LEVELS OF PEROXYACETIL NITRATE IN ROME URBAN AIR

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Abstract
The daily PAN trends are compared with the Ox variable in different meteorological conditions. During the high-pressure period the Ox variable shows minimum values below the ozone background and maximum daytime values which can easily exceed this value (maximum Ox values range between 120-160 ppb). The presence of intense radical activity is confirmed by the trend of PAN concentrations (maximum PAN values range between 20-30 ppb). Basically, the increases of PAN concentrations during the morning day coincide with the maximum positive derivate of Ox. PAN is the only member of nitrogenous compounds produced by photochemical processes and it is the specific indicator of anthropogenic photochemical air pollution.

Key words: PAN; Photochemical pollution; Urban atmosphere.

1. INTRODUCTION
Peroxyacetil nitrate (PAN) is the principal member of a family of nitrogenous compounds produced by action of sunlight on NOx and reactive hydrocarbons. PAN has been known to be a phytotoxicant and lachrymator (Taylor, 1969). There has also been considerations with regard to the role of PAN in human health effects due to exposure to ambient air, especially in the presence of elevated O3. PAN is a suggested agent of skin cancer in photochemically active areas and a possible bacterial mutagen. Damage of various non-biological materials has been reported.

PAN and O3 are the two most important components of photochemical smog, but there are differences in the characteristics of these two compounds. PAN has only very low natural background concentrations in contrast to ozone which has a relevant source in stratosphere. The lifetime of PAN in the atmosphere strongly depends on the ambient temperature and this enables PAN to persist for a longer time at low temperature. Furthermore, PAN is removed only slowly from the atmosphere through dry deposition contrary to ozone where dry deposition represents an effective destruction mechanism. Therefore, long-range transport if PAN is likely to occur and it is generally suggested that PAN might constitute the largest fraction of the natural NOx reservoir. This is supported by observations of the high PAN/NOx ratios in the cool middle free troposphere (Ridley et al., 1990), and the dominance of PAN as the major nitrogen compound in the Artic (Bottenheim and Gallant, 1989).

Precursors of PAN in the polluted areas are specific non-methane hydrocarbons (particularly propene, 1- and 2-butene, 2-pentene), aldehydes (acetaldehyde) and NO2. Its abundance, particularly in air masses polluted by motor vehicle emissions, increases PAN mixing ratios up to several ppbv.

Natural Volatile Organic Compounds (VOCs) such isoprene are of minor importance in urban and near urban atmospheres, where the PAN is the very specific indicator of anthropogenic photochemical air pollution).

In this paper we report measurements of PAN in the urban area of Rome carried out during the period May 2007-April 2008. We also discuss the meteorological conditions that can lead to elevated PAN concentrations and describe the relationships between measured concentrations of PAN, O3, NO2 and HCHO in this environment.

2. EXPERIMENTAL PART
Measurements of PAN were carried out by means of a gas-chromatography (Carlo Erba Instruments, Milan, Italy). An Electron Capture Detector (ECD) equipped with a 106Ni-foil of 10 mCi, was used and a glass tube (length 30 cm, i.d. 2 mm) packed with 10% Carbonwax on Chromosorb 80/100 mesh served as column. Carrier-gas was nitrogen (purity of 99.99%). The flow-rate through the column was 20 mL min-1. The temperature of the GC oven was kept at 35°C, whereas the detector’s temperature was 100°C. An external pump (flow-rate 800 mL min-1) supplied the GC with ambient air, and every 15 min air samples (sampling loop volume 2 mL) were automatically injected into the GC system through a 4-port valve regulated by pressurized air. For the GC conditions described above the PAN retention time was usually about 2 min. The estimated accuracy of the measurements was about ±20%, its precision ±10% and the detection limit is 0.001 ppb. Data were recorded by a Shimazu integrator.

For prepare small PAN amount a mixture of 50 ppm of isobutene and 5 ppm of NO2 diluted in synthetic air was undergone to irradiation by vapor Hg lamp (Schurath and Wipprecht, 1980). Ozone and NO2 have been measured by means of a Differential Optical Absorption Spectrometry (DOAS, Opsi, Sweden) based on the Lambert-Beer's law. For describing the dynamic of the low boundary layer meaning the

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atmospheric stability/instability conditions was used the natural radioactivity by means of the $\beta$-radioactivity of short-lived decay products of Radon (SM200, Opsis) (Avino et al., 2003).

The sampling site was located in downtown Rome (37 m a.s.l.; 41°54'N and 12°30'E; 2.7 million inhabitants), site characterized by high density of autovehicular traffic (about 2.5 millions among cars, motorcycles and bus, source from Automobil Club Italia) and domestic heating. The measurements covered 12-months from May 2007 to April 2008.

3. RESULTS AND DISCUSSION

3.1. PAN levels in Rome

The monthly average PAN concentrations measured during the entire campaign are reported in Table 1. The PAN concentrations reached a maximum of 30.3 ppb with an average daily maximum of 5.7 ppb in summertime and a maximum of 7.3 ppb with an average daily minimum of 2.1 ppb in wintertime.

<table>
<thead>
<tr>
<th>PAN level</th>
<th>Average value</th>
<th>Range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rome (this work)</td>
<td>2.1 (winter)</td>
<td>0.1-7.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.7 (summer)</td>
<td>0.1-30.3</td>
<td></td>
</tr>
<tr>
<td>Santiago</td>
<td>2.4</td>
<td>0.1-7.6</td>
<td>Rubio et al., 2007</td>
</tr>
<tr>
<td>Mexico City</td>
<td>15.0</td>
<td>0.1-34</td>
<td>Marley et al., 2007</td>
</tr>
<tr>
<td>Antartica</td>
<td>9.3</td>
<td>0.8-33.2</td>
<td>Mills et al., 2007</td>
</tr>
</tbody>
</table>

3.2. Trends of PAN, O$_3$ and NO$_2$

In Figures 1 and 2 typical daily trends of PAN determined inside a green park, Villa Ada, in downtown Rome during summer and winter periods, respectively, are reported.
First of all, a clear difference about the amount is shown. During the summer period, the solar irradiation is strong and consequently the PAN production reaches very notable levels (up to 30 ppb) compared with low levels in wintertime (maximum 5 ppb). The really interesting consideration is the occurring of photochemical smog episodes also during cold period when the solar irradiation is very low but the VOC emissions are very significant because both the autovehicular traffic and domestic heating, especially in a great urban area such as Rome. Even if the episodes are limited and PAN does not reach high values, the occurring of this phenomena is important to understand the dynamic of the atmospheric pollution in this area and how the air quality is affected.

In Rome, the total VOC composition (around 80 ppbv) is very complex and almost all the hydrocarbons in the range C2-C9 are present: in particular, alkanes 44.3%, alkenes 36.5% and aromatic 19.2%. An other interesting consideration is the high contribution of ethane (23.6%) and ethene (70.4%) to alkane and alkene fractions, respectively. Considering the origin of these two species (Mayrsohn et al., 1977), the values are due to the strong diesel-vehicle density in downtown Rome.

As it can be seen in Figures 1 and 2, the PAN behavior is almost regular depending strictly on both the meteo conditions and the ozone and HCHO levels in atmosphere, overall the VOC such as described above.

The ozone formation kinetic is also influenced by other factors such as VOC species, the relative reaction coefficients for producing RO2 and OH radicals. It is well-known that nitrous acid (HNO2) and formaldehyde (HCHO) play a fundamental role in processes occurring in atmosphere (Crutzen and Fishman, 1977). In Figures 3 and 4 the trends of PAN, ozone and formaldehyde determined in downtown Rome, are reported.

Figure 3 shows the high correlation between PAN and ozone (Pearson’s coefficient of correlation 0.84) meaning a strict relationship between them. These considerations can be evident especially during stability atmospheric conditions (investigated using the natural radioactivity, i.e. radon trend) when the pollutant dispersion is not favored (from 7th to 18th) whereas during the other periods it shows a low correlation depending on the chemical reactions occurring in atmosphere.

Figure 4 shows that high HCHO concentrations are present in the late morning and afternoon whereas minimum values are found during high solar radiation hours: in particular, the higher levels are determined in the hour range 13.00-15.00 when the highest ozone concentrations are detected. Further, it is possible to evidence that the pollutant behaviors are interesting. In fact, the kinetic between PAN and HCHO is different: in the atmosphere, the formation reaction of HCHO is more rapid than the relative PAN formation whereas the PAN removal is very
quickly. This means that during regular atmospheric mixing conditions (instability conditions) no pollutant accumulation is possible; on the contrary, during stability conditions (i.e., pollutant dispersion is not favored) smog photochemical episodes can occur. The intensity of such phenomena depends on variables above described but the results are higher instantaneous PAN and HCHO levels and consequently maximum concentrations of ozone. Finally, for a photochemical pollution prevention it is important evaluating the relation between ozone and its precursors (VOCs and NOx). This evaluation has been always performed by mathematical models. In this approach we have considered the daily ratios of VOCs/NOx determined in downtown Rome: they range between 1.3 and 5.5.

4. CONCLUSIONS

The daily trends of ozone and PAN are reported and discussed together with the NO2 and HCHO behaviors in relationship with the concentrations of the natural radioactivity (radon) used as parameter for describing the dynamic of low atmospheric boundary layer. PAN has a low chemical reactivity and it represents a selective index of photochemical activity in atmosphere also because it is almost negligible the natural sources on its budget. Furthermore, PAN measurements are also important for investigating photochemical pollution transport phenomena.

5. ACKNOWLEDGEMENTS

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References


