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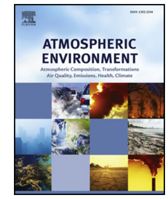

Small-scale variations in ozone concentration in low mountains

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ABSTRACT

In a relatively low mountain area adjacent to Matsuyama city in Japan, ozone concentration variations were studied at spatial scales of $O(10) \sim O(10^3)$ m. Walking mobile measurements were complemented by vertical profiling, wind measurements, and passive sampling. The broad-scale distribution at $O(10^2) \sim O(10^3)$ m was found to depend on time of day, atmospheric stability, and geography in ways consistent with previous studies. Well-defined areas of low ozone concentrations $O(10)$ m in width were found at several locations. No distinctive features of these locations were immediately discernible, but detailed examination of the temporal variations coupled with the wind field suggested that the distribution of the low-ozone areas was determined by subtle differences in the terrain topography.

1. Introduction

This paper presents an observational study of spatial variations in ozone (O^3) concentration in a relatively low mountain area. Ozone in mountains has been studied mainly for its deleterious effects on plants. These effects are reviewed by Karnosky et al. (2007), and their implications in terms of large ecosystems are discussed in Wang et al. (2016). Ozone concentrations are high at high elevations due to the lack of sources of nitric oxide (NO), a major ozone sink, and to the residual ozone that, having been produced photochemically in the daytime boundary-layer, lingers in the upper layer due to the weak sinks at those elevations. These high ozone concentrations have led to decays of ozone-sensitive forests at high elevations in many countries. However, even at a given elevation, the extent of plant damage varies considerably from place to place (Yamane et al., 2007). Spatial variations in ozone concentrations may explain some of the spatial variation in plant damage, but other factors such as water stress and insect feeding may also contribute.

Previous studies on ozone distributions in mountain areas were conducted at spatial scales of $O(10^2) \sim O(10^4)$ m. A comprehensive review of this topic may be found in Monteiro et al. (2011). What follows is a brief discussion of the topic to situate the present study. Brodin et al. (2010) analyzed ozone concentrations at multiple monitoring stations along an elevation gradient in Colorado, USA, and found that the elevation dependence differed between summer and winter: monotonic increase with elevation in winter, but stepwise increase in summer. By using small ozone monitors that could easily be deployed at temporary stations, Burley and co-workers measured ozone at high spatial densities in Yosemite National Park (Burley and Ray, 2007), the White Mountains (Burley and Bytnerowicz, 2011), and Joshua Tree National Park (Burley et al., 2014) in the USA. Panek et al. (2013) deployed passive samplers in the southern Sierra Nevada, CA, USA, and found sub-regions of high, low, and variable ozone exposure. Broder et al. (1981) measured ozone distribution in a valley using a tethered balloon and ground stations. They found an unexpectedly large night-time destruction rate of ozone, which could be explained by a closed cross-valley circulation in which decomposition of ozone occurs within a layer of downslope winds along the valley side walls. Omori et al. (2016) conducted mobile ozone measurements using the same portable monitor as in the present study. They observed distinct ozone-concentration distribution regimes on the sides of the Tanzawa mountains, Kanagawa, Japan, facing towards and away from the nearby urban area.

Kanda (2015) reported broad-scale variations in ozone concentration along a low hill using a portable semiconductor sensor. The accuracy of the portable sensor was confirmed by parallel measurements using both the semiconductor monitor and a UV-absorption portable monitor. The parallel measurements confirmed the overall accuracy of the semiconductor sensor. However, sharp drops in ozone concentration were observed only sporadically due to the slow response of the semiconductor sensor (~1 min for step decrease and ~3 min for step increase). In contrast, the UV absorption monitor's faster response (~20 s) allowed clearer and more reproducible detection of the concentration drops.

This study is concerned with variations in ozone concentration at spatial scales smaller than are generally investigated ($O(10^2) \sim O(10^3)$

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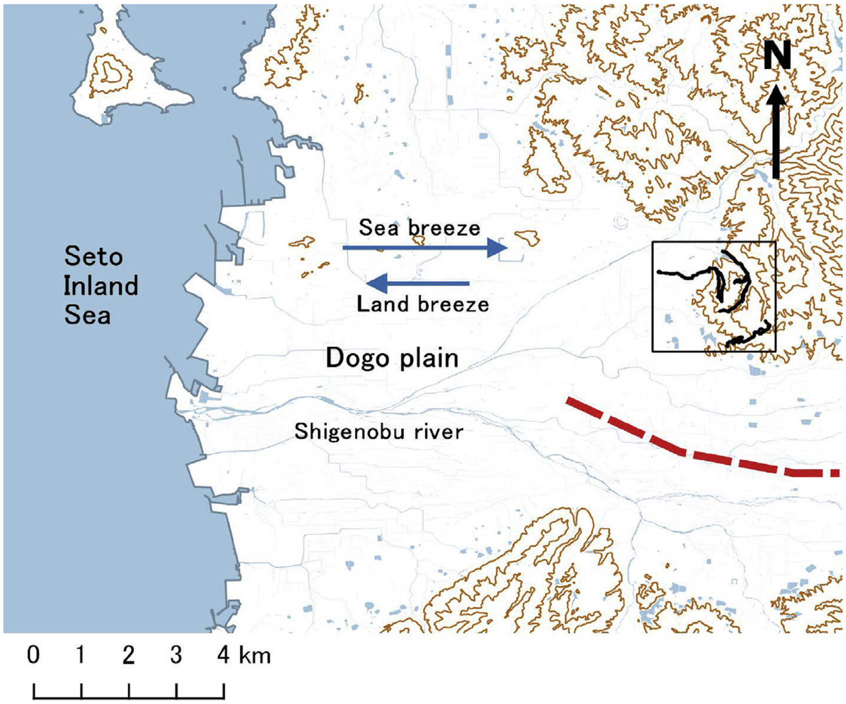

Fig. 1. Map of the Dogo plain. The elevation contour interval is 100 m. The cyan patches indicate water. Black lines indicate mobile measurement paths and the enclosing box is the boundary of Fig. 2 (a). The red dashed line is the axis of a valley along the Shigenobu river. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

m). The objective of this study is to identify the cause of the sharp drops in ozone concentration observed in some areas. Furthermore, this study seeks to confirm that the study area is not a singular terrain in terms of ozone chemistry and transport but rather that results can be generalized to other regions. As described below, the low-ozone areas are found to be ubiquitous in the area, although their characteristics depend on the exact location.

2. Study site

The observations were conducted in the mountains and valleys near Mt. Awajigatou (peak elevation 273 m above sea level (a.s.l.)) in the eastern part of Matsuyama city in Japan. The study site is shown in Fig. 1. Most of the residential area of Matsuyama city is on the Dogo plain, which faces the Seto Inland Sea to the west and the Shikoku Mountains to the east. This geography creates a clear land-sea breeze circulation with westerly winds prevailing in the day time and easterly winds prevailing at night (arrows in Fig. 1). The vegetation around Awajigatou is a mix of species including red pine, oak, and chestnut. The maximum tree height is about 15 m, and the majority of the underbrush is fern.

In the study site, many walking trails exist to facilitate maintenance visits to the power transmission towers that are installed every few hundred meters. The trails and roads, with widths ranging from 0.6 to 5 m, that were used in this study are shown in Fig. 2. Photographs at representative sites (α_1, α_2, and β_1) are shown in Fig. 3.

3. Methods

The primary method of observation was walking mobile measurements using a portable UV-based ozone monitor (Model 202, 2B Technologies, Boulder, CO, USA), a temperature and pressure monitor (TR-73U, T&D Co., Matsumoto, Japan), a humidity monitor (TR-77Ui, T &D), and a GPS logger (iBlue 747 Pro, TranSystem Inc., Hsinchu, Taiwan). The sensing ports were held around 70–80 cm above the ground. The walking speed was maintained around 5 km h^{-1}. The observations were conducted during four campaigns: February 2014–April 2014, July 2015–August 2015, December 2015–March 2016, and December 2016. For the daytime observations during all campaigns and all observations from December 2015 onward, the thermistor temperature sensor of TR-73U was set inside a forcefully ventilated dual-duct housing to reduce the impact of solar radiation on the measurement. For observations conducted before dawn and before December 2015, the temperature sensor was exposed directly to the ambient air. The recording intervals of 2B–202, TR-73U, and TR-77Ui were 10 s, 1 or 2 s, and 1 or 2 s, respectively. The response times of 2B–202, TR-73U, and TR-77Ui were 20 s, 75 s, and 20 s, respectively. When faster response times for the temperature measurement were considered necessary, a Pt100 with a response time of about 40 s was used in parallel. The housing for the thermistor sensor had little influence on the response time. Before or after each measurement campaign except for the last one, 2B202 was calibrated against an SI-traceable ozone monitor (OA-781, Kimoto Electric, Osaka, Japan). No substantial drift occurred through the first three campaigns. As will be described later, the observed ozone concentration often showed negative correlation with the relative humidity, which raises a question that 2B202 might be inherently humidity sensitive. This is not the case because each calibration measurement spanned more than 24 h during which the ambient relative humidity changed from 50 to 80 percent, but the difference between 2B202 and OA-781 remained within a few ppb irrespective of the magnitude of relative humidity.

In addition, at some locations wind speed and direction were measured by an ultrasonic anemometer (CYG81000, R.M.Young Co., MI, USA) or using smoke visualization. A balloon-borne electrochemical concentration cell (ECC) ozone sensor (EnSci, CO, USA) (Komhyr, 1969) was used to measure the vertical profile of ozone concentration throughout the tree canopy. Ogawa passive NOx samplers (Ogawa Inc., Kobe, Japan) and the ECC sensor were used to determine the presence of chemical species such as NO and HONO.

In the following, ozone concentration, temperature, and relative humidity are denoted as C, T, and ϕ, respectively.

4. Results

4.1. Broad-scale behavior

We first describe the variations in ozone concentration at the diurnal time scale and at spatial scales of $O(10^2)$ m or greater. In the