Determination and Role of Peroxyacetil Nitrate in Photochemical Processes in Atmosphere

P. Avino[1], M.V. Russo[2] and K. Movassaghi[3]

[1]Istituto Superiore per la Prevenzione e la Sicurezza del Lavoro (ISPESL), Rome, Italy. [2]Faculty of Agricultural Science, University of Molise, Campobasso, Italy. [3]Dept. Chemistry, University of Isfahan, Isfahan, Iran.

Abstract

Peroxyacetil nitrates (PAN) is the most characteristic photoxidant of a range of secondary pollutants formed by the photochemical reaction of hydrocarbons with nitrogen oxides in the atmosphere: it is phytotoxic and shows an increasing role in human health effects due to ambient air exposure, expecially in presence of high ozone concentrations.

In this paper we report PAN concentrations determined in Rome urban area during winter- and summer-period. PAN measurements were carried out by means of a gas-chromatograph equipped with an ECD detector. Furthermore, there are investigated the relationship between PAN and the variable O_x (=NO_2+O_3) which describes the oxidation process evolution.

Introduction

Peroxyacetil nitrate (PAN, $CH_3C(O)OONO_2$) is the principal member of a family of nitrogenous compounds produced by action of sunlight on nitrogen oxides and reactive hydrocarbons [1]. PAN has been known to be a phytotoxicant and lachrymator. There has also been considerations with regard to the role of PAN in the human health effects due to the exposure in ambient air, especially in the presence of high levels of ozone. PAN is a suggested agent of skin cancer in photochemically active areas and a possible bacterial mutagen.

Even the background level of PAN is not defined, it has very low natural background concentrations [2] so it is very specific indicator of anthropogenic photochemical air pollution; on the contrary ozone has relevant sources in troposphere and consequently the level is high. It should be underlined that very few data of PAN levels in ambient atmosphere are present in literature and so it is very difficult to identify guideline values in air quality evaluation.

Precursors of PAN in the polluted areas are specific non-methane hydrocarbons (NMHC) (particularly, propene, 1-butene, 2-butene, 2-pentene, etc.), aldehydes (formaldehyde, acetaldehyde) and NO_2. Especially in air masses polluted by anthropogenic emissions (i.e., autovehicular traffic, industrial emission and space heating), the NMHC abundance causes a rising of PAN mixing ratios sometime up to several ppbv.

In this paper we report measurements of PAN in the urban area of Rome carried out during the period May 2008-April 2009. We also discuss the meteorological conditions that can lead to elevated PAN concentrations.

Materials & Methods

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 ^{63}Ni-foil of 10 mCi was used a glass tube (lenght 30 cm, i.d. 2 mm) packed with 10% Carbonwax on Chromosorb 80/100 mesh served with a 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. The measurement estimated accuracy was about ±20%, its

precision ±10%, the detection limit is 0.001 ppb.

Ozone and nitrogen oxides were measured by means of Differential Optical Absorption Spectrometry (DOAS) at ISPESL Pilot Station.

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) and domestic heating. The measurements covered 12-months from May 2008 to April 2009.

Results

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.

A clear difference about the amount in these two period is shown. During the summer period (Figure 1), 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). During cold period PAN does not reach high values.

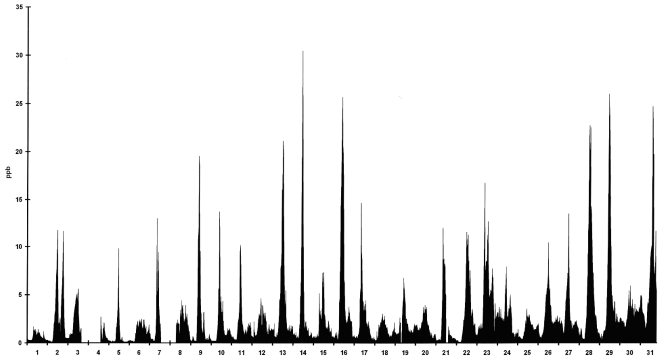

Fig. 1; Typical daily trend of PAN (ppbv) during a summer period.

The PAN behavior is almost regular depending strictly on both the meteorological conditions and the ozone and HCHO levels in atmosphere, overall the Volatile Organic Compounds (VOCs). In particular, O_x variable, sum of O_3 and NO_2, describes the atmospheric radical conditions: when no reactions occur, the daily trend of the O_x variable is constant because O_3 and NO_2 have a specular behavior depending strictly on the solar radiation, i.e. high ozone levels in the early morning and NO_2 removal and opposite in the rest of the morning. During photochemical smog episodes, higher levels of HCHO and PAN are found: simultaneously, the various reactions cause an ozone accumulation and the relative sum of ozone and NO_2 is not constant during the day. The O_x behavior can be considered an index of the occurrence of a smog photochemical episode.

Conclusions

The daily trends of ozone and PAN are reported and discussed 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.

References

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