Assessment of high to low frequency variations of isoprene emission rates using a neural network approach

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Abstract

Using a statistical approach based on artificial neural networks, an emission algorithm (ISO_LF) accounting for high (instantaneous) to low (seasonal) frequency variations was developed for isoprene. ISO_LF was optimised using an isoprene emission data base (ISO-DB) specifically designed for this work. ISO-DB consists of 1321 emission rates collected in the literature, together with 34 environmental variables, measured or assessed using NCDC (National Climatic Data Center) or NCEP (National Centers for Environmental Predictions) meteorological databases. ISO-DB covers a large variety of emitters (25 species) and environmental conditions (10° S to 60° N). When only instantaneous environmental regressors (air temperature and photosynthetic active radiation, PAR) were used, a maximum of 60% of the overall isoprene variability was assessed and the highest emissions were underestimated. Considering a total of 9 high (instantaneous) to low (up to 3 weeks) frequency regressors, ISO_LF accounts for up to 91% of the isoprene emission variability, whatever the emission range, species or climate. Diurnal and seasonal variations are correctly reproduced for Ulex europaeus with a maximum factor of discrepancy of 4. ISO-LF was found to be mainly sensitive to air temperature cumulated over 3 weeks T21 and to instantaneous light L0 and air temperature T0 variations. T21, T0 and L0 only accounts for 76% of the overall variability. The use of ISO-LF for non stored monoterpene emissions was shown to give poor results.

1 Introduction

Chemistry-Transport models (CTMs) are commonly used to assess the distribution of tropospheric species, such as ozone, at local or global scales. Appropriate and accurate emission data are needed to initialise their chemical modules. Emissions of gaseous compounds in the atmosphere can be related to human activities and natural processes. Volatile organic compounds (VOC) emitted from foliage, usually referred
to as biogenic VOC or BVOC, are key species in atmospheric chemistry processes. Indeed, (i) their global emissions are believed to exceed the VOC anthropogenic inputs by a factor of 10 (Müller, 1992; Guenther et al., 1995) and, (ii), on a global to regional scale, due to their high reactivity, they are believed to significantly influence atmospheric chemistry and climate (Fehsenfeld et al., 1992; Simpson, 1995; Poisson et al., 2000; Steinbrecher et al., 2000; Sanderson et al., 2003). Therefore, assessment of accurate and highly resolved BVOC emission fluxes is a major goal for environmental issues. Many efforts have been undertaken to understand the biological and physical processes involved in BVOC emissions. Some BVOC emission parameterisations have thus been developed, mainly for isoprene and monoterpenes (Tingey et al., 1979; Guenther et al., 1991; Guenther et al., 1993; Sharkey and Loreto, 1993; Lehning et al., 2001; Guenther et al., 2006). These parameterisations were based on the recognition that incident photosynthetic active radiation (PAR) and leaf temperature intensities are key parameters in BVOC emission rate regulations. However, most of these parameterisations account for relatively short term (minutes to hours) plant adaptations to ambient light and temperature changes. Nevertheless, tree capacity to release BVOC into the atmosphere was observed to be highly dependent as well on lower frequency (e.g. seasonal) variations of environmental conditions (see review section hereafter). Such seasonal adaptations were recognised to significantly account for the overall variability observed for BVOC emissions (Pier and McDuffie, 1997; Goldstein et al., 1998; Boissard et al., 2001) and thus to represent a major source of discrepancies from actual BVOC emission assessments (Guenther et al., 1995). Some attempts were made to understand and predict BVOC emission variations other than the instantaneous ones (Pier and McDuffie, 1997; Geron et al., 2000; Staudt et al., 2000; Hakola et al., 2001; Lehning et al., 2001; Petron et al., 2001; Guenther et al., 2006) but were not broadly validated.

In this manuscript, a new approach (a multiple non-linear regression based on artificial neural networks – ANNs) is employed to develop an isoprene emission rate algorithm, ISO-LF, which accounts for high (minutes to hours) to low (seasonal) frequency
variations. ANNs were trained using an appropriate database (ISO-DB) specifically built for this work. First, we present a review of the current understanding of BVOC emission seasonal variations. ISO-LF development, performances and sensitivity are then presented and discussed together with its use to other BVOC emissions (non stored monoterpene).

2 Seasonal variability of BVOC emissions: a review

Among the numerous works undertaken on BVOC emissions, a significant number directly or indirectly focused on their seasonal aspects. The impacts on BVOC emissions of the growth conditions recorded from few days to few weeks before the measurements have been screened over a large range of environmental conditions and for different species (Table 1). This section reviews (i) the main seasonal observations reported in the literature for isoprene, monoterpenes, and other BVOC, (ii) the environmental indicators shown to be able to describe some of the observed variations and, (iii), our understanding of some of the mechanisms underlying the observed variability.

Low frequency variations of BVOC emissions represent a significant and, in some cases, the major part of the overall observed emission fluctuations, whatever the plant species, the location or the type of compound emitted by the plants. One of the first evidence was observed for $\alpha$-pinene emissions of *Pinus densiflora* (Yokouchi et al., 1984) and isoprene emissions of *Quercus serrata* (Ohta, 1986). Both studies, carried out in Japan, reported, as expected, much higher emission rates during early summertime, with a factor of 16 and 2 of difference between observed minimum and maximum emission rates for pine and oak respectively. Differences in the local environmental conditions (air temperature and light intensity) that a leaf experiences during measurements, can no explain all this observed emission variability. Indeed, when BVOC emission rates are standardised to normalised temperature – 303 K – and light intensity – 1000 $\mu$mol m$^{-2}$ s$^{-1}$ – (G93 algorithms, Guenther et al., 1993) – the observed variations remain as large as few orders of emission magnitude, whatever the BVOC,
the emitting species or the environmental conditions. For isoprene, this seasonal variability were found to occur over 2 to 3 orders of magnitude of standardised emission rates (Monson et al., 1994; Geron et al., 2000; Petron et al., 2001). Similarly, Janson (1993) reported for monoterpenes emissions from Pinus sylvestris and Picea abies (two emitters with monoterpenes storage organs) in Sweden, a seasonal ratio of 22 between the maximum and the minimum standardised total monoterpenes emissions. In southern Germany, an even higher ratio of 62 was observed for Pinus sylvestris emissions (Komenda and Koppman, 2002). When measurements were carried out over an entire growing period, seasonal variations of more than one order of magnitude were observed for total monoterpenes emissions emitted by Quercus ilex, a non-stored monoterpenes emitter, independent of its location (Bertin et al., 1997; Kesselmeier et al., 1997; Llusia and Peñuelas, 2000; Peñuelas and LLusia, 1999; Sabillon and cremades, 2001), with highest emissions usually observed between springtime and summertime, and occasionally, during autumn too. In the tropical and subtropical environment, monoterpenes emissions were also observed to vary seasonally, but with a much lower magnitude for Eucalyptus ssp in Australia (He et al., 2000) and deciduous trees (Hymenaea courbaril and Apeiba tibourbou) in Brazil (Kuhn et al., 2004). Monoterpenes composition in broadleaf trees is generally relatively stable over the season, the observed interspecies fluctuations being attributed to genetics differences (Bertin et al., 1997; Staudt et al., 2001 and Fishbach et al., 2002 for Quercus ilex; Hakola et al., 2001 for Betula pendula and Betula pubescens). On the contrary, the monoterpenes emissions from Pinus pinea grown in air conditioned greenhouse were found to be dominated by limonene and trans-β-ocimene during winter and summer respectively (Staudt et al., 2000). These results suggest that monoterpenes seasonal variations may be complicated due to their respective ecological roles, e.g., for attracting pollinators, or as defence substances (Litvak and Monson, 1998; Rapparini et al., 2001; Llusia and Peñuelas, 2000).

As other BVOC (sesquiterpenes, oxygenated VOC in particular) emissions are concerned, their seasonal pattern is, so far, still poorly documented. However, some re-
cent data obtained in California, suggest that direct biogenic emissions of acetone and methanol are likely to influence the seasonal variations of their ambient air concentrations (Schade and Goldstein, 2006). In California too, Arey et al. (1995) reported some significant seasonal variations for total sesquiterpene emissions. However, as for monoterpenes, the sesquiterpene relative composition can seasonally fluctuate. The capacity of leaves to emit BVOC, apparently closely correlates with leaf developmental stage. In the case of isoprene for instance, a first period of emission induction (from few days to few weeks) has been noticed after bud break before the emissions start to increase, until a maximum level was reached in mature leaves. A more or less regular decrease of emissions down to non detectable levels has then been observed during the leaf senescence of Populus tremuloides (Monson et al., 1994), Populus trichocarpa (Petron et al., 2001), Quercus alba (Geron et al., 2000) and Quercus macrocarpa (Petron et al., 2000). However, this regular ‘bell shape’ trend has not systematically been observed for all BVOC. Indeed, some unexpected high monoterpene emissions were recorded too during autumn for Quercus ilex in the Mediterranean area (Bertin et al., 1997) and for Pinus sylvestris in a boreal environment (Janson, 1993) suggesting some complex unexplained regulation processes. Some rather simple environmental indicators, such as the amount of energy accumulated by the plant as heat or incident light, have been successfully used to predict the early season increase and the late season decrease of emissions. Induction was observed to occur after 200, 300 or 400 degree day (d.d.) after bud break for Quercus trichocarpa (Petron et al., 2001) and Quercus macrocarpa (Petron et al., 2000) and Populus tremuloides (Monson et al., 1994) respectively. A total of 600 (700 respectively) d.d. after bud break was then needed for Q. alba (Q. macrocarpa respectively) isoprene emissions to reach their maximum levels. Depending on local environmental conditions, these d.d. values correspond to temperatures cumulated within a few days to a maximum of 3 weeks for branch measurements and up to 4 weeks for canopy fluxes (Canadian temperate forest, Fuentes and Wang, 1999). Onset of total
monoterpene emissions from birch were similarly shown to occur when an Effective Temperature Sum (ETS) above 5°C of 400 d.d. was reached (Hakola et al., 2001). However the emission decline was more variable for different birches and could not be parameterised. When individual monoterpenes were considered, *Betula pubescens* linalool emissions were observed to dominate for ETS>400 d.d. (flowering stage) and decrease when ETS reached a value of 800 d.d. from which sesquiterpene (mainly caryophyllene) emissions then dominated. In addition to the more general seasonal trend, emission potentials may vary also in response to recent weather conditions. Sharkey et al. (1999) found that isoprene emission rate variations from mature oak leaves were significantly correlated with air temperatures averaged over the previous 1, 2 and 7 days (T1, T2 and T7 respectively) and with photosynthetic active radiations averaged over the previous 2 days (PAR2), the strongest correlation being with T2×PAR2. Rapid (over 1 day) changes of basal oak isoprene emission rates early in the growing season were found to be best described by T1×PAR1. More recently, time lags of 1 and 10 days are considered for effects of cumulated temperature in the isoprene MEGAN emission model (Guenther et al., 2006).

Variations of isoprene and monoterpene emissions being related to their enzymatic synthase activity (Lehning et al., 1999; Fishbach et al., 2002), plant growth conditions and acclimations to more or less long term environmental changes are in fact more critical than leaf developmental stage only. Isoprene synthase activity of *Quercus robur* was shown to adapt within 24 to 48 h to new temperature and light conditions (Lehning et al., 1999; Zimmer et al., 2000). Acclimation to new growth temperature only was observed to be as rapid (<24 h) for Sphagnum moss (Hanson and Sharkey, 2001). Elevated temperature growth conditions were found to shorten the delay of kudzu isoprene onset to one week compared to 2 weeks under cold growth conditions (Wiberley et al., 2005). The light acclimation was observed to be more complex, with a first adaptation occurring within few hours and a second one after 4–6 days (Hanson and Sharkey, 2001). Bertin et al. (1997) found some similar impacts of long term shading adaptations for *Q. ilex* monoterpene emissions (a factor of 17 differences was
observed between sunlit and shaded branch standardized emission rates), and water availability which was suggested to be responsible of the observed high fall emissions. Water influence on monoterpene emissions was also suspected for *Pinus sylvestris* and *Picea abies* (Janson, 1993). Drought was found to dramatically increase the proportion of assimilated carbon lost as isoprene from *Populus deltoides* (Pegoraro et al., 2004, 2005). However, over periods with longer and more severe water stress, these isoprene emissions were shown to decrease again, probably due to a depression of the photosynthetic activity when any alternative carbon pools are eventually depleted for isoprene formation.

3 Method

3.1 The overall strategy

Since variation in isoprene emission capacity was observed, for different emitters and in various locations (see previous Review section) to present a fairly reproducible seasonal pattern, an emission rate algorithm (ISO-LF) was developed for isoprene. ISO-LF was also tested for emission rates of the monoterpenes from plant species that, like isoprene, do not store these after synthesis.

Most current approaches for assessing BVOC emissions assign an emission factor to an emitter or a group of emitters, which is then modulated by the prevalent instantaneous ambient conditions or linked to leaf carbon assimilation (Guenther et al., 1993, 2006; Arneth et al., 2007). However, the ‘emissions factors’ may actually represent all the proportion of the emission intensity that is not yet parameterised. Thus, as summarised in the previous section, large uncertainties in the value of the emission factors exist. Table 1 provides an overview over BVOC emission studies that explicitly reported seasonal variation in emission capacity. Interestingly, among the data reported in this table, the magnitude in the observed seasonal variation from bud break to after senescence were found to be strongly ($r^2 = 0.83$, n=13) correlated with local
environmental conditions. Indeed, as shown in Fig. 1, the ratio $R_{\text{max}}/\text{min}$ between the maximum and minimum standardised emission rates of isoprene ($n=6$), monoterpenes ($n=4$) and oxygenated BVOC ($n=3$) was found to increase with the absolute value of the measurement latitude, $L$ (taken as surrogate for average growth conditions at a given location), following an exponential relation as:

$$R_{\text{max}}/\text{min} = 0.716 \exp^{0.084 \times |L|}$$

Because generally cooler conditions are prevailing at higher latitudes, the magnitude of environmental differences between the coldest and the warmest periods, in other words between the worst and optimal environmental conditions for isoprene emissions, increases.

A statistical approach, a multiple non-linear regression based on an artificial neural network (ANN), was thus used to weight the overall impact of various selected environmental variables on the isoprene emission rate variability. Among the various available statistical methods, ANNs present the advantage of being the most parsimonious (Dreyfus et al., 2002), which means that a same level of error can be obtained with much fewer regressors than with other methods. Moreover, the ANN approach, as the other non-linear regression methods, is not, or not very, sensitive to the regressor co-linearity (see for example Bishop, 1995 and Dreyfus et al., 2002). Such an approach has already been successfully applied for isoprene emission rates of *Ulex europaeus* (Lasseron, 2001), showing that the consideration of low frequency environmental regressors such as temperatures cumulated over 2 and 3 weeks ($T_{14}$ and $T_{21}$ respectively) were significantly reducing the uncertainty in assessing isoprene emission variations. This work extended this first approach to a broader set of emitters and environmental conditions. ANNs were thus trained and optimised using an appropriate database (ISO-DB) specially built for this study.
3.2 Neural network principle and description

The neural network developed in this study was based on a commercial version of the Netral NeuroOne software (v. 5.0 – http://www.netral.com, France), used as a Multi Layer Perceptron (MLP) in order to calculate multiple non-linear regressions between a set of input regressors $x_i$ (the environmental variables) and the output data $y_{calc}$ (the isoprene emission rates). Further details concerning the MLP theory can be found, for instance, in Aleksender and Morton (1990) and White (1992). Basically, an artificial neuron consists of a parameterised asymptotic ”S” shape function $f$ that calculates the weighted sum $w_i \times x_i$ of the input data before transferring it to the output layer ($f$ is thus sometimes referred to as ’transfer function’). Within an ANN, a different number of neurons $N_j$ can be used and arranged in a network of different layers. However, whatever the network, every input regressors $x_i$ is connected to each neuron $N_j$, all are connected together and to the final output data. Figure 2 presents an example of an ANN based on 2 neurons. The output value $Y_{calc}$ is then calculated according to:

$$Y_{calc} = w_0 + \sum_{j=1}^{j=N} \left[ w_j \times f \left( w_{0,j} + \sum_{i=1}^{i=n} w_i \times x_i \right) \right]$$

(2)

where $w_0$ is the connecting weight between the bias and the output, $N$ the number of neurons $N_j$, $f$ the transfer function, $w_{0,j}$ the connecting weight between the bias and the neuron $N_j$, $w_i$ the connecting weight between the input and the neuron $N_j$, and $x_i$ the $n$ input regressors. Optimised weights are assessed during a training phase which consists, starting from random values of $w_j$, in minimising the difference $E$ between the calculated and measured outputs. For this study, $E$ was calculated as follows:

$$E = \frac{1}{2} \sum_{k=1}^{k=z} (Y_{calc} - Y_{mes})^2$$

(3)

where $l$ is the number of the $z$ output values. For ISO-LF development, a large number (300) of iterations were selected for every ANN run in order to make sure that $E$ did
not correspond to a local error minimum. During a validation phase, or blind validation, the ANN performance was then assessed using the mean square root (MSR) obtained with data that were not used during the training phase. A special set of validation data was thus saved before start. Training and validation data splitting represents a key step in neural approach. For this work, the training-validation division was, first, carried out regarding the different climates and types of emitter present in ISO-DB. For each of the 4 climates considered here (tropical, temperate with dry summer, temperate without dry summer, and cold and humid) data were classified according to their emission strength (strong, medium and small as in Guenther et al., 1995). A total of 11 sub datasets were thus considered. Each of them was then split between training data (80%) and data used for the blind validation (20%), using a Kullback-Leibler distance function (Kullback, 1951) for statistical homogeneity. The final training (n=1062) and validation (n=259) databases consist of the union of each training and validation sub-datasets. As shown in Fig. 3 for isoprene emission rates, both databases were found to be statistically homogeneous, with training mean, first second and third quartile values of 30.01, 1.87, 14.57 and 38.53 µgC (g foliar dry weight)\(^{-1}\) h\(^{-1}\) (hereafter, µgC g\(_{dwt}\)\(^{-1}\) h\(^{-1}\)) respectively, similar to validation values of 30.39, 2.75, 16.08 and 38.50 µgC g\(_{dwt}\)\(^{-1}\) h\(^{-1}\) respectively. Note that the highest (3.3×10\(^2\) µgC g\(_{dwt}\)\(^{-1}\) h\(^{-1}\)) and smallest (5.0×10\(^{-4}\) µgC g\(_{dwt}\)\(^{-1}\) h\(^{-1}\)) isoprene emission rates belong to the training database, since the neural approach is only valid within interpolation.

3.3 ISO-DB description

The isoprene database ISO-DB designed for this study consists of:

1. 1321 isoprene emission rate values, collected in the literature from previous in-situ studies. (note that not all of them were carried out over a seasonal range, therefore they are not necessarily extracted from Table 1 whom only half of the 16 studies dealt with seasonal aspects of isoprene emissions). All emission rates represent branch level measurement, most of them (93%) were obtained using branch
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ISO-DB covers a total of 25 different emitting species from different families of deciduous and coniferous trees grown under environmental conditions ranging from tropical (10° S) to boreal (60° N) climates (Table 2). Emission rates values were shown to vary over more than 4 orders of magnitude, from, approximately, $5 \times 10^{-4}$ to $3 \times 10^{2} \mu g_{C} g_{dwt}^{-1} h^{-1}$ (Appendix A), much larger than could be attributed to discrepancies between sampling methods. Most species included are representative for moderate to high isoprene emitters (i.e. standardised emission rates higher than 35 and 70 $\mu g_{C} g_{dwt}^{-1} h^{-1}$ respectively, as in Guenther et al., 1994). ISO-DB mean and median emission rate values are 30.1 and 14.8 $\mu g_{C} g_{dwt}^{-1} h^{-1}$ respectively.

2. temperature (T0) and PAR (L0) values, recorded at times when samples for emission analysis were taken, hereafter referred to as ‘instantaneous’, although these parameters were integrated over the whole sampling period ranging from about 5 to 25 minutes; temperature (respectively PAR) was found to range from 2 to 42°C (0 to 2400 $\mu$mol m$^{-2}$ s$^{-1}$, respectively), with a mean and median value of 25.1 and 25.5°C (680 and 590 $\mu$mol m$^{-2}$ s$^{-1}$, respectively).

3. 32 other medium to low frequency environmental regressors were examined (Appendix B) for their ability to account for the overall environmental change on isoprene emission variations during and before the emission measurement. Some of them have been previously recognised (cumulated air temperature and light intensity), or suspected (rainfall, soil temperature and water content, minimum and maximum air temperatures) to directly or indirectly influence BVOC emission variations (see review section). Based on the observations obtained for isoprene emission acclimation to temperature and light changes (see previous review section) all input regressors were summed from 1 day (the shortest ac-
climatic time reported for isoprene synthase activity) up to three weeks. However, no information is available to evaluate if such lag times are relevant for inputs other than temperature and light intensity. Expect for instantaneous temperature and light intensity values that were extracted together with the isoprene emission values from the literature references used for this work, the other environmental parameters, seldom recorded during the emission measurements, were all derived from the NCDC (National Climatic Data Center) meteorological data (http://www.ncdc.noaa.gov/oa/ncdc.html) for air temperatures and rainfall, or NCEP (National Centers for Environmental Predictions) reanalysis data (http://www.ncep.noaa.gov) for soil variables and solar radiations. All the selected meteorological stations were within a distance of 30 km of each site measurement, except for the Kuhn et al. (2002, 2004) data obtained in Brazil where no meteorological station was available within 200 km. However, since tropical climatic conditions are fairly stable within the same season, the potential bias of using distant meteorological station data was hypothesised to be minor, especially for low frequency variables. Similarly, environmental data were not available in 1984 at the Nagoya station for Ohta (1986) *Quercus serrata* measurements. Meteorological data available in 1984 at the nearest station, Shionomisaki located approximately at a distance of 200 km was corrected by the differences obtained between both stations over the 1994–2004 period. Canopy effects on the amount of light received by a leaf through the canopy and the temperature were accounted for shaded leaf emission data according to the Lamb et al. (1993) model. The daylight length $D$ was considered for its capacity in discriminating which period in the seasonal emission pattern was calculated as:

$$D = \frac{24}{\pi} \arccos(-\tan \lambda \cdot \tan(\arcsin(\sin \delta \cdot \cos[\frac{2\pi}{n}(r - 172)])))$$  \hspace{1cm} (4)$$

where $\lambda$ is the latitude, $\delta=23.45^\circ$ the Earth inclination, $r$ the day of the year, and $n$ the number of day in a year (365 or 336 for bissextile years).
3.4 Data pre-processing

Since input regressors are expressed in different units, their absolute value can range over a huge magnitude. To prevent input variables $x_i$ from having an artificially stronger weight in the neural network, they were thus all centrally-normalised as follows:

$$X_i(CN) = \frac{x_i - \bar{x}_i}{s_{x_i}}$$

(5)

where $\bar{x}_i$ is the mean of the variable $x_i$, and $s_{x_i}$ its associated standard deviation calculated for the entire ISO-DB. Output data (isoprene emission rates) were similarly treated. In addition, due the large range of variation (5 orders of emission magnitude), the log of the pre-processed isoprene emission rates was used in the neural network.

4 Results and discussion

Note that, when not mentioned, the results hereafter presented were obtained with validation data.

4.1 Are L0, T0, L1 and T1 sufficient to account for the overall BVOC emission variability?

In order to make sure that the variability of ISO-DB emissions is not only a response to high frequency environmental changes, L0, T0, L1 and T1, recognised for their role in describing short term acclimation of isoprene emissions (Guenther et al., 1993; Geron et al., 2000; Lehning et al., 2001) were tested in ANNs. Two series of runs were conducted: (i) the ANN0 case, using L0 and T0 only, and, (ii) the ANN01 case with T0, T1, L0 and L1. Results obtained for validation data are compared in Table 3 with the measured isoprene emission rates. The consideration of L0 and T0 only was shown to account for less than 60% of the isoprene emission variability. Adding L1 and T1
variables (ANN01 case), the results were significantly improved at the 95% confidence level, with up to 70% of the overall variability explained (see detailed results in Table 3). The remaining 30% were mainly associated with the highest emission values which were underestimated by up to two orders of magnitude (results not shown).

4.2 Development of ISO-DB, an isoprene emission algorithm accounting for high to low frequency variations

The isoprene emission algorithm ISO_LF was obtained from an optimum combination of environmental regressors (selected among the 34 inputs available in ISO-DB) and network structure (number of neurons, transfer function, number of iterations, network structure). Combinations of 3 transfer functions (the arctangent atn, the hyperbolic tangent tanh and the sigmoid sig) and up to 7 neurons were tested. For each neural network run, 300 initialisations were performed and a second order Quasi-Newton back-propagation method used. In order to avoid overtraining, one of the main problem in statistical regressions, the number of input regressors must be kept as small as possible. Using the statistical probe technique (Stoppiglia, 1997) and a covariance analysis, inputs which were shown to have no statistical influence on isoprene emissions, or which have a weak influence but were strongly ($r^2 > 0.97$) correlated with other dominating input regressors, were rejected. In addition, regressors $x_i$ for whom $\frac{\Delta \log E}{\Delta x_i}$ was found to be of the same order of magnitude or higher than the isoprene emission rate $E$ itself were considered to have very little influence and were also rejected ($\Delta x_i$ corresponds to $x_i$ range of variation in ISO-DB). A best validation mean squared error $\text{MSE}_{\text{validation}}$ of 0.086 was eventually obtained with the tanh function, 4 neurons set in one layer and 9 input regressors: the instantaneous air temperature $T_0$ and light intensity $L_0$, the (d-1) day mean ($T_1$) and minimum ($T_1m$) air temperatures, solar radiation ($L_1$) and soil temperatures ($ST_1u$), the precipitation cumulated over 2 and 3 weeks ($P_{14}$ and $P_{21}$ respectively), and the air temperature cumulated over 3 weeks $T_{21}$ (Appendix B). When a single one of these 9 variables was excluded from the statistical
analysis, isoprene emission assessment error was, at the 95% confidence level, significantly increased. One third of ISO-LF variables represents low frequency adaptations (of at least one week) and more than half (T0, L0, L1, T1m and T21) was previously reported as positively influencing isoprene emissions under in-situ conditions. Note that the use of more than 4 neurons led to an overtraining phenomenon with validation MSE\textsubscript{validation} values higher than MSE\textsubscript{training} (data not shown). Further details of neural training can be found in Dutot et al. (2007). The general equation of ISO-LF is given in Appendix C.

The isoprene algorithm ISO-LF was found to explain 90% of the overall variability of isoprene emissions (Fig. 4a), a result which was shown to be, at the 95% confidence level, significantly better than the one obtained using the ANN0 (60%) or ANN01 cases (70%, Appendix B). Moreover, a good agreement was observed for assessments over the whole emission range, including the highest values. A few points were poorly reproduced, but these could not be attributed to any specific species or climate type. Some of these outliers were found to correspond to statistically poorly represented situations (e.g.: sudden occurrence of clouds during sampling or summer late afternoon sampling with low light intensity but still elevated temperature for some of the *Ulex europaeus* measurements). As the cumulated air temperature has been previously observed to be important for the seasonality of isoprene emissions (see previous review section), the specific impact of T21 was tested within the ANN021(T0, L0, T21) and ANN0121(T0, L0, T1, L1, T21) models and compared to the former ANN0 and ANN01 cases. As shown in Table 3, when T21 was additionally considered, r\textsuperscript{2} values of 0.76 and 0.85 were obtained for ANN021 and ANN0121 respectively, compared to 0.56 and 0.70 for ANN0 and ANN01 respectively. Still, ISO-LF performances were at the 95% confidence level better (r\textsuperscript{2} of 0.90). Moreover, highest and lowest emission rate values were poorly matched using ANN021 and ANN0121 compared to ISO-LF (data not shown).
4.3 ISO-LF sensitivity

The evaluation of the input sensitivity is not straightforward for non-linear regressions. However, in order to have an idea to which environmental variable $x_i$ ISO-LF is more sensitive, $S_{x_i}$ was calculated as follows:

$$S_{x_i} = \left| \left( \frac{\Delta \log E}{\Delta x_i} \right) \right|_{\bar{x}}$$

where $E$ is the isoprene emission rate, $j = i - 1 \ (j \neq i)$ and $\bar{x}$ the mean of the input $j$. $S_{x_i}$ was calculated (i) for the entire dataset and (ii) for ISO-DB data obtained from 4 different types of climate (temperate with and without a dry summer, tropical and cold and humid) over the different seasons (only summer for cold climate). As shown in Fig. 5a, ISO-LF is mainly sensitive to $T_0$ and $L_0$, (the instantaneous air temperature and light intensity respectively) and to $T_{21}$, (the air temperature cumulated over 3 weeks) whatever the climate or the season. Further tests showed that, when $L_0$, $T_0$ and $T_{21}$ only were used, 76% of the isoprene emission variability was assessed. $T_1$ and $T_{1m}$ (the (d-1) day mean and minimum air temperatures respectively) and $P_{21}$ (the precipitation cumulated over the 3 weeks) are found to have a smaller weight in isoprene emission regulations. ISO-LF lowest sensitivity was observed for $ST_{1u}$ and $L_1$. Lowest $s_{x_i}$ values were generally obtained for tropical climate data ($S_{x_i}<0.15$, Fig. 5b) probably reflecting the more stable environmental conditions under which the plants were growing. On the contrary higher $S_{x_i}$ values were generally found for more variable climate. The distribution of the relative input importance observed for all data was similar when different climates and seasons were distinguished, expect for a higher relative contribution noticed for $ST_{1u}$ ($ST_{1u}$ is the second dominating environmental input in winter under temperate climate, Fig. 5e) and for $P_{14}$ in autumn for temperate with dry summer climate data. The interpretation of such $ST_{1u}$ predominance is speculative since there are no in-situ observations of the direct impact of soil temperature on isoprene
emissions. However, soil nutrient uptake, such as nitrogen, is known to be strongly dependent on the micro-organism activity, which is itself directly controlled by the soil temperature (see for instance Bassirirad, 2000). For temperate climates with dry summer, the regulations of isoprene emissions appear to be very critical to autumnal conditions, since high $S_x$ values are for all inputs except $T0$ and $L0$ (Fig. 5d). Unexpected high monoterpene emissions have been previously measured in the Mediterranean area in October (Bertin et al., 1997; Owen et al., 1998). These observations and our finding suggest that autumnal assessments of BVOC emissions under Mediterranean type climates could be very sensitive to environmental condition changes, in particular to low frequency variations of the air temperature ($ST21 > 2$). For temperate climate data (Fig. 5e), the highest $S_x$ values are obtained during winter and spring and the lowest ones during summer and autumn. $T21$ remains the dominant input, in particular during Winter and Spring, which is in good agreement with in-situ observations reported for isoprene emission onset of *Populus tremuloides* (Monson et al., 1994) and *Quercus alba* (Geron et al., 2000). The elevated $S_x$ observed in winter (Fig. 5e) may reflect a statistical poor representation of isoprene emission data for this season (mainly *Ulex europaeus* emission rates). More data are needed for further interpretation.

### 4.4 Application of ISO-LF to other non stored BVOC

As for isoprene, some monoterpene are not stored in the plant before their release into the atmosphere. Instant emission regulation of such non-stored monoterpenes (MTns) has thus been shown to be described by the same parameterisations than established for isoprene. ISO-LF was thus applied on a MTns database (MTns-DB, $n=707$) specifically compiled using the same principles described for ISO-DB. Most of the data was measured on *Quercus ilex* emission rates and mainly in the Mediterranean area (Table 4). Other data are for *Apeiba tibourbou*, *Arbutus unedo* and *Erica arborea*. ISO-LF was found to poorly ($y=0.40+0.15$, $r^2=0.23$, Fig. 6) described MTns emission variations. Even if a part of this discrepancy can be attributed to the statistical differences between MTns-DB and ISO-DB (see Fig. 7), it is more likely that the processes regul-
5 Summary and future developments

Using a statistical approach, a multiple non-linear regression based on artificial neural networks (ANNs) was implemented to develop an isoprene emission algorithm accounting for high (instantaneous) to low (seasonal) frequency of emission variations. ANNs were trained on an isoprene database (ISO-DB) specifically compiled for this study. ISO-DB consists of (i) 1321 isoprene emission rates collected in the literature for 25 different deciduous and coniferous species, grown under latitudes ranging from 10° S to 60° N, and, (ii) 34 high to low (3 weeks) frequency environmental regressors which were assessed for each isoprene emission rates. A maximum of 60% of the overall isoprene emission variability was found to be assessed when instantaneous environmental regressors (air temperature T0 and light intensity L0) only were considered. A value of 70% was reached when (d-1) day light (L1) and temperature (T1) information was added, with the remaining 30% unexplained variability being mostly associated with the highest emission rates. When the (d-1) day minimum air and soil temperatures (T1m and ST1u respectively), the precipitations cumulated over 2 and 3 weeks (P14, P21 respectively), and the cumulated air temperature over 3 weeks (T21) were additionally considered in the optimised (4 neurons, transfer function \textit{tanh}) algorithm ISO-LF, up to 90% of the overall isoprene variability is accounted for. ISO-LF was found to be mainly sensitive to T0 and L0 (which were previously observed to account for rapid acclimation to environmental changes) and to T21. More precisely, T21 was found to be particularly critical during spring for temperate climates which is also in agreement with the fact that cumulated air temperature was previously observed to describe the spring onset of isoprene emissions from \textit{Populus tremuloides} (Monson et al., 1994) and \textit{Quercus alba} (Geron et al., 2000). On the contrary, in temperate climates with dry summers, T21 (as other inputs except T0 and L0) was found to be critical for
isoprene emissions during autumn. Such a finding on isoprene may help to explain some unexpected high autumnal emissions previously observed for monoterpene in the Mediterranean area (Bertin et al., 1997; Owen et al., 1998). Without additional parameterisation, ISO-LF did poorly for non-stored monoterpenes.

ISO-LF can be routinely updated and improved by adding new emission data in ISO-DB. Thus, the impact of factors not considered in this study because of a lack of available data (e.g. nitrogen content, soil characteristics known to affect the plant water and nutrient uptake) or broadly assessed with meteorological datasets could be assessed. An even longer period of 3 weeks before the emission could also be tested for some relevant variables. The validation with ad-hoc seasonal campaigns (measurements of isoprene emissions and environmental information before and between sampling) is however recommended.

Such an approach could also be employed for other BVOC emissions such as monoterpene or sesquiterpene, although their emission variations appear to be even more complex than for isoprene. Canopy fluxes, rather than emission rates, of BVOC would also be good candidates for a neuronal approach, but new relevant regressors should then be considered.
Appendix A

Reported isoprene emission rates vs the Day of Year of their measurement for the 25 species present in ISO-DB.
| Climate type | Coniferous tree | Deciduous tree | Other |
|-------------|----------------|----------------|-------|
| C           |                | △ 🌲 Populus tremula |       |
|             |                | ○ 🌲 Salix phillicifolia |       |
| T           | ⬤ 🌲 Pseudosuga menziesii | ◆ 🌲 Liquidambar (shaded) | ◆ 🌲 Ulex europaeus |
|             | ⬤ 🌲 Thuja plicata | ◆ 🌲 Liquidambar (sunlit) |       |
|             | □ 🌲 Tsuga mertensiana | + 🌲 Pseudosuya orientalis |       |
|             |                 | ◆ 🌲 Populus balsamifera |       |
|             |                 | – 🌲 Quercus alba |       |
|             |                 | × 🌲 Quercus rubra |       |
|             |                 | □ 🌲 Quercus serrata |       |
| Td          | ◆ 🌲 Abies borisi | ◆ 🌲 Eucalyptus globulus | ◆ 🌲 Erica arborea |
|             |                 | + 🌲 Quercus frainetto | ▲ 🌲 Myrtus communis |
|             |                 | □ 🌲 Quercus pubescens |       |
| TR          |                 | ▲ 🌲 Astronium graveolens |       |
|             |                 | ◆ 🌲 Ficus insipida |       |
|             |                 | + 🌲 Hymenea courbaril |       |
|             |                 | ◆ 🌲 Luehea semenii |       |
|             |                 | ◆ 🌲 Soroea guillenminiana |       |
|             |                 | ▲ 🌲 Spondias monbin |       |

Emission rates measured within cold climates (C) are represented in white, those obtained under temperate climates (T) in blue, under temperate climates with dry summer (Td) in red, and those under tropical climates (TR) in green, according to the hereafter symbols:
Appendix B

Environmental input regressors considered during this work for the development of the isoprene emission algorithm ISO-LF.

| Environmental information | Frequency |
|----------------------------|-----------|
|                            | High (instantaneous) | Medium | Low |
|                            | (d-1) day | cum_{days} | cum_{week} | cum_{weeks} | cum_{weeks} |
| Day length                 | D         |           |           |           |           |
| Temperature                | T0        | T1        | T7        | T14       | T21       |
| mean                       |           |           |           |           |           |
| maximum                    |           |           |           |           |           |
| minimum                    |           |           |           |           |           |
| Solar flux                 | L0        | L1        | L7        | L14       | L21       |
| Rain falls                 | P1        | P3        | P7        | P14       | P21       |
| Upper layer                | ST1u      | ST7u      | ST14u     | ST21u     |
| (0-10 cm)                  |           |           |           |           |
| Temperature                | W1u       | W7u       | W14u      | W21u      |
| Water content              |           |           |           |           |
| Deep layer                 | ST1d      | ST7d      | ST14d     | ST21d     |
| (10-200 cm)                |           |           |           |           |
| Temperature                | W1d       | W7d       | W14d      | W21d      |
| Water content              |           |           |           |           |

Bold letters are regressors eventually considered in ISO-LF.

Air and soil temperatures are daily mean. Day length D is in hour, air and soil temperatures in °C, L0 in μmol m⁻² s⁻¹, solar fluxes L in W m⁻², precipitations in mm and soil water contents in fraction (0–1).

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Appendix C

Calculation of isoprene emission rates $E_{[ISO-LF]} (\mu g_c g_d h^{-1})$ using the ISO-LF algorithm

\[
E_{[ISO-LF]} = 10^{\log E_{[ISO-LF]}}
\]

where

\[
\log E(ISO - LF) = \log E(ISO - LF_{(CN)}) \times s + m
\]

and

- $s$ is the standard deviation of Log(ISO-DB) isoprene emission rates (1.2122)
- $m$ is the mean of Log(ISO-DB) isoprene emission rates (0.7553)

\[
\log E_{[ISO-LF(CN)]} \text{ is the central-normalised log}_{10} \text{ of isoprene emissions rates}
\]

\[
\log E_{[ISO-LF(CN)]} = w_{40} + w_{41} \times \tanh(N_1) + w_{42} \times \tanh(N_2) + w_{43} \times \tanh(N_3) + w_{44} \times \tanh(N_4)
\]

where:

\[
N_1 = w_0 + \sum_{i=1}^{9} \sum_{j=1}^{9} w_{i,j} x_{i,j}
\]

\[
N_2 = w_{10} + \sum_{i=11}^{19} \sum_{j=1}^{9} w_{i,j} x_{i,j}
\]

\[
N_3 = w_{20} + \sum_{i=21}^{29} \sum_{j=1}^{9} w_{i,j} x_{i,j}
\]

\[
N_4 = w_{30} + \sum_{i=31}^{39} \sum_{j=1}^{9} w_{i,j} x_{i,j}
\]

\[
w_{i,j}: \text{ the optimised weights as follows:}
\]
\[ w_0 = -0.89846 \]

\[ w_1 = -0.27948 \quad w_{12} = 0.15894 \quad w_{23} = -0.19168 \quad w_{34} = -2.03039 \]

\[ w_2 = -0.20780 \quad w_{13} = 4.78860 \quad w_{24} = -0.88332 \quad w_{35} = 5.49218 \]

\[ w_3 = -0.11346 \quad w_{14} = -8.04591 \quad w_{25} = 0.50996 \quad w_{36} = 0.90825 \]

\[ w_4 = 0.04658 \quad w_{15} = 14.91701 \quad w_{26} = 0.32972 \quad w_{37} = -0.67121 \]

\[ w_5 = -0.28604 \quad w_{16} = 2.27811 \quad w_{27} = 0.09713 \quad w_{38} = -0.77617 \]

\[ w_6 = -0.01218 \quad w_{17} = -0.13261 \quad w_{28} = 0.03432 \quad w_{39} = 0.24809 \]

\[ w_7 = 0.08509 \quad w_{18} = -2.52531 \quad w_{29} = 0.11136 \quad w_{40} = -3.08618 \]

\[ w_8 = 0.15142 \quad w_{19} = 0.11231 \quad w_{30} = 3.07818 \quad w_{41} = -2.35616 \]

\[ w_9 = -0.00431 \quad w_{20} = 4.87766 \quad w_{31} = -0.04267 \quad w_{42} = -2.66701 \]

\[ w_{10} = 9.06389 \quad w_{21} = -0.01802 \quad w_{32} = 0.03061 \quad w_{43} = 1.71583 \]

\[ w_{11} = 0.02752 \quad w_{22} = 2.73633 \quad w_{33} = 1.24757 \quad w_{44} = 2.71897 \]

\[ x_i: \text{the selected input regressors as follows:} \]

\[
\begin{array}{cccccccccc}
  x_1 & x_2 & x_3 & x_4 & x_5 & x_6 & x_7 & x_8 & x_9 \\
  T0 & L0 & T1m & T1min & T21 & P14 & P21 & ST1u & L1 \\
\end{array}
\]

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Table 1. List of the main in-situ BVOC emission studies reported in the literature and focusing on their seasonal variations. (1) Baker et al. (2005), (2) Bertin et al. (1997), (3) Boissard et al. (2001), (4) Fishbach et al. (2002), (5) Fuentes et al. (1999), (6) Fuentes and Wang (1999), (7) Geron et al. (2000), (8) Goldstein et al. (1998), (9) Guenther (1997), (10) Hakola et al. (2001), (11) Harley et al. (1997), (12) He et al. (2000), (13) Holzke et al. (2006), (14) Janson (1993), (15) Karl et al. (2003), (16) Kempf et al. (1996), (17) Kesselmeier et al. (2002), (18) Kim (2001), (19) Komenda and Koppman (2002), (20) Kuhn et al. (2004), (21) Lehning et al. (2001), (22) Lerdau et al. (1994), (23) Llusià and Peñuelas (2000), (24) Monson et al. (1994), (25) Ohta (1986), (26) Otter et al. (2002), (27) Peñuelas and Llusià (2001), (28) Petron et al. (2001), (29) Pier (1995), (30) Pier and McDuffie (1997), (31) Pressley et al. (2004), (32) Pressley et al., 2006, (33) Rapparini et al. (2001), (34) Sabillon and Cremades, 2001, (35) Schnitzler et al. (1997), (36) Simon et al. (1994), (37) Staudt et al. (1997), (38) Staudt et al. (2000), (39) Staudt et al. (2001), (40) Street et al. (1996), (41) Street et al. (1997), (42) Villanueva-Fierro et al. (2004), (43) XiaoShan et al. (2000), (44) Yatagai et al. (1995), (45) Yokouchi et al. (1984).

D: deciduous tree. C: conifer tree. EG: Evergreen tree. B: bush and other vegetation type. Climate types are: TR = tropical, C = cold, Td = temperate with dry summer, T = temperate without dry season. ° Measurements carried out using water supply. °° Measurements carried out water and fertilizer supply. * Seasonal study carried out over the whole plant development stage (before bud break till senescence). n.a.: no standardised emission rates available.
Table 1.

| Emitting species | Emitted compounds | Site location | Latitude | Climate type | Period of measurement | Magnitude of variation (mg.m\(^{-2}\).h\(^{-1}\)) | Reference |
|------------------|------------------|---------------|----------|--------------|-----------------------|---------------------------------|-----------|
| *Pinus pinea* | D | Barcelona, Spain | 41.4 | Mediterranean | June 1992 | 0.26 - 3.3 | (1) |
| *Quercus ilex* | D + EG | Madrid, Spain | 40.4 | Mediterranean | June 1992 | 0.26 - 3.3 | (1) |

Note: D = Direct measurement; EG = Environmental chamber; C = Controlled environment chambers; TR = Temperature rise; MT = Meteorological conditions; ISO = International Organization for Standardization; T = Temperature; C = Climate; C + C = Combined effects of temperature and climate; E = Emission rate; ISO = International Organization for Standardization; MT = Meteorological conditions; T = Temperature; C = Climate.
Table 2. Content and details of the isoprene database ISO-DB (n=1321) specifically built and used for this work. (1) Boissard et al. (2001); (2) Drewitt et al. (1998); (3) Hakola et al. (1998); (4) Hansen et al. (1997); (5) Harley et al. (1997); (6) Harrison et al. (2001); (7) Keller and Lerdau (1999); (8) Kesselmeier (personnel communication); (9) Kuhn et al. (2002); (10) Kuhn et al. (2004); (11) Nunes and Pio (2001); (12) Ohta (1986); (13) Pier (1995): (14) Simon et al. (1998); (15) Steinbrecher et al. (1997); (16) Xiaoshan et al. (2000). Data are available at http://www.lisa.univ-paris12.fr/~boissard.

| Emitter Measurement information | References |
|---------------------------------|------------|
| **Emitter** | **Measurement information** | **References** |
| | | |
| Abies Borisii-regis | 39.54 | 21.44° E | Pertouli, GRC | 08/1997 | 217–222 | 105 (6) |
| Astronium graveolens | 9.1 | 79.6° W | Panama city, PAN | 02/1997 | 42 | 7 (7) |
| Erica arborea | 41.6 | 12.5° E | Castelporziano, ITA | 05/1994 | 143,144 | 33 (4) |
| Eucalyptus globulus | 40.4 | 8° W | Tabuá, PRT | 03/1994 | 81,82 | 36 (1) |
| Ficus insipida | 9.1 | 79.6° W | Panama city, PAN | 02, 07/1997 | 37,38,39,41,202,206 | 56 (7) |
| Hymenaea courbaril | –10.08 | 62.54° W | Rondônia, BRA | 05/1999 | 128, 129, 295, 296 | 51 (9) (10) |
| Liquidambar styraciflua | 33.8 | 84.33° W | NE d’Atlanta, USA | 06/1993 | 160–166, 168–172 | 32 (5) |
| Luehea seemanii | 9.1 | 79.6° W | Panama city, PAN | 07/1996 | 36, 37, 41, 42, 204, 205, 206, 208 | 59 (7) |
| Myrtus communis | 41.6 | 12.5° E | Castelporziano, ITA | 05/1994 | 146 | 20 (4) |
| Pendula loud | 40 | 116.4° E | Pékin, CHN | 08/1998 | 226 | 10 (16) |
| Platanus orientalis | 40 | 116.4° E | Pékin, CHN | 10/1998 | 288 | 37 (16) |
| Populus balsamifera | 49.1 | 122.8° W | Lower Fraser Valley (LFV), CAN | 09/1995 | 139, 159, 173, 197, 229, 259 | 34 (2) |
| Populus tremula | 60.4 | 25° E | Nord d’Helsinki, FIN | 09/1996 | 164, 169, 177, 250 | 8 (3) |
| Pseudotsuga menziesii | 49.1 | 122.8° W | LFV, CAN | 06/1995 | 181 | 11 (2) |
| Quercus alba | 35.57 | 84.17° W | Oak ridge, USA | 07, 08/1992 | 211, 215 | 91 (5) |
| Quercus frainetto | 41.6 | 12.5° E | Castelporziano, ITA | 05/1994 | 146 | 47 (15) |
| Quercus pubescens | 43.45 | 3.45° E | Viols en Laval, FRA | 06/1995 | 171–173, 181 | 100 (8) (14) (15) |
| Quercus rubra | 34.51 | 87.16° W | Rogersville, USA | 10/1992 | 225–288 | 302 (13) |
| Quercus serrata | 35.2 | 136.9° E | Nagoya, JPN | 10/1984 | 193, 269, 301 | 32 (12) |
| Salix phylicifolia | 60.4 | 25° E | Nord d’Helsinki, FIN | 05, 06, 08/1996 | 143,145,169,220, 226, 247 | 12 (3) |
| Soroea guilleminiana | –10.08 | 62.54° W | Rondônia, BRA | 10/1999 | 283,284 | 25 (10) |
| Spondias mombin | 9.1 | 79.6° W | Panama city, PAN | 02/1997 | 45 | 7 (7) |
| Thuja plicata | 49.1 | 122.8° W | LFV, CAN | 08/1995 | 243 | 12 (2) |
| Tsuga mertensiana | 49.1 | 122.8° W | LFV, CAN | 08/1995 | 235 | 12 (2) |
| | | | | | 284, 320, 339, 11 |
| Ulex europaeus | 54.2 | 2.6° W | Wray, GBR | 09/1994 to 09/1995 | 55, 68, 114, 128 | 140 (1) |
| | | | | | 201, 228, 259 |
| | | | | | 166,167 | 42 |
Table 3. Comparison of the statistical performances of different neural networks trained with an input regressor combination of (L0, T0) – ANN0 case, (L0, T0, L1, T1) – ANN01 case, (L0, T0, T21) and (L0, T0, L1, T1, T21) – ANN0121 case. The best values of slope s, correlation coefficient $r^2$, root mean square error RMSE, mean square error MSE and mean bias error MBE obtained are presented.

|                | ANN0(L0, T0) | ANN01(T0, L0, T1, L1) | ANN(T0, L0, T21) | ANN(L0, T0, T1, L1, T21) | ISO-LF |
|----------------|--------------|-----------------------|------------------|--------------------------|--------|
| s              | 0.567        | 0.683                 | 0.739            | 0.82                     | 0.898  |
| $r^2$          | 0.564        | 0.695                 | 0.763            | 0.846                    | 0.901  |
| RMSE           | 0.775        | 0.649                 | 0.486            | 0.383                    | 0.293  |
| MBE            | −0.014       | −0.035                | −0.011           | −0.004                   | −0.002 |
Table 4. Content and details of the non stored monoterpene database MTns-DB (n=707) built and used for this study. (1) Bertin et al. (1997), (2) Ciccioli et al. (1997), (3) Kesselmeier et al. (1997), (4) Kesselmeier et al. (1998), (5) J. Kesselmeier (personnal communication), (6) Kuhn et al. (2002), (7) Llusía and Peñuelas (2000), (8) Nunez et al. (2002), (9) Peñuelas and LLusia (1999), (10) Sabillon and Cremades (2001), (11) Simon et al. (1998).

| Emitter                  | Measurement information | References |
|--------------------------|--------------------------|------------|
| Lat. Lon. Location Date  | Lat. Lon. Location Date  | Lat. Lon. Location Date  |
| Apeiba tibourbou –10.08 62.54°W Rondônia, BRA 05, 10/199 | 124–125, 291–292 | 35 (6) |
| Arbutus unedo 41.27 2.07°E Barcelone, ESP 07, 11/1997 | 42, 114, 206, 311 | 12 (7) |
| Erica arborea 41.27 2.07°E Barcelone, ESP 07, 11/1997 | 42, 114, 206, 311 | 12 (7) |
| Quercus cocifera 41.27 2.07°E Barcelone, ESP 07, 11/1997 | 42, 114, 206, 311 | 12 (7) |
| Quercus ilex 43.45 3.4°E Viols en Laval, FRA 06/1995 | 171–174 | 137 (2) (4) (5) (11) |
| 41.27 2.07°E Barcelone, ESP 07, 11/1997 | 42, 114, 206, 311 | 11 (7) |
| 41.6 12.5°E Castelporziano, ITA 05/1994 | 135, 137, 144–146, 214–216, 98, 299 | 358 (1) (2) (3) (5) |
| 40.6 3.4°W NE Madrid, ESP 10/2000 | 273, 277 | 19 (8) |
| 41.38 2.01°E Montcau, ESP 07/1996 | 134, 179, 211 | 17 (9) |
| 41.5 2°E Terrassa, ESP 07/1998 | 9, 42, 75, 107, 117, 176, 197 | 94 (10) |
Fig. 1. Exponential increase of $\frac{\text{ERs}_{\text{max}}}{\text{ERs}_{\text{min}}}$ versus $L$. $\text{ERs}_{\text{max}}$ (respectively $\text{ERs}_{\text{min}}$) is the maximum (respectively minimum) standardised (according to the Guenther et al., 1993 algorithm) emission rates of isoprene (square, $n=6$; Boissard et al., 2001; Fuentes et al., 1999; Geron et al., 2000; Kuhn et al., 2004; Llusia and Peñuelas, 2000; Street et al., 1996) monoterpene (circle, $n=4$; Holzke et al., 2006; Komenda and Koppman, 2002; Pier and McDuffie, 1997; Staudt et al., 2000) and oxygenated BVOC (triangle, $n=3$; Karl et al., 2003) obtained during seasonal in-situ studies carried out over the whole period of emitter development (before bud break until senescence), and $L$ the absolute value of the measurement latitude.

$y = 0.716e^{0.0835x}$, $r^2 = 0.83$ (n=13)
Fig. 2. Schematic representation of the structure and functioning principles of an artificial neural network (ANN) based on 2 neurons.
Fig. 3. Comparison of the statistical characteristics of ISO-DB isoprene emission rates for, both, training (n=1065) and validation (n=259) databases. The lower (respectively medium and upper) horizontal bar corresponds to the first (respectively median and 3rd) quartile. Mean values are represented by crosses. Minimum and maximum values are represented by the vertical bars.
Fig. 4. Comparison between the Log$_{10}$ of the isoprene emission rates calculated using the ISO-LF algorithm vs the measured isoprene emission rates for (a) the validation database and (b) the training data. The 1:1 line is shown (dotted line).
Fig. 5. Sensitivity of the Log of isoprene emission rates assessed using the ISO-LF algorithm to the 9 input regressors $x_i$ used in ISO-LF, for (a) all ISO-DB data, (b) tropical climate data (wet and dry season), (c) cold climate data (summer only), (d) temperate climate with dry summer (all seasons), and (e) temperate climate (all seasons).
Fig. 6. Comparison between the Log$_{10}$ of the non stored monoterpene emission rates MTns calculated using the ISO-LF algorithm and the measured MTns emission rates. The 1:1 line is shown (dotted line).
Fig. 7. Comparison of the statistical characteristics of the non stored monoterpane (MTns) emission rate data (n = 707) with training and validation ISO-DB isoprene emission rates. The lower (respectively medium and upper) horizontal bar corresponds to the first (respectively median and 3rd) quartile. Mean values are represented by crosses and minimum and maximum values are by the vertical bars.