28.7	21.5	36.0	8.3	28.8	12	100
Total VOC	27	217	40	532	44	1016	30	724	159	105	92	178	45	105	62	411

and 1-octene were found the most abundant. As for alkanes the nighttime concentrations of alkenes were found significantly higher than the daytime ones. C_2–C_3 alkenes were not detected due to their too high volatility for the sampling method used. The detection of significant concentrations of 2-methyl-1-butene around oil refineries is confirmed by results reported by Chang *et al.* (2005) for a Taiwan petroleum refinery, although they found ethylene to be the most abundant alkene compound detected.

Total alkanes reached 330 and 47 μg/m^3, respectively, at R and CM sites during the day and 645 and 300 μg/m^3 in the night, on average. The daytime average of total alkenes measured at R and CM sites was respectively 43 and 12 μg/m^3, while the nighttime one increased up to 197 and 100 μg/m^3.Thus, while the ratio between total alkane contents at the two sites was about one order of magnitude at daytime, it dropped down to a factor of ~2 at night. By contrast the same ratio for the total alkenes contents exhibits a lower daytime-nighttime variation (3.6 to 2). The time series of VOC collected at both R and CM sites are shown in Figure 3.

Compared with values reported by different authors (Ciccioli, 1992, 1993) for urban and rural areas of Rome, the diurnal concentration of total alkanes at site CM is in good agreement with the value measured at a rural site (13.2 μg/m^3), while the diurnal concentration at the site R is twice the concentrations measured at noon in the urban area (133 μg/m^3). Both daily and period average of total alkenes at R site

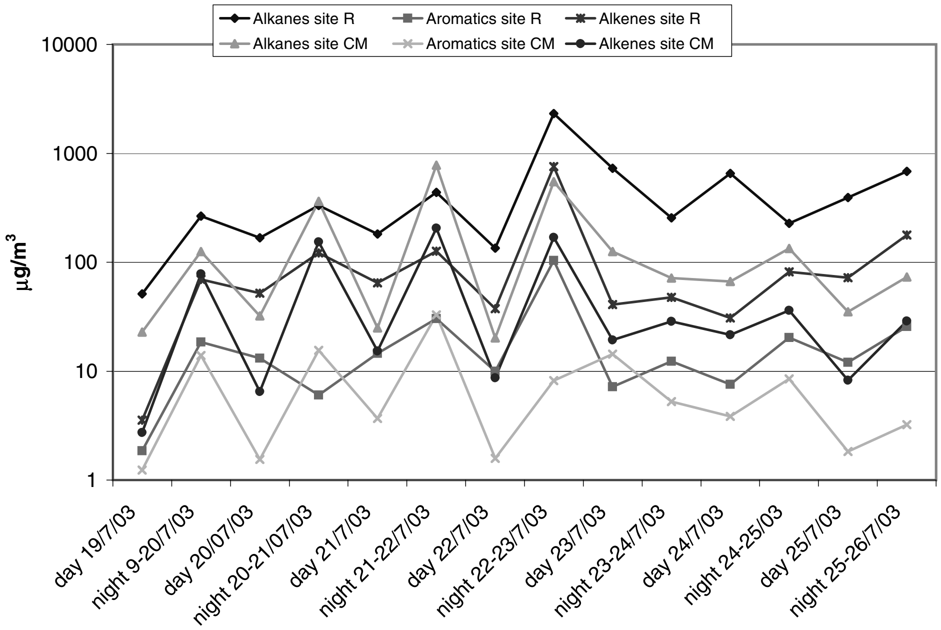

Figure 3. Time series of ground concentrations of Alkanes, Alkenes and Aromatics VOC compounds at Refinery and Castel Malnome monitoring stations.

are similar respectively with values reported by Ciccioli *et al.* (1992) in downtown Rome at noon (67 μg/m^3), and with data reported by Brocco *et al.* (1997) (104.9 μg/m^3) for the same city. The observed total alkenes concentration at R site are also in agreement with values reported by Na *et al* (2001) for a Korean industrial area and with daytime data provided by Chang *et al.* (2005) for a Taiwan petroleum refinery. If we compare data referring to aliphatics and aromatics, sink processes developing in the atmosphere seem to be more effective on alkanes than on BTX. All VOC present broad differences between daytime and nighttime concentrations. Similarly, the increase of both alkanes and alkenes concentrations, starting from the night of July 21st was more pronounced than that of aromatics. In particular, a high load of total alkanes and alkenes was observed during the nights of 22nd and 23rd, when also benzene, toluene and xylenes reached their absolute maxima. This phenomenon was observed at both sites, although with different extent.

3.2. METEOROLOGY AND ITS INFLUENCE ONTO HYDROCARBON LEVELS

During the analyzed period the studied area was characterized by a high pressure system, with high temperatures and insulation. A land-sea breeze regime dominated the area. A light wind blowing from North was prevailing during nighttime. By contrast, at daytime, the high insulation produced convection with a vertical remixing of the atmosphere; concurrently, a sea breeze developed, blowing from either SW or NW sectors, with wind speed raising during the day. Figure 4 shows the surface measurements of both wind speed and direction collected at the MML station.

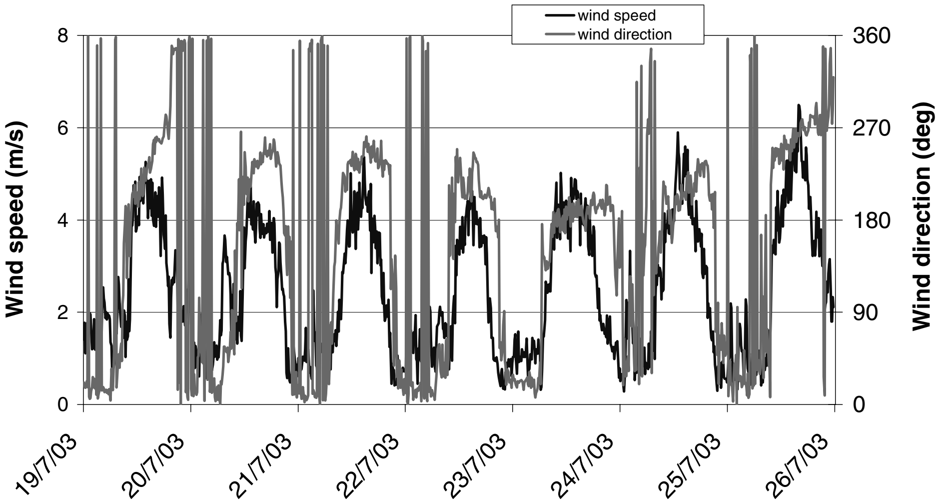

Figure 4. Observed values of surface wind speed and direction measured by MML.

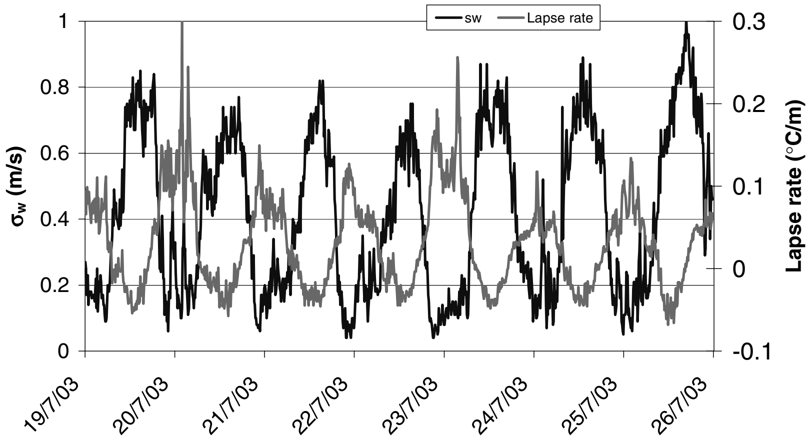

Figure 5. Observed values of surface σ_w and surface lapse rate measured by MML.

To better investigate the lower layers of the PBL, which have great effect on both BTX and VOC loads, surface turbulence and SODAR data were analyzed, with special concern on the standard deviation of vertical wind component (σ_w) and surface lapse rate (SLR). Figure 5 shows the surface measurements of both σ_w and SLR. The σ_w data exhibit peak values during the day in coincidence with a strong convective mixing of the atmosphere. The same results were observed for turbulence kinetic energy (TKE), whilst the SLR showed negative peaks confirming the instability of the lower layer of the atmosphere in that time. These conditions favour decreasing of VOC concentrations. It must also be considered that the sea breeze developed during the day might transport fresh maritime air to the sites increasing the dilution of the pollutants. On the other hand, SRL exhibited positive peak values during the night, when σ_w was at the minimum values. These findings reveal the existence of a stable boundary layer, where the poor mixing of the atmosphere contributes to the pollutants accumulation and, consequently, the increase of their air concentrations. At night time the land breeze conditions might also bring polluted air both from the highway located 1 Km north of the refinery and from the urban area of Rome. However, two outliers were detected on nights of 20th and 24th, when strong σ_w (0.4 and 0.5 m/s respectively) and low SLRs (from 0.29 to 0.06 °C/m on July 20th) were measured, addressing to a remixing of the local atmosphere induced by thermally driven winds.

A special attention was paid to analysis of data from 21st to 23rd when a progressive increase of both BTX and VOC concentrations was observed. Nightime results of σ_w revealed a very poor remixing of the atmosphere, while SLR reached values higher than 0.12 °C/m. It is also worth noting that the time period with σ_w values lower than 0.2 m/s, which indicates low turbulence conditions, extended for 56, 66 and 93% of total night time, respectively, on nights of July 21st, 22nd and

23rd. This phenomenon was likely to cause the progressive increase of BTX values due to the accumulation of the pollutants. Remarkable results are also the nocturnal σ_{w} and SLR data of 23rd with the latter reaching values up to 0.26 °C/m and the former always close to 0.1 m/s, indicating extremely stable conditions. This night BTX concentrations exhibit the highest values.

Figure 6 shows the wind vector of SODAR data collected on 22nd–23rd night in coincidence with peaks of BTX and VOC. A well developed surface-based inversion can be identified from these data. Two different layers are detected. The lower one, below 80 m asl, was characterized by weak wind conditions and low σ_{w}. A very shallow stable boundary exists in this layer which supports pollutants accumulation. The higher layer extended from 80 up to 220 m asl. Stronger winds up to 8.5 m/s were detected in this residual layer together with a secondary σ_{w} peak. The surface-based inversion produced the decoupling of the local atmosphere, allowing the detection of a strong vertical reflectivity.

3.3. BTX RATIO ANALYSIS

To investigate possible relationships existing among pollutants, their co-variance and possible common emission sources, their concentration ratios were calculated and analyzed. To get advantage of the better statistics available, in terms of number of samples, the study was conducted on the BTX dataset obtained by means of the semi-continuous sampler.

A strong daily modulation was observed for the benzene/toluene ratio at both sites. This modulation seemed less pronounced for both benzene/($m + p$-xylene) and toluene/($m + p$-xylene) ratios. The hourly dispersion of BTX ratios at the site R is shown in Figure 7. At night time, BTX ratios exhibit average values quite constant with a low dispersion. At daytime the benzene/toluene and benzene/($m + p$)-xylene ratios are higher both in average and standard deviation, whilst the toluene/($m + p$)-xylene ratio maintains the same behavior as at nighttime. The behavior observed at CM is similar, though the daytime benzene/toluene and benzene/($m + p$)-xylene ratios are twice than those measured at R. Table IV reports a few statistical indexes calculated for BTX ratios at both sites.

The benzene/toluene ratio shows interesting features. While at night time it was quite similar at both sites, during the day it increases more at CM than at R (by a factor of 3 and 2, respectively). This ratio is similar to that calculated by Lin *et al.* (2004) for a petroleum refinery in Taiwan. To explain the daytime difference between benzene/toluene ratio at the two sites, it must be considered that in these hours the prevailing wind blows from North-East sectors locating the CM site upwind respect to the refinery. So the BTX values observed at the CM site, are probably related to background values produced by emissions in a portion of rural territory upwind to this site. Those background values are certainly affected by photochemical reactions. Since benzene is quite stable in the atmosphere, while toluene is subjected to photochemical decomposition, this combined effect modifies the

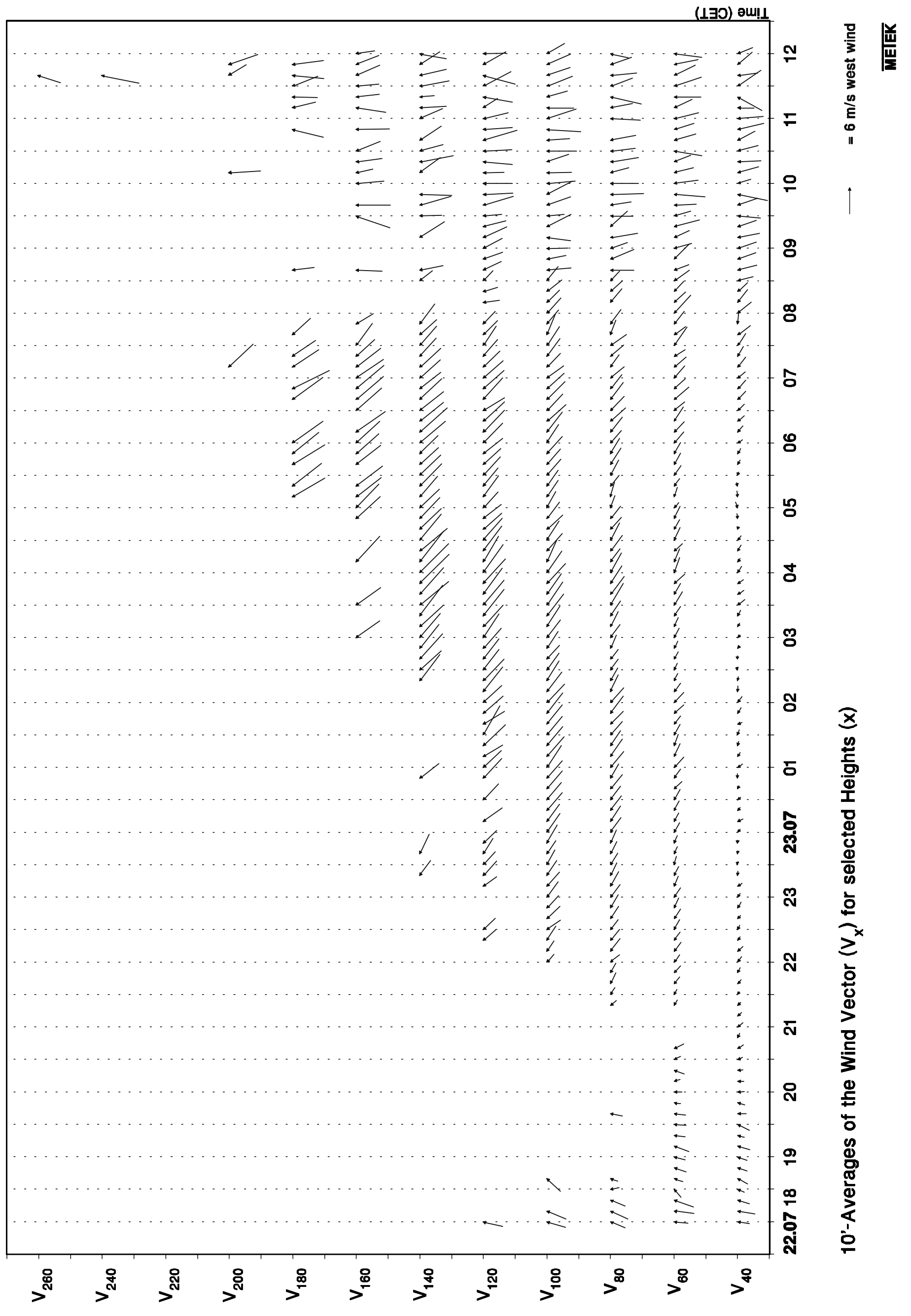

Figure 6. Wind vectors on night 22nd–23rd as detected by the SODAR.

TABLE IV

Statistical indexes for BTX ratios calculated at Refinery and Castel Malnome sites

	Refinery (R)			Castel Malnome (CM)		
	Benz./Tolu.	Benz./Xile.	Tolu./Xile.	Benz./Tolu.	Benz./Xile.	Tolu./Xile.
Daytime						
Average (avg.)	0.7	1.6	2.4	1.5	7.4	4.9
Standard dev. SD	0.3	1.2	1.5	0.7	5.7	2.8
SD/Avg.	0.4	0.7	0.6	0.5	0.8	0.6
Nighttime						
Average (avg.)	0.3	1.0	3.1	0.4	1.5	4.0
Standard dev. SD	0.2	0.6	0.9	0.2	2.0	1.3
SD/Avg.	0.7	0.7	0.3	0.6	1.3	0.3

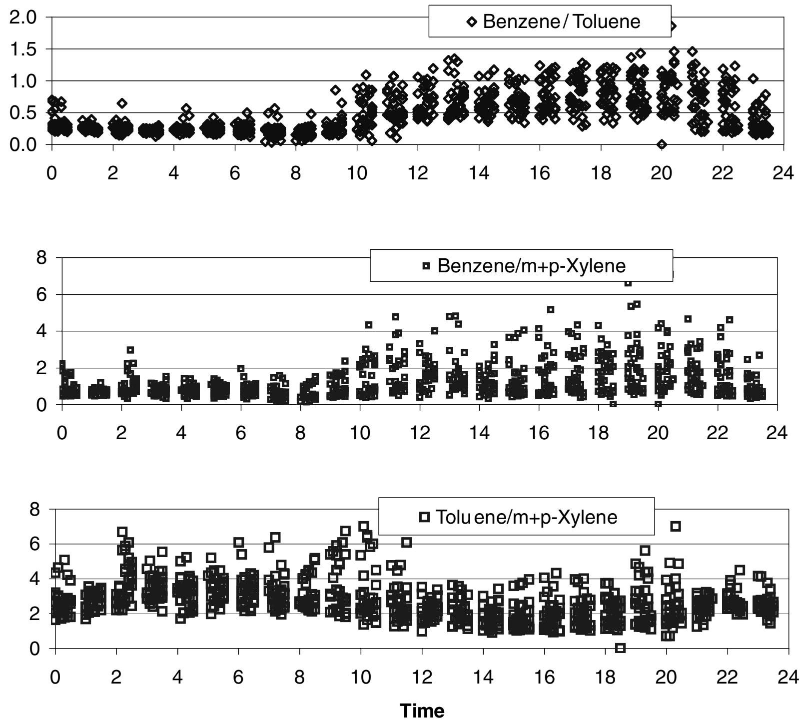

Figure 7. Hourly dispersion of BTX ratios calculated at the Refinery site.

BTX ratio at CM site. Conversely in these wind conditions the R site is downwind a few particular hydrocarbons emission sources located inside the refinery plant. In this case the fresh emission components of each compound is predominant respect to the photochemical one and works on both factors of the considered ratio.

The benzene/($m + p$)-xylene ratio confirms the pattern of the benzene/toluene ratio, with the daytime value resulting much higher at site CM than R (7.4 and 1.6, respectively). Xylene was confirmed as more photochemically susceptible than toluene.

Since toluene and xylene are both reactive, the ratio between the corresponding contents in air do not show any variability during the day. Indeed, the night and day values are comparable (3.1 and 2.4, respectively, at R), with a factor of two between the daily values at the two sites (2.4 and 4.9 for site R and CM respectively).

4. Conclusions

A high industrialized area close to Rome has been selected as a case study to assess the impact of air pollutants emitted by the industrial facilities located in the Valle Galeria area, with particular attention to the Volatile Organic Compounds. An intensive field campaign has been conducted during summer, where VOC have been sampled and analyzed with both automatic and non-automatic instruments at two different sites. In order to assess the possible meteorological effects on the monitored pollutants, high resolution surface and upper air meteorological measurements were conducted during the field campaign.

High concentrations of VOC have been detected at nighttime during stable meteorological conditions. Much lower concentrations were observed during the day, in correspondence of strong convection episodes produced by high solar insulation.

Among the VOC measured, the alkanes were the most abundant components. In particular *n*-butane, *i*-pentane and *n*-pentane accounted for 70% of C_4–C_{10} measured VOC. The alkane fraction reached twice higher concentrations than the ones reported for downtown Rome, whilst aromatics were lower. Trans-2-pentene, 2-methyl-1,3-butadiene, 2-methyl-1-butene and 1-octene were found the most abundant alkenes detected in the monitored sites. The VOC profile was similar at the two monitoring sites, while the total loads were quite different, as a consequence of the atmospheric dispersion. The VOCs fingerprint profile was compatible with that characterizing petroleum refinery emission. Any significant contribution was not detected for other sources.

Surface and upper air meteorological data analysis demonstrated that the high VOC (including BTX) concentrations observed at night time, were caused mainly by the state of atmosphere at the local scale. In particular, the highest BTX pollution episode was produced by a very stable nocturnal boundary layer, as revealed by the surface turbulence σ_w data. In addition, a strong vertical decoupling of the atmosphere was detected by means of SODAR data revealing the existence of a surface-based inversion layer.

The benzene/toluene and benzene/xylene ratios showed a similar time profile, with nearly constant values and a low standard deviation during the night, and higher and spread values in the day, suggesting that photochemically induced reactions affected toluene as well as xylene during transport in the atmosphere from the emission sources to the monitored sites. Significant differences were found in the BTX ratios calculated at the two monitored sites, with much higher values at the site located farther away from the main emission sources, addressing to a stronger chemical reaction of hydrocarbons with oxidants.

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