Study of Volatile Organic Compounds Precursors Ozone in the Metropolitan Area of Sao Paulo

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Introduction

The standards of air quality in the metropolitan area of São Paulo (MASP), with approximately 20 million inhabitants, are violated by gases from vehicles.

Ozone (O_3) is a pollutant that presents great concern in terms of air quality in the MASP. In 2012 were observed 98 days of exceedances of the standard time air quality for this pollutant in the MASP [1].

Trajectory model OZIPR (Ozone Isopleth Package for Research) is used for determination of the main Volatile Organic Compounds (VOCs) a scale of increment of reactivity for O_3 specific for the MASP in order to provide data to assist the development of strategies to reduce this pollutant.

Methods

Sampling

Site: Air Monitoring Station CETESB IPEN/USP/City of University.
Period: Sep 2011 until Aug 2012 – 07:00 am to 09:00 am.
N.º samples: 66 hydrocarbons, 62 of aldehydes and 42 of ethanol.

Analyses of samples

➢54 VOCs quantified.
➢Gas Chromatography: Hydrocarbons (HC) → C2-C4: flame ionization (FID) e HC > C4 mass spectrometry (MS) and FID, Aldehydes → HPLC with UV and Ethanol → CG/FID.

Determination of the main precursors of O_3

➢Input data: meteorological parameters, adjust the hourly emissions of CO, NO_x and VOCs, planetary boundary layer and rate of deposition of NO_x and O_3 for the period studied.
➢Adjustment parameters for the model to reproduce the real concentrations of CO, NO_x and O_3 measured during the sampling.
➢Determine the potential of formation of O_3 for each VOCs, using the incremental O_3 reactivity scale (IR)
➢IR → Mean positive IR (IR_+) and negative (IR_-), calculated by the increase and decrease, respectively, 0.2% of the total concentration (μg m^{-3}) of VOCs each species VOCs [2].

Results

Considering the concentration of VOCs analyzed and the incremental reactivity determined by the model OZIPR in the atmosphere of MASP for the year 2011-2012, the aldehydes were responsible for 74% of the ozone formation in the atmosphere (61.2% of this number corresponds to acetaldehyde).

Table 1. Initial Concentration of VOCs (ppmC), NO_x and CO (ppm) during the seasons 2011-2012 at the CETESB IPEN/USP station

Compounds	Spring	Summer	Autumn	Winter
VOCs	0.74	0.74	0.67	0.79
NO_x	0.04	0.06	0.04	0.07
CO	0.47	0.36	0.30	0.45

Table 2. Mean concentration of the most abundant VOCs

Compounds	Concentration (ppbv)
Ethanol	36.3
acetaldehyde	28.7
formaldehyde	21.7
acetone	10.9
propane	5.56
ethene	4.84
ethane	2.98
butane	2.94
1-ethyl-4-Methylbenzene	2.85
1,2,4-trimethylbenzene	2.43

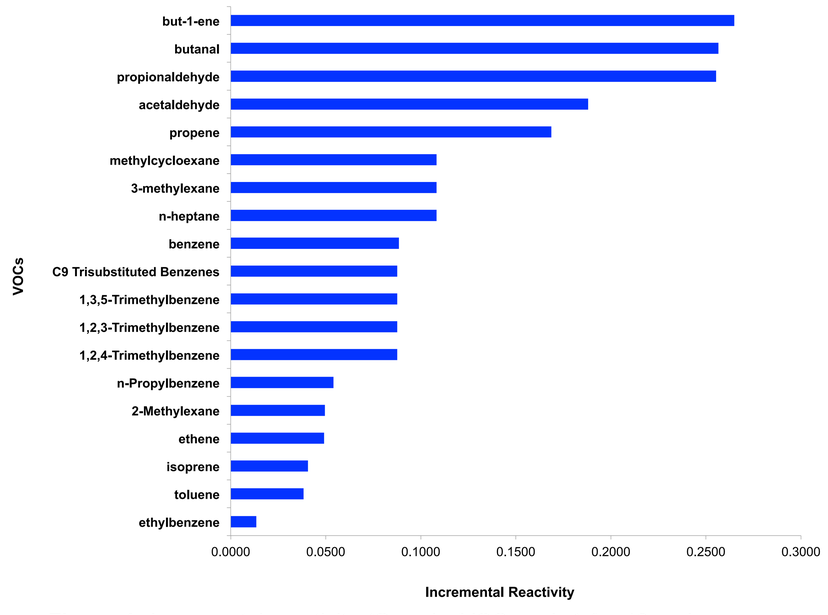

Figure 1. Incremental reactivity (O_3 ppbv/VOCs ppbc) for 19 major precursor of O_3 in the atmosphere of the MASP, calculated for VOCs measured in Air Monitoring Station CETESB IPEN/USP.

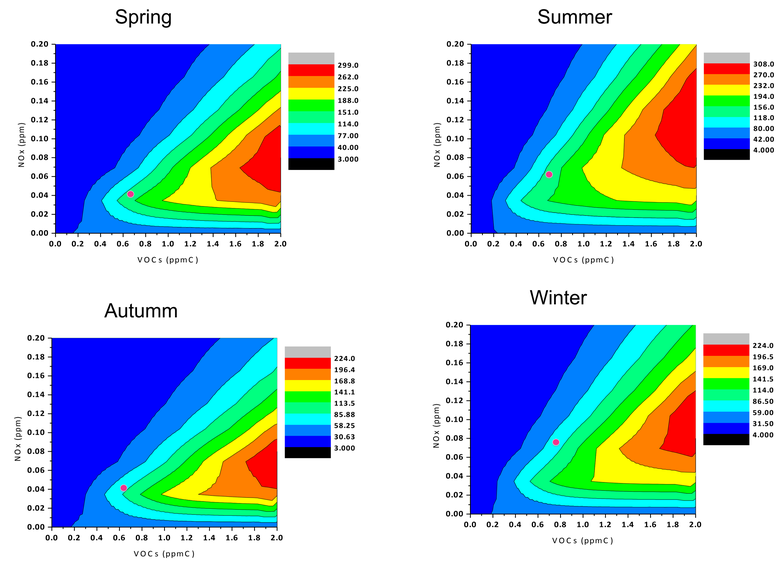

Figure 2. Ozone isopleths (ppb) for various concentration of VOCs (ppmC) and NO_x (ppm) for the campaing in the year 2011-2012 in the air monitoring station CETESB IPEN/USP.

Conclusion

➢The class of aldehydes represented 35.3% of VOCs concentrations analyzed in the atmosphere, ethanol 22.6%, aromatics 15.7%, alkanes 13.5%, ketones 6.8%, alkenes 6.0% and alkadienes <0.1%.
➢VOCs analyzed, the class of aldehydes contributed with 74% of the production of O_3, aromatics 14.5%, alkenes 10.2%, alkanes 1.3% and alkadienes (isoprene) 0.03%.
➢These results are important for understanding what measures would be effective in controlling the formation of ozone in the atmosphere MASP
➢Decrease in the concentration of VOCs in the MASP will result in the decrease of the ozone concentration. The ratio VOCs/NO_x found during this study for the spring, summer, autumn and winter seasons were 4, 3, 3 and 2, respectively.

References

1. CETESB. Report of air quality in the state of São Paulo. 2011, 2012.
2. Tonnesen, G. S. 2000. User's Guide for Executing OZIPR.

Acknowlegements

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