ORIGIN OF MONOTERPENE EMISSIONS FROM BOREAL TREE SPECIES: DETERMINATION OF DE NOVO AND POOL EMISSIONS BY $^{13}CO_2$ LABELING

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INTRODUCTION

Boreal forests are dominated by monoterpenes emitting tree species (Rinne *et al*., 2009). Traditionally the monoterpene emissions from coniferous tree species are assumed to originate as evaporation from large storage pools (Guenther *et al*., 1991). Thus their diurnal cycle would depend only on temperature. However, there is indication that a significant part of the monoterpene emission would originate directly from synthesis (e.g. Shao *et al*., 2001). Such *de novo* emission would be rapidly labelled with ^{13}C were the plant fed with $^{13}CO_2$ (Figure 1). Thus this method can be used to quantify the fraction of the emission originating directly from synthesis.

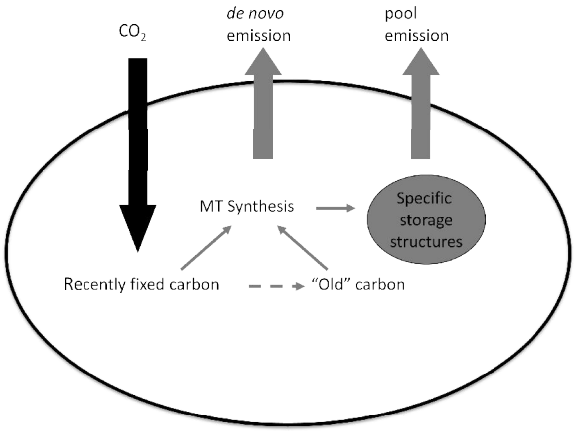

Figure 1: Schematic of the monoterpene emission pathways in monoterpene-storing coniferous trees.

METHODS

By applying $^{13}CO_2$ fumigation and analyzing the isotope fractions with proton transfer reaction mass spectrometry (PTR-MS) and classical GC-MS we studied the origin of monoterpene emissions from some major Eurasian boreal and alpine tree species. We determined the fractions originating from de novo biosynthesis and from large internal monoterpene storages for three coniferous tree species with specialized monoterpene storage structures and one dicotyledon species without such structures. An example of data from labelling experiments is shown in Figure 2. The labelled fraction of emitted isoprene was used to estimate the relative amount of "old carbon" used for monoterpene synthesis (Ghirardo *et al*., 2010).

To assess the applicability of the emission algorithm based on these laboratory experiments to natural ecosystems we evaluated the algorithm against measured ecosystem scale monoterpene emission. The

emission measurements were conducted by disjunct eddy covariance method at a Scots pine forest (Rinne *et al*., 2007).

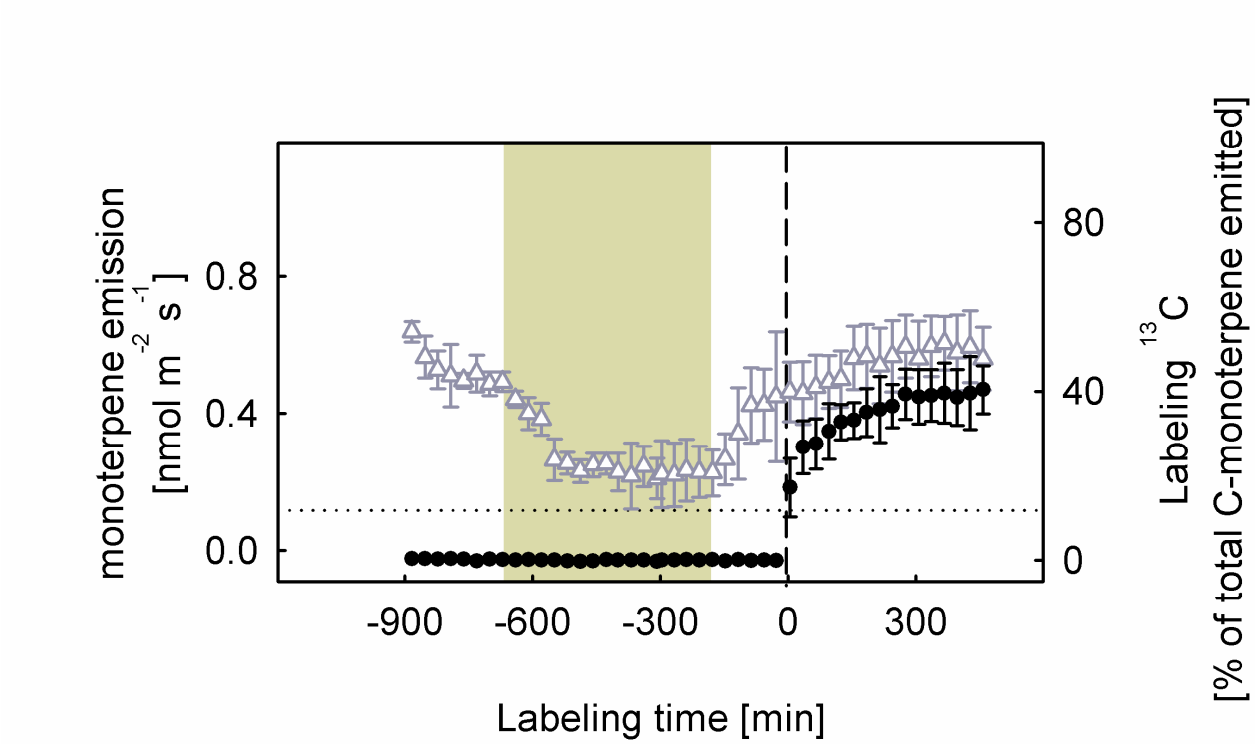

Figure 2. Example of data from a single labeling experiment with Scots pine. The open triangles are measured monoterpene emissions (left axis) and black dots indicate the percentage of emitted monoterpenes that are labelled with ^{13}C (right axis). the shaded area indicates when the plant chamber was in dark and vertical dashed line indicates the starting on $^{13}CO_2$ fumigation (Ghirardo *et al*., 2010).

CONCLUSIONS

Tree species	Percentage of de novo emission %
Pinus sylvestris	58
Picea abies	34
Larix decidua	10
Betula pendula	100
Quercus ilex	100

Table 1. Percentages of monoterpene emissions originating directly from synthesis.

The emission from dicotyledon species Betula pendula originated solely from the de novo synthesis (Table 1). The origin of the emissions from coniferous species was mixed with varying fraction originating from de novo synthesis and the rest from large internal monoterpene storage pools. Thus we formulated an algorithm for monoterpene emission, *E*, as

$$E = E_0[f C_T C_L + (1 - f)\gamma], \quad (1)$$

where E_0 is the emission potential, f is the fraction of emission of de novo origin, C_T and C_L are the activity factors for temperature and light in the isoprene emission algorithm of Guenther (1997), and γ is the exponential activity factor for traditional monoterpene emission algorithm (Guenther 1997). Application of the observed fractions of emission originating from de novo synthesis and large storage pools in a hybrid emission algorithm (Eq. 1) resulted in a better description of ecosystem scale monoterpene emissions from a boreal Scots pine forest stand (Figure 3). The correlation coefficient

between hybrid model and measurements was 0.85 instead of that of 0.78 between traditional algorithm and measurements.

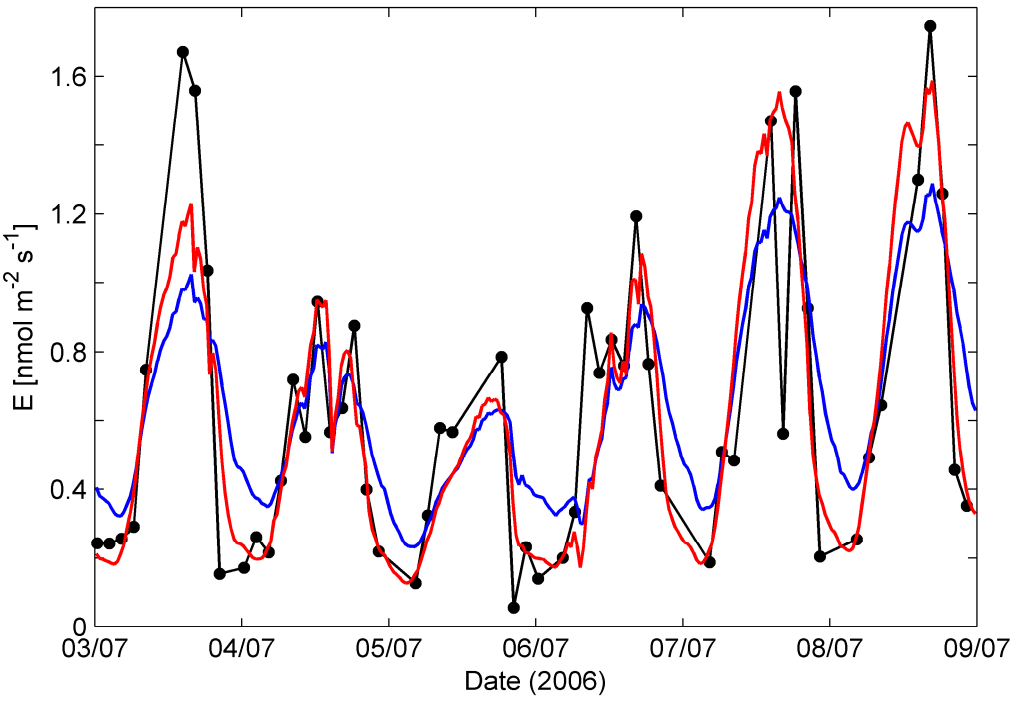

Figure 3. Ecosystem scale monoterpene emission measured by the disjunct eddy covariance method (black dots) at a Scots pine forest, emissions calculated by the traditional algorithm (blue line), and emissions calculated by the hybrid algorithm (Eq. 1, red line, Ghirardo *et al.*, 2010).

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