Relationships among Particle Fractions of Urban and Non-urban Aerosols

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Data on mass concentrations of PM_{10} and $PM_{2.5}$, obtained at four urban sites in western Taiwan from 1998 to 2000, were analyzed to examine the pattern of seasonal and yearly variations in the $PM_{2.5}/PM_{10-2.5}$ ratio, the relationship among particle fractions and the variability of each particle fraction. The results were compared with those reported in the literature for urban and non-urban areas in several countries. Even though the annual mean of the $PM_{2.5}/PM_{10-2.5}$ ratio at a site might fall within a relatively narrow range over several years, the seasonal mean of the ratio could still vary considerably within a year. These results imply that there is no long-term characteristic value of the ratio for a community. Furthermore, different urban areas did not necessarily have similar ranges of the ratio. Results for the relationship among particle fractions and the variability of each particle fraction also indicated significant differences between communities. For the areas where both $PM_{2.5}$ and $PM_{10-2.5}$ are moderately correlated with PM_{10}, separate measurements of $PM_{2.5}$ and $PM_{10-2.5}$ are needed for a better assessment of the underlying causes for the health effects of particulate matter.

Keywords: ambient aerosol, fine particles, coarse particles, $PM_{2.5}$, PM_{10}

1. Introduction

Complexity in physical and chemical characteristics of ambient aerosols has led to considerable difficulty in identifying the determinants in particulate pollutants that are responsible for adverse health effects. As a consequence, air quality standards for particulate pollution have made use of indicators such as TSP, PM_{10}, and $PM_{2.5}$, instead of concentrations of specific chemical species. Over past decades, the PM indicator has progressively narrowed in particle size range, as the scientific understanding of the association between particulate pollutants and health effects has advanced. Although the recent establishment of $PM_{2.5}$ standards in the U.S. was based on the results of definitive epidemiological studies, a lack of concentration data on this particle fraction poses a problem for other countries to consider adopting $PM_{2.5}$ as an indicator in air quality standards. Measurements of $PM_{2.5}$ concentrations are therefore being made in many countries both as part of scientific studies and as test runs of routine monitoring. Relationships between different particle fractions have also been studied, partly with the objective of examining the possibility of using PM_{10} as a surrogate for $PM_{2.5}$ or PM_{10}.

Taiwan, as in many newly industrialized countries, has been tackling serious particulate pollution problems over the past three decades. The sources of particulate pollutants in urban areas include vehicular exhausts, fugitive dust from construction sites, resuspended road dust, products

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of gas-to-particle conversion by chemical reactions that involve gaseous pollutants, and emissions from smokestacks in nearby industrial parks. The relative contributions of these sources have changed over the years. Construction activities during the early stages of urbanization contributed a significant amount of coarse particles, while the contribution of vehicular emissions to fine particles has markedly increased in urban centers in the 1990s. Consequently, the concentration of fine particles has remained at relatively high levels, even though the PM_{10} concentration has been leveling off owing to the implementation of various pollution control programs.

The Taiwan Environmental Protection Administration began to set up air quality monitoring stations in 1982. As of 2001, the number of monitoring stations had increased to 72. PM_{10} has been one of the criteria pollutants monitored at these stations. The monitoring of $PM_{2.5}$ began in 1997 at four selected stations in urban areas and one station near a major highway in western Taiwan. This study analyzes the data on mass concentrations of $PM_{2.5}$ and PM_{10} obtained at the four urban stations from December 1997 to November 2000. The seasonal and year-to-year variations in the $PM_{2.5}/PM_{10\text{-}2.5}$ ratio, the relationship among $PM_{2.5}$, $PM_{10\text{-}2.5}$, and PM_{10}, and the variability of each particle fraction are calculated. The calculated results are compared with those for urban and non-urban areas in Australia, Canada, U.K., and U.S.A. to examine whether any general pattern exists in the relationship between particle fractions.

2. Methods

The four monitoring stations were Kuting (KT) in the metropolitan Taipei area, Chungming (CM) in the metropolitan Taichung area, and Fengshan (FS) and Linyuan (LY) in the metropolitan Kaohsiung area. All the four stations are in the western part of the island. Kuting and Chungming stations are in northern and central Taiwan, respectively, while both Fengshan and Linyuan stations are in southern Taiwan. Linyuan station, located on the urban fringe, is just 2 km away from a major petrochemical industrial park.

The monitoring stations used beta gauge systems with preselector inlets to obtain hourly concentration data on $PM_{2.5}$ and PM_{10}. The aerosol samplers were placed on roof-tops at 11.43 – 16.15 m above the ground surface. The beta gauge system was not equipped with a heating unit and therefore the PM data were not corrected for humidity effects. The data reported by the monitoring stations were compared with those obtained using dichotomous samplers and cascade impactors placed in the vicinity of some stations. The data were found to be reasonably consistent.

The data obtained from the four stations were first examined for validity. The data sets that had $PM_{2.5}$ concentrations higher than the corresponding PM_{10} concentrations were rejected. Only days with at least 16 valid hourly concentration measurements were included in the analysis. Calculations of daytime and nighttime average concentrations were made only for the daytime and nighttime periods that had at least 8 valid hourly concentration measurements. The mass concentration of $PM_{10\text{-}2.5}$ was calculated as the difference between those of PM_{10} and $PM_{2.5}$. The $PM_{2.5}$ and $PM_{10\text{-}2.5}$ concentrations were therefore approximately equal to the concentrations of fine and coarse particles, respectively. The daily average concentrations, the daytime average concentrations, and the nighttime average concentrations were calculated and then used to compute respective ratios of $PM_{2.5}$ to $PM_{10\text{-}2.5}$. The daytime period, representing the duration from 7 a.m. – 7 p.m., included the morning rush hours from 7 – 9 a.m. and the evening rush hours from 5 – 7 p.m.

The data were grouped according to season, winter (December to February), spring (March to

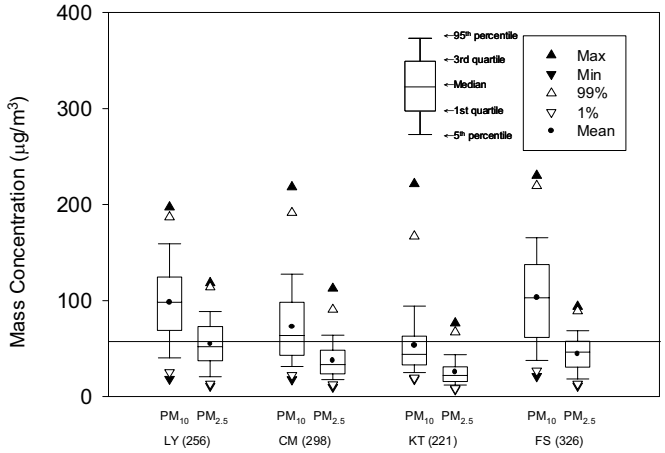

Figure 1. Mass concentration of PM_{10} and $PM_{2.5}$ at the four stations from December 1999 to November 2000. The number in parentheses following the station name is the sample size. The U.S. $PM_{2.5}$ standard (24-hr average) is 65 μg m^{-3}.

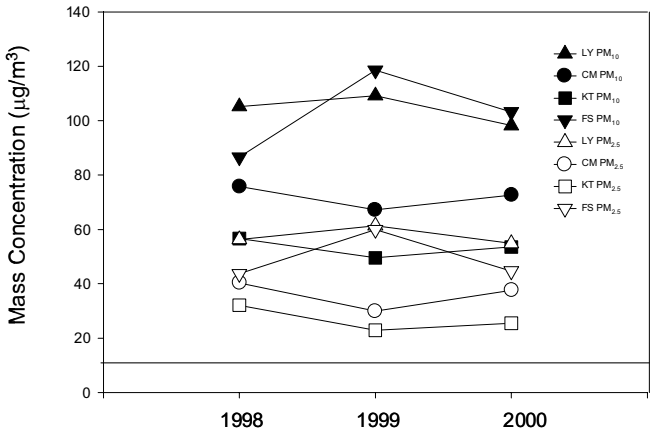

Figure 2. Variations in mass concentrations of $PM_{2.5}$ and PM_{10} at the four stations from 1998 to 2000. The U.S. $PM_{2.5}$ standard (annual average) is 15 μg m^{-3}.

May), summer (June to August), and fall (September to November). Accordingly, one year referred to the 12 months from December of the preceding year to November of the current year. The seasonal and annual mean concentrations were calculated from the daily average concentrations, and the seasonal and annual means of the $PM_{2.5}/PM_{10}$ ratio were computed from the daily values of the ratio.

The coefficients of determination (R^2) for the relationships among particle fractions at each station were calculated for each season and each year. The coefficient of variation (CV, the standard deviation divided by the mean) was used to examine the variability of $PM_{2.5}$, $PM_{10\text{-}2.5}$, and PM_{10} concentrations. To determine which particle fraction had a greater influence on the variation of PM_{10} concentrations, the contribution of each of the two components, $PM_{2.5}$ and $PM_{10\text{-}2.5}$, to the variability of PM_{10} was calculated by dividing the standard deviation of each component by the mean of PM_{10} concentrations.

3. Results and Discussion

3.1 $PM_{2.5}$ and PM_{10} Concentrations

The frequency distributions of the daily average PM_{10} and $PM_{2.5}$ concentrations at each station were approximately lognormal when the data were plotted for each year. The distributions were similar to those of the PM_{10} concentrations at several sites in southern California, as analyzed by Kao and Friedlander (1995). Although the frequency distributions obtained in this study were only approximately lognormal and the geometric mean and geometric standard deviation varied to some extent from year to year at each station, they were sufficiently consistent to suggest that the factors that influence aerosol concentrations, such as emission rate and meteorological conditions, did not have an abnormally high number of extreme cases.

Figure 1 shows the mass concentrations of PM_{10} and $PM_{2.5}$ at the four stations from December 1999 to November 2000. The mean concentrations of both PM_{10} and $PM_{2.5}$ differed considerably among various stations. For instance, the annual mean PM_{10} concentrations ranged from 54 to 103 μg m^{-3} and the annual mean $PM_{2.5}$ concentrations ranged from 25 to 55 μg m^{-3}. Metropolitan Kaohsiung, located in southern Taiwan, is surrounded by several industrial parks and therefore has a serious particulate pollution problem, as indicated by the

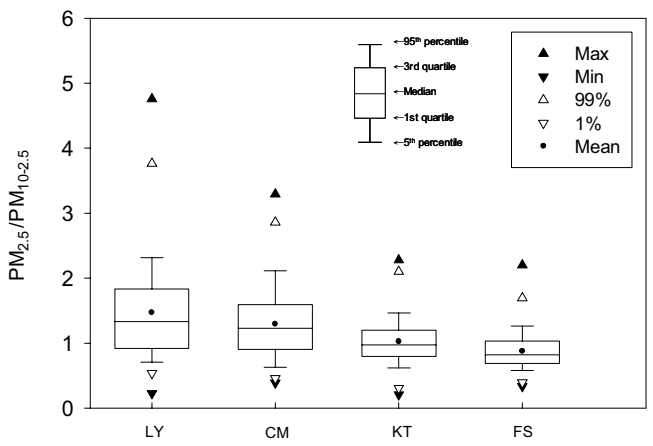

Figure 3. Daily $PM_{2.5}/PM_{10\text{-}2.5}$ ratios at the four stations from December 1999 to November 2000.

high particle concentration levels at stations LY and FS.

The annual mean mass concentrations of PM_{10} and $PM_{2.5}$ did not change significantly at the four stations except at FS, during the three years from 1998 to 2000 (Fig. 2). Since the surge in annual mean mass concentrations in 1999 took place at FS, but not at LY, both of which are in metropolitan Kaohsiung, the marked surge in mass concentration at FS suggests an abnormal influence of local particle sources.

3.2 $PM_{2.5}$/ $PM_{10\text{-}2.5}$

Figure 3 shows the ratio of $PM_{2.5}$ to $PM_{10\text{-}2.5}$ at the four stations from December 1999 to November 2000. The annual mean values of the ratio at the four stations fell within the narrow range from 0.88 to 1.47, in contrast to the annual mean mass concentrations of $PM_{2.5}$ and PM_{10}, both of which varied by a factor of around 2.

Table 1 compares the annual mean values of the $PM_{2.5}$/ $PM_{10\text{-}2.5}$ ratio obtained in this study with those reported for various types of sites and regions in the United States, Canada, and Australia. Interestingly, the ratios in western Taiwan, southern California, and Canada vary over similar ranges. The ratios for the primarily non-urban sites across the United States were in a much wider range because they covered a greater variety of regions with different types of particle sources. The ratios for the six urban sites in Australia were relatively high because most of the measurements were made during a four-week period of high emissions of fine particles from domestic wood-fires.

Several factors drive the change in $PM_{2.5}$/ $PM_{10\text{-}2.5}$. The ratio increases with the emissions from motor vehicles and high-temperature processes. It also increases as a result of stronger photochemical reactions or fewer resuspended coarse particles from road surfaces. Other meteorological conditions, such as rain, solar radiation and atmospheric stability, may also affect the ratio.

Table 1. Ranges of the annual mean of the $PM_{2.5}/PM_{10\text{-}2.5}$ ratio for various regions.

Region	Range of $PM_{2.5}/PM_{10\text{-}2.5}$	References
Taiwan[a]	0.88 – 1.48	
U.S.[b]	0.69 – 2.70	Eldred et al., 1997
Southeastern U.S.[c]	1.38 – 3.55	Parkhurst et al., 1999
Southern California[d]	1.07 – 1.46	Kim et al., 2000
Canada[e]	0.56 – 1.86	Brook et al., 1997
Australia[f]	1.27 – 4.00	Keywood et al., 1999

[a] Four urban sites during the period from December 1997 to November 2000.

[b] Means of seasonal means for the 1993 seasonal year at 12 non-urban sites.

[c] 13 urban and rural sites from 1982 to 1991, but the mean at each site is based on one-year data.

[d] Five urban sites for the period from January 1995 to February 1996.

[e] 19 urban and rural sites for the period from 1984 to 1993, but the values at some sites cover periods of fewer years.

[f] Six urban sites for the period from August 1996 to August 1997, but the value at each site covers only a period of four weeks.

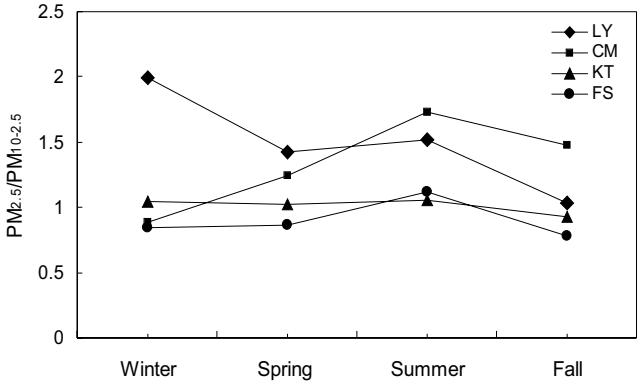

Figure 4. Seasonal variations of $PM_{2.5}/PM_{10\text{-}2.5}$ at the four stations from December 1999 to November 2000.

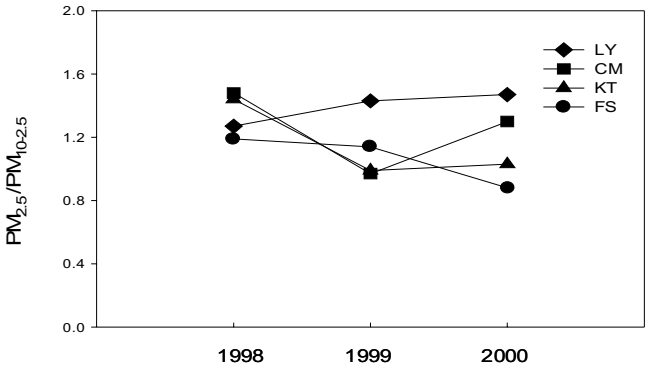

Figure 5. Variations in $PM_{2.5}/PM_{10\text{-}2.5}$ for the four stations from 1998 to 2000.

The results of this analysis indicate that rainfall and traffic volume did not significantly influence the seasonal variations of the $PM_{2.5}/PM_{10\text{-}2.5}$ ratios at the four sites. Comparing weekday and weekend $PM_{2.5}/ PM_{10\text{-}2.5}$ ratios in the daytime of sunny days showed that the weekend ratios were, in general, only slightly higher than the weekday ratios at all four stations. It suggests that vehicular emissions contributed only slightly more than other sources during the weekend. Similarly, the means of the daytime values of the ratio were only slightly higher than those of the nighttime values. The analysis did not yield a clear trend in the effects of rainfall. Heavy rainfall wets road surfaces, thereby suppressing the resuspension of coarse particles. On the other hand, raindrops preferentially remove fine particles that consist of more soluble components such as sulfate and nitrate.

The pattern of seasonal variations of the $PM_{2.5}/ PM_{10\text{-}2.5}$ ratio differed to some extent across stations from December 1999 to November 2000 (Fig. 4). Kuting station had a relatively narrow range of seasonal mean $PM_{2.5}/PM_{10\text{-}2.5}$ ratios (0.93-1.06), indicating that the contribution from motor vehicles, the main source, to ambient aerosol remained relatively constant throughout the year. The range over which the seasonal mean ratio varied at the other three stations was somewhat wider but still varied within a factor of 2.

In the absence of $PM_{2.5}$ data, it is tempting to estimate $PM_{2.5}$ concentrations from the $PM_{2.5}/PM_{10}$ ratio (calculated from existing data), on the assumption that each community has a characteristic annual mean of the ratio. Such an assumption needs close examination. As shown above, the seasonal mean ratio can vary considerably over time at a site. The pattern of year-to-year change in the ratio also differs from site to site (Fig. 5).

Neither the seasonal variation of the $PM_{2.5}/ PM_{10\text{-}2.5}$ ratio at urban sites nor that at the non-urban sites exhibits a clear pattern. Data obtained in Birmingham, U.K., show that the mean of the ratio was 4.88 from October 1994 to March 1995 and 0.72 from May to September 1995. In an analysis of particulate concentrations measured at 42 sites in the Interagency Monitoring of Protected Visual Environments (IMPROVE) network in Class I visibility areas throughout the United States during the 1993 seasonal year, Eldred et al. (1997) reported the seasonal mean of the ratio for 12 sites. For these primarily non-urban sites, the ratio generally varied within a factor of 2 at each site. The only major exception was Rocky Mountain, for which the ratio was 0.33 in winter and 1.04 in spring. Kim et al. (2000b) reported two distinct types of the ratio in the South Coast Air Basin of southern California. The first was a high ratio due to high formation of fine particles, such as 4.26

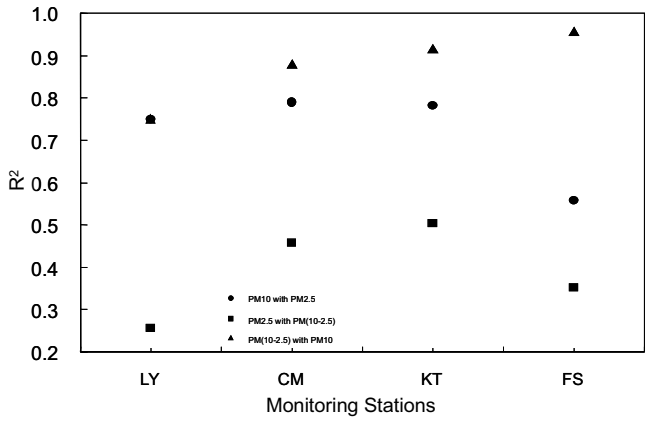

Figure 6. Coefficient of determination (R^2) for the relationships among particle fractions at the four stations from December 1999 to November 2000.

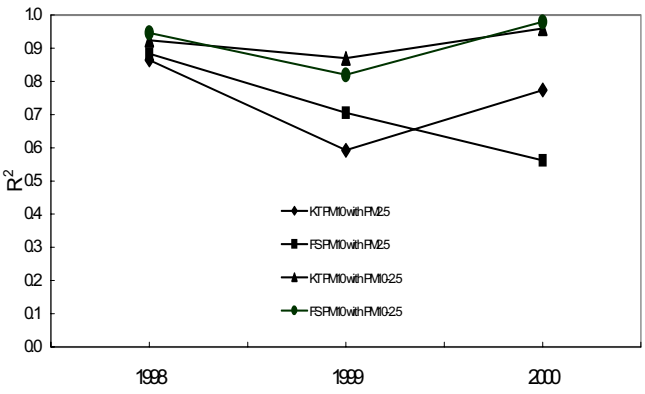

Figure 7. Variations in the coefficient of determination (R^2) for the relationships among particle fractions at KT and FS from 1998 to 2000.

observed at downtown Los Angeles on a day under stagnation conditions. The second type was a low ratio due to blowing dust, such as 0.28 observed at Rubidoux on a Santa Ana wind day. The ratio may exhibit small spatial variations in a metropolitan area such as Philadelphia, where $PM_{2.5}$ is the predominant contributor to particulate pollution. The aerosol concentrations measured at eight sites located within metropolitan Philadelphia during the summers of 1992 and 1993 (Burton et al., 1996) showed that the mean values of the ratio at the eight sites were similar, ranging only from 2.45 to 3.35. The relatively high values for the ratio in metropolitan Philadelphia are not necessarily typical of urban areas. For instance, downtown Los Angeles had a value of 1.46 (Kim et al., 2000a) and the ratios at the urban sites in Canada ranged from 0.56 to 1.44. The results shown in Table 1 also indicate that the ratios at non-urban sites do not fall within a narrow range.

3.3Relationship among Particle Fractions

The temporal variation of aerosol concentrations is an important parameter used in time-series epidemiological studies to test the relationship between particulate matter indicators and health outcomes. If an association between PM_{10} concentrations and human mortality rates exists, then the usefulness of various PM indicators can be further examined by comparing the relationships among particle fractions (Wilson and Suh, 1997). $PM_{2.5}$ is a better indicator than $PM_{10-2.5}$, if $PM_{2.5}$ and PM_{10} are highly correlated but $PM_{10-2.5}$ and PM_{10} are poorly correlated. On the contrary, $PM_{10-2.5}$ is a better indicator if $PM_{2.5}$ and $PM_{10-2.5}$ are highly correlated but $PM_{2.5}$ and PM_{10} are poorly correlated. If both $PM_{2.5}$ and $PM_{10-2.5}$ are moderately correlated with PM_{10}, then both can serve as indicators and separate measurements of $PM_{2.5}$ and $PM_{10-2.5}$ are needed for a better assessment of the underlying causes of health effects.

Figure 6 shows the relationship among particle fractions as indicated by the coefficient of determination (R^2) for the four monitoring stations from December 1999 to November 2000. The correlation between PM_{10} and $PM_{2.5}$ and the correlation between PM_{10} and $PM_{10-2.5}$ were both relatively high (R^2 in the ranges of 0.56-0.79 and 0.75-0.96, respectively). However, the correlation between $PM_{2.5}$ and $PM_{10-2.5}$ was moderate (R^2 in the range of 0.25-0.50). In contrast, the Philadelphia aerosols during the summers of 1992 and 1993 exhibited a high correlation (average R^2=0.90) between $PM_{2.5}$ and PM_{10}, a moderate correlation (average R^2=0.35) between PM_{10} and $PM_{10-2.5}$, and a low correlation (average R^2=0.11) between $PM_{2.5}$

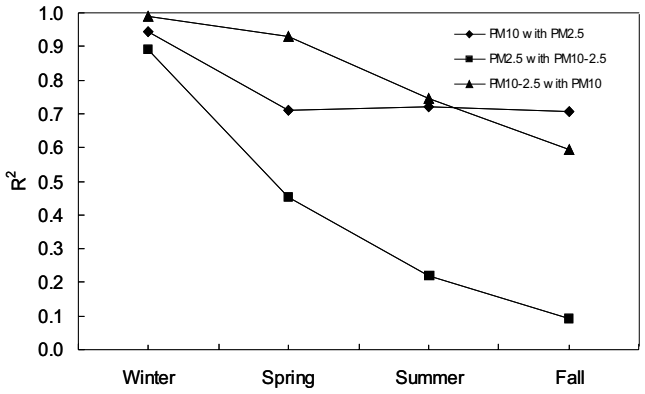

Figure 8. Seasonal variations of the coefficient of determination (R^2) for the relationships among particle fractions at FS from December 1999 to November 2000.

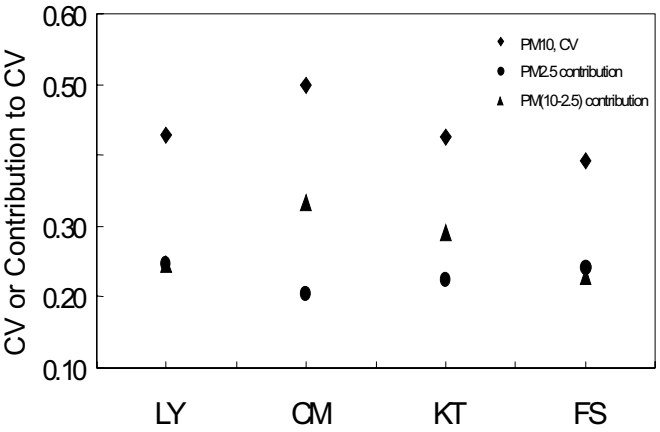

Figure 9. Coefficient of variation (CV) for PM_{10} concentrations and the contributions of $PM_{2.5}$ and $PM_{10\text{-}2.5}$ to PM_{10} CV at the four stations from December 1999 to November 2000.

and $PM_{10\text{-}2.5}$ (Wilson and Suh, 1997). The difference in relationships among particle fractions between Philadelphia and western Taiwan arises mainly because the Philadelphia aerosols had much higher $PM_{2.5}/PM_{10\text{-}2.5}$ ratios (2.45-3.35) than the aerosols in western Taiwan (0.78-1.99).

The pattern of year-to-year variations in R^2 for the relationships among particle fractions differed across stations from 1998 to 2000 (Fig. 7). The value of R^2 for the relationship between PM_{10} and $PM_{2.5}$ decreased considerably at the FS station over the period, while that between PM_{10} and $PM_{10\text{-}2.5}$ did not change much. In contrast, the values of R^2 remained relatively constant at the KT station. Figure 8 shows the seasonal variations of the coefficient of determination for the relationships among particle fractions at the FS station from December 1999 to November 2000. The coefficient of determination showed a moderate seasonal variation for the relationship between PM_{10} and $PM_{2.5}$, but a higher variation between PM_{10} and $PM_{10\text{-}2.5}$. The marked variation in the coefficient of determination for the relationship between $PM_{2.5}$ and $PM_{10\text{-}2.5}$ suggested that the driving forces for fluctuations in concentration of these two particle fractions changed independently of each other from season to season.

3.4Variability of PM_{10}, $PM_{2.5}$, and $PM_{10\text{-}2.5}$

The underlying causes of the association between PM_{10} concentrations and human mortality rates can also be examined by comparing the variability of various particle fractions. Figure 9 shows that, for all four stations from December 1999 to November 2000, $PM_{2.5}$ and $PM_{10\text{-}2.5}$ contributed almost equally to the coefficient of variation of PM_{10} concentrations. However, further calculations indicated that the relative contributions of $PM_{2.5}$ and $PM_{10\text{-}2.5}$ to the variability of PM_{10} varied considerably from season to season at each site, from year to year at each site, and from site to site for each year.

4. Conclusions

For both urban and non-urban sites, the seasonal mean of the $PM_{2.5}/PM_{10\text{-}2.5}$ ratio could vary considerably within a year. Different urban areas have ratios with markedly different ranges. Care must therefore be taken when estimating $PM_{2.5}$ from the ratio by assuming that the ratio has a characteristic value for a community.

The relationships among particle fractions and the variability of each particle fraction could differ

significantly between communities. Even though epidemiological studies indicate that increases in human morbidity and mortality rates are associated with the mass concentration of ambient particles in a certain size fraction, the properties of the particles that cause adverse health effects remain unknown. The mass concentration of particles in a certain size fraction is unquestionably a simple and convenient index for monitoring and regulatory purposes. The current rationale for using $PM_{2.5}$ and PM_{10} as separate indices follows mainly from the observation that the chemical compositions of fine and coarse particles in many communities differ greatly. Exception may arise in regions where fine particles contain a substantial amount of crustal material. Additional questions arise if the mass concentration of particles in a certain size fraction is simply a surrogate of short-lived, difficult-to-quantify, but biochemically active compounds. Friedlander and Yeh (1998) provided evidence of the involvement of peroxides in particulate pollutants in causing adverse health effects. This study indicates that PM_{10} and $PM_{10\text{-}2.5}$ are highly or moderately correlated in some communities. For these areas, data on both PM_{10} and $PM_{2.5}$ are still needed for epidemiological studies. If resources are limited, $PM_{2.5}$ can be monitored only in urban centers where $PM_{2.5}$ is the predominant contributor to PM_{10}. Before biologically active chemical species that actually cause the adverse health effects are clearly identified, extensive monitoring of $PM_{2.5}$ is not well justified in areas with low $PM_{2.5}/PM_{10\text{-}2.5}$ ratios.

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