Measurements of ozone vertical distribution in a hinoki (Chamaecyparis obtusa) forest using a sensitive ozone passive sampler

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We measured the ozone vertical distribution inside a hinoki (Chamaecyparis obtusa) forest in a mountainous area of Aichi prefecture, Japan, by using a sensitive passive sampler. The vertical profile of the ozone concentration in the forest had a sigmoid pattern: the concentration decreased in the canopy, increased under the canopy, and decreased again at the ground surface. The profiles were analyzed using the concentration ratios at each measurement point and were compared between daytime and night time. As a result, the sigmoid patterns were found in both day and night time. This result suggests that not only uptake of ozone through stomata but also adsorption on the surface of leaves, stems or soils are essential. Keywords: ozone, passive sampler, hinoki (Chamaecyparis obtusa), vertical distribution

Introduction

Ozone is a secondary pollutant produced by photochemical reactions of nitrogen oxides, carbon monoxide, and hydrocarbons. Polluted air emitted from urban areas is transported with photochemical reactions to rural mountainous areas (Chang et al. 1989) and produces ozone by which forest trees might be influenced. It is well known that ozone affects physiology of forest trees (McLaughlin 1985; Darrall 1989; Heath and Taylor 1997). Ozone causes various effects on plants, including visible leaf injury, growth reduction, and altered freezing tolerance (Waite et al. 1994). It is reported that tropospheric ozone is increasing in the 1990s especially in East Asian Pacific rim region (Lee et al. 1998). Therefore, ozone deposition and its effects on forests in mountainous areas have become subjects of discussion.

The degree of ozone deposition on forests have been mainly evaluated by calculating ozone flux. The flux is obtained from a gradient of ozone concentration at two heights in forests (Fuentes et al. 1992; Duyzer et al. 1995; Ro-Poulsen et al. 1998), or from an ambient ozone concentration using a simple gas exchange model (Wieser and Havraneck 1993, 1995) or using a eddy-correlation model (Amthor et al. 1994; Padro 1995; Pilegaard et al. 1995). For the estimation of ozone flux, it is essential that the height and various factors such as monitoring period for ozone measurement should be decided based on actual ozone profile inside forest. In addition this, from the viewpoint of ozone effect on tree physiology, actual ozone profiles inside forest should give some important information. However, though a large number of reports concerning the ozone flux have been published, only a few paper showed a detailed vertical

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(Received: Dec. 14, 2001)
profile of ozone inside forest (Fontan et al, 1992; Pleijel et al, 1995) because of a problem of limited electric facility for ozone analyzer in mountainous area. On the other hand, Ikeura and Mizoguchi (1991) have developed a simple diffusive ozone sampler with high sensitivity as a complementary analyzer for a usage in non-electricity area.

The purpose of this study is to observe a vertical distribution of ozone inside a hinoki (Chamaecyparis obtusa) forest in a mountainous area of Aichi prefecture, Japan, by using a sensitive passive sampler.

**Materials and Methods**

The observation site was in a 31-year-old hinoki (Chamaecyparis obtusa Sieb. et Zucc.) plantation forest in the Nagoya University Forest (35°11′N, 137°33′E), located northeast of Nagoya city. The altitude is approximately 980 m, and the annual precipitation and average temperature are 2000 mm and 8°C, respectively. The soil type is brown forest soil originated from granite. A 9-m tower was built in the forest where the ground slope is 30°~40° and the average tree height and bole length were 7.5 m and 3.5 m, respectively. The canopy was closed and there was no understory.

The ozone concentration in the ambient air inside the forest was measured by a modified fluorescence determination method using a sensitive passive sampler for ozone (Ikeura and Mizoguchi 1991). The passive sampler, containing acetamidophenol solution, was exposed to ambient air through a membrane filter. During the exposure, the acetamidophenol reacted with ozone and condensed to the biphenyl compound, which fluoresces strongly. After 1-h exposure, the reaction was stopped by the addition of L-ascorbic acid solution. After bring back to the laboratory, the fluorescence intensity excited at 327 nm was measured at 422 nm with a fluorescence spectrophotometer (RF-5000, Shimadzu Co. Ltd. Kyoto, Japan). The detection limit of the sampler was reported to be 2 ppb for 1-hr exposure (Ikeura and Mizoguchi 1991). Since the reaction is affected by the ambient temperature (Ikeura and Mizoguchi 1991), the measured fluorescence intensity was corrected with the ambient temperature measured at the sampling site. The linearity between the ozone concentration and the fluorescence intensity was confirmed and calibrated with a UV photometric ozone analyzer (Model 49, Thermo Environmental Instruments Inc., Franklin, MA, U.S.A.). The reproducibility of the method using the passive sampler was confirmed as follows: Six passive samplers were simultaneously exposed to ambient air on the Nagoya University campus for 1 h, and the fluorescence intensities of the reactant solutions were measured. The experiment was repeated 8 times. The correlation coefficient between the fluorescence intensity of the reactant solution in the passive sampler and the ozone concentration measured by O₃ analyzer was 0.99. The average relative standard deviation of 8 measurements was 6.6% at around 50 ppb.

Twelve passive samplers for ozone were attached to the tower, one above the other. Sampler No. 1 was set above the canopy. Samplers No. 2~9 were set inside the canopy. Nos. 10 and 11 were under the canopy, and No. 12 was just above the ground surface. The measurements were conducted on 25 August, 14 September, 20 and 21 October, 10, 11, 22 and 23 November, 1 December 1994, and 8 and 22 August 1995. Samples were taken for every 4 hours.

The weather during the sampling period was fine or slightly cloudy, except at 4:00 and 8:00 of 21 October 1994. To evaluate the effect of wind on ozone distribution, the wind velocity above canopy (50 cm higher than the apex) was measured with an Anemomaster (AM-A11, Nippon Kagaku Kogyo, Japan).

**Results and Discussion**

Figure 1 shows a time series of ozone concentration above the canopy for five observations.
These data indicate that the maximum ozone concentration did not always occur in the afternoon. It is known that ozone concentration increases after sunrise and reach to maximum in the afternoon since ozone is produced through photochemical reactions (Fuhrer et al. 1997; Wieser and Havranek 1993). On the other hand, Chang et al. (1989) reported that the time when the maximum concentration of ozone is observed depends on the distance from a highly polluted area and the possibility of wet deposition during the transportation of polluted air. The maximum ozone concentration during our observation periods was 57 ppb. In the Inabu mountainous area no data of ozone concentration has been obtained because of no official observation site. An estimate based on a study of air pollution on the Nohbi plain (Mori and Kitada 1999) indicates that the ozone concentration in this area may sometimes reach more than 100 ppb in summer. In Europe, the critical level concept for ozone effects on vegetation had been discussed and the threshold concentration was set at 40 ppb (Fuhrer et al. 1997). Although the ozone data are still few in the mountainous area in Inabu, trees are possible to be exposed to an enough high level of ozone over the critical level in these area.

The vertical profiles of ozone concentration in the forest stand from 20th to 21st of October 1994 is shown in Fig. 2 as a representative data. The concentration of ozone at 16:00 was highest and that at 20:00 was lowest. The profile has a sigmoid pattern: the concentration decreased in the canopy, increased under the canopy, and decreased again at the ground surface. This pattern means that ozone is absorbed by or adsorbed onto leaves, branches or stems in the canopy. The sigmoid pattern was distinct in daytime and was still found after sunset. This sigmoid pattern and daily tendency were found in the other observation days. Fontan et al. (1992) reported the vertical ozone profiles in a pine forest by measuring ozone at five heights and showed a simple decrease toward ground surface. Since they did not measure ozone concentration inside canopy, no detail distribution of ozone in canopy was obtained.

To analyze the vertical profile of ozone in the forest, we calculated and summarized the concentration ratios at each measurement point (Table 1). The decrease in ozone inside the canopy is shown as the ratio of the ozone concentration at the center of the canopy to that in the above canopy. In the same way, the decreases under the canopy and at ground surface are shown as the ratios of the ozone concentration under the can-
Fig. 2. Vertical profiles of ozone concentration from 20th to 21st October 1994. The plots at the highest point corresponded to No. 1 sampler and these at 0m corresponded to No. 12 sampler.

Table 1. Profile analysis of ozone concentration in canopy

<table>
<thead>
<tr>
<th></th>
<th>average (n=40)</th>
<th>daytime (n=25)</th>
<th>nighttime (n=15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decrease in canopy</td>
<td>B/A</td>
<td>0.87</td>
<td>0.86^a</td>
</tr>
<tr>
<td>Decrease under canopy</td>
<td>C/A</td>
<td>0.92</td>
<td>0.92^a</td>
</tr>
<tr>
<td>Decrease at ground surface</td>
<td>D/C</td>
<td>0.88</td>
<td>0.85^a</td>
</tr>
</tbody>
</table>

Daytime 7:00-18:00  Nighttime 19:00-6:00
A: ozone concentration above the canopy
B: ozone concentration at center of the canopy
C: ozone concentration under the canopy
D: ozone concentration at ground surface

Values labeled with different letters are significantly different (p<0.05) by t-test.


...continues...
trees is also a potential mechanism of ozone decrease inside canopy and it appears distinctly at night time.

Table 1 shows that the decrease in ozone concentration under the canopy was smaller than the decreases within the canopy and at ground surface and not related to time of the day. The ozone concentration under the canopy is considered to be affected by lateral invasion of wind. Figure 3 shows the relationship between the wind speed measured above the canopy and the ozone concentration ratio of under to above the canopy. This figure indicates that the ratios were relatively low when the wind speed was \( \leq 1.5 \text{ ms}^{-1} \). This means that, when the wind is enough strong to invade from lateral direction, the concentration of ozone under the canopy might be almost the same level as ambient. Namely, in this hinoki forest the ozone concentration measured under the canopy could reflect the ambient ozone level if the wind is enough strong.

On the other hand, the decrease in ozone concentration at the ground surface was significantly different between daytime and night time in confidence with 95\%. That is, the absorption or adsorption of ozone into the ground surface in daytime is more effective than at night. Pilegaard et al. (1995) suggested that the destruction of ozone through a reaction with NO emitted from soil through nitrification process by microbiological activity should be taken into consideration. Therefore, not only a simple adsorption to soils but also microbiological activity in soils might related to the decrease in ozone concentration at the ground surface.

**Conclusion**

From the measurement of ozone concentrations in hinoki (Chamaecyparis obtusa) forest in a mountainous area of Aichi prefecture using a sensitive passive sampler, we observed a sigmoid pattern in ozone vertical profile. That is, 10–15% of the ambient ozone was decreased in the canopy, and the concentration of ozone under the canopy was higher than that in the canopy probably caused by wind invasion. The daily variation in the vertical profile of ozone suggests that that not only ozone uptake through stomata but also ozone deposition to leaf external surfaces, branches, stems or soil is important for ozone distribution in forest. To evaluate a chronic stress on forest trees by ozone, the accumulation of ozone concentration and distribution data in mountainous areas using a sensitive passive sampler should be important.

**Acknowledgements**

The authors would like to thank technicians, Mr. Y. Imaizumi and Mr. N. Yamaguchi, of the Nagoya University Forest for carrying out the series of experiments.

**Literature cited**


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高感度オゾン簡易測定器を用いたヒノキ林におけるオゾンの鉛直分布測定

竹中千里・日比野道子・栗山芳留代

愛知県の山地において、高感度オゾン簡易測定器を用いてヒノキ林内のオゾン濃度の鉛直分布を調べた。林内のオゾン濃度鉛直分布としては、樹冠内で減少し、生枝下で再び増加し、地表面で減少するというシグモイド型のパターンが得られた。このパターンを濃度比で表し昼夜別に解析した結果、昼夜に関わりなく、シグモイド型の分布になっている傾向が認められた。これらの結果より、葉の気孔を通じてのオゾンの取り込みだけでなく、葉、枝、樹幹や土壌への吸着も林内のオゾン濃度分布に重要な役割を果たしていることが示された。

キーワード：オゾン，簡易型測定器，ヒノキ，鉛直分布