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# Long-term measurement of terpenoid flux above a *Larix kaempferi* forest using a relaxed eddy accumulation method

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## HIGHLIGHTS

- Terpenoid flux above a *Larix kaempferi* forest was measured during four seasons.
- More than 800 flux measurement data points were collected for this site.
- The monoterpene flux depended on temperature, regardless of season.
- However, several unusual high fluxes were observed after rain fall events.
- The annual flux was estimated by considering temperature and soil water content.

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## ABSTRACT

Terpenoids emitted from forests contribute to the formation of secondary organic aerosols and affect the carbon budgets of forest ecosystems. To investigate seasonal variation in terpenoid flux involved in the aerosol formation and carbon budget, we measured the terpenoid flux of a *Larix kaempferi* forest between May 2011 and May 2012 by using a relaxed eddy accumulation method. Isoprene was emitted from a fern plant species *Dryopteris crassirhizoma* on the forest floor and monoterpenes from the *L. kaempferi*. α-Pinene was the dominant compound, but seasonal variation of the monoterpene composition was observed. High isoprene and monoterpene fluxes were observed in July and August. The total monoterpene flux was dependent on temperature, but several unusual high positive fluxes were observed after rain fall events. We found a good correlation between total monoterpene flux and volumetric soil water content ($r = 0.88$), and used this correlation to estimate monoterpene flux after rain events and calculate annual terpenoid emissions. Annual carbon emission in the form of total monoterpenes plus isoprene was determined to be 0.93% of the net ecosystem exchange. If we do not consider the effect of rain fall, carbon emissions may be underestimated by about 50%. Our results suggest that moisture conditions in the forest soil is a key factor controlling the monoterpene emissions from the forest ecosystem.



## 1. Introduction

Biogenic volatile organic compounds (BVOCs), including terpenoids (e.g., isoprene, monoterpenes, and sesquiterpenes) as well as oxygenated hydrocarbons (e.g., acetone and methanol), are emitted from vegetation into the atmosphere. In particular, isoprene and monoterpenes emitted from vegetation are dominant. The annual global emissions of BVOCs were estimated to be 1150 Tg $yr^{-1}$ (Guenther et al., 1995), which is higher than that of anthropogenic volatile organic compounds (AVOCs) (Singh and Zimmerman, 1992).

BVOCs are known to play an important role in atmospheric chemistry. Because of their higher atmospheric reactivity with OH radicals and $O_3$, the lifetimes of BVOCs are shorter than those of most AVOCs (Atkinson and Arey, 2003). These BVOCs contribute to the formation of photochemical oxidants (such as ozone) in the troposphere (Guenther et al., 1995) that can adversely affect air quality.

On the other hand, BVOCs are involved in the formation of secondary organic aerosols (SOAs) that are produced by reactions of

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BVOCs with $O_3$ and OH radicals (Yokouchi and Ambe, 1985). The SOAs may scatter sunlight and, through reactions in the atmosphere, become cloud condensation nuclei (CCN) (Kanakidou et al., 2005). SOAs may fairly suppress global warming (IPCC, 2007) and, therefore, are considered to be important components in the earth's atmosphere.

Isoprene and monoterpenes include 5 and 10 atoms, respectively, of carbon in each molecule. This indirect emission of carbon in the form of BVOCs may significantly contribute to the carbon budget of a forest ecosystem or its net ecosystem exchange (NEE). Bouvier-Brown et al. (2012) reported that total BVOC emissions account for 4% of the annual NEE of the ponderosa pine plantation in North America.

To estimate BVOC emissions from vegetation, it is essential to develop a BVOC emission inventory. Changes in BVOC emissions caused by climate change can be simulated using models based on BVOC inventories (Constable et al., 1999). So far, considerable efforts have been devoted to determining the extent of BVOC emissions from vegetation. The emission of isoprene is mainly controlled by light intensity and temperature (Guenther et al., 1993). In general, monoterpenes in resin or other pools are emitted as a function of temperature. In addition, other parameters such as mechanical disturbance (Mochizuki et al., 2011a), humidity (Schade et al., 1999), and leaf expansion (Kuhn et al., 2004) are known to influence monoterpene emission.

The techniques used to measure BVOC emissions from trees are either micrometeorological or enclosure methods. Touching tree branches when covering them with an enclosure bag has been considered to be a factor that enhances monoterpene emission by stimulating and, in some cases, mechanically damaging the branches.

The advantages of micrometeorological techniques are to avoid stimulating trees and disturbing their emission behavior. These methods provide the flux averaged over the footprint area. Eddy covariance (EC) is the most direct method, but it requires a gas analyzer with a rapid response (10 Hz). For example, Karl et al. (2001) has demonstrated the applicability of proton transfer reaction-mass spectrometry (PTR-MS) to EC measurements for a wide range of chemical species. However, the number of compounds measured within a short period of time (<1 s) is limited. Since PTR-MS cannot distinguish compounds having the same molecular weight, individual monoterpene species cannot be quantified.

In general, the relaxed eddy accumulation (REA) method coupled with a GC instrument has been widely used as a theoretically simple micrometeorological technique (Businger and Oncley, 1990). The data of BVOC composition is important because lifetimes of terpenoid compounds differ among terpenoid species. The seasonal variation in BVOC composition may be caused by phenological events (Kuhn et al., 2004). Short-term BVOC flux measurements using REA method have been conducted mainly in Europe and America (e.g. Baker et al., 1999; Christensen et al., 2000). However, there is no report on long-term BVOC flux measurement using a REA method so far.

*Larix kaempferi* is endemic to Japan and corresponds to 5% of the total forest area in Japan. Its congeneric species *Larix sibirica* and *Larix gmelinii* widely occur in boreal coniferous forests in Siberia and north Europe. BVOC flux from these forests has been rarely measured (Ieda et al., 2006).

In the present study, terpenoid flux of a *L. kaempferi* forest was measured using the REA method from May 2011 to May 2012. Field flux data over 52 measurement days were intermittently acquired. We investigated the effects of seasonality and meteorological disturbances, such as rain fall, on terpenoid fluxes. By comparing terpenoid fluxes and NEE, we calculated annual carbon emission from the forests in the form of terpenoids.

## 2. Materials and methods

### 2.1. Measurement site and date

The study was conducted at the Fuji-Hokuroku Flux Research Site (35° 26′ N, 138° 45′ E), which is located at an elevation of 1100 m (slope: 3–4°) in a *L. kaempferi* plantation (tree ages: 45–50 years, canopy height: 20–25 m) in the foothills of Mt. Fuji in Yamanashi Prefecture, Japan. The soil type is coarse-grain volcanic ash. The *L. kaempferi* trees were uniformly planted in approximately 150 ha including this study area. The site is interspersed with an evergreen coniferous tree species (*Pinus densiflora*) and mixed broadleaved tree species (*Swidacontroversa*). Because the forest canopy is open, the forest floor is covered with understory including the fern species *Dryopteris crassirhizoma*. In 2011, the annual mean air temperature and annual precipitation measured at the meteorological flux tower were 9.1 °C and 2256 mm, respectively.

The eddy covariance method was used to measure the fluxes of sensible heat and $CO_2$ at a height 35 m by using a sonic anemometer (DA600, Kaijo, Japan) and a closed path infrared $CO_2$ gas analyzer (LI-6262, Li-Cor, USA). Details of the micrometeorological measurements and net ecosystem exchange calculation have been described by Hirata et al. (2007).

The terpenoid flux was measured at a height of 35 m above the ground level using a 31 m meteorological tower. Sampling was carried out from May 2011 to May 2012 (Table 1). The terpenoids were collected at 30 min intervals from 8:00 to 17:00. Measurements within four days after rainfall are noted in Table 1 and are categorized as "Days after rain." In our measurements, 17 days were included in the category.

### 2.2. Relaxed eddy accumulation method

Terpenoid fluxes were measured using the REA method (Businger and Oncley, 1990). The terpenoid fluxes, $F$, were calculated according to the following equation.

$$F = b\sigma_w\left(C^+ - C^-\right) \quad (1)$$

where $\sigma_w$ is the standard deviation of vertical wind velocity ($w$, m s$^{-1}$) and $b$ is an empirical constant specific for the REA method. $C^+$ and $C^-$ are the terpenoid concentrations in the air sampled when $w$ is upward and downward, respectively.

**Table 1**
Dates of the terpenoid flux measurements.

| Month | Day |
|---|---|
| **2011** | |
| May | 13, 14, 15, 16, 18, 19 |
| June | 4, 5, 20, 29 |
| July | 1, 2, 3, 9, 17, 18, 22, 24, 25 |
| August | 3, 6, 11, 12, 13, 14, 24, 28, 29 |
| September | 6, 7, 8, 9, 24, 25 |
| October | 11, 12, 13, 24, 25, 26 |
| November | 24, 25 |
| December | 19, 20 |
| **2012** | |
| January | 23, 24, 31 |
| February | 1 |
| March | |
| April | 28, 29, 30 |
| May | 1 |

Numbers underlined indicate days in which the volumetric soil water content increased "after rainfall."