

## ISOPRENE EMISSION ESTIMATE IN REGION CONTAINING EUCALYPTUS FOREST AND ITS RELATIONSHIP WITH LOCAL TROPOSPHERIC OZONE: CASE STUDY

Ana Paula dos Santos Zepka and Kelly Ribeiro

**ABSTRACT.** In order to study the biogenic emissions of isoprene by a commercial eucalyptus forest and its relationship with the local tropospheric ozone, two intensive surveys were conducted in Fibria Celulose e Papel company, Caçapava, Vale do Paraíba, São Paulo State, Brazil. The samples were analyzed for isoprene via thermal desorption gas chromatography. Ozone was monitored using a UV Photometric O<sub>3</sub> Analyzer, Model 49i. The highest mixing ratios of isoprene were detected at noon and ranged from the maximum of 8.3 ppbv on November 29, 2010 to 3.5 ppbv on June 30, 2011. On the evaluated days, it was observed that isoprene and ozone peaked with about two hours delay; this is explained by the time required for the isoprene to react with other precursors and, in the presence of sunlight, to form ozone. During the winter days when both temperature and photosynthetic active radiation are lower, the emission of isoprene was also 65% lower than in the summer. Based on the maximum ozone (27.9 ppbv) detected, the atmosphere in this region is considered clean according to Conselho Nacional do Meio Ambiente (CONAMA) stipulates a maximum of 81.5 ppbv of ozone for good air quality.

**Keywords:** commercial forest, chemical compounds, atmospheric chemistry.

**RESUMO.** Com o objetivo de estudar a emissão de isopreno biogênico por floresta comercial de eucalipto e sua relação com o ozônio troposférico local, foram realizadas duas campanhas intensivas na companhia Fibria Celulose e Papel, em Caçapava, no Vale do Paraíba Paulista. As amostras coletadas de isopreno foram analisadas por cromatografia gasosa via dessorção térmica. O ozônio foi monitorado pelo Analisador UV Photometric O<sub>3</sub>, Modelo 49i. Ao meio-dia foram detectadas as maiores razões de mistura de isopreno, variando do máximo de 8,3 ppbv em 29 de novembro de 2010 a 3,5 ppbv em 30 de junho de 2011. Nos dias avaliados, observou-se que o ozônio apresentou pico máximo atrasado em cerca de duas horas em relação ao máximo de isopreno, o que é justificável devido ao tempo necessário para que este gás reaja com outros precursores, e que na presença de luz solar levem à formação de ozônio. Durante os dias avaliados de inverno, com temperatura e radiação fotossinteticamente ativa menores, a emissão de isopreno foi 65% menor do que na semana estudada do verão. Baseado no máximo detectado de ozônio (27,9 ppbv), a atmosfera dessa região é considerada limpa de acordo com o Conselho Nacional do Meio Ambiente (CONAMA) que estipula o máximo de 81,5 ppbv de ozônio para um ar de boa qualidade.

**Palavras-chave:** floresta comercial, compostos químicos, química atmosférica.

## INTRODUCTION

Global climate changes are related to increased concentrations of greenhouse gases. Reforestation programs using fast-growing species are alternatives to control global warming since they participate in the carbon cycle (Grainger, 1990).

In São Paulo, eucalyptus (*Eucalyptus* sp.) is one of the most common species used in reforestation because of its rapid growth, the variety of applications for its wood and its use in the pulp and paper industry (Campinhos Jr., 1999).

In particular, this study investigates the biogenic emissions of isoprene by a commercial eucalyptus forest and its relationship with the local tropospheric ozone. The region, where the Fibria Celulose e Papel company is located was chosen for the data collection, in Caçapava, Vale do Paraíba Paulista. This area is explored and suitable for reforestation; however, it is deeply degraded due to its high density of arable soil with low fertility.

Forest areas are potentially volatile organic compounds (VOC<sub>s</sub>) emitters. These are emitted by biogenic sources and have significant impact on tropospheric chemistry, especially in the formation of ozone (O<sub>3</sub>) when combined with nitrogen oxides (NO<sub>x</sub>) (Chameides et al., 1988). In this group, the biogenic isoprene is highlighted since it is released by the vegetation in quantities larger than any other non-methane hydrocarbon (Guenther et al., 1995). Isoprene is often the most abundant VOC<sub>s</sub> (Fehsenfeld et al., 1992) found in the atmosphere over forests, at a mixing ratio of 0.2 to 30 ppbv (Seinfeld & Pandis, 1998).

The isoprene emission increases exponentially with increasing temperature, especially in the warmer summer days (Harley et al., 2003). As a result, emissions increase over time in areas that tend to have higher temperatures due to climate change (Lathiere et al., 2006; Wiedinmyer et al., 2006). Moreover, gas emissions increase with radiation (Guenther et al., 2000), so that the highest mixing ratios of isoprene are observed in the summer, at noon. Thus, the maximum mixing ratios generally coincide with periods of maximum production of photochemical ozone, in a way that the oxidation of isoprene produces ozone more efficiently than other VOC<sub>s</sub> stored in the plants, such as monoterpenes. The effect of isoprene on ozone production is also strongly dependent on the high levels of NO<sub>x</sub> in the atmosphere (Li et al., 2007). The oxidation of isoprene in the presence of high concentrations of NO<sub>x</sub> increases the levels of O<sub>3</sub> by photolysis, i.e., by means of reactions triggered by solar radiation (Pacific et al., 2009).

National air quality standards have been established by IBAMA in Normative No. 348, from 1990, which has been transformed into CONAMA Resolution No. 003/90 (Cetesb, 2009). The air quality standard (AQS) sets a limit of 81.5 ppbv (160 μg m<sup>-3</sup>) of ozone in the air while higher values characterize "polluted air".

This case study evaluates the isoprene emissions by a commercial eucalyptus forest and the local tropospheric ozone mixing ratios through the study of atmospheric chemistry of the region.

## METHODOLOGY

The characterization of chemical compounds derived from biogenic emissions is an analytical challenge that requires precise and accurate identification and quantification of hydrocarbons. In Brazil, there are no specific standards established for analysis of volatile organic compounds (VOC) and, therefore, this work is based on the protocol of Methods TO-15 and 17 of USEPA (1997, 1999), used worldwide as a reference in this line of research.

The samples were collected in commercial eucalypt forests that belong to the paper company Fibria Celulose e Papel (23°07'S, 45°37'W, 625 m), in Caçapava, Vale do Paraíba, São Paulo State. Two intensive campaigns, five days in the summer of 2010 and three days in the winter of 2011, were performed. An operational ground-level weather station was installed in the company for this work. Specific sensors measured the air temperature (°C) and photosynthetically active radiation (PAR) (μmol s<sup>-1</sup>) every 15 min, generating information that was recorded so it would be possible later on to determine the atmospheric behavior in the region.

Isoprene was collected in Air Toxics denuders coupled to a portable air pump. The denuders' treatment consisted of conditioning, a specific cleaning process aiming to remove possible residual contaminants. This conditioning process was performed during 30 min at 300°C, and flow rate of 50 mL min<sup>-1</sup> carrier (nitrogen) gas in automatic TurboMatrix 350 ATD thermal Desorber manufactured by PerkinElmer, the same used in the data analysis. After cleaning, the denuders were wrapped in aluminum, stored in glass jars and kept in a refrigerator free of organic solvent at 4°C.

A total of five liters of air were sampled for each denuder during 60 min at a flow rate of 90 mL min<sup>-1</sup>. After pre-concentration, via the thermal desorption, the denuders were analyzed by gas chromatography equipped with FID detector (PerkinElmer, 2005).

Calibration curves of the standard gas were plotted to quantify the chemical compounds identified in the chromatographic analysis. The calibration curve is a function that describes the detector response over a wide concentration range and allows determining the species of interest. To this end, a minimum of three (50, 60 and 70 mL) and a maximum of five (40, 50, 60, 70 and 80 mL) volumes of standard gas were used to reach the relative accuracy of 2.8% for the isoprene. The volumes have been adapted to improvements in the analytical method. The three-volume method was chosen due to analytical system linearity, i.e., the one that for a determined operating range responds proportionally to the

concentration of the chemical compound in the sample and provides efficient calibration by measuring two or three different volumes of the standard.

The standard reference gas certified by White Martins containing  $99 \pm 10$  ppbv of n-butane (normal butane) and  $84 \pm 8$  ppbv isoprene in ultrapure, dry nitrogen, bottled in a 2.3-m<sup>3</sup> aluminum cylinder was used. The standard gas is a predetermined mixture of compounds whose mixing ratio is known and selected according to the components to be detected in the air samples.

The ozone monitoring was performed by the UV Photometric O<sub>3</sub> Analyzer, Model 49i, with mean flow rate from 1 to 3 L min<sup>-1</sup> and a wide range mixing concentration ratio from 0.05 to 200 ppbv. This model is based on the principle that the ozone molecules absorb ultraviolet light (UV) at a wavelength of 254 nm, so that the amount of UV light absorbed is directly proportional to the ozone concentration.

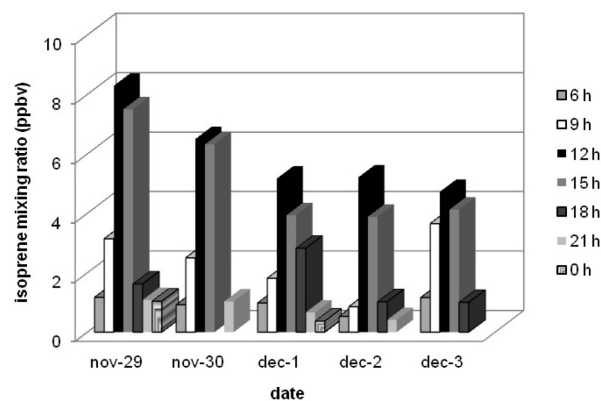
The Methods TO-15 and 17 of USEPA (1997, 1999) establish decisive criteria for a qualified sampling procedure to ensure the viability of the analytical method employed. One of these parameters is the method's limit of detection (LOD), which is calculated from the standard deviation of the analytical response and defined for each system by seven repeat measurements of the same standard gas volume close to the LOD expected, or within a factor of five. The standard deviation was calculated for the seven measurements and the value multiplied by 3.14 (ICH, 1995). After analyzing seven times 10 mL of the standard gas used in this work, the average for isoprene was  $0.52 \pm 0.10$  ppbv with a LOD of 0.31 ppbv ( $0.86 \text{ mg m}^{-3}$ ) while for n-butane, average was  $0.38 \pm 0.05$  ppbv and LOD, 0.16 ppbv ( $0.38 \text{ mg m}^{-3}$ ). Thus, the method limit of detection criterion of  $\leq 0.5$  ppbv was satisfied. In addition to this, the criteria for accuracy within 20% for both analytical duplicates for standard gas samples and within 30% for mixing ratios usually expected in air samples (0.5 to 2 ppbv), were also calculated. The analytical duplicates accuracy was calculated at 15% and 21% accuracy for each sampling day, considering the area of isoprene for standard and observed values.

## RESULTS AND DISCUSSION

The mixing ratio of isoprene calculated for the first five days of the intensive survey is shown in Figure 1.

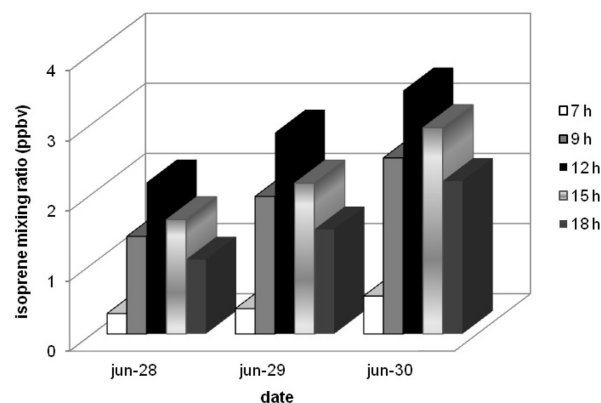
The maximum mixing ratios of isoprene were always detected at noon during the evaluated period, which peaked (8.3 ppbv) on November 29, 2010, as shown in Figure 1. From 9 p.m., the mixing ratio of the gas reached 0.8 ppbv average. The rainfall (1.6 mm average for the period) prevented sampling at midnight in three of the five days of the survey, but despite this, the two data for that time showed that during the night mixing ratios were lower than

in the day, reaching 1 and 0.4 ppbv on November 29 and December 1, respectively. This result shows that the emissions of this compound by eucalyptus are strongly dependent on radiation, as already stated by Harley et al. (2004). Between August and October 2004, Rizzo (2006) surveyed the Amazon region and observed that isoprene peaked at 7.8 ppbv in the early afternoon while decreasing to 0.7 ppbv in the evening, revealing a mixing ratio similar to this work during nighttime. Also in the Amazon region, Karl et al. (2007) detected the highest isoprene peaks at noon, with an average of 5.4 ppbv and radiation close to  $1600 \mu\text{mol s}^{-1}$ . In Canada, Jobson et al. (1999) studied a eucalyptus forest in 1992 and reported isoprene emission peaks of 5 ppbv also at noon.



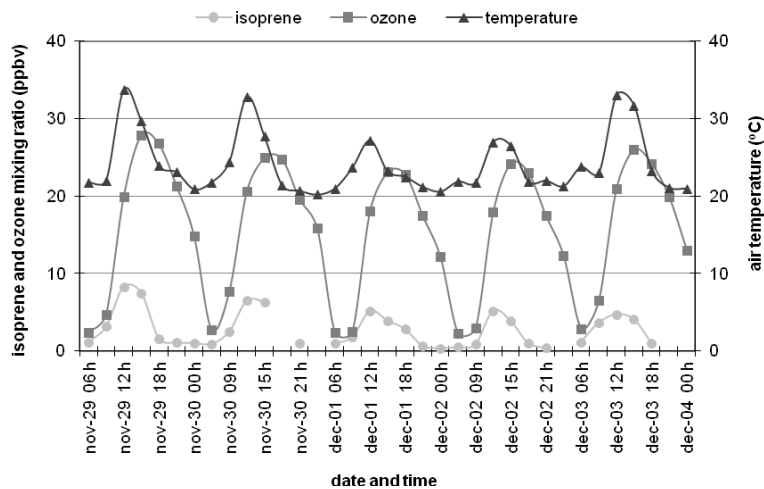
**Figure 1** – Isoprene mixing ratio in the region of Fibria, Vale do Paraiba, during the first intensive survey in the summer 2010, for hourly collection (local time).

The mixing ratio of isoprene calculated for the three days of the second intensive survey is shown in Figure 2.

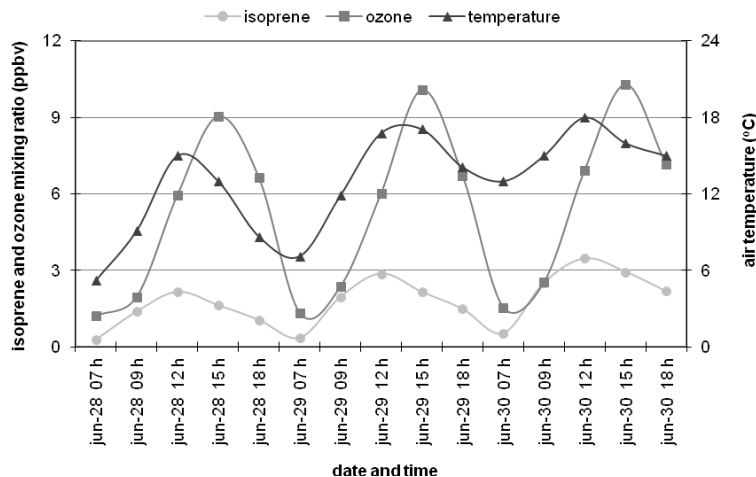


**Figure 2** – Isoprene mixing ratio in the Fibria region, Vale do Paraiba, during the second intensive survey in the winter 2011, for hourly collection (local time).

Figure 2 shows that the isoprene mixing ratios peaked (3.5 ppbv) again at noon on June 30, 2011. Because this survey was conducted in the winter and sunset occurs at approximately 5:30 p.m., a sharp drop was observed in the gas mixing ratio of the sample collected at 6:00 p.m. In the first collection,



**Figure 3** – Comparison between isoprene and ozone mixing ratios with air temperature in the Fibria region, Vale do Paraiba, for five sampling days during summer 2010.



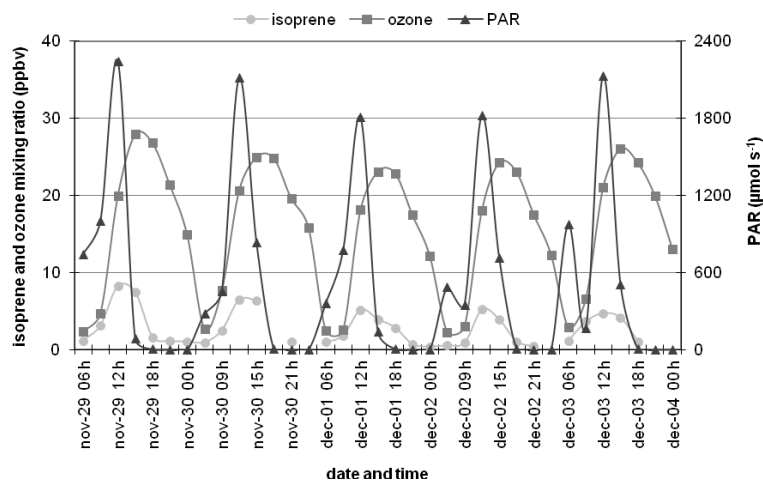
**Figure 4** – Comparison between isoprene and ozone mixing ratios with air temperature in the Fibria region, Vale do Paraiba, for three sampling days during winter 2011.

isoprene peaked at 8.3 ppbv, which is 4.8 ppbv higher than the highest value of the second survey, on June 30. This variation is attributed to the relationship between the gas concentration and temperature (Figs. 3 and 4), and the photosynthetically active radiation (Figs. 5 and 6) on the dates specified. This relationship demonstrated in this work and already provided in the literature (Guenther et al., 1995; Fuentes et al., 2000) is related with the fact that the isoprene synthase (expressed by the gene *ISPs*), which catalyzes the isoprene synthesis, is stimulated by intense radiation and high temperatures (Fares et al., 2006). Therefore, they directly influence the diurnal variations observed gas emissions, revealing a dependence that is controlled by the activity of the key enzyme of this process (Monson et al., 1992).

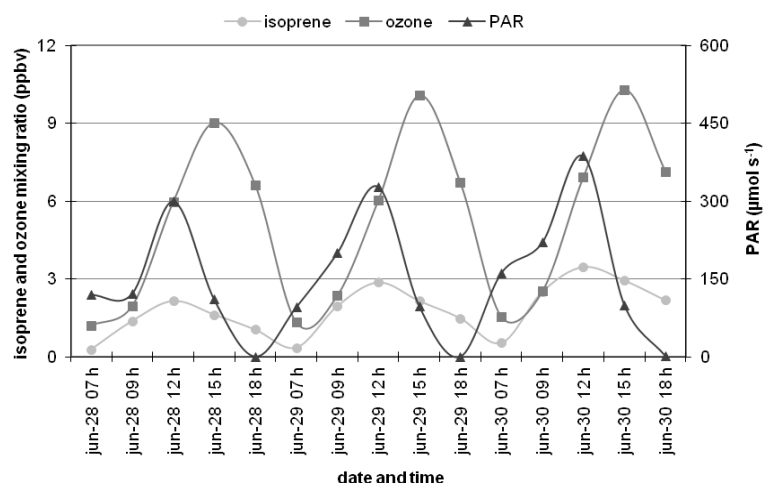
Figures 3 to 6 display the relationship between ozone and isoprene in the region studied. For static and windless environment, it is possible to identify that during the evaluation period, ozone peaked with about two hours delay after isoprene. This delay is justifiable due to the time required for isoprene and other precursors, such as  $\text{NO}_x$ , to react in the atmosphere in the presence of sunlight and form  $\text{O}_3$ .

In the second intensive survey, isoprene and ozone peaked at 3.5 and 10.3 ppbv (Figs. 5 and 6) while, in the first, they peaked at 8.3 and 27.9 ppbv, respectively (Figs. 3 and 4).

In the days with higher air temperature and photosynthetically active radiation (PAR), the emission of gases was also higher as shown in the figures. However, in the remaining days of



**Figure 5** – Comparison between isoprene and ozone mixing ratios with photosynthetically active radiation (PAR) in the Fibria region, Vale do Paraíba, for five days during summer 2010.



**Figure 6** – Comparison between isoprene and ozone mixing ratios with photosynthetically active radiation (PAR) in the Fibria region, Vale do Paraíba, for three days during winter 2011.

winter 2011, gas emission was 65% lower than that of the summer 2010, showing a seasonal variation in isoprene emission by the eucalyptus forest, which is justified by the relationship of this gas with the above meteorological parameters. Rizzo (2006) also reported that in the Amazon region, isoprene mixing ratio was high in the warmer months, reaching 29 ppbv, decreasing an average 6.9 ppbv during cooler periods. The temperature controls the activation of the isoprene synthase enzyme, i.e., the isoprene emission increases with temperature parallel to the enzyme activity (Kuzma & Fall, 1993).

Thus, as already described by Hewitt et al. (1995), which identified air temperature and photosynthetically active radiation as the two most influential factors affecting the emission of this gas,

this study shows a relationship between gas emission peaks and higher temperatures, as well as higher light incidence. Temperature and radiation play an important role in controlling seasonal, year-to-year, and spatial variations of  $\text{VOC}_S$ .

## CONCLUSION

The results show that the atmosphere studied can be characterized as clean, based on the observed ozone mixing ratio peak of 27.9 ppbv well below the levels established by CONAMA (81.5 ppbv) and given the prevailing weather condition in the region, with hot summers and dry winters.

The isoprene emitted by the commercial eucalypt forest was within the reference range estimated for this gas from  $-0.2$  to

30 ppbv (Seinfeld & Pandis, 1998), according to the methodology used. The isoprene emissions peaked (8.3 ppbv in 2010 and 3.5 ppbv in 2011) at noon, the period during which the temperature and photosynthetically active radiation remained higher (33.7°C and 2243  $\mu\text{mol s}^{-1}$  on November 29, 2010 and 18°C and 387  $\mu\text{mol s}^{-1}$  on June 30, 2011), directly influencing plant metabolism by stimulating the synthesis of isoprene synthase, leading to the production and release of isoprene.

On the days assessed, the isoprene and ozone peaks displayed a delay of about two hours, underlying the fact that the photochemical reactions between chemical precursors that lead to ozone production need a time interval to happen.

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