

Monitoring of tropospheric ozone precursors in the Metropolitan Area of São Paulo.

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Abstract

In recent years, the ambient concentrations of tropospheric ozone in the Metropolitan Area of São Paulo (MASP) reached levels of more than five times those considered safe for public health according to the World Health Organization (WHO). Since volatile organic compounds (including hydrocarbons, carbonyl compounds and alcohols), NO_x and ultraviolet radiation ($\lambda \leq 394\text{nm}$) have a key role in the formation of this pollutant, the current study presents data from continuous sampling and analysis of these precursors to the formation of tropospheric ozone in São Paulo city. The hydrocarbons and ozone were continuously sampling and analyzed automatically 24 hours a day. Statistical analyses were applied to the base data to evaluate the winds direction effects on the hydrocarbons variability. The main focus was to find specific tracers for the fuels used in São Paulo.

Introduction

Ozone (O₃) is an important secondary pollutant in the troposphere and also a major oxidant. Ozone and other oxidants, such as peroxy nitrates and hydrogen peroxide (H₂O₂) formed in polluted areas mainly by atmospheric reactions involving two classes of precursor pollutants, volatile organic compounds (VOCs) and nitrogen oxides (NO_x). High ozone concentrations are strongly related to meteorological conditions and usually occur during sunny days, when primary pollutants (NO_x and VOCs) interact photochemically, supported by strong solar radiation and high temperatures [1, 2]. World Health Organization (WHO) [3] points out a risk to human health and vegetation due to the increased concentration of ozone in troposphere. Ozone adversely affects the respiratory organs, and as a result of this effect mortality has increased in areas of increased ozone concentrations [4].

Tropospheric ozone represents one of the main atmospheric pollutants in megacities such as the Metropolitan Area of Sao Paulo (MASP), a megacity located in southern Brazil, which actually has a population of almost 20 million inhabitants. According to the latest report from CETESB [5] – the government agency responsible for monitoring air quality in the MASP, the year 2011 had the highest number of days exceeding the standard of quality since 2002, 96 days overtaking. National standards for air quality (CONAMA Resolution N° 03 of 28/6/90) establish that ozone concentration does not exceed the average hourly limits of 160 $\mu\text{g m}^{-3}$ (80 ppbv), and the value has not to be exceeded more than once a year. In 2011, the stations of quality air monitoring from CETESB, IPEN-USP station, Sao Caetano do Sul station and Ibirapuera station, presented significant increase in the

standard of quality when compared with previous years and presented several exceedances of the standard, 72 days, 58 days and 47 days, respectively.

Since this pollutant is formed in the atmosphere by photochemical reactions that depend on solar radiation, among other factors, ozone occurs most frequently in the period between September and March (Spring and Summer), with warmer weather and higher incidence of radiation on top of the solar atmosphere. In order to characterize meteorological effects and establish the behavior pattern for some VOCs compounds (especially the volatile non-methane hydrocarbons – NMHC) and its contribution in the tropospheric ozone formation, automatic unattended hourly campaign was carried out during spring season (October, 2012) in MASP.

Methodology

The sampling point is located in a west region of São Paulo, inside the University Campus and surrounded by principal roadways with intense vehicular traffic.

The ozone precursor automated measurement system of Perkin Elmer® was used. This system is based on: 1) a Thermal desorption unit (ATD650) fitted with an air sampler accessory, in which the dried sample was concentrated in an electrically cooled sorbent trap ($-30\text{ }^{\circ}\text{C}$) in the TD. In a second stage, the concentrated sample was desorbed by rapid heating at a rate of $40\text{ }^{\circ}\text{C s}^{-1}$ up to $325\text{ }^{\circ}\text{C}$, maintained for 6 min, and transferred by a helium carrier flow into the chromatographic system. 2) A Clarus 500 GC – FID with two chromatographic columns: PLOT ($\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$, $50\text{ m} \times 0.32\text{ mm} \times 5\text{ }\mu\text{m}$) and BP1 ($50\text{ m} \times 0.22\text{ mm} \times 1\text{ }\mu\text{m}$) and two ionization flame detectors (FID). Ultra-pure helium (6.0) is used as carrier gas, and the temperature program for the GC oven was hold at $46\text{ }^{\circ}\text{C}$ (15 min), up to $170\text{ }^{\circ}\text{C}$ ($5\text{ }^{\circ}\text{C min}^{-1}$), up to $200\text{ }^{\circ}\text{C}$ ($15\text{ }^{\circ}\text{C min}^{-1}$), and hold at $200\text{ }^{\circ}\text{C}$ (6 min). Under these operating conditions it was possible to separate in 47.8 min more than 50 NMHC C2–C11 in the GC – FID. Operation was optimized for systematic online measurement every hour. Ambient air samples were collected during the Spring period (October, 2012), which is of main interest for local ozone episodes in the area.

Of the almost 60 compounds identified only 23 of them were evaluated, due to having the greatest number of cases.

Results and discussion

The results indicated that most abundant compounds are trans-2-hexene, toluene, ethane, ethylene, p-xylene, 2,3-dimethyl-butane e 1,2,4-trimethyl-benzene, which are related with a greater photochemical ozone potential formation following the MIR reactivity scale of Carter [6]. These results are consistent to the ones found in other NMHC long-term campaigns [7, 8].

Statistical correlation analysis classified the data into groups with similar characteristics and

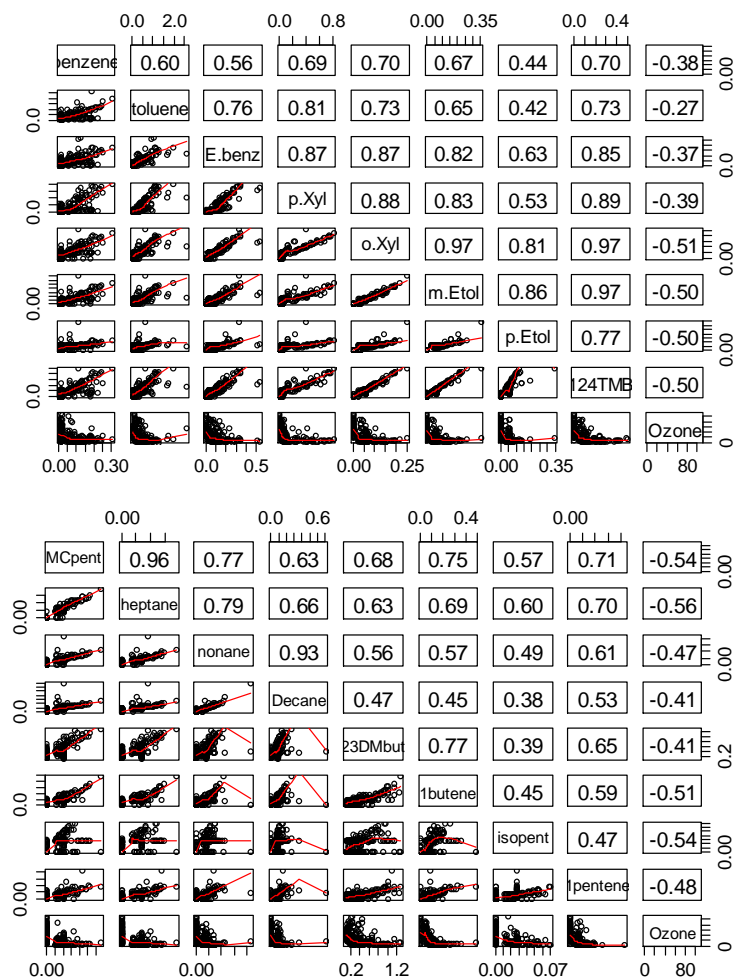


Figure 1. Correlation matrix of some NMHC and Ozone of C₄-C₅: 1-pentene (pentene), 1-butene, 2, 3-dimethylbutane (23DMbut).

In addition, negative correlation coefficients resulted between NMHCs and ozone. Better results were represented by methylcyclopentane (MCpent), n-heptane (heptane), isopentane (isopent), 1-butene and o-xylene (o.xyl).

In order to understand behavior patterns, the time variation of some hydrocarbons was evaluated. The hourly average evolution can be seen in Figure 2. As can be observed, most of the compounds follow a similar pattern with a maximum concentration at night and a minimum concentration during the day. This behavior is inverted when compared to the ozone daily pattern, explained by the hydrocarbons consumption reactions that lead to ozone formation in the presence of sunlight and NO_x.

infers possible emission sources of each group. The matrices of Figure 1 show the results of multiple regression analysis. As can be seen, there are high correlation coefficients between aromatic compounds as toluene, ethyl benzene (E.benz), p-xylene (p.xyl), o-xylene (o.xyl), p-ethyl toluene (p.Etol), m-ethyl toluene (m.Etol) and 1,2,4-trimethyl benzene (124TMB). Emissions from motor vehicles were the dominant source of aromatic hydrocarbons in our area of study.

Furthermore, high correlations were found between heavier alkanes C₇-C₁₀: n-heptane (heptane), n-nonane (nonane), n-decane (Decane), and between alkenes and hydrocarbons derived

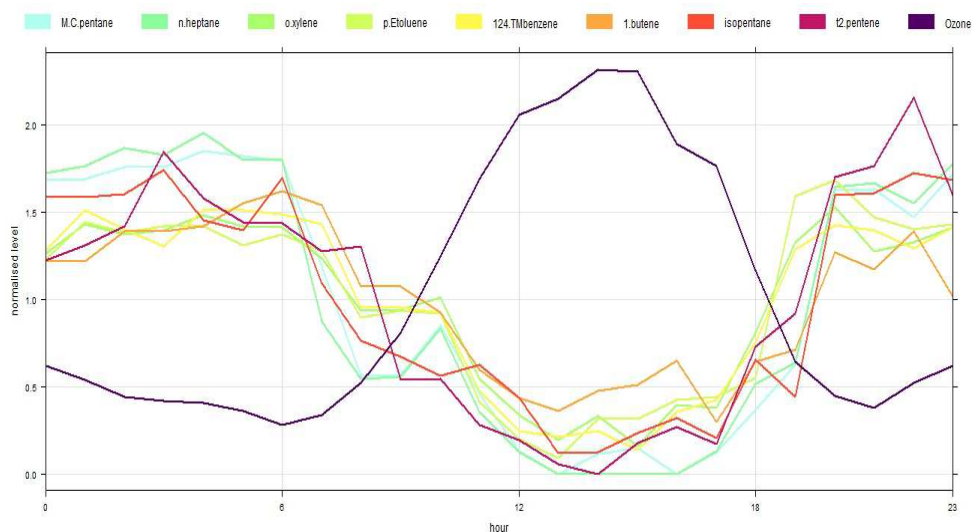


Figure 2. Evolution of the hourly average pattern of some selected NMHC and Ozone (normalized)

Meteorological parameters were recorded at the IAG-USP monitoring station [9], located at same place of Ozone precursor measurement system. The wind direction and speed data were incorporated in the NMHC database to analyze them concurrently. Meteorological data cover all the measuring period of NMHC measurements.

Hourly mean pollutant concentrations were assigned to the corresponding wind direction, when the wind speed is not calm (wind speed = 0 ms^{-1}). We explored the frequency of the wind directions associated with each pollutant for different concentration ranges. In figure 3 the pollution wind rose diagrams are presented for some compounds during measuring period. The dominant wind direction was SE-E.

Diagrams represent proportion of each concentration range (%) by wind direction at the monitoring point. In the case of 1-butene we can notice that higher concentration is correlated only with east wind direction while lower concentrations do not have a specific direction. O-xylene pollution rose shows a predominant SE direction for higher concentrations and a little contribution from NNE direction. Besides that, for methylcyclopentane, 1,2,4-trimethyl benzene and n-heptane roses we can find a similar behavior with greater concentrations coming through from the SE, E and NE directions. However, for isopentane was not observed one predominant wind direction.

Moreover, we evaluated the frequency contribution of each range (NMHCs) by wind in relationship with ozone concentrations. It can be seen at Fig 4, where according to what was shown in Fig 2, higher concentrations of ozone are related with lower concentration of NMHC.

Conclusions

In summary, with this methodology based on automatic GC-FID system, we have collected continuous hourly data for more than 50 NMHC during long periods. These systems produce a large amount of complex data, whose treatment and processing require a great time and understanding.

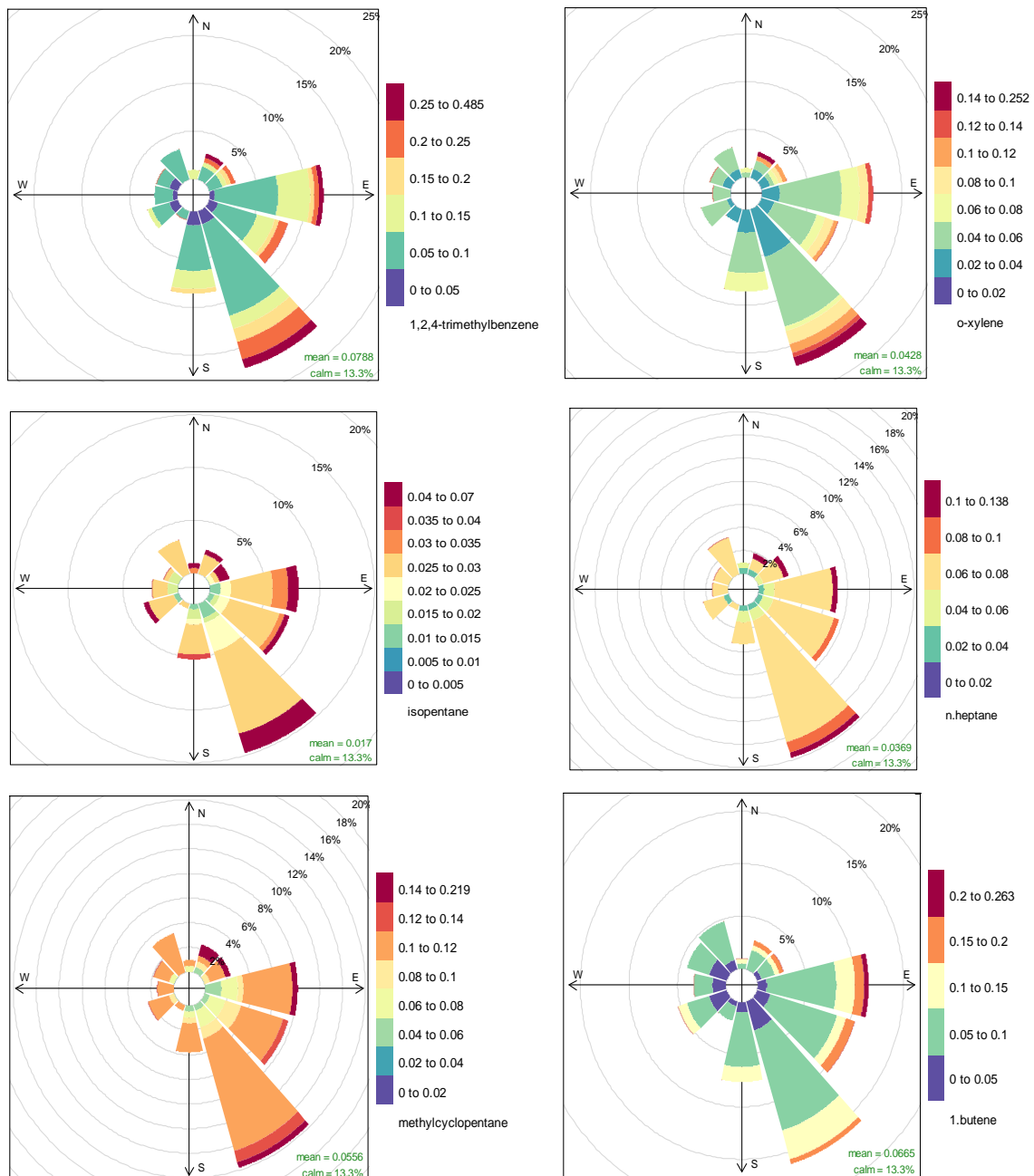


Figure3. Pollution rose diagram of some compounds.

Statistical correlation analysis combined with multivariate techniques were applied for inferring the organic compound sources. High correlations findings between some types of compounds (alkanes, aromatics, alkenes) as well a simple meteorology analyses, allows us to have a better understanding of the likely sources of emission of ozone precursors compounds.

Future seasonal campaigns achieved improve our understanding of the annual cycle of each compound and as the wind and other meteorological variables determine the presence and concentration of each.

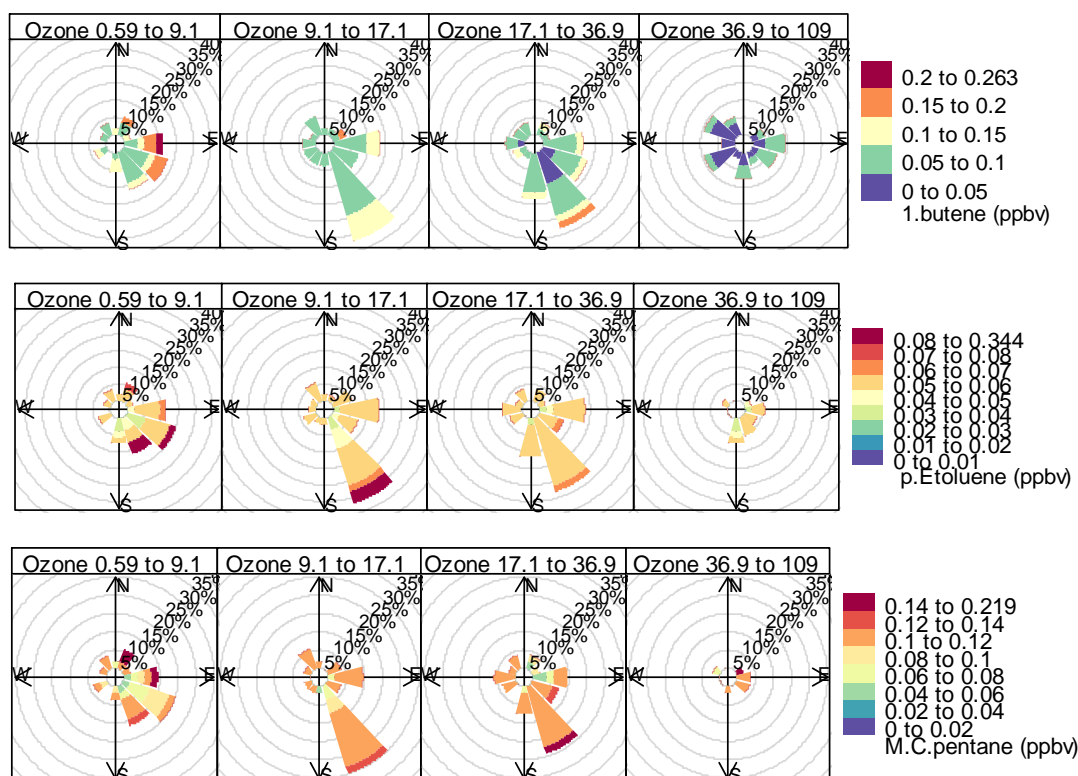


Figure 4. Frequency of counts by wind directions and the relationship with ozone concentration

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References

- [1] R. Atkinson, Atmospheric chemistry of VOCs and NO_x, *Atmos Environ* 34(2000) 2063-2101.
- [2] D.J. Jacob, Heterogeneous chemistry and tropospheric ozone, *Atmos Environ* 34(2000) 2131-2159.
- [3] WHO, Health risks of ozone from long-range transboundary air pollution. Regional Office for Europe, Copenhagen, Denmark. 2008.
- [4] D.V. Bates, Ambient ozone and mortality, *Epidemiology* 16(2005) 427-429.
- [5] CETESB, Relatório Anual de Qualidade do Ar no Estado de São Paulo 2011., 2012.
- [6] Carter (2010) Updated maximum incremental reactivity scale and hydrocarbon bin reactivities for regulatory applications. University of California, Riverside.
- [7] Durana, N., Navazo, M., Gómez, M. C., Alonso, L., García, J. A., et al. (2006). Long term hourly measurement of 62 nonmethane hydrocarbons in an urban area. *Atmos. Env.*, 40, 2860–2872.
- [8] M. Navazo, N. Durana, L. Alonso, M. C. Gómez, J. A. García, et al. (2008). High temporal resolution measurements of ozone precursors in a rural background station. A two-year study. *Environ Monit Assess* (2008) 136:53–68
- [9] MASTER. Meteorologia Aplicada a Sistemas de Tempo Regionais. <http://www.master.iag.usp.br/>
- [10] R Core Team (2012). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0.