# Regional Isoprenoid Emission from Eucalyptus grandis Forests in Northeastern Argentina

**Article** *in* International Journal of Agriculture and Biology · May 2016

CITATIONS
0

READS
93

**4 authors**, including:

Klaus Richter
Instituto Nacional de Tecnología Agropecuaria
**11** PUBLICATIONS **8** CITATIONS
SEE PROFILE

Carlos Marcelo Di Bella
Instituto Nacional de Tecnología Agropecuaria
**79** PUBLICATIONS **1,448** CITATIONS
SEE PROFILE

Gabriela Posse
Instituto Nacional de Tecnología Agropecuaria
**36** PUBLICATIONS **360** CITATIONS
SEE PROFILE

INTERNATIONAL JOURNAL OF AGRICULTURE & BIOLOGY
ISSN Print: 1560–8530; ISSN Online: 1814–9596
15–528/2016/18–3–615–622
DOI: 10.17957/IJAB/15.0137
http://www.fspublishers.org

*Full Length Article*

# Regional Isoprenoid Emission from *Eucalyptus grandis* Forests in Northeastern Argentina

**Klaus Richter[1], Mauro Centritto[2], Carlos Di Bella[1,3] and Gabriela Posse[1*]**
[1]*Instituto de Clima y Agua – Instituto Nacional de Tecnología Agropecuaria (INTA), Hurlingham, Provincia de Buenos Aires, Argentina*
[2]*Trees and Timber Institute, National Research Council, Via Madonna del Piano 10, 50019 Sesto Fiorentino (FI), Italy*
[3]*Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina*
[*]For correspondence: posse.gabriela@inta.gob.ar; posse.gabriela@gmail.com

## Abstract

Eucalyptus species are strong source of isoprenoid emission. The objective of the present study was to estimate isoprenoid emissions from *Eucalyptus grandis* forest crops in the Entre Rios province in the Mesopotamia region of Argentina. The emission rates of isoprene and monoterpenes were measured on individual leaves under; controlled environmental conditions. At 30°C and with a PPFD of 1000 µM $m^{-2}$ $s^{-1}$ the emission rate of isoprene emission was 12.5 ± 1.9 nM $m^{-2}$ $s^{-1}$ and monoterpenes 15.1 ± 3.1 nM $m^{-2}$ $s^{-1}$. Emission was significantly affected by leaf position and decreased significantly from East to West. The most abundant compound emitted was limonene, accounting for between 50 and 68% of the total monoterpene emission. The time course of the isoprene emission course showed its strong dependence on light. On sunny days 42% of the isoprene emission comes from top of the canopy and only 2% from bottom of the canopy. But on overcast days, the relative contribution of diffuse radiation may be larger and can exceed the contribution of direct radiation. A model procedure in a Geographic Information System was implemented to estimate isoprene emissions at a regional scale. A forest inventory, data from a meteorological station and leaf area indices derived from satellite data served as inputs for the model. For the Entre Rios province (78781 $km^2$), the isoprene emission totals up to 39.5 t $d^{-1}$ on a clear summer day. The methodology applied to estimate isoprenoid emissions on a regional scale contributes to the understanding of carbon exchange between biosphere and atmosphere. 

**Keywords:** Biogenic emission; Isoprenoid; Gas exchange measurements; *Eucalyptus grandis*; Argentina

## Introduction

Terrestrial ecosystems play an important role in carbon cycling, and interact in multiple ways with atmospheric processes. The emission of volatile organic compounds (mainly isoprene and monoterpenes) from terrestrial vegetation represents a global input of 1 Pg of carbon into the atmosphere (Guenther *et al*., 2012). Isoprenoids are highly reactive and as a consequence significantly affect the chemical and physical properties of the atmosphere (Chameides *et al*., 1988; Centritto *et al*., 2011); through the formation of tropospheric $O_3$ and secondary organic aerosols, in addition to influencing the lifetime of powerful greenhouse gases including methane (Trainer *et al*., 1987; Fuentes *et al*., 2000; Claeys *et al*., 2004).

Isoprene (C5) and monoterpenes (C10) are formed in the chloroplast through the methyl erythritol phosphate pathway using newly fixed carbon during photosynthesis (Brilli *et al*., 2007; Grote *et al*., 2014). Experimental evidence shows that isoprenoid emission depends upon many factors that are likely to be affected by global change (Peñuelas and Staudt, 2010; Li and Sharkey, 2013; Grote *et al*., 2014; Sharkey and Monson, 2014): (1) environmental conditions that raise emission, such as temperature (Sharkey and Loreto, 1993; Fares *et al*., 2011; Brilli *et al*., 2013) and photosynthetically active radiation (Sharkey and Loreto, 1993; Loreto and Centritto, 2008); (2) factors that decrease emission rates, such as improper spectral composition of the light (Pallozzi *et al*., 2013a, b), abiotic and biotic stresses (Brilli *et al*., 2007; Loreto and Schnitzler, 2010; Niinemets, 2010; Brilli *et al*., 2013; Harrison *et al*., 2013); (3) atmosphere concentration of $CO_2$ and $O_3$ (Lerdau, 2007; Loreto *et al*., 2007); (4) plant form, development and functional type (Brilli *et al*., 2013; Harrison *et al*., 2013; Loreto and Fineschi, 2015); and (5) land-use changes (Geron *et al*., 2006; Ciccioli *et al*., 2014; Sharkey and Monson, 2014). Quantitative predictions of global isoprenoid emissions to climate change are extremely complex due to the multifaceted interactions amongst the multiple determinants that control emission rates.

**To cite this paper:** Richter, K., M. Centritto, C.D. Bella and G. Posse, 2016. Regional isoprenoid emission from *Eucalyptus grandis* forests in Northeastern Argentina. *Int. J. Agric. Biol*., 18: 615–622

Nonetheless, global change is expected to dramatically increase the level of isoprenoid emission, mostly through the influence of rising temperatures (Peñuelas and Staudt, 2010; Sharkey and Monson, 2014).

At present, models estimate that the global emission of isoprene, the most abundant VOC, accounts for approximately 0.5 Pg C $yr^{-1}$ (Arneth *et al*., 2008; Ashworth *et al*., 2013), whereas the annual estimate of monoterpene emissions ranges between 0.03 and 0.15 Pg (Ashworth *et al*., 2013). However, scaling up isoprenoid emissions from the leaf to larger scale remains a major challenge, as the amount and components of isoprenoid emission vary geographically depending upon the vegetation type, the dominant species and canopy structure (Ashworth *et al*., 2013; Guenther, 2013; Grote *et al*., 2014). Furthermore, little information regarding isoprenoid emission in the southernmost regions of South America is currently available.

The objective of the present study was therefore to estimate isoprenoid emissions from *Eucalyptus grandis* forests in the Entre Rios province. Here we present a case study aimed at implementing a methodology for upscaling leaf level data to estimate potential emissions at a canopy scale. We have focused on isoprene, as unlike monoterpenes, isoprene emissions can be modelled with relatively high reliability (Arneth *et al*., 2008). Meteorological data and spatial distributed leaf area indices derived from data of the Moderate Resolution Imaging Spectroradiometer (MODIS) were used to estimate forest emissions during the study period by applying methodologies described by Müller *et al*. (2008).

## Materials and Methods

### Study Area

The Entre Rios province of Argentina occurs between 30.2° and 33.8° Southern Latitude and 57.8° and 60.5° Western Longitude, with an area of 78781 $km^2$. The climate is subtropical; with an average maximum temperature over the past 30 years of 32.3°C (January) and 17.9°C (July). The mean annual precipitation is 1345 mm, with the maximum in April (151 mm) and minimum in July (53 mm). *Eucalyptus grandis* is the most important commercial species and most planted tree in the Entre Rios province: *E. grandis* plantations cover nearly 103000 ha (SAyDS, 2007; MAGyP - DPF - Area SIG e Inventario Forestal 2008/2009). The average time when plantation destination is wood sawmills is 10–15 years. One-year old saplings were planted in spring of 2002. Measurements were performed on eight-year old plants, approximately 24–25 m in height. The forest stand had a density of 1111 trees per ha.

### Gas Exchange Measurements

Photosynthesis ($A_n$), stomatal conductance ($g_s$), intercellular [$CO_2$] ($C_i$) and isoprenoid emissions were measured in situ between 10:00 and 16:00 h. A round portion (6 $cm^2$) of fully expanded leaf of *E. grandis* was clamped in the cuvette of the portable IRGA system (LI-6400, Lincoln, Nebraska, USA). To measure the basal rate of isoprenoid emissions, all gas exchange measurements were made in ambient [$CO_2$] (380 μM $M^{-1}$), at PPFD (photosynthetic photon flux density) of 1000 μM $m^{-2}$ $s^{-1}$, relative humidity of 50–55% and leaf temperature of 30°C. The measurements were made in March 2010 on leaves selected from the centre, east and west parts of ten *E. grandis* trees.

When $A_n$ became steady, the chamber outflow was disconnected from IRGA and diverted into a silcosteel cartridge packed with 200 mg of Tenax (Markes International Limited, UK). A volume of 2 L of air was pumped through the trap at a rate of 200 mL $min^{-1}$. The cartridges were then analyzed through a thermal desorber UNITY (Markes International Limited, UK) by using a gas chromatograph (GC-Agilent 6850, Agilent Technologies, Wilmington, DE, USA) equipped with a splitless injector and a HP-5MS capillary column (30 m in length, 250 μm i.d. and 0.25 μm film thickness) and coupled with a mass selective detector (MS-Agilent 5975C, Agilent Technologies, Wilmington, DE, USA). Helium was used as a carrier gas. The concentration of each volatile compound was calculated by comparison with the peak area of a gaseous standard. The GC-MS system was calibrated weekly using cylinders with a standard of each detected compound (Rivoira, Milan, Italy) and the concentration of each volatile compound was calculated by comparison with the peak area of the gaseous standard. Different compounds were identified via the NIST library provided with the GC/MS Chem Station software (Agilent). Gas chromatography peak retention time was substantiated by analysis of parent ions and main fragments on the spectra. Following isoprenoid sampling, measurements of dark respiration ($R_d$) were also made at ambient $CO_2$ concentration on the same leaves by switching off the light in the cuvette and measuring the $CO_2$ emission rate.

### Input Data

Meteorological input data for the isoprene emission model consisted of global radiation, temperature and relative humidity. The data were measured at one of the meteorological stations of the Instituto Nacional de Tecnología Agropecuaria (INTA), located in Concordia in Eastern Entre Rios at a height of 48 m asl (31º 23´ S, 58º 02´ W). The model calculations were carried out using the meteorological values for a day in late summer (March 24, 2010) with clear sky, a maximum mean hourly global radiation level of 888 W $m^{-2}$, temperatures between 13°C (in the early morning) and 30°C (in the late afternoon) and values of relative humidity between 26% (in the afternoon) and 97% (in the morning). The leaf area indices were taken from a NASA MODIS product (http://modis.gsfc.nasa.gov), which provides composite images every 8 days, with a

spatial resolution of 0.5' (roughly 1 km). We used LAI data from 22 to 29 March 2010 as this covered the measurement period. The model calculations were carried out for 70 LAI classes, ranging from 0.1 to 7, the highest LAI of the MODIS product. Twenty eight percent of LAI values were between 1.0 and 2.0, 22% between 2.0 and 3.0 and 29% between 6.0 and 7.0. Isoprenoid emissions were calculated for all LAI classes (in steps of 0.1) on the grid of leaf area indices. The emissions were weighed in each grid cell with the portion of area covered by *Eucalyptus* forests as given by the forest inventory. The maps were created with a Geographical Information System, ArcGIS (ESRI, Redlands, USA), which allows software development with Visual Basic to realize the model computations.

**Dependence of Isoprene Emissions on Temperature and PPFD**

The dependence of isoprene emission $E_{ISO}$ (nM $m^{-2}$ $s^{-1}$) per leaf area on temperature and radiation was calculated as (European Emission Agency, 2007):

$$E_{ISO} = E_{ISO,S} \cdot C_T \cdot C_{PPFD} \quad (1)$$

Where, $E_{ISO,S}$ is isoprene emission at standard conditions (leaf temperature $T_S$ = 30°C and photosynthetic photon flux density active radiation $I_S$ = 1000 μM quanta $m^{-2}$ $s^{-1}$), $C_T$ and $C_{PPFD}$ are correction factors which take into account deviations from standard conditions. For the dependence of the emissions on leaf temperature and PPFD we used semi-empirical equations recommended by Guenther *et al*. (1993). The correction factor $C_T$ describes the dependence of the isoprene emission on leaf temperature $T$:

$$C_T = \frac{\exp\left(\frac{c_{T1} \cdot (T - T_S)}{R \cdot T \cdot T_S}\right)}{c_{T3} + \exp\left(\frac{c_{T2} \cdot (T - T_M)}{R \cdot T \cdot T_S}\right)} \quad (2)$$

Where, $R$ (= 8.314 $J^{-1}$ $M^{-1}$ $K^{-1}$) is the universal gas constant, $c_{T1}$ (= 95 000 J $M^{-1}$), $c_{T2}$ (= 230 000 J $M^{-1}$) and $T_M$ (= 314 K) are empirical coefficients and $c_{T3}$ (= 0.96) assures that $C_T$ is equal to one at standard temperature (Guenther, 1997). The correction factor increases with temperature, but decreases after a maximum at 39°C. The dependence on PPFD is given by:

$$C_{PPFD} = \frac{\alpha \cdot c_{L1} \cdot I}{\sqrt{1 + \alpha^2 \cdot I^2}} \quad (3)$$

Where, $I$ is PPFD (μM $m^{-2}$ $s^{-1}$ per leaf area) and $\alpha$ (= 0.0027) and $c_{L1}$ (= 1.066) are empirical coefficients. The function is zero at night and reaches its maximum asymptotically with increasing radiation. The two functions are suitable to describe the isoprene emission variation for a number of different plants including *Eucalyptus* (Guenther *et al*., 1993).

**Leaf Temperature**

Leaf temperature was calculated with the leaf energy budget of Campbell and Norman (1998) and Monteith and Unsworth (2008). The energy budget requires the energy absorbed by the leaf, which comprises PPFD, near-infrared radiation (NIR) and long-wave radiation from sun, sky and soil. The contributions of long-wave radiation from the canopy, sky and soil are calculated with the Stefan-Boltzmann equation (Goudriaan and van Laar, 1994). The absorption of short-wave and long-wave radiation depends on leaf height in the canopy as described by Wang and Leuning's model (1998). Sky emissivity was calculated according to Brunt's equation (Brunt, 1932), using FAO parameterization (FAO, 1990). The energy budget also takes into account energy lost through thermal radiation, by heat flow due to the difference between the leaf and ambient air, and by transpiration. To calculate transpiration the measured stomatal conductance (Table 1) was used, and its variation in response to PPFD was estimated using a rectangular hyperbola (Jarvis, 1976; Baldocchi *et al*., 1987). The energy budget equation is solved by iterative application of the Newton-Raphson method (Dai *et al*., 2004; Steinbrecher *et al*., 2009). As the absorbed shortwave radiation is different for sunlit and shaded leaves, different leaf temperatures were calculated for these leaves.

**Canopy Model for Radiation**

Because isoprene emission is strongly influenced by radiation, a model considering light extinction in the canopy was applied to scale up isoprene emissions from leaves to the whole canopy. To apply the radiation canopy model, the radiation above the canopy has to be subdivided into its components, e.g. direct and diffuse radiation. These components were estimated on the basis of global radiation and solar elevation angle according to the methodology described by de Pury and Farquhar (1997). One half of the energy flux is assumed to be in the range of the photosynthetically active radiation (400 – 700 nm) (Monteith and Unsworth, 2008). The direct and the diffuse photosynthetically active radiation is then calculated with a methodology described by de Pury and Farquhar (1997). To convert the energy flux to quantum flux a conversion factor of 4.57 μ M quanta $J^{-1}$ can be applied, for diffuse radiation the conversion factor is 4.24 μ M quanta $J^{-1}$ (McCree, 1972). The resultant direct and diffuse PPFD values serve as inputs for the canopy model. The radiation canopy model applied equations and parameters given by Goudriaan and van Laar (1994), de Pury and Farquhar (1997), Campbell and Norman (1998) and Friend (2001) to compute the radiation absorbed by sunlit and shaded leaves in the canopy. The radiation absorbed by shaded leaves takes into account diffuse radiation as well as scattered radiation. The radiation absorbed by sunlit leaves takes into account the additional direct irradiation from the sun.

### Canopy Model for Biogenic Emissions

The output of the canopy model for radiation are the sunlit and shaded absorbed PPFD values, $I_{sun}$ and $I_{sha}$, at the depth of the canopy corresponding to the cumulated leaf area index $L$ downwards from the top of the canopy. Canopy isoprene emission, $E_{ISO}^{cpy}$, is then calculated with equation (1), which is integrated over the cumulated leaf area index $L$ downwards from the top of the canopy:

$$E_{ISO}^{cpy} = \int_0^{LAI} E_{ISO}(T_{sun}, I_{sun}) \cdot f_{sun} dL + \int_0^{LAI} E_{ISO}(T_{sha}, I_{sha}) \cdot f_{sha} dL \quad (5)$$

The first and the second summand on the right side of this equation represent isoprene emission by the sunlit and shaded portions of the canopy, respectively. The variables $f_{sun}$ and $f_{sha}$ are the fractions of sunlit and shaded leaves at the canopy depth corresponding to the cumulated leaf area index $L$, which adopts values between the integral limits L = 0 and L = LAI, whereas LAI is the leaf area index of the canopy. The integrals were computed numerically using the Newton-Cotes method (Törnig, 1979). For the application of this method seven values of the integrand were calculated for different values of the cumulated leaf area index $L$. The values of the integrand are then multiplied with coefficients given by the Newton-Cotes method and summed up. The method was checked with test functions and exhibited a very high accuracy with integration errors of less than 1%.

### Model Procedure

The model procedure (Fig. 1) is carried out for LAI values up to LAI = 7. For each LAI value emission values for sunlit and shaded leaves at seven different canopy heights are used to calculate the whole canopy emission by integration. The model procedure is carried for a whole day in time steps of one hour. The daily emission of isoprene is spatially distributed corresponding to the MODIS LAI and the occurrence of *Eucalyptus* in the forest inventory.

## Results

### Gas Exchange Measurements

There were significant differences in gas-exchange parameters among leaf location (Table 1). Photosynthesis was significantly higher in leaves to the east and centre of the tree than of west. Stomatal conductance was not statistically different between the central and west leaves, but significantly increased in the east leaves. The different dynamics of $A_n$ and $g_s$ resulted in a significantly higher $A_n$ in east than central leaves, while no differences were detected between east and west leaves. There were no significant differences in $R_d$ among the different leaf location.

**Table 1:** Net photosynthesis (An), dark respiration (Rd), stomatal conductance (gs) and intercellular [$CO_2$] (Ci) of E. grandis

| | Unit | Centre | East | West |
|---|---|---|---|---|
| An | μmol $CO_2$ $m^{-2}$ $s^{-1}$ | 9.50 ± 0.86 b | 9.60 ± 0.79 b | 7.24 ± 0.57 a |
| Rd | μmol $CO_2$ $m^{-2}$ $s^{-1}$ | –2.69 ± 0.27 | –2.37 ± 0.32 | –2.54 ± 0.30 |
| gs | mol $H_2O$ $m^{-2}$ $s^{-1}$ | 0.079 ± 0.010 a | 0.101 ± 0.009 b | 0.076 ± 0.004 a |
| Ci | μmol $CO_2$ $mol^{-1}$ | 170 ± 9 a | 206 ± 9 b | 191 ± 7 ab |

**Table 2:** Emission of isoprene and monoterpenes (nmol $m^{-2}$ $s^{-1}$) from *E. grandis* measured at leaf temperature 30 °C and PPFD of 1000 μmol $m^{-2}$ $s^{-1}$

| Compound | | Centre | East | West |
|---|---|---|---|---|
| Isoprene | | 11.1 b | 18.8 c | 7.4 a |
| | Mean | | 12.5 ± 1.9 | |
| Monoterpenes | | | | |
| α-pinene | | 0.994 b | 1.254 c | 0.638 a |
| Camphene | | 0.112 a | 0.174 b | 0.122 a |
| Sabinene | | 0.294 a | 0.233 a | 0.597 b |
| β-pinene | | 0.227 b | 0.348 c | 0.074 a |
| β-myrcene | | 0.884 b | 1.749 c | 0.270 a |
| α-phellandrene | | 0.068 b | 0.155 c | 0.016 a |
| 3-carene | | 0.078 ab | 0.110 b | 0.032 a |
| a-terpinene | | 0.053 b | 0.050 b | 0.009 a |
| p-cymene | | 0.857 b | 1.031 c | 0.400 a |
| 1-8 cineole | | 0.962 b | 2.038 c | 0.695 a |
| Limonene | | 9.788 b | 16.850 c | 2.948 a |
| γ-terpinene | | 0.098 b | 0.195 c | 0.024 a |
| α-terpinolene | | 0.078 a | 0.196 b | 0.034 a |
| Linalool | | 0.128b | 0.046 a | 0.065 a |
| Camphor | | 0.077 | 0.088 | 0.070 |
| | Total | 14.7 b | 24.5 c | 6.0 a |
| | Mean | | 15.1 ± 3.1 | |

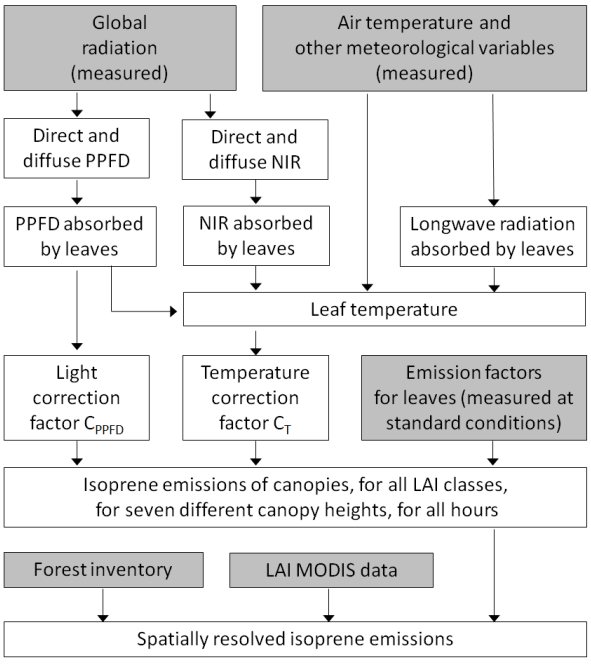


**Fig. 1:** Simplified scheme of the model procedure to estimate isoprene emissions. The grey boxes represent the model input data

Isoprene and monoterpene emission was also significantly affected by leaf position (Table 2). Emissions of both compounds decreased significantly from east to west. In general, a similar pattern was seen also in the predominant monoterpene compounds of the emitted blend of VOCs. The most abundant compound emitted was limonene, accounting for between 50 and 68% of the total monoterpene emission in the different leaf types, followed by 1-8 cineole, β-myrcene and α-pinene.

### Model Simulations

The photosynthetically active radiation above the canopy derived from the global radiation reached values of about 361 and 74 W $m^{-2}$ for direct and diffuse radiation (Fig. 2), respectively. The estimated leaf temperatures typically differed by a few degrees from the air temperature. The computations suggest that at midday, in a canopy with a high LAI, sunlit leaves were about 2 K warmer than air, while shaded leaf temperature hardly differed from air temperature. As expected, PPFD absorbed by the leaves within a canopy decreased with the canopy depth, as a result of the attenuation of diffuse light (data not shown). At LAI = 7 the isoprene emission on the selected day (March 24, 2010) reached a value of 51.8 mg $m^{-2}$ $d^{-1}$. The diurnal variation of the isoprene emission at LAI = 7 was a maximum of 7.9 mg $m^{-2}$ $h^{-1}$ (Fig. 3). In such a canopy, 42% of the isoprene emission comes from the top of the canopy (L = 0 – 1), and only 2% from the bottom. The time course of the isoprene emission course showed its strong dependence on light (Fig. 4). The spatial distribution of the emission (Fig. 5) was determined by the occurrence of Eucalyptus forests, which are mainly found in the Eastern part of the Entre Rios province. The maps show averaged values of 100 LAI grid cells with a resolution of 5' × 5'. For the whole study area the isoprene emission totalled 39.5 t $d^{-1}$.

## Discussion

*Eucalyptus* species are strong isoprene and monoterpene emitters, with large amounts of monoterpenes stored in specialised leaf cavities (Ashworth *et al*., 2013; Brilli *et al*., 2013). In such species, monoterpenes are largely emitted by evaporation in response to mechanical stress and warming (Ashworth *et al*., 2013). However, it has been demonstrated that emission rate of monoterpenes is not completely decoupled from their biosynthesis (Staudt *et al*., 1997; Komenda and Koppmann, 2002), as between 30–90% of total emission derives from light-dependent newly synthesized monoterpenes. The values of isoprene and monoterpene emissions recorded in this study reported in the literature for a number of *Eucalyptus* species (He *et al*., 2000; Brilli *et al*., 2013). Furthermore, isoprene measurements carried out above canopies of other species and ecosystems are also available, such as scrubland,

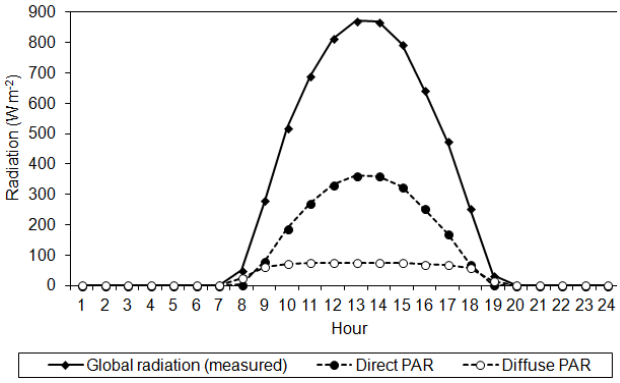


**Fig. 2:** Diurnal variation of the hourly global radiation based on measurements at the meteorological station in Concordia, Entre Rios, on March 24, 2010, and the calculated incident direct and diffuse PAR (photosynthetic active radiation) above the canopy

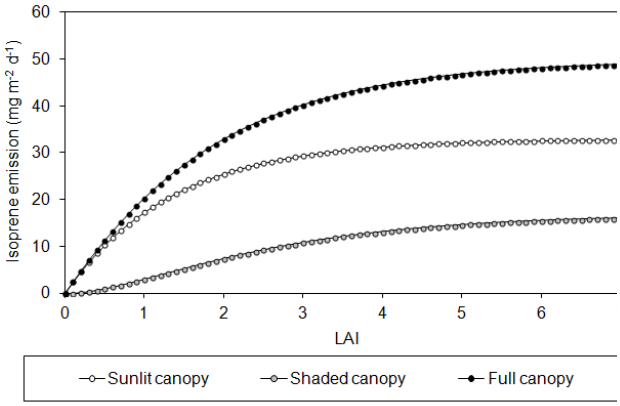


**Fig. 3:** Isoprene emission of the sunlit and the shaded fraction of the Eucalyptus canopy and of the total canopy at March 24, 2010, in dependence on the leaf area index, as calculated by the model

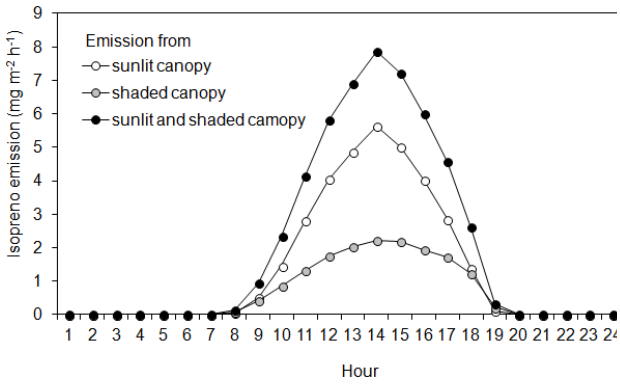


**Fig. 4:** Diurnal variation of isoprene emissions of an Eucalyptus canopy (LAI = 7), as calculated by the model

grassland and bogs in regions with temperate and tropical climate (Pacifico *et al*., 2009). The maximum fluxes of isoprene above forest canopies ranges between 2.2 mg $m^{-2}$ $h^{-1}$ for a tropical evergreen broadleaf forest in Amazonia (Rinne *et al*., 2002; Müller *et al*., 2008) and 29 mg $m^{-2}$ $h^{-1}$ for a temperate deciduous broadleaf forest in Michigan (Pressley *et al*., 2005). Our estimate of the maximum isoprene flux (7.9 mg $m^{-2}$ $h^{-1}$) for the Eucalyptus forest is thus within this measurement range.

Due to the asymptotic behaviour of the light dependency (Equation 3), maximum isoprene emission is easily achieved by leaves exposed to strong direct radiation. In contrast, shaded leaves are exposed to lower diffuse radiation, thus an increase of diffuse radiation leads to a more efficiently increase of isoprene emissions than found in sunlit leaves. Shaded leaves therefore constitute an important part of the canopy, and contribute significantly to biogenic emissions. In the present study, direct and diffuse PAR fluxes have been computed based on the global radiation for a clear sky. On such a day, diffuse radiation is much smaller than direct radiation, and exhibits little variation over the course of the day. However, during overcast skies, the contribution of diffused radiation may be larger and can exceed the contribution of the direct radiation. Therefore, to estimate biogenic emissions over longer periods it would be recommended to apply a method, which takes into account cloudiness, or to measure both components of radiation towards their use as inputs for the radiation canopy model. The light-dependence of isoprene emissions is relatively similar for a variety of plants (see e.g. Pacifico, 2009), so these estimations of isoprene emissions can be considered to be quite reliable.

Isoprene is predominantly emitted from the sunlit fraction of the canopy, but also the shaded fraction exhibited to diffuse light. Light strongly determines isoprene emissions and the equation that describes this dependency is well known (Equation 3). In contrast, monoterpene emissions depend strongly on temperature, and a exponential function has been proposed to describe the temperature dependency (Tingey *et al*., 1980). Approaches exist to describe the biosynthesis and emission of terpenoids in a mechanistic way. Bäck *et al*. (2005) described the synthesis of monoterpenes in a model including photosynthesis and photorespiration, which also requires a high number of model parameters not known in the present study. Other models (Niinemets and Reichstein, 2002; Noe *et al*., 2006) take into account monoterpene emission kinetics, related to the pools where monoterpenes are stored. These models require a greater number of input parameters, but in future studies may possibly be considered to replace the current empirical equation for monoterpenes.

The separation of the two components of PPFD (i.e., direct and diffuse PPFD) allows describing the light-dependent processes in the canopy. Due to the asymptotic behaviour of the light dependency (Equation 3), the maximum level of isoprene emission is easily reached for leaves exposed to strong direct radiation. In contrast, shaded leaves are exposed to lower diffuse radiation and an increase in diffuse radiation leads to a more efficient increase in isoprene emission than in sunlit leaves. Shaded leaves therefore constitute an important part of the canopy, and contribute significantly to biogenic emissions (Fig. 3).

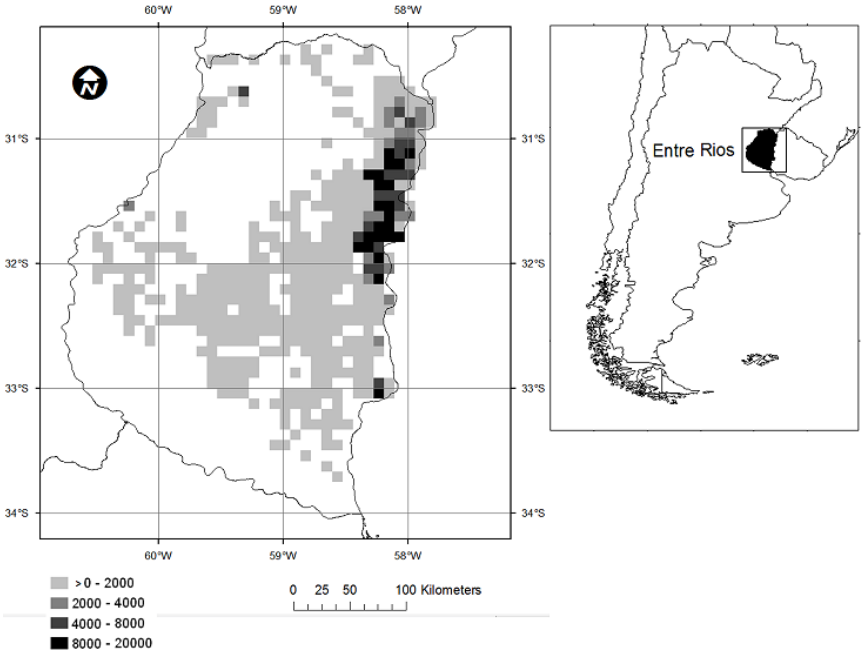


**Fig. 5:** Isoprene emission in µg $m^{-2}$ in the Argentine Entre Rios province on March 24, 2010. To improve the visual presentation, the values of 100 LAI grid cells have been averaged

In overcast skies the contribution of diffuse radiation to emission of isoprenoids may be even larger and exceed the contribution of direct radiation.

The difference between leaf and air temperature is strongly affected by the radiation absorbed the leaves. Leaves at the top of a canopy receive more shortwave radiation than leaves inside the canopy because radiation decreases with canopy depth. However, leaves at the top of a canopy receive relatively little thermal radiation from the sky in comparison with leaves fully surrounded by canopy, because the sky has a lower emissivity (approximately 0.80 in our case study) than leaves, which have an emissivity of nearly one. The wind speed profile within the canopy - with decreasing wind speeds from top to down (Monteith and Unsworth, 2007) - leads to a decreasing tendency for the energy exchange by transpiration and convection with ambient air (Campbell and Norman, 1998). When the model is performed with a leaf temperature equal to air temperature, the daily isoprene emission becomes 3% smaller and the maximum isoprene emission is reduced by 0.4 mg $m^{-2}$ $s^{-1}$. This indicates that in the present study of a single day, the difference between air and leaf temperature does not have a major influence on the emission estimates. However, on a global scale, isoprene emission is reported to be 18% higher when leaf temperature is used instead of air temperature (Müller *et al*., 2008); as a consequence, to conduct a more comprehensive approach an estimation of leaf temperatures is preferable.

## Conclusion

The present study utilises the results of field gas exchange measurements of a *Eucalyptus* species with the aim of estimating spatially resolved and time-dependent isoprene emissions in the Entre Rios province of Argentina. These measurements, combined with meteorological measurements, forest inventory and satellite-based data (leaf area indices), suggest emissions of up to approximately 39.5 t $d^{-1}$ isoprene in the course of a clear summer day. Future studies could take into account a higher resolution of meteorological input data, in addition to leaf age nutrient conditions, soil moisture and stress situations of the plant. Furthermore, other model approaches could be tested taking into consideration the internal $CO_2$ concentration of leaves. For this, however, more gas exchange and field measurements are needed. These measurements could include seasonal dependencies of the emissions and should cover the whole spectrum of tree species in the Mesopotamian region of Argentina.

## Acknowledgments

K.R. gratefully acknowledges support from the Centrum für internationale Migration und Entwicklung (CIM), Germany. Financial support was provided by INTA (proj. AERN 294421 and PNNAT 1128024) and by Ministero dell'Istruzione dell'Università e della Ricerca of Italy: PRIN 2010–2011 "PRO-ROOT" and Progetto Premiale 2012 "Aqua". The authors wish to thank field work assistance to Eugenia Beget and Alejandra Kemerer and to Dr. Matthew Haworth who assisted in the proof-reading of the manuscript.

## References

Arneth, A., R.K. Monson, G. Schurgers, U. Niinemets and P. Palmer, 2008. Why are estimates of global isoprene emissions so similar (and why is this not so for monoterpenes)? *Atmos. Chem. Phys. Discus*., 8: 7017–7050

Ashworth, K., C. Boissard, G. Folberth, J. Lathière and G. Schurgers, 2013. Global modelling of volatile organic compound emissions. *In: Biology, Controls and Models of Tree Volatile Organic Compound Emissions*, pp: 451–487. Ü. Niinemets and R.K. Monson (eds.). Springer, Dortrecht, Netherlands

Bäck, J., P. Hari, H. Hakola, E. Juurola and M. Kulmala, 2005. Dynamics of monoterpene emissions in *Pinus sylvestris* during early spring. *Boreal Environ. Res*., 10: 409–424

Baldocchi, D.D., B.B. Hicks and P. Camara, 1987. A canopy stomatal resistance model for gaseous deposition to vegetated surfaces. *Atmos. Environ*., 21: 91–101

Brilli, F., C. Barta, A. Fortunati, M. Lerdau, F. Loreto and M. Centritto, 2007. Response of isoprene emission and carbon metabolism to drought in white poplar (*Populus alba*) saplings. *New Phytol*., 175: 244–254

Brilli, F., T. Tsonev, T. Mahmood, V. Velikova, F. Loreto and M. Centritto, 2013. Ultradian variation of isoprene emission, photosynthesis, mesophyll conductance and optimum temperature sensitivity for isoprene emission in water-stressed *Eucalyptus citriodora* saplings. *J. Exp. Bot*., 64: 519–528

Brunt, D., 1932. Notes on radiation in the atmosphere. *Q. J. R. Meteorol. Soc*., 58: 389–418

Campbell, G.S. and J.M. Norman, 1998. *An Introduction to Environmental Biophysics*. Springer Science+Business Media, Springer–Verlag, Inc., New York. USA

Centritto, M., R. Tognetti, E. Leitgeb, K. Střelcová and S. Cohen, 2011. Above ground processes: Anticipating climate change influences. *In*: *Forest Management and the Water Cycle: An Ecosystem-Based Approach*, pp: 31–64. Bredemeier, M., S. Cohen, D.L. Godbold, E. Lode, V. Pichler and P. Schleppi (eds.). Ecological Studies 212. Springer, Dordrecht, The Netherlands

Chameides, W., R. Lindsay, J. Richardson and C. Kiang, 1988. The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study. *Science*, 241: 1473–1475

Ciccioli, P., M. Centritto and F. Loreto, 2014. Biogenic volatile organic compound emissions from vegetation fires. *Plant Cell Environ*., 37: 1810–1825

Claeys, M., B. Graham, G. Vas, W. Wang, R. Vermeylen, V. Pashynska, J. Cafmeyer, P. Guyon, M.O. Andreae, P. Artaxo and W. Maenhaut, 2004. Formation of secondary organic aerosols through photooxidation of isoprene. *Science*, 303: 1173–1176

Dai, Y., R.E. Dickinson and Y.P. Wang, 2004. A two-big-leaf model for canopy temperature, photosynthesis, and stomatal conductance. *J. Clim*., 17: 2281–2299

de Pury, D.G.G. and G.D. Farquhar, 1997. Simple scaling of photosynthesis from leaves to canopies without the errors of big-leaf models. *Plant Cell Environ*., 20: 537–557

European Environment Agency, 2007. *EMEP/CORINAIR Emission Inventory Guidebook*. Group 11: Other sources and sinks. Copenhagen, Denmark

FAO, 1990. Annex V. FAO Penman-Monteith formula. Food and Agriculture Organization of the United Nations, Rome, Italy

Fares, S., T. Mahmood, S. Liu, F. Loreto and M. Centritto, 2011. Influence of growth temperature and measuring temperature on isoprene emission, diffusive limitations of photosynthesis and respiration in hybrid poplars. *Atmos. Environ*., 45: 155–161

Friend, A.D., 2001. Modelling canopy $CO_2$ fluxes: are 'big-leaf' simplifications justified? *Glob. Ecol. Biogeogr*., 10: 603–619

Fuentes, J.D., M. Lerdau, R. Atkinson, D. Baldocchi, J.W. Bottenheim, P. Ciccioli, B. Lamb, C. Geron, L. Gu, A. Guenther, T.D. Sharkey and W. Stockwell, 2000. Biogenic hydrocarbons in the atmospheric boundary layer: a review *Bull. Amer. Meteorol. Soc*., 81: 1537–1575

Geron, C., S. Owen, A. Guenther, J. Greenberg, R. Rasmussen, J.H. Bai, Q.J. Li and B. Baker, 2006. Volatile organic compounds from vegetation in southern Yunnan Province, China: Emission rates and some potential regional implications. *Atmos. Environ*., 40: 1759–1773

Goudriaan, J. and H.H. van Laar, 1994. *Modelling Crop Growth Processes*, p: 238. Kluwer, Amsterdam, The Netherlands. Textbook with Exercises, Kluwer Academic Publisher. Dordrecht, The Netherlands

Grote, R., C. Morfopoulos, Ü. Niinemets, Z. Sun, T.F. Keenan, F. Pacifico and T. Butler, 2014. A fully integrated isoprenoid emissions model coupling emissions to photosynthetic characteristics. *Plant Cell Environ*., 37: 1965–1980

Guenther, A., 1997. Seasonal and spatial variations in natural volatile organic compound emissions. *Ecol. Appl*., 7: 34–45

Guenther, A., P.R. Zimmerman, P.C. Harley, R.K. Monson and R. Fall, 1993. Isoprene and monoterpene rate variability: model evaluations and sensitivity analyses. *J. Geophys. Res*., 98: 12609–12617

Guenther, A., X. Jiang, C.L. Heald, T. Sakulyanontvittaya, T. Duhl, L.K. Emmons and X. Wang, 2012. The model of emissions of gases and aerosols from nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions. *Geosci. Model Dev*., 5: 1471–1492

Guenther, A., 2013. Upscaling biogenic volatile compound emissions from leaves to landscapes. *In*: *Biology, Controls and Models of Tree Volatile Organic Compound Emissions*, pp: 391–414 Niinemets, Ü. and R.K. Monson (eds.). Springer Netherlands, Dortrecht

Harrison, S.P., C. Morfopoulos, K.G.S. Dani, I.C. Prentice, A. Arneth, B.J. Atwell, M.P. Barkley, M.R. Leishman, F. Loreto, B.E. Medlyn, Ü. Niinemets, M. Possell, J. Peñuelas and I.J. Wright, 2013. Volatile isoprenoid emissions from plastid to planet. *New Phytol*., 197: 49–57

He, C., F. Murray and T. Lyons, 2000. Monoterpene and isoprene emissions from 15 Eucalyptus species in Australia. *Atmos. Environ*., 34: 645–655

Jarvis, P.G., 1976. The interpretation of the variations in leaf water potential and stomatal conductance found in canopies in the field. Philosophical *Trans. Roy. Soc. Ldn., Series B*, 273: 593–610

Komenda, M. and R. Koppmann, 2002. Monoterpene emissions from Scots pine (*Pinus sylvestris*): field studies of emission rate variabilities. *J. Geophys. Res*., 107 (D13): 4161, doi: 10.1029/2001JD000691

Li, Z. and T.D. Sharkey, 2013. Molecular and pathway controls on biogenic volatile organic compound emissions. *In: Biology, Controls and Models of Tree Volatile Organic Compound Emissions,* pp: 119–151. Niinemets, Ü. and R.K. Monson (eds.). Springer, Dortrecht, The Netherlands

Lerdau, M., 2007. A positive feedback with negative consequences. *Science*, 316: 212–213

Loreto, F., M. Centritto, C. Barta, C. Calfapietra, S. Fares and R.K. Monson, 2007. The relationship between isoprene emission rate and dark respiration rate in white poplar (*Populus alba* L.) leaves. *Plant Cell Environ*., 30: 662–669

Loreto, F. and M. Centritto, 2008. Leaf carbon assimilation in a water-limited world. *Plant Biosyst*., 142: 154–161

Loreto, F. and J.P. Schnitzler, 2010. Abiotic stresses and induced BVOCs. *Trends Plant Sci*., 15: 154–166

Loreto, F. and S. Fineschi, 2015. Reconciling functions and evolution of isoprene emission in higher plants. *New Phytol*., 206: 578–582

McCree, K.J., 1972. Test of current definitions of photosynthetically active radiation against leaf photosynthesis data. *Agric. Meteorol*., 10: 443–453

Monteith, J. and M. Unsworth, 2008. *Principles of Environmental Physics*. Third edition. Academic Press, London

Müller, J.-F., T. Stavrakou, S. Wallens, I. De Smedt, M. Van Roozendael, M.J. Potosnak, J. Rinne, B. Munger, A. Goldstein and A. Guenther 2008. Global isoprene emissions estimated using MEGAN, ECMWF analyses and a detailed canopy environment model. *Atmos. Chem. Phys*., 8: 1329–1341

Niinemets, Ü. and M. Reichstein, 2002. A model analysis of the effects of nonspecific monoterpenoid storage in leaf tissues on emission kinetics and composition in Mediterranean sclerophyllous *Quercus* species. *Glob. Biogeochem. Cycle*, 16: 57-1–57-26

Niinemets, Ü., 2010. Mild versus severe stress and BVOCs: thresholds, priming and consequences. *Trends Plant Sci*., 15: 145–153

Noe, S.M., P. Ciccioli, E. Brancaleoni, F. Loreto and Ü. Niinemets, 2006. Emissions of monoterpenes linalool and ocimene respond differently to environmental changes due to differences in physico-chemical characteristics. *Atmos. Environ*., 40: 4649–4662

Pacifico, F., S.P. Harrison, C.D. Jones and S. Sitch, 2009. Isoprene emissions and climate. *Atmos. Environ*., 43: 6121–6135

Pallozzi, E., A. Fortunati, G. Marino, F. Loreto, G. Agati and M. Centritto, 2013a. BVOC emission from *Populus × canadensis* saplings in response to acute UV-A radiation. *Physiol. Plant*., 148: 51–61

Pallozzi, E., T. Tsonev, G. Marino, L. Copolovici, Ü. Niinemets, F. Loreto and M. Centritto, 2013b. Isoprenoid emissions, photosynthesis and mesophyll conductance in response to blue light in *Populus x canadensis*, *Quercus ilex* and Citrus reticulata. *Environ. Exp. Bot*., 95: 50–58

Peñuelas, J. and M. Staudt, 2010. BVOCs and global change. *Trends Plant Sci*., 15: 133–144

Pressley, S., B. Lamb, H. Westberg, J. Flaherty, J. Chen and C. Vogel, 2005. Long-term isoprene flux measurements above a northern hardwood forest. *J. Geophys. Res*., 110, D07301

Rinne, H.J.I., A.B. Guenther, J.P. Greenberg and P.C. Harley, 2002. Isoprene and monoterpene fluxes measured above Amazonian rainforest and their dependence on light and temperature. *Atmos. Environ*., 36: 2421–2426

SAyDS, D.B, 2007. *Primer Inventario Nacional de Bosques Nativos* (PINBN) – Informe Nacional de la Dirección de Bosques (DB) de la Secretaría de Ambiente y Desarrollo Sustentable (SAyDS), Argentina. ISBN 978-96256-6-8

Sharkey, T.D. and F. Loreto, 1993. Water-Stress, temperature, and light effects on the capacity for isoprene emission and photosynthesis of kudzu leaves. *Oecologia*, 95: 328–333

Sharkey, T.D. and R.K. Monson, 2014. The future of isoprene emission from leaves, canopies and landscapes. *Plant Cell Environ*., 37: 1727–1740

Steinbrecher, R., G. Smiatek, R. Köble, G. Seufert, J. Theloke, K. Hauff, P. Ciccioli, R. Vautard and G. Curci, 2009. Intra- and inter-annual variability of VOC emissions from natural and seminatural vegetation in Europe and neighbouring countries. *Atmos. Environ*., 43: 1380–1391

Staudt, M., N. Bertin, U. Hansen, G. Seufert, P. Ciccioli, P. Foster, B. Frenzel and J.L. Fugit, 1997. Seasonal and diurnal patterns of monoterpene emissions from *Pinus pinea* (L.) under field conditions. *Atmos. Environ*., 31: 145–156

Tingey, D.T., M. Manning, L.C. Grothaus and W.F. Burns, 1980. Influence of light and temperature on monoterpene emission rates. *Plant Physiol*., 65: 797–801

Törnig, W., 1979. *Numerische Mathematik für Ingenieure und Physiker*, Band 2. Springer-Verlag, Germany

Trainer, M., E.J. Williams, D.D. Parrish, M.P. Buhr, E.J. Allwine, H.H. Westberg, F.C. Fehsenfeld and S.C. Liu, 1987. Models and observations of the impact of natural hydrocarbons on rural ozone. *Nature*, 329: 705–707

Wang, Y.P. and R. Leuning, 1998. A two-leaf model for canopy conductance, photosynthesis and partitioning of available energy I. Model description and comparison with a multi-layered model. *Agric. For. Meteorol*., 91: 89–111

**(Received 16 May 2015; Accepted 12 October 2015)**