



Volatile organic compound levels at one site in Rome urban air

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ABSTRACT

Volatile organic compound (VOC), nitrogen dioxide (NO₂) and ozone (O₃) concentrations were measured at one site in Rome urban air during 2011. The seasonal mean concentrations of VOCs varied from 78 µg m⁻³ in winter to 37 µg m⁻³ in summer. Total aromatic concentration was reduced by 59% during summertime, alkanes of 39% and alkenes of 71%. VOC diurnal pattern exhibited a primary peak during the morning and a secondary peak in the evening hours coinciding with rush-hour traffic. The high correlation between benzene and toluene evidenced their common origin probably due to vehicular traffic. In summer isoprene diurnal profile showed both biogenic and anthropogenic origin. NO₂ and O₃ daily trends during summertime evidenced both photostationary state typical conditions and photochemical smog episodes. VOC and O₃ trends also evidenced a reduction in VOC levels during O₃ formation. Based on the Maximum Incremental Reactivity scale, the highest contributors to ozone production in Rome were propene, ethene and toluene. Comparing data found in Rome at the same site in 1992, 2007 and 2011, a decreasing trend in VOC levels was observed, suggesting the effectiveness of European Directives on air quality. In addition, our results were confirmed by similar data found in other urban areas around the world.

Keywords: Volatile organic compounds, isoprene, vehicle emissions, ozone, Maximum Incremental Reactivity



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1. Introduction

Quantification of volatile organic compounds (VOCs) in the ambient air is important for air quality assessment and for understanding the photochemical formation of smog. One of the main constituents of photochemical smog is ozone (O₃) which has adverse effects on human health at high concentrations. O₃ is formed by a series of complex atmospheric reactions between nitrogen oxides (NO_x) and VOCs in the presence of sunlight and under favorable meteorological conditions.

Researchers have focused on urban VOC levels, especially aromatic organic compounds, due to the carcinogenic nature of some compounds. Benzene is a known carcinogen and exposure to high ambient concentrations represents a considerable health risk, while toluene is toxic for the central nervous system (WHO, 1986). VOCs are emitted from various urban, industrial and natural sources. Previous works have shown that the dominant anthropogenic sources in the urban areas are vehicle exhaust, gasoline evaporation, emissions from the commercial and industrial use of solvents and from liquefied petroleum gas (LPG) (Perry and Gee, 1995; Na et al., 2004; Barletta et al., 2008; Parra et al., 2009). In rural areas, biogenic emissions may contribute significantly to the levels of VOCs (Guenther et al., 1993; Borbon et al., 2001; So and Wang, 2004), but in urban areas this contribution is often negligible.

Several studies have been carried out to investigate the VOC levels in urban (Broderick and Marnane, 2002; Fernandez-Villarrenaga et al., 2004; Xie et al., 2008) and rural areas (Borbon et al., 2004; Wang et al., 2004a; Parra et al., 2006) around the world, but only a few studies, regarding atmospheric VOC concentrations

in Italy, have been published (Brocco et al., 1997; Latella et al., 2005; Meinardi et al., 2008; Fuselli et al., 2010). Concerning Rome urban air, only two studies have been reported, however both of them have some limitations: Brocco et al. (1997) dealt with twenty year older data, whereas a limited number of VOCs have been analyzed by Fuselli et al. (2010). Over the last two decades, European Directives have been introduced to improve the parameters of air quality affected by traffic-related emissions. In particular Directive 2008/50/EC (CEU, 2008) recommended that a whole list of VOC ozone precursors should be measured so their trends could be analyzed, the efficiency of emission reduction strategies checked and sources of emissions determined. Moreover, Directive recommended that the mandatory measuring station should be preferably located in the urban background and should not be directly influenced by strong local sources such as traffic or large industrial installations. However, the full VOC spectrum monitoring at least at one traffic site has been recommended. Rome is the largest city in Italy with surface area of 1 300 km², 2.5 million inhabitants and has the highest number of vehicles (~2.5 million as of 31.12.2010) among Italian cities. In the area around Rome there are no heavy industries and the nearest power plant is at about 100 km from the urban area.

Air pollution originates primarily from motor vehicle traffic (60%) and secondarily from home heating devices (30%), which together account for more than 90% of gaseous pollutants and airborne particles (Kirchmayer et al., 2005).

In this study, continuous concentration data of VOCs, O₃ and nitrogen dioxide (NO₂) were measured in the urban air of Rome from December, 2010 to the end of 2011. Twenty six VOCs were measured and the European Legislation recommended the

determination for 24 of them. We reported diurnal and seasonal variations of VOC levels and their influence on the formation of photochemical smog.

In addition, as a VOC decreasing trend has been reported in studies conducted in different European cities (EMEP/CCC, 2002; Plass-Dulmer et al., 2002; Plass-Dulmer and Berresheim, 2007; von Schneidmesser et al., 2010) and in the Air Quality in Europe report (EEA, 2012), VOC mean concentrations were compared with data measured in Rome at the same site in 1992, 2007 and 2011. Moreover, in order to put the Rome data in a global perspective, we discussed our VOC levels with those obtained in other urban areas of the world.

The obtained results enabled us to get some answers about the effectiveness of European Directives to reduce traffic-related emissions in Rome and provided a recent baseline data, performed after European Directive enforcement, from which to monitor future changes in the ozone precursor levels.

2. Methods

2.1 Sampling site description

The measurements presented in this work were carried out at the pilot station located in a street canyon in downtown Rome at the Italian National Institute for Occupational Safety and Prevention building (near S. Maria Maggiore Cathedral). The site, characterized by high density of vehicular traffic, is representative of urban center. Benzene levels of this site correspond to those measured in Rome at the Regional Environmental Protection Agency (ARPA Lazio) monitoring stations classified as traffic.

Meteorological data of 2011 were collected by a weather station (STMAIR; NESAs) located on the roof of the building (25 m in height). The average temperature varied from 9 °C (winter) to 26 °C (summer) while total average radiation increased from 67.32 W m⁻² in winter to 307.69 W m⁻² in summer.

2.2. VOC, NO₂ and O₃ measurements

Continuous measurements of VOC, O₃ and NO₂ concentrations were carried out between December 21, 2010 and December 31, 2011.

A Syntech Spectras 955 gas chromatograph (GC) was used for continuous measurements of 26 hydrocarbon concentrations with 30 minute time intervals. The height of air intake was 3.5 m above the ground level. The daily averages were taken into account when the measurements covered more than 90% of the daily hours.

The Syntech Spectras solution is an analytical system consisting of two sampling systems and two separate column systems: one for the C₂–C₅ and one for the C₆–C₁₀ fraction. The analytical system is equipped with three detectors: two photo ionization detectors (PID) and a flame ionization detector (FID). A detailed description of the analytical setup can be found elsewhere (Wang et al., 2004b; Xie et al., 2008).

FID was used for the light hydrocarbons (C₂–C₅), C₆–C₁₀ analysis was performed by PID and FID. For each analysis, an air sample with a volume of 250 mL was sampled. Instrument calibration was performed before each seasonal campaign by using a gas standard containing 29 target species with mixing ratios of 1 ppm in nitrogen (Sapio, Italy), prepared by the gravimetric method (ISO, 2001). The detection limits are estimated to be 0.01 to 0.2 µg m⁻³, and the uncertainty is estimated to be 5%.

NO₂ and O₃ concentrations were measured by means of a Differential Optical Absorption Spectroscopy (DOAS) (mod. AR500,

OP SIS, Sweden). The DOAS technique is described elsewhere (Hallstadius et al., 1991; Platt, 1994). The distance between emitter and receiver is 280 m. The DOAS monitors only gaseous pollutants. Some gases are monitored independently, while some are examined simultaneously. Therefore, the number of gases examined and the amount of time chosen to monitor each gas affects the overall measurement cycle of the instrument. For this application, the measurement cycle was 5 min, the monitoring times for NO₂ and O₃ were 30 seconds and 2 min respectively. For the pollutants monitored, the manufacture specifies a detection limit of 1 µg m⁻³ for NO₂ and 3 µg m⁻³ for O₃ with a linearity of ±1%.

The contributions of VOCs to local O₃ production were estimated by the Maximum Incremental Reactivity (MIR) values (Carter, 1994; Carter, 2010). MIR is the amount (in grams) of O₃ formed per gram of VOC added to an initial VOC–NO_x mixture, showing how much a compound may contribute to the O₃ formation in the air. This dimensionless coefficient (gram of O₃ formed per gram of VOC emitted), multiplied by the measured VOC concentrations indicates how much the compound may contribute to O₃ formation in the air.

2.3. Data analysis

One-way ANOVA analysis, followed by Student Newman Keuls post-hoc analysis, was performed to compare seasonal VOC variations. Pearson correlation test was carried out to study the relationship between compounds. $p < 0.05$ was considered significant, $p < 0.001$ highly significant.

3. Results and Discussion

3.1 Seasonal concentrations of VOCs

Table 1 lists the seasonal mean concentrations of 26 monitored VOCs. A large and statistically significant ($p < 0.05$) variations was evaluated in seasonal VOC levels, ranging from 78 µg m⁻³ in winter to 37 µg m⁻³ in summer. One-way ANOVA results showed significantly ($p < 0.05$) higher concentrations in winter compared to summer period for all the VOCs, except for ethane. Low variability of ethane could be derived by accumulation in the air due to its relatively long atmospheric life.

Alkanes provided the largest contribution to the total VOCs, followed by aromatics. The most abundant species among alkanes was *i*-pentane which contributed from 38% to 51% of the alkanes and from 22% to 24% of the total VOCs in winter and summer, respectively. Among aromatic hydrocarbons, toluene was the most abundant species which contributed from 48% to 53% of the aromatics and from 13% to 14% of the total VOCs in winter and summer, respectively, followed by *m,p*-xylene and benzene. Ethene and propene were the most abundant species among alkenes and only ethene contributed to 12% (wintertime) and 7.5% (summertime) to the total VOCs.

A recent study (Montero et al., 2010) on a detailed characterization of hydrocarbon emissions from modern two-stroke mopeds (pre-Euro, Euro 1 and Euro 2) showed a larger fraction of unburned alkanes rather than aromatics. In particular, a large rate of *i*-pentane and ethene was revealed. In Rome motorcycles (~404 000) have become an important mode of transportation due to inadequacy of public transport system, traffic congestion, and scarce parking. Based on obtained results we cannot exclude the possible influence of moped emissions on alkane and alkene levels.

In order to compare our data with global ones we considered only studies carried out in recent years (since 2007) and those reporting only the ratio between VOCs and CO have not been considered.

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