Atmospheric Environment 42 (2008) 7915–7923

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Influence of the public transportation system on the air quality of a major urban center. A case study: Milan, Italy

Simone Meinardi [a,*], Paul Nissenson [b], Barbara Barletta [a], Donald Dabdub [b], F. Sherwood Rowland [a], Donald R. Blake [a]

[a] Department of Chemistry, University of California, 531 Rowland, Irvine, CA 92697-2025, USA
[b] Department of Mechanical and Aerospace Engineering, University of California, Irvine, USA

ARTICLE INFO

Article history:
Received 14 February 2008
Received in revised form 27 June 2008
Accepted 2 July 2008

Keywords:
Gas-chromatography
Non-methane hydrocarbons
Urban pollution
Tropospheric ozone
Vehicular emission

ABSTRACT

A sampling campaign was conducted in the city of Milan, Italy before and during a transportation strike in January 2004. This strike provided a unique opportunity to investigate the influence of public transportation on the air quality in a major metropolitan area. Twenty-four air samples were collected each day around the city on January 2nd, 7th and 9th. The samples were analyzed for methane, carbon monoxide, non-methane hydrocarbons (NMHCs), halocarbons and alkyl nitrates. Significant differences in the mixing ratios were observed among the three days of sampling, with January 2nd showing the lowest concentrations as a result of decreased activity in the city during the holiday season. January 9th showed the highest NMHC concentrations because of increased vehicular activity in the city due to a public transportation strike. This paper investigates the correlation between the increased number of vehicles and decreased air quality because of a reduction in public transportation. Computer simulations were able to reproduce measurements of ozone production during the January 2004 strike and a July 2005 strike. The measurements and simulations suggest that reduced VOC emissions due to the existence of public transportation lowers peak ozone by 11–33% during the summer months.

1. Introduction

Volatile organic compounds (VOCs) and nitrogen oxides (nitrogen monoxide, NO, and nitrogen dioxide, NO_2) are the most important chemical precursors of tropospheric ozone (O_3) formation in the urban environment (Seinfeld and Pandis, 1998). Volatile organic compounds undergo a series of chemical and physical transformations, depending both on the specific organic compound and the composition of the troposphere. The most important chemical reaction of VOCs in the troposphere is with the hydroxyl radical (OH) (Finlayson-Pitts and Pitts, 2000). Following the initial reaction with OH, a complex series of chemical transformations occur, leading to the oxidation of NO to NO_2. The photolysis of NO_2 ($\lambda < 420$ nm) releases oxygen in its ground state, which can react with molecular oxygen to form ozone.

Non-methane hydrocarbons (NMHCs) generally constitute the majority of the VOCs in urban areas. Most of the NMHCs in urban areas are emitted from anthropogenic sources, such as power plant combustion, vehicular emissions, and industrial usage. Air quality has been studied extensively in rural areas (Hagerman et al., 1997; Gioia et al., 2006), urban areas (see review articles such as Fenger, 1999; Mayer, 1999; Baldasano and Jimenez, 2003), and megacities worldwide (Molina and Molina, 2004; Gurjar and Lelieveld, 2005; Guttikunda et al., 2005; Goyal et al., 2006). However, few studies focus on the impact of public

* Corresponding author.
E-mail address: smeinard@uci.edu (S. Meinardi).

1352-2310/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2008.07.046

transportation on the air quality of a large urban center (Gambini-Rossano et al., 2006) and instead concentrate on the emission of gases and particulate matter by buses, showing increased amounts of carcinogenic pollutants such as polycyclic aromatic hydrocarbons (Tavares et al., 2004; Kado et al., 2005; Lim et al., 2005).

Milan is the most important city of Italy economically, with a population of 1.7 million people (3% of the total population of Italy). A large public transportation system supports the three million people living in the greater metropolitan area of Milan (including the surrounding suburbs). A 1995 survey showed that 28% of the population in or around Milan used public transportation as the main mode of transportation, increasing to 41% within the city (ATM, 2006). At the end of 2005, 122 different public transport routes operated in Milan, including three underground lines, 21 electric powered lines and 58 routes for buses equipped with catalytic converters and particulate filters. As of 2006, the public transportation system reached an average of 20 bus stops per km, not including the underground system (ATM, 2006).

Several field campaigns have examined the air quality in the area around Milan. For example, in 1998 the Pianura Padana Produzione di Ozono (PIPAPO) campaign investigated the impact of emissions originating from Milan on the regional air quality of the northern Po Valley (Neftel et al., 2002). At sites downwind of Milan, ozone mixing ratios as high as 195 ppbv have been measured (Dommen et al., 2002; Polla Mattiot et al., 2002; Baertsch-Ritter et al., 2003). Furthermore, a study was conducted on the sensitivity of ozone production to the VOC/NO_x ratio (Spirig et al., 2002). However, the PIPAPO campaign focused primarily on ozone formation in the northern Po Valley. This study complements the PIPAPO campaign by including a speciation of NMHCs in the metropolitan area of Milan during different traffic regimes. In addition, the absence of an active public transportation system during this study provides a unique opportunity to quantify the effect of increased private traffic on air quality.

This paper quantifies the importance of the public transportation system on the air quality of a large industrial city (Milan, Italy). Three sampling days in January 2004 (2nd, 7th and 9th) represent three snapshots of the VOC composition in the atmosphere of Milan. The data from this sampling campaign are extrapolated to create a more general picture of the Milan atmosphere in the absence of a public transportation system.

2. Experimental

During the month of January 2004, 72 whole air samples were collected on three different days around the city of Milan, Italy, then shipped back to the University of California, Irvine, where they were analyzed for methane (CH_4), carbon monoxide (CO), carbon dioxide (CO_2), and VOCs (see Colman et al., 2001 for a complete description of the analytical system). The accuracy and precision are 1% and 2 ppbv, respectively, for both CH_4 and CO, and 1% and 3 ppmv for CO_2. The accuracy for the NMHCs ranges from 1 to 10%, while the precision of the measurements varies by compound and by mixing ratio. For example, the measurement precision is 2% or 1.5 pptv (whichever is larger) for the alkanes and alkynes, and 3% or 3 pptv (whichever is larger) for the alkenes. The limit of detection for the NMHCs is 10 pptv.

The first 24 samples were collected on January 2nd (Friday) at different locations throughout Milan, namely in parks or open areas away from local point sources in order to collect integrated ambient air. These samples were assumed to be representative of the background of the city during the wintertime holiday season. In Italy, schools were closed throughout the Christmas break of 2003/2004 until January 6th, 2004, during which time many people were away from the city, particularly during the days following Christmas and New Year's Day. In addition, most family businesses were closed and large industries slowed production during the holiday season. However, all activities returned to normal levels by January 7th (Wednesday). The second set of 24 samples was collected on January 7th, which was representative of an average working day in Milan. The last set of 24 samples was collected on January 9th (Friday) during a public transportation strike that affected the movement of vehicles in and around the city. It should be noted that during the entire winter season, public vehicles not equipped with catalytic converters are not allowed in the city during rush hours (7 a.m. to 10 a.m. and 4 p.m. to 7 p.m. local time). In addition, only vehicles with special permits can circulate in the downtown area. However, during the public transportation strike these restrictions were not enforced and all vehicles were permitted to circulate in the city, resulting in a significantly different car fleet that included old vehicles with no catalytic converters. During the sampling campaign the meteorological conditions did not vary much, with drizzling rain and average temperatures for the three days of sampling ranging between 3.5 °C and 5.0 °C.

3. Results and discussion

Carbon monoxide, CO_2, CH_4 and a total of 69 NMHCs, including 29 C_2–C_{11} alkanes, 23 C_2–C_8 alkenes, three alkynes (ethyne, propyne and 2-butyne), and 14 aromatics were quantified in this study. To determine whether air masses originating from different regions could have influenced the sampling campaign, 4-day back trajectories were calculated using the National Oceanic and Atmospheric Administration (NOAA) HYbrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT), (NOAA, 2006). No significant differences were observed in the back trajectories for January 7th and 9th (Fig. 1b,c) with air masses passing over France and reaching Milan from the southwest. In contrast, the air mass for January 2nd originated from the northeast (Fig. 1a). However, the low NMHC mixing ratios found on January 2nd are most likely due to the extremely low number of circulating vehicles (see discussion below), even though a different air mass composition cannot be completely ruled out.

The minimum, maximum, median and average mixing ratios of the 20 most abundant NMHCs for the combined three days of sampling are listed in Table 1. This subset of hydrocarbons accounts for about 90% of the total measured NMHC abundance. Methyl tert-butyl ether (MTBE) and 1,3-

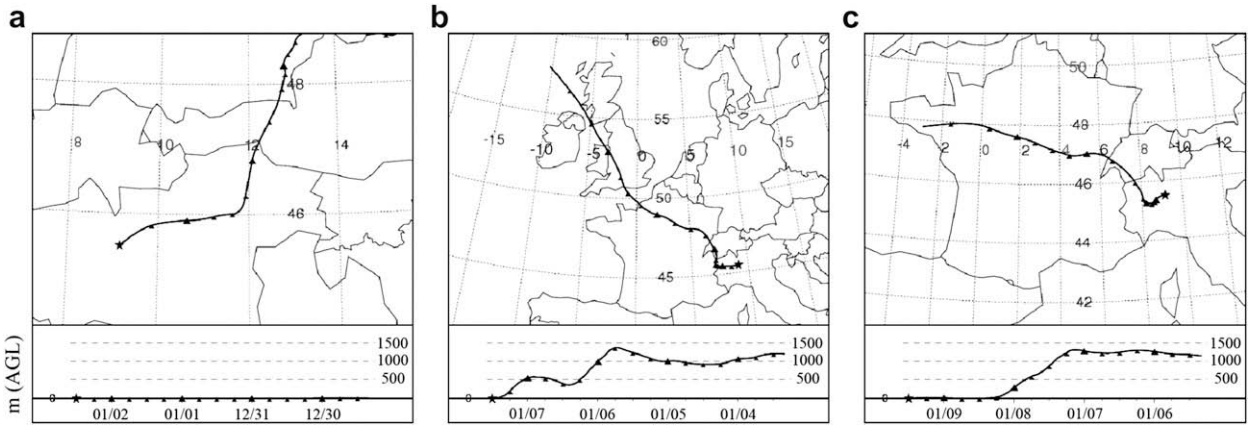

Fig. 1. Four days back trajectories calculated using the NOAA HYSPLIT model for the city of Milan, Italy on (a) January 2nd, (b) 7th and (c) 9th 2004 respectively. (source 45.50 N, 9.16 E. AGL; above ground level).

butadiene are also included in Table 1 because 1,3-butadiene is a toxic and carcinogenic compound (EPA, 2007) and MTBE is a useful vehicular emission tracer emitted into ambient air through tailpipe exhaust and evaporation of gasoline (Chang et al., 2003, Wu et al., 2006). Ethane, ethene, ethyne, and propane were the most abundant compounds during the three days of sampling, with the same ranking order. It can be also noted that half of the measured aromatic species (seven out of 14) were among the 20 most abundant gases. Benzene and toluene measured in this study can be compared to measurements carried out in the city of Verzago (about 35 km north of downtown Milan; Steinbacher et al., 2005). In Verzago, samples collected in a semi-rural environment in June 1998 and August 2002 had benzene mixing ratios lower than 1 ppbv, while in September 2003 levels up to about 2 ppbv were measured. In the same location, the majority of the samples collected in June 1998 and August 2002 had toluene mixing ratios between 0.5 and 2.5 ppbv, while higher levels were reported in September 2003 (1–4 ppbv).

Table 1
Minimum, maximum, median, and average concentration for a subset of NMHCs measured in January 2004 in Milan

Species	Min	Max	Median	Average	SD
CO (ppbv)	430	2220	970	990	310
CO_2 (ppmv)	390	530	440	440	30
CH_4 (ppmv)	1.963	2.496	2.252	2.212	0.161
Ethane	3980	13020	9330	8600	2770
Ethene	2760	13320	7800	7410	2500
Ethyne	2750	17760	7210	7100	2640
Propane	1980	11990	5680	5300	2090
Toluene	920	8560	3590	3720	1690
n-Butane	1250	5850	3400	3350	1220
i-Pentane	930	6540	3300	3210	1300
i-Butane	670	8130	1910	1920	1040
Propene	410	3080	1530	1510	640
Benzene	700	2800	1570	1500	440
2-Methylpentane	300	3130	1270	1280	660
m-Xylene	280	3030	1100	1090	530
n-Pentane	330	2150	960	1050	500
3-Methylpentane	160	2710	630	720	480
o-Xylene	160	1540	560	560	260
n-Hexane	90	4760	270	540	700
2,2-Dimethylbutane	120	1200	510	510	220
1,2,4-Trimethylbenzene	130	1260	430	470	220
p-Xylene	120	1270	470	460	220
Ethylbenzene	130	1180	460	460	210
1,3-Butadiene	58	340	150	150	60
MTBE	56	560	190	200	100

All the mixing ratios are in parts per trillion by volume unless otherwise stated. SD, standard deviation.

During our study within the urban area of Milan, higher concentrations were measured for both aromatic compounds compared to Verzago (Fig. 2). Steinbacher et al. (2005) also reported benzene and toluene levels measured in Bresso, 5 km north of downtown Milan. Measurements were conducted at a location inside the freeway belt around Milan with heavy traffic present at all times. As a result of the direct impact of vehicle emissions, high levels of VOCs were observed, with benzene peaks of up to about 7 ppbv and toluene levels between 1 and 6 ppbv in the majority of the samples collected (toluene mixing ratios higher than 10 ppbv were measured in several samples). Concentrations measured on the last two days of sampling of our Milan campaign, in particular on January 9th, were comparable to the mixing ratios measured at the Bresso location.

The general trend observed for benzene and toluene, with increasing concentrations from the first to the last day of sampling (Fig. 2) was also observed for the other gases. A significant enhancement in mixing ratios was observed when comparing the emissions of January 2nd with those for January 7th and 9th. An average increase of 40 and 55% in the total mixing ratios was calculated for January 7th and 9th respectively, compared to January 2nd.

A possible correlation with the vehicular fleet was investigated because no relevant meteorological changes were observed for January 7th and 9th. A public transportation strike occurred on January 9th allowing for unrestricted vehicular movement throughout the city at any time. Video recorded traffic data are available for four different locations in Milan: one in downtown (Via Senato), one in an urban area (Viale Eginardo), and the last two (Via Stephenson and Corsico) in the suburbs close to the main access roads to the city. The videos were analyzed and the

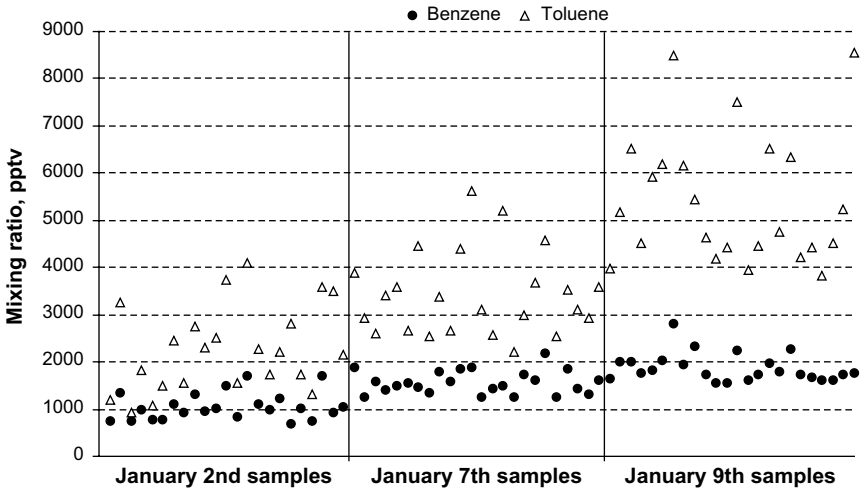

Fig. 2. Mixing ratio of benzene and toluene for all samples collected in Milan.

vehicles segregated in three different categories according to their lengths (cars 1–7 m, trucks 7–14 m, and over 14 m vehicles mainly trailer-trucks-). Table 2 reports the average number of vehicles for the three categories. The number of vehicles in the car category was higher at all stations on January 9th than on January 7th as a result of the transportation strike. The two urban locations experienced the highest increase in traffic likely due of the larger flux of cars towards downtown Milan.

When vehicular emitted compounds were investigated, different levels were observed during each subsequent day of sampling, particularly between the first and the last two days (Fig. 3). For all gases displayed in Fig. 3, average mixing ratios were twice as high on January 9th compared to January 2nd. In addition, average mixing ratios on January 9th were 20–50% higher than on January 7th. For example, the gasoline additive MTBE averaged 284 ± 93 pptv on January 9th compared to 210 ± 82 pptv and 116 ± 49 pptv on January 7th and January 2nd, respectively. On January 9th, the mixing ratio of ethyne, which is a combustion tracer, was about twice that measured on the first sampling day (9.5 ± 2.3 ppbv versus 4.5 ± 1.2 ppbv) and about 30% higher when compared to January 7th.

Table 2
Average number of vehicles at four locations in the city of Milan

Location	Location type	Length (m)	January 2nd	January 7th	January 9th
Viale Eginardo	Urban	1–7	12298	18969	20769
		7–14	300	318	653
		>14	299	79	418
Via Senato	Downtown	1–7	11097	19196	23450
		7–14	418	672	926
		>14	345	425	415
Via Stephenson	Suburb	1–7	37031	54327	55590
		7–14	1610	3150	3716
		>14	568	1065	1471
Corsico	Suburb	1–7	13757	17035	19023
		7–14	861	1842	1928
		>14	457	818	1076

Measurements of NMHCs at the same location on different sampling days were compared because the NMHC sources present within the city could have varying impacts at different urban sites due to the complex nature of mass transport and gas-phase chemistry. Using Stanford Graphics' inverse square method, concentration matrices were calculated for the different gases studied. Fig. 4 shows concentration color contours of CO, ethene, benzene, toluene and tetrachloroethene (C_2Cl_4) for the three sampling days. Carbon monoxide, ethene, and benzene were selected because they are recognized tracers of vehicle emissions (Baldasano and Jimenez, 2003; Calbó et al., 2005); toluene because it has both industrial and vehicular sources; C_2Cl_4 is a widely used industrial solvent (Simpson et al., 2004). The enhancement areas throughout the city were the same for the well-known combustion species CO, ethene and benzene (Fig. 4). Toluene showed similar enhancements, although some areas in the east side of the city had different trends when compared to the other combustion products (Fig. 4). A dual emission component (vehicular and industrial) was most likely responsible for this toluene enhancement. The presence of additional industrial emissions for January 9th, compared to January 7th, is supported by the increase of C_2Cl_4, dichloromethane (CH_2Cl_2), and trichloroethene (C_2HCl_3) mixing ratios, both used as solvents in many industrial activities. However, enhancement areas for the halogenated solvents were different from those of the vehicular emitted species, confirming different sources for these two classes of compounds. The meteorological parameters recorded by the fixed monitoring stations measured an average wind speed of 5.4 km/h for the week of the sampling (ARPA Lombardia, 2006), corresponding to a ventilation time of 3 h for the urban area of Milan. During the sampling campaign, meteorological conditions showed the absence of a stagnant air mass, suggesting that different industrial emissions were responsible for the solvent enhancements measured on the sampling days. Increases in industrial emissions were expected, as a result of the resumption of many activities following the holiday season.

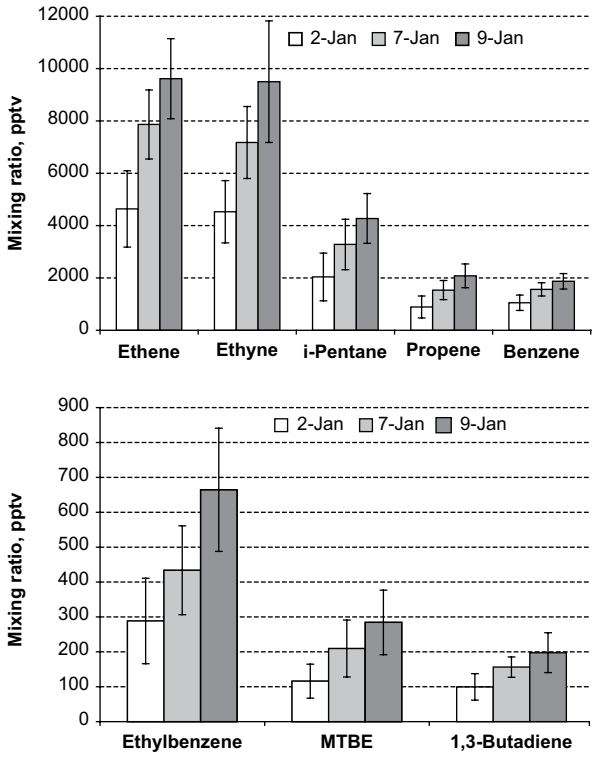

Fig. 3. Average mixing ratio of selected NMHCs measured on January 2nd, January 7th and January 9th, 2004 in Milan. The bar represents the 1-sigma standard deviation.

The correlation and the slope between selected compounds were investigated to determine further the role of vehicular emissions on the measured levels of NMHCs. Overall, the coefficient of determination with respect to CO and ethyne for vehicular emitted compounds (especially alkenes) were higher for the samples collected on January 9th compared to January 7th, suggesting that the increased traffic circulation was responsible for the enhanced mixing ratios throughout the city. For instance, when the samples collected on January 7th are considered, the coefficient of determination (R^2) calculated for the plot of CO versus ethene and CO versus ethyne were 0.71 and 0.55, respectively. Higher coefficients of determination (R^2 of 0.85 and 0.74) were then calculated for the same correlation plots on January 9th (Fig. 5). Also, the R^2 calculated between ethyne and benzene on January 7th ($R^2 = 0.74$) improved to 0.89 on January 9th.

The composition of the vehicle fleet was affected significantly by the public transportation strike on January 9th; vehicles not equipped with catalytic converters were allowed in the city during the strike but not on January 7th. The ethene/ethyne ratio is a good indicator of the presence of a fleet equipped with catalytic converters; vehicles without a catalytic converter produce lower ethene/ethyne ratios (about 1; Hoekman, 1992) compared to vehicles with a catalytic converter (3 or greater; Duffy and Nelson, 1996). The ratio calculated on January 9th was much lower than the ratio calculated on January 7th (0.57 versus 0.96), demonstrating that the fleet likely gained vehicles without catalytic converters during the strike. In addition, a change in the ratio of the two combustion products 1,3-butadiene and CO between January 7th and January 9th (0.18 versus 0.29) was observed, probably due to a change in the vehicle fleet. In summary, the elevated levels and different slopes of selected NMHCs measured on January 9th are attributed to the lack of the public transportation system in Milan, which resulted in a different mix of circulating vehicles.

Many other parameters – such as NO_x emissions and meteorological conditions – must be considered in order to determine whether the enhanced NMHCs (attributed to the increased number of circulating vehicles) would effectively lead to a larger ozone production. In order to better understand the data, a box model was developed to simulate chemical and physical processes in Milan. The size of the modeling region was set to 13.67×13.67 km ($187\ km^2$) with a 500-m boundary layer height (Argentini et al., 1999; Allegrini et al., 1994). Emission rates were calculated for each gas, and NO_x concentrations were obtained from the public monitoring network (ARPA Lombardia, 2006). Despite the lack of specific data regarding the height of the planetary boundary layer (PBL) in Milan for the days studied, literature data for other Italian cities (Del Guasta, 2002), together with the current meteorological conditions in Milan at the time of the sampling, were used to determine this parameter.

In general, the concentration of species i follows the atmospheric reaction diffusion equation:

$$\partial c_i/\partial t + \partial u c_i/\partial t = D(\partial^2 c_i/\partial t^2) + Q_{\mathrm{chem},i} + Q_{\mathrm{depos},i} + S_i \quad (1)$$

where c_i is the concentration of species i, u is the air mass velocity, D is the diffusion constant, $Q_{\mathrm{chem},i}$ is the rate change of species i from gas-phase chemistry, $Q_{\mathrm{depos},i}$ is the loss rate of i due to deposition, and S_i is the emission rate of i.

It was assumed that the air mass entering Milan contained species at rural area concentrations. These concentrations were incorporated in the model as Dirichlet boundary conditions (Haberman, 2004). The dry deposition mechanism was adapted from the CIT model (Shieh et al., 1986), and was incorporated in the modeling region as a bottom boundary condition. Rates of dry deposition were calculated assuming that the entire Milan area is 'mixed urban' containing residential, commercial and industrial structures. The top of the modeling region incorporated a no-flux boundary condition because of the existence of a boundary layer at that height. Inside the well-mixed cell the model accounts for 124 species that may undergo 361 reactions. The chemical mechanism used is the Caltech atmospheric chemistry mechanism (Griffin et al., 2002).

The box model inputs are emission rates (NMHCs and NO_x), temperature, wind speed, relative humidity, total solar radiation, and UV radiation. Due to limited data, the box model assumed that these parameters were uniform over the entire Milan area at a given time. The temperature, wind speed, relative humidity, and total solar radiation were obtained from the fixed stations of the monitoring network in Milan (ARPA Lombardia, 2006). It was assumed that the UV radiation was attenuated by 70% on January 7th and 9th as a result of an overcast sky (Calbó et al., 2005).

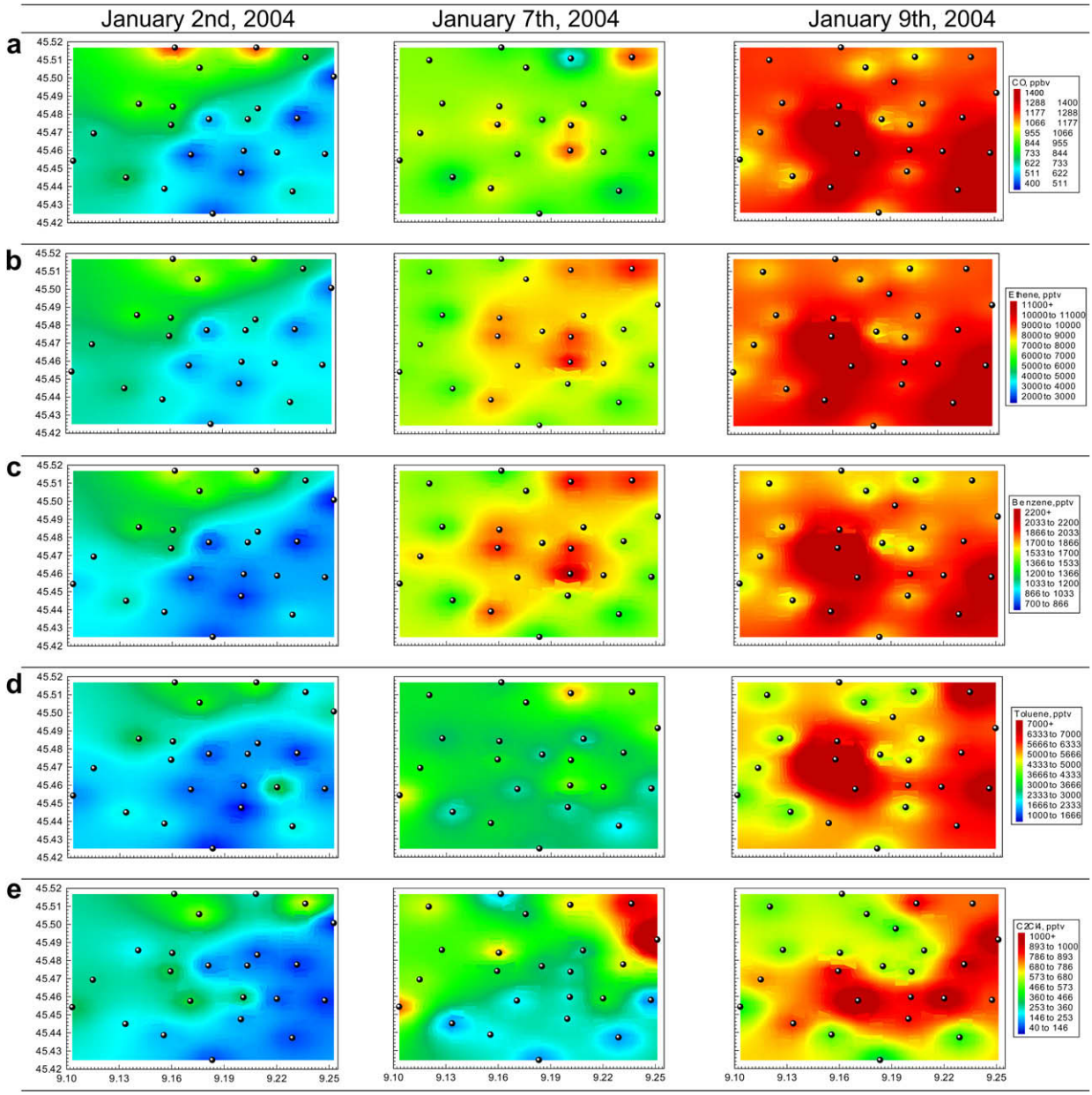

Fig. 4. Concentration color contour plots of (a) CO, (b) ethene, (c) benzene, (d) toluene and (e) C_2Cl_4 for January 2nd, 7th and 9th 2004.

Simulations were performed until steady state results were observed, typically after about five simulation days. The results obtained for January 7th and January 9th are in good agreement with the measured ozone peak values recorded through the fixed monitoring stations. For January 7th, an ozone peak of 4.2 ppbv (peak VOC/$NO_x = 10.1$ ppbC/ppbv) was calculated by the model against a measured value of 6.2 ppbv. For January 9th the calculated and measured values for the ozone peak were 2.5 ppbv (peak VOC/$NO_x = 7.7$ ppbC/ppbv) and 3.2 ppbv, respectively. The agreement between the calculated and the measured values suggests that both the NMHC calculated emission rates and the chosen PBL height are adequate representations of the boundary layer composition in Milan during the sampling campaign. The low ozone concentration is attributed to the scarce photochemistry because of the meteorological conditions and the large NO_x concentrations present at the time, which reacted with the ozone formed.

The public transportation strike of January 2004 occurred during a period of relatively low solar radiation due to overcast skies and a low solar zenith angle. In an attempt to describe the effect of a similar public transportation strike during the summer months (a period of relatively high solar radiation), calculations were performed assuming the same vehicular emission rates during

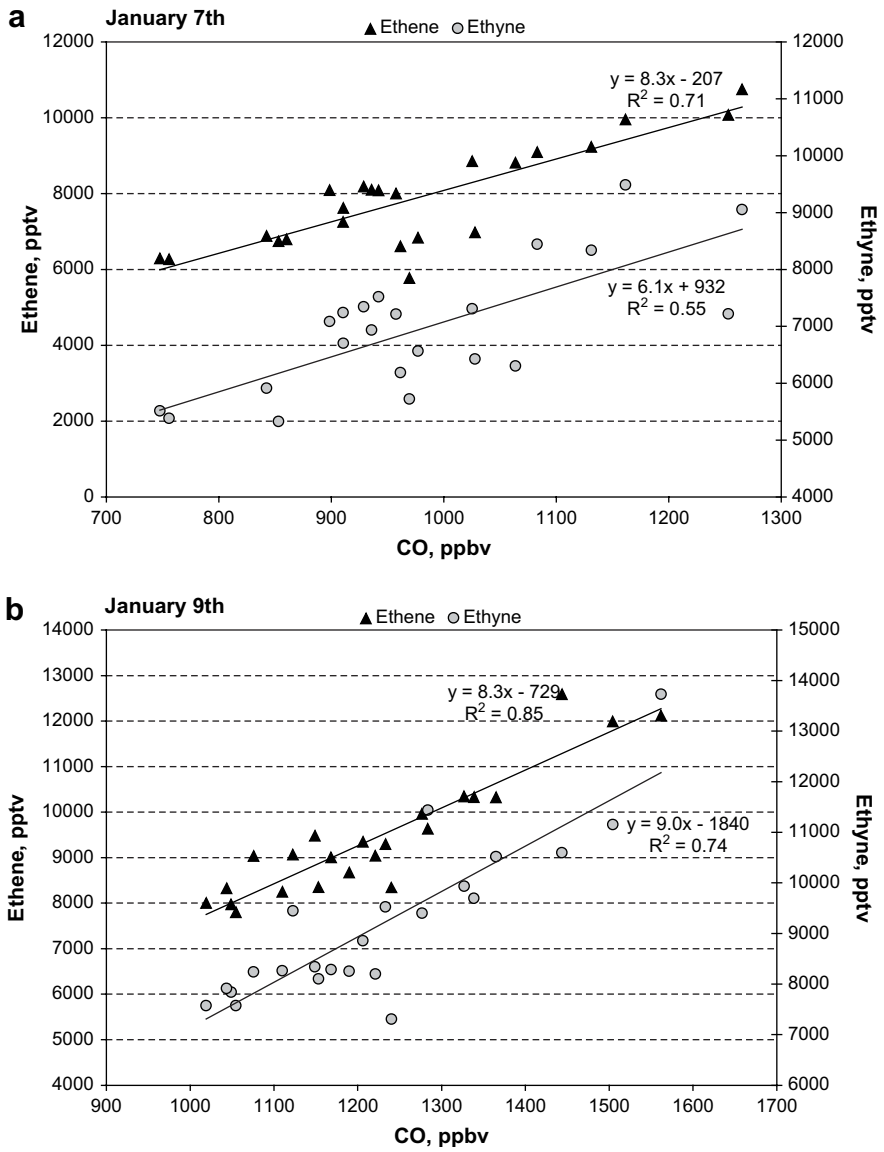

Fig. 5. CO versus ethene and ethyne for (a) January 7th and (b) January 9th, 2004. An exceptionally high ethyne mixing ratio measured on January 7th was excluded from the overall correlation (11 ppbv), while one exceptionally high mixing ratio of CO was excluded on January 9th (2.2 ppmv).

winter and summer. July 14th and 15th 2005 were chosen since a public transportation system strike occurred on the 15th and the meteorological conditions were the same during both days. Summer NO_x emission rates (calculated using data from the monitoring network of Milan) were used, together with the NMHC emission rates calculated from the winter.

Two sets of simulations were performed to study the summer episode. The first set was conducted using the January 7th NMHCs emissions coupled to the NO_x emissions for July 14th, plus the January 9th NMHC emissions coupled to the NO_x emissions for July 15th. July 14th was chosen as a reference day (representing a normal summer working day) for comparison with the day of the strike (July 15th) because, as noted above, almost identical meteorological conditions (sunny and clear skies) were reported for the two days. The meteorological parameters used in all of the summer simulations were the actual conditions recorded through the fixed network of monitoring stations (ARPA Lombardia, 2006). This first set of simulations predicted an ozone enhancement of 33% on July 15th compared to July 14th. However, this first set of simulations produced high VOC/NO_x ratios.

A second set of simulations was performed by multiplying the NO_x emission rates by a factor of three, so that a VOC/NO_x ratio of about 8 was obtained at the end of the calculation. A VOC/NO_x ratio of 8 is similar to the ratio obtained for Milan during the winter season. This VOC/NO_x ratio decrease caused the ozone peak to increase by 11% on July 15th compared to July 14th. Through the fixed

monitoring network, ozone peaks of 86 ppbv were measured on July 15th, or a 21% increase compared to 68 ppbv measured on July 14th. Despite using NMHC winter emission rates as a surrogate for summer values and the possibility of underestimated biogenic species (mostly isoprene) for the summer simulations, good agreement is still achieved between the calculated and measured ozone peaks in terms of percentage enhancement.

4. Conclusions

The sampling campaign performed in Milan during the winter of 2004 was used to determine the impact of the public transportation system on air quality. The samples were collected during a 3-day period, with the last day of sampling occurring during a public transportation system strike. All of the NMHC concentrations were highly enhanced during the strike. These enhancements were a result of the presence of a stronger combustion source (i.e. vehicular emissions) throughout the city, as indicated by the recorded increase of circulating vehicles. Modeled ozone concentrations for the winter episode were in good agreement with measured values. Emission rates calculated using the winter measurements were then used to determine ozone concentrations during a public transportation strike in the summer. Box model simulations indicate that for summer months the public transportation strike in Milan resulted in 11–33% more local ozone. These calculated enhancements are in good agreement with the measured ozone peaks for the selected days, which showed that the measured ozone peak increased 21% on the day of the public transportation strike.

Measurements and model simulations demonstrate that the public transportation system for Milan impacts air quality by reducing ozone levels during the photochemically active summer months. Milan is representative of other major European cities and it is expected that this result applies to other urban areas. Increasing the availability of public transportation has the potential to improve significantly the air quality of major metropolitan regions.

Acknowledgements

We want to thank Dr Silvana Angius of the Associazione Regionale per l'Ambiente and Dr Mita Lapi of the Fondazione Lombardia dell'Ambiente for their help in the retrieval of the meteorological and chemical parameters data recorded through the fixed monitoring station of the city of Milan. We thank also Dr Isobel Simpson for her collaboration, Brent Love and Gloria Liu for technical support, and the Comer Foundation for financial support.

References

Allegrini, I., Febo, A., Pasini, A., Schiarini, A., 1994. Monitoring of the nocturnal mixed boundary layer by means of particulate radon progeny measurement. J. Geophys. Res. 99 (D9), 18765–18777.

Argentini, S., Mastrantonio, G., Lena, F., 1999. Case studies of the wintertime convective boundary-layer structure in the urban area of Milan. Italy Boundary-Layer Meteorol 93 (2), 253–267.

Associazione Regionale per l'Ambiente (ARPA) Regione Lombardia, http://www.arpalombardia.it (accessed June 2006).

Azienda Municipale Tranviaria (ATM) di Milano, http://www.atm-mi.it (accessed June 2006).

Baertsch-Ritter, N., Prévôt, A.S.H., Dommen, J., Andreani-Aksoyoglu, S., Keller, J., 2003. Model study with UAM-V in the Milan area (I) during PIPAPO: simulations with changed emissions compared to ground and airborne measurements. Atmos. Environ. 37 (29), 4133–4137.

Baldasano, J.V.E., Jimenez, P., 2003. Air quality data from large cities. Sci. Total Environ. 307 (1-3), 141–165.

Calbó, J., Pagès, D., González, J.-A., 2005. Empirical studies of cloud effects on UV radiation: a review. Rev. Geophys. 43, RG2002. doi:10.1029/2004RG000155.

Chang, C.-C., Lo, S.-J., Lo, J.-G., Wang, J.-L., 2003. Analysis of methyl tert-butyl ether in the atmosphere and implications as an exclusive indicator of automobile exhaust. Atmos. Environ. 37 (34), 4747–4755.

Colman, J.J., Swanson, A.L., Meinardi, S., Sive, B.C., Blake, D.R., Rowland, F.S., 2001. Description of the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-Tropics A and B. Anal. Chem. 73 (15), 3723–3731.

Del Guasta, M., 2002. Daily cycles in urban aerosols observed in Florence (Italy) by means of an automatic 532–1064 nm LIDAR. Atmos. Environ. 36 (17), 2853–2865.

Dommen, J., Prévôt, A.S.H., Neininger, B., Bäumle, M., 2002. Characterization of the photooxidant formation in the metropolitan area of Milan from aircraft measurements. J. Geophys. Res. 107 (D22) LOP 10.

Duffy, B.L., Nelson, P.F., 1996. Non-methane exhaust composition in the Sydney harbor tunnel: a focus on benzene and 1,3-butadiene. Atmos. Environ. 15, 2759–2768.

Environmental Protection Agency (EPA), 2007. Integrated Risk Information System – 1,3-Butadiene. http://www.epa.gov/iris/subst/0139.htm (accessed September 2007).

Fenger, J., 1999. Urban air quality. Atmos. Environ. 33 (29), 4877–4900.

Finlayson-Pitts, B.J., Pitts, J.N., 2000. Chemistry of the Upper and Lower Atmosphere. Academic Press, San Diego.

Gambini-Rossano, L., Passerini, G., Tascini, S., 2006. Impact of local policies on transport pollutant emission. WIT Trans. Ecol. Environ. 86 (Air Pollution XIV), 657–665.

Gioia, R., Steinnes, E., Thomas, G.O., Mejier, S.N., Jones, K.C., 2006. Persistent organic pollutants in European background air: derivation of temporal and latitudinal trends. J. Environ. Monit. 8 (7), 700–710.

Goyal, S.K., Ghatge, S.V., Nema, P., Tamhane, S.M., 2006. Understanding urban vehicular pollution problem vis-a-vis ambient air quality – case study of a megacity (Delhi, India). Environ. Monit. Assess 119 (1-3), 557–569.

Griffin, R.J., Dabdub, D., Seinfeld, J.H., 2002. Secondary organic aerosol: 1. Atmospheric chemical mechanism for production of molecular constituents. J. Geophys. Res. 107 (D17), 4332. doi:10.1029/2001JD000541.

Gurjar, B.R., Lelieveld, J., 2005. New directions: megacities and global change. Atmos. Environ. 39 (2), 391–393.

Guttikunda, S.K., Tang, Y., Carmichael, G.R., Kurata, G., Pan, L., Streets, D.G., Woo, J.-H., Thongboonchoo, N., Fried, A., 2005. Impacts of Asian megacity emissions on regional air quality during spring 2001. J. Geophys. Res. 110 (D20), D20301/1–D20301/18.

Haberman, R., 2004. Applied Partial Differential Equations: with Fourier Series and Boundary Value Problems, fourth ed. Pearson Prentice Hall, New Jersey.

Hagerman, L.M., Aneja, V.P., Lonneman, W.A., 1997. Characterization of non-methane hydrocarbons in the rural southeast United States. Atmos Environ. 31 (23), 4017–4038.

Hoekman, S.K., 1992. Speciated measurements and calculated reactivities of vehicle exhaust emissions from conventional and reformulated gasoline. Environ. Sci. Technol. 26, 1206–1216.

Kado, N.Y., Okamoto, R.A., Kuzmicky, P.A., Kobayashi, R., Ayala, A., Gebel, M.E., Rieger, P.L., Maddox, C., Zafonte, L., 2005. Emissions of toxic pollutants from compressed natural gas and low sulfur diesel-fueled heavy-duty transit buses tested over multiple driving cycles. Environ. Sci. Technol. 39 (19), 7638–7649.

Lim, M.C.H., Ayoko, G.A., Morawska, L., Ristovski, Z.D., Jayaratne, E.R., 2005. Effect of fuel composition and engine operating conditions on polycyclic aromatic hydrocarbon emissions from a fleet of heavy-duty diesel buses. Atmos. Environ. 39 (40), 7836–7848.

Mayer, H., 1999. Air pollution in cities. Atmos. Environ. 33 (24–25), 4029–4037.

Molina, M.J., Molina, L.T., 2004. Megacities and atmospheric pollution. J. Air Waste Manage. Assoc. 54 (6), 644–680.

National Oceanic and Atmospheric Administration (NOAA), ARL HYSPLIT model, http://www.arl.noaa.gov/ready/hysplit4.html (accessed June 2006).

Neftel, A., Spirig, C., Prévôt, A.S.H., Furger, M., Stutz, J., Vogel, B., Hjort, J., 2002. Sensitivity of photooxidant production in the Milan basin: an overview of results from a EUROTRAC-2 Limitation of Oxidant Production field experiment. J. Geophys. Res. 107 (D22) LOP 1/1–LOP 1/10.

Polla Mattiot, F., Gariazzo, C., Buttini, P., Carizi, G., Levy, A., Rebesco, E., 2002. Ozone episode in the Milan metropolitan area: a comparative evaluation of UAM-V and CALGRID models. Water Air Soil Pollut. Focus 2, 471–486.

Seinfeld, J.H., Pandis, S.N., 1998. Atmospheric Chemistry and Physics. John Wiley & Sons, New York.

Shieh, C.M., Wesely, M.L., Walcek, C.J., 1986. A dry deposition module for regional acid deposition. EPA report under agreement DW89930060-01.

Simpson, I.J., Meinardi, S., Blake, N.J., Rowland, F.S., Blake, D.R., 2004. Long-term decrease in the global atmospheric burden of tetrachloroethene (C_2Cl_4). Geophys. Res. Lett. 31. doi:10.1029/2003GL019351.

Spirig, C., Neftel, A., Kleinman, L.I., Hjorth, J., 2002. NO_x versus VOC limitation of O_3 production in the Po Valley, local and integrated view based on observation. J. Geophys. Res. 107 (D22) LOP 4/1–LOP 4/19.

Steinbacher, M., Dommen, J., Ordonez, C., Reimann, S., Gruebler, F.C., Staehelin, J., Prevot, A.S.H., 2005. Volatile organic compounds in the Po Basin. Part A: Anthropogenic VOCs. J. Atmos. Chem. 51 (3), 271–291.

Tavares, M., Pinto, J.P., Souza, A.L., Scarminio, I.S., Solci, M.C., 2004. Emission of polycyclic aromatic hydrocarbons from diesel engine in a bus station, Londrina, Brazil. Atmos. Environ. 38 (30), 5039–5044.

Wu, B.-Z., Hsieh, L.-L., Sree, U., Chiu, K.-H., Lo, J.-G., 2006. Determination and impact of volatile organics emitted during Rush Hours in the ambient air around gasoline stations. J. Air Waste Manage. Assoc. 56 (9), 1342–1348.