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Spatial variations of ground level ozone concentrations in areas of different scales

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Abstract

The spatial variation of ground level ozone concentrations was investigated for areas of three different scales: (1) an air quality management district (a region about $100 \times 70 \text{ km}^2$) in northern Taiwan, (2) the neighborhood (about 2 km in radius) of an air quality monitoring station, and (3) an open field (about $400 \times 600 \text{ m}^2$) surrounded by 3- and 4-storey buildings in an elementary school. Analysis of data on hourly ozone concentration, obtained at 13 m above the ground at 21 monitoring stations in the air quality management district, showed that the stations downwind of the urban center in the district had significantly higher ozone concentrations. Measurements for 8-h average ozone concentrations at 1.5 m above the ground by passive samplers showed that, in a flat area about 2 km in radius, the ratios of the ozone concentration at open areas to that at the monitoring station (0.86–0.93) were significantly higher than those obtained at areas with higher traffic flow and density of buildings (0.60–0.68). For the open field in an elementary school, the 8-h average ozone concentrations at 1.5 m above the ground at sites less than 10 m from the nearest building were considerably lower than those at sites farther away from buildings. The results indicated that, in areas of small scales, the spatial distributions of ozone concentration were highly non-uniform and there were appreciable day-to-day variability in spatial distribution. Such variability should be taken into account in determining the extent to which an individual is exposed to ozone. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Recent epidemiologic studies have shown that ground level ozone even at concentrations lower than 80 ppb (8-h average) can exacerbate asthma symptoms (Avol et al., 1998; Delfino et al., 1998). In view of the fact that such a concentration level has been adopted as an ambient air quality standard, improved quantitative assessments of the relationship between ozone and adverse health outcomes are needed to help establish protective levels of the ozone concentration standard.

The assessments have been complicated by factors such as characteristics of the microenvironments where individuals spend their time and the representativeness of data obtained at air quality monitoring stations.

Ozone is highly reactive and therefore has variability greater than other pollutants in both spatial and temporal distributions. Previous studies on the spatial variation of ozone concentration have mainly focused on areas of large size scales such as an air quality management district, or a neighborhood of an air quality monitoring station. Mulholland et al. (1998) reported that there were substantial spatial variations of ozone concentration during ozone episodes in the 20-county Atlanta metropolitan area (over an area about 60 km in all directions from the city center). Their

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study showed that locations of high ozone concentration were consistent with the daily, spatially averaged wind velocity data. A quantitative measure for the spatial representativeness of ground level ozone concentrations has been described as a means for comparing modeled and measured data by Stefan and Joerg (1998). They applied the principal component analysis to routinely measured diurnal variations at more than 300 sites in Germany, and inferred a radius of representativeness of about 4 km. Information on the radius of representativeness is useful for a broad indication of the ground level ozone concentration in the neighborhood of a monitoring station. From the viewpoint of health risk assessment, however, information on the spatial variation in areas of smaller size scales is needed. Different individuals living and working in the same neighborhood of a monitoring station may receive different ozone exposures if the microenvironments where they spend their time differ in ozone concentration. The objective of this study was to compare the patterns of the spatial variation of ground level ozone concentration in areas of different size scales. We selected, for this study, three areas with sizes varying from about $400 \times 600 \text{ m}^2$ to about $100 \times 70 \text{ km}^2$.

2. Methods

2.1. Study areas

To study the spatial variation of ground level ozone concentrations in different size scales, we selected the following three areas

2.1.1. An air quality management district (about $100 \times 70 \text{ km}^2$ in area)

The Northern Air Quality Management District, with a population of over 8 million, was selected for this study. This district consists of three basins and a river valley surrounded by mountains. There are 21 air quality monitoring stations in the district operated by the Taiwan Environmental Protection Administration. Fig. 1 shows the locations of the monitoring stations and the topographical features of the district. Ozone concentrations at a height of approximately 13 m above the ground were monitored by an ultraviolet photometer in each station.

Among the 21 monitoring stations, Stations B1–B10 are located in the Taipei basin, Stations O1–O4 in the outskirts of the basin, Stations C1–C5 in the coastal area, and Stations M1 and M2 in the mountainous

Fig. 1. Locations of monitoring stations in Northern Air Quality Management District in Taiwan. The lighter shades represent higher elevations.

Fig. 2. Locations of the sampling sites in an area about 2 km in radius where Monitoring Station B10 was located. Shaded boxes represent sampling sites at a height of 1.5 m, except Site 1 which was at the vicinity of Station B10 (13 m above the ground).

region. Taipei city, the most populated urban center in the District, has five air quality monitoring stations (B1, B3, B4, B6 and B7).

2.1.2. The neighborhood of an air quality monitoring station (about 2 km in radius)

The neighborhood of Monitoring Station B10 was selected for study. It is a flat area of about 2 km in radius. Fig. 2 shows the 9 sampling sites within this area. The sampler was placed at 1.5 ± 0.2 m above the ground at all sampling sites, except at Site 1 where the sampler was placed next to Monitoring Station B10 (13 m above the ground) as a reference.

All sampling sites except the reference Site 1 were classified into three groups according to the characteristics of each site's surroundings. Sites 2 and 3, located in the outskirts of the business center, had the lowest traffic flow and density of buildings; Sites 4–6, situated between the outskirts and the business center, had the medium traffic flow; and Sites 7–9, located on sidewalks of major thoroughfares in the business center of the town, had the highest traffic flow and density of buildings. The distance from the nearest building was greater than

10 m for all sampling sites except Site 7 which was 5 m from the nearest building.

2.1.3. An open field (about 400×600 m² in area)

We selected an open field surrounded by 3- and 4-storey buildings in an elementary school, where Monitoring Station B10 was located, for the area of the smallest size scale in this study. There were 12 sampling sites in the area, of which 7 sites were on the ground in the open field and 5 sites on the rooftop of the surrounding buildings. Among the sampling sites on the rooftop, one site was adjacent to the monitoring station (Fig. 3).

3. Field sampling and chemical analysis

3.1. Field sampling

There were 19 sampling days during March to September 2000 for the study in the neighborhood of Monitoring Station B10 and 16 sampling days during December 1999–July 2000 for the open field. Passive

Fig. 3. Locations of the sampling sites in an open field (about $400 \times 600 \text{ m}^2$) surrounded by buildings (not to scale). Shaded circles and rectangles represent the sampling sites and buildings, respectively. The samplers in the open field were placed 1.5 m above the ground, while the rooftop samplers were about 13 m above the ground.

samplers (Ogawa & Co. Inc., Pompano Beach, Florida, USA) were used to determine average ozone concentrations at about $1.5 \pm 0.2 \text{ m}$ above the ground. A total of 336 ambient samples were collected. The passive sampler with nitrate-coated filters has been used in measurement of ambient ozone (Koutrakis et al., 1993). In the presence of ozone, the sodium nitrite coated on the filter gets oxidized to nitrate:

In the field, the sampler was covered with a PVC protective cup to reduce the effect of wind speed on the collection rate. Sampling was carried out for 8 h, from 8:30 to 16:30, on each sampling day. During transfer between the laboratory and the field, all samplers were kept in zip-lock bags and placed in sealed bottles. For each sampling day, three samplers were used as field blanks.

3.2. Chemical analysis

At the end of sampling, the samplers were immediately brought back to the laboratory for chemical analysis. The two filters in each sampler were transferred to a 10 ml test tube containing 5 ml of distilled and de-ionized water. The water suspensions were sonicated twice for 15 min. The sample extracts were then filtered (by filters with $0.2\text{-}\mu\text{m}$ pore size) and analyzed for nitrate

by ion chromatography (DX-120, Dionex Corp., Sunnyvale, CA, USA).

4. Data analysis

4.1. Data from monitoring stations

The data on hourly ozone concentrations were acquired from the 21 monitoring stations of Northern Air Quality Management District in Taiwan for the period from June 1999 to May 2000, and analyzed for the pattern of spatial distribution and seasonal variation of ground level ozone concentration. A high ozone concentration day was defined as a day when the maximum 8-h running mean of ozone concentration exceeded 80 ppb. The percentage of high ozone concentration days in the total number of days with valid ozone concentration data was calculated for each monitoring station and compared with factors such as season, wind direction and topographical features that may influence the spatial distribution of ozone concentration in the district.

4.2. Data from field sampling

For analysis of the data sets obtained from field sampling in the neighborhood of Monitoring Station

B10, we used the concentration ratio to eliminate the effect of daily variation in ozone concentrations. The concentration ratio was defined as the 8-h average ozone concentration obtained from field sampling divided by the 8-h average ozone concentration obtained at Monitoring Station B10 for the same period of time during which the field sample was taken. As for the data sets obtained from sampling in the open field in the elementary school, we used the ratio of the concentration obtained at each site to that obtained at the site adjacent to Station B10.

5. Results and discussion

5.1. Spatial variations of ground level ozone concentration

5.1.1. In an air quality management district

Table 1 shows the percentage of high ozone concentration days at each of the 21 monitoring stations in Northern Air Quality Management District in Taiwan during the period from June 1999–May 2000. The results showed that spring 2000, with an average percentage of high ozone concentration days of 5.6%, was the worst ozone pollution season in the district. In the spring season, the typical meteorological conditions (low wind speed and high intensity of ultraviolet radiation)

combined with higher emissions of volatile organic compounds from biological sources in the district contributed to the frequent occurrence of ozone episodes. Due to strong wind and lower intensity and shorter duration of solar radiation, ozone episodes rarely occurred in winter. Only two stations reported 8-h average ozone concentrations higher than 80 ppb in winter 1999 (both on December 4).

During the daytime, sea breezes enter the Taipei basin from the estuary at the northwestern shore. The percentage of high ozone concentration days was generally higher at the monitoring stations downwind of the urban center such as Stations B4–B10. For instance, the percentage in summer 1999 was 5.6% and 6.7% at Stations B10 and B6, respectively, but was 0 at both Stations B1 and O2. The result indicated that wind direction was the primary factor that affected the ozone distribution in the air quality management district, similar to the conditions described by Mulholland et al. for Atlanta (1998).

5.1.2. In the neighborhood of a monitoring station

Fig. 4 shows the ratio of the concentration at each sampling site to the concentration monitored at Monitoring Station B10. The concentration ratio for Site 1 which was located next to the monitoring station was 1.04 ± 0.1 , indicating that the ozone concentration determined from passive samplers was consistent with

Table 1

The percentage of high ozone concentration days in the total number of days with valid ozone data in each season at the 21 monitoring stations in Northern Air Quality Management District in Taiwan during June 1999–May 2000

Monitoring station	Summer (06/1999–08/1999)	Fall (09/1999–11/1999)	Winter (12/1999–02/2000)	Spring (03/2000–05/2000)
B1	0.0	1.3	0.0	3.5
B2	2.2	2.5	0.0	4.4
B3	2.7	2.3	0.0	1.1
B4	4.9	4.7	0.0	6.7
B5	3.4	1.3	0.0	12.1
B6	6.7	3.7	0.0	6.5
B7	3.3	2.2	0.0	7.6
B8	3.6	2.3	0.0	9.2
B9	4.4	3.9	0.0	10.1
B10	5.6	6.0	0.0	9.8
O1	3.3	2.3	0.0	4.4
O2	0.0	1.2	0.0	3.4
O3	1.1	1.2	0.0	2.3
O4	2.2	1.2	0.0	3.4
C1	1.1	0.0	0.0	1.1
C2	4.6	2.3	0.0	9.8
C3	1.1	1.3	0.0	0.0
C4	1.1	2.4	1.2	3.3
C5	2.3	2.6	1.4	5.8
M1	1.1	2.2	0.0	6.8
M2	1.1	2.4	0.0	5.5
Mean	2.7	2.3	0.1	5.6

Fig. 4. Ratios of the ozone concentration at each sampling site to that at Monitoring Station B10 during March–September 2000. Each error bar indicates the 95% confidence interval of the mean value.

the value monitored at the station. The ratio decreased as the traffic flow and density of buildings increased (from Sites 2–9). The decrease in ozone concentration is likely to be caused by reactions of ozone (with vehicular emissions and surface materials) and poor convection. Analysis of the data showed that, on a given day, the difference in the mean ozone concentration between the business center (Sites 2 and 3) and the outskirts (Sites 7–9) were statistically significant, even though they were only about 2 km apart. Density of buildings and traffic flow appeared to be the likely factors giving rise to the non-uniformity in spatial distribution of ozone concentrations at 1.5 m height.

Based on each day's prevailing wind direction, sampling sites were divided into upwind sites and downwind sites. The ratio of the mean ozone concentration of the downwind sites to that of the upwind sites was in the range of 2.2–0.7, with a median of unity. The result indicated that wind direction had no significant effect on the spatial distribution of ozone concentration at the height of 1.5 m in an area of about 2 km in radius.

A linear regression of concentration ratios on the distance of each site from the reference station showed that the correlation between them was not statistically significant.

5.1.3. In an open field

Fig. 5 shows the relationship between the ozone concentration ratio and the distance from the nearest

building. The mean concentration ratio, defined as the ratio of the concentration at each site to that at the site next to the monitoring station, rose from 0.73 to 0.98 as the distance from the nearest building increased from 3 to 25 m. The concentrations at sites less than 10 m from the nearest building were considerably lower than the concentrations at sites farther away from buildings. The results indicated possible decay of ozone by reactions on painted surfaces of concrete buildings. On the other hand, the mean concentration ratio at sites greater than 20 m from the nearest building leveled off to 0.94, suggesting that the influence of nearby buildings on the spatial distribution of ozone concentration was relatively insignificant at such distances. On the rooftop where the effect of nearby buildings was negligible, the ozone concentration had a relatively uniform distribution as indicated by the narrow range of concentration ratio (0.90–0.92) for the 4-rooftop sites.

5.2. Comparison of the spatial variation patterns in areas of different scales

The following five different categories of area in Northern Air Quality Management District were compared: (I) the entire district, (II) the Taoyuan county which is in a basin in the southwestern region of the district, (III) an area consisting of Taipei city and Taipei county, which includes the Taipei basin and part of

Fig. 5. The relationship between the ozone concentration ratio and the distance from the nearest building in an open field surrounded by buildings during December 1999–July 2000. The concentration ratio is the ratio of the concentration at each sampling site to that measured by a passive sampler placed next to a monitoring station. Each error bar indicates the 95% confidence interval of the mean value.

Table 2

The maximum distance between paired sites and the mean and standard deviation (SD) of site-to-site correlation coefficients of ozone concentrations for all paired sites in each category of area in Northern Air Quality Management District in Taiwan, in the neighborhood of Station B10, and in the open field in an elementary school during March–July 2000

Area number	Category of area	Maximum distance between paired sites (km)	Correlation coefficients	
			Mean	SD
I	The entire district ^a	70	0.74	0.19
II	The Taoyuan county ^a	35	0.88	0.09
III	Taipei city and Taipei county ^a	30	0.82	0.18
IV	The Taipei basin ^a	15	0.91	0.09
V	The high ozone concentration area ^a	15	0.92	0.08
	The neighborhood of Station B10 ^b	4	0.77	0.12
	The open field in an elementary school ^b	0.25	0.88	0.07

^aSampling height : ~13 m above the ground.

^bSampling height : 1.5 ± 0.2 m above the ground.

surrounding mountains, (IV) the Taipei basin, and (V) the high ozone concentration area downwind of the urban center. Fig. 1 indicates the sizes and locations of these sub-regions in the district. It is to be noted that some of these sub-regions overlap each other.

To examine the pattern of spatial variation of ozone concentrations, the site-to-site correlation of 8-h average ozone concentrations was determined for each category

of area. For the purpose of comparison, the calculations for site-to-site correlation were carried out only for those days when field sampling was conducted in the neighborhood of Monitoring Station B10. Table 2 shows the maximum distance between paired stations and the mean and standard deviation of site-to-site correlation coefficients for all pairs in each category of area in the district, in the neighborhood of Station B10,

and in the open field in the elementary school. In the air quality management district, the maximum distance between paired stations was 70 km. Although the mean value of the site-to-site correlation coefficients for the entire district was the lowest among all categories of area, the ozone concentrations at various stations in the district were still fairly well correlated ($r = 0.74$). All other categories of area in the district had a mean value of site-to-site correlation coefficients greater than 0.82, indicating that the ozone concentrations monitored at the stations were highly correlated within each category of area. The sub-region consisting of Taipei city and Taipei county had complicated topographic characteristics including urban centers, countrysides, and mountains. The mean value of site-to-site correlation coefficients in this category was the lowest ($r = 0.82$) among the four sub-regions in the district. In general, the results indicate that the topographical features played a key role in the spatial variation pattern of ozone concentrations in the air quality management district. Nevertheless, all the stations in the monitoring network of the district appeared to respond to change in ozone concentration fairly concurrently. The day-to-day variability in ozone concentration at one station therefore should be a fairly good measure of the average variability across the district.

It is interesting to compare the site-to-site correlations for ozone concentrations acquired at monitoring stations, which were located at least 10 m above the ground, with those for ozone concentrations obtained from field sampling at about 1.5 m above the ground. Also shown in Table 2 is the mean value of the correlation coefficients between paired sites in the neighborhood of Station B10 ($r = 0.77$). It was lower than those in all the sub-regions in the air quality management district. The results indicated that the spatial distribution of ozone concentration at 1.5 m above the ground had greater day-to-day variability than those at the elevations where monitors are located. For the smallest size area studied, the open field in an elementary school, the mean value of the site-to-site correlation coefficients (0.88) was considerably higher than that for the neighborhood of Station B10, and its standard deviation (0.07) was the lowest among all categories of area given in Table 2. The difference of the correlation coefficients between the two smaller study areas was reasonable because the open field was considerably smaller in size (a maximum separation distance of only 250 m) and there were no barriers in the field to obstruct the transport of ozone. Although the high site-to-site correlations for the two areas may reduce the power of spatial distributions to an epidemiologic study, data on local spatial distributions are still useful for assessing ozone exposure of specific groups.

The results obtained at different heights have different implications and therefore are not to be integrated. The 13 m measurements, representing the prevailing concentrations in the medium-scale environment, are useful in giving a broad indication of the ozone pollution problem in the area but do not reflect the influence of local transport and sinks. There is no need to monitor the 13 m concentration at more than one site within the medium-scale environment because it is uniform over such an area. On the other hand, the concentration to which an individual is exposed varies with the local environment and therefore differs to some extent from the 13 m concentration. Measurements at 1.5 m reflect the local conditions and therefore can provide the data needed for exposure assessments. Since 1.5 m concentrations depend strongly on local conditions, it is not useful to compare them at various sites in a large-scale environment.

6. Conclusions

Analysis of data on hourly ozone concentrations measured at approximately 13 m above the ground at all monitoring stations in Northern Air Quality Management District in Taiwan showed that the occurrence of high ozone concentration at downwind air monitoring stations were consistent with prevailing wind directions (northwestern sea breeze). The result for the site-to-site correlation coefficients in the district showed that the monitored ozone concentrations reported by the air quality network responded to change fairly concurrently. In a small town of about 2 km in radius and in an open field (about $400 \times 600 \text{ m}^2$ in area) surrounded by buildings, the spatial distribution of ozone concentration at 1.5 m above the ground was highly non-uniform and there was appreciable day-to-day variability in spatial distribution. The marked spatial variations of ground level ozone concentrations and day-to-day variability in spatial distribution should be taken into consideration in determining the extent to which an individual is exposed to ozone.

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