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The Effect of Particulate Matter on Visibility in Hangzhou, China

ABSTRACT

Hangzhou, a humid subtropical city of China, was studied to investigate the effect of particulate matters (PMs) and its fractions (e.g., $PM_{2.5}$ and $PM_{2.5\sim10}$) and levels of relative humidity (10 to >90%) on atmospheric visibility. It was found that finer fractions of PM have greater negative effect on visibility. This inverse relationship was pronounced during winter season, having the highest $PM_{2.5}$ concentrations and the lowest visual range. Summer season exhibited the highest visual range and least $PM_{2.5}$ fractions, along with autumn. Furthermore, lower relative humidity coincides with higher visual range regardless of the PM fractions. As the levels of relative humidity went up (>90%), lower values of visual range were measured. The results from this study suggest that lower target levels of $PM_{2.5}$ is needed for Hangzhou in order to prevent episodes of poor visibility.

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INTRODUCTION

Visibility is a convenient indicator for the public to evaluate air quality. Poor visibility often leads to serious concerns, or sometime even causes panic in the general public due to its indication of the potential hazard to human health.(*Pui et al. 2014; Yang et al. 2013; Zhao et al. 2013*) Therefore, it is crucial to understand what may affect visibility under various circumstances so that appropriate pollution control policies can be made to mitigate visibility degradation. With the increase of public awareness about visibility degradation or hazy weather, Chinese governments have made regulatory efforts to fight against air pollution in recent years, for instance, the China Ministry of Environmental Protection promulgated a new $PM_{2.5}$ standard in early 2012. In line with this, many local authorities have overhauled regional standards for air pollution control and proposed roadmaps to improve air quality, accordingly.

The success of these efforts would not be possible without the sufficient understanding of the characteristics of air pollution and its relationship with visibility, as China is such a large country with various industries unevenly distributed in different regions. Moreover, the climate in China varies from one region to another since the country is a massive one. Therefore, in order to obtain a better understanding of the relationship between the visibility and the concentration of PM2.5, the investigations of air pollution should be carried out in Chinese cities in different regions.

The relationship between visibility and particulate matters (PMs) has been examined in several major cities in eastern Asia in recent years.(*Han et al. 2014; Kuo et al. 2013; Pui et al. 2014; Wang et al. 2013*) For instance, Chen et. al. studied the effects of relative humidity (RH) and water soluble components in PM2.5 on atmospheric visibility in Beijing under different meteorological conditions.(*Chen et al., 2014*) The analysis of $PM_{2.5}$ samples collected in Spring 2012 shows that water soluble species takes up 38.1% of the total mass of $PM_{2.5,}$ among which NO_{3-} was the most abundant constituent, followed by SO_4^{2-}, NH_4^+ and water soluble organic matter. Their correlation analysis further revealed that visibility was better correlated with the total mass of water soluble constituents (WSC) compared to the total aerosol loading of $PM_{2.5}$. The visual range was the most sensitive factor to both WSC and $PM_{2.5}$ in a RH of 30-70%. Severe visibility impairment was observed for RH ≥ 70% with the least sensitivity to WSC and $PM_{2.5}$. In another study by Deng and his coworkers, they investigated the changing trend of visibility in Taiwan Strait and its influence factors, including the effects of $PM_{2.5}$ and PM10.(*Deng et al. 2014*) They found negative correlations of airborne PMs with visibility with r-values between -0.58 and 0.76, which suggests the significant contribution of PMs to light extinction. The associations between $PM_{2.5}$ and visibility have more negative correlation coefficients than that between PM_{10} and visibility, suggesting that, $PM_{2.5}$ played a more important role in visibility deterioration over the cross-strait region than PM_{10}.

Hangzhou is situated in a subtropical area with distinct seasonal weather conditions, and is 50-km away from the western rim of the Pacific Ocean. Hangzhou is experiencing both fast urbanization and growing environmental issues: (*Xiao et al. 2011*) as of 2010, the population of Hangzhou ranked sixth in China, and the population density was 1,214 km^{-2}. While the city is a traditional hotspot for national and international tourists, it also suffered from severe air pollution due to the fact that the city is located in the Yangtze River Delta (YRD), one of the most developed regions in China. In recent years, hazy weather with poor visibility becomes frequent in Hangzhou. However, only few studies have analyzed the key factors that are detrimental to visibility.(*Xiao et al. 2011*) Moreover, along with the fast economic growth and the evolvement of local industries, the chemical composition of pollutants also varies significantly over the past few years.

The understanding of the relationship between visibility and PM pollution is indispensable for the pollution control in cities like Hangzhou. To this end, we conducted an extensive investigation in Hangzhou from Dec. 1, 2012 to Nov. 30, 2013. In addition, the correlation between visibility and the chemical composition of $PM_{2.5}$ from Oct. 13, 2013 to Nov. 1, 2013 was analyzed as a case study. As Hangzhou is a typical humid subtropical city with four distinctive seasons, visibility and the concentrations of fine ($PM_{2.5}$) and coarse ($PM_{2.5\sim10}$) particulate matter for the seasons were firstly discussed. $PM_{2.5\sim10}$ represents particulate matters with an aerodynamic diameter of 2.5~10μm. The statistical correlation among visibility, PMs, and RH in Hangzhou was then examined. Finally, the effects of different chemical species on visibility were investigated to provide additional information for the understanding of the alleviation of poor visibility.

METHODOLOGY

Site Description

All in situ measurements of aerosol optical properties and meteorology factors were conducted at Zhaohui station (30°17'28.4"N, 120°10'39.7"E) (**Figure 1**). The instruments at the station were installed on the roof of a building. They are at 20 m above ground level (AGL). The station is in the convergence of commercial, residential and educational zones without apparent industrial pollution sources, thus the air quality at this place can be considered as typical for Hangzhou urban areas. There is no industrial activity near the site.

Duration of Sampling

Sampling, other than those for chemical analysis, was conducted at the Zhaohui station from Dec. 1, 2012 to Nov. 30, 2013. For chemical analysis, sampling period was from Oct. 13, 2013 to Nov. 1, 2013. As the sampling region was raining frequently, $PM_{2.5}$ samples were only concurrently collected at the Zhaohui station during non-raining days. On each sampling day, samples were collected for 20 hours so that the total volume of air sample is equivalent to the average volume of air a

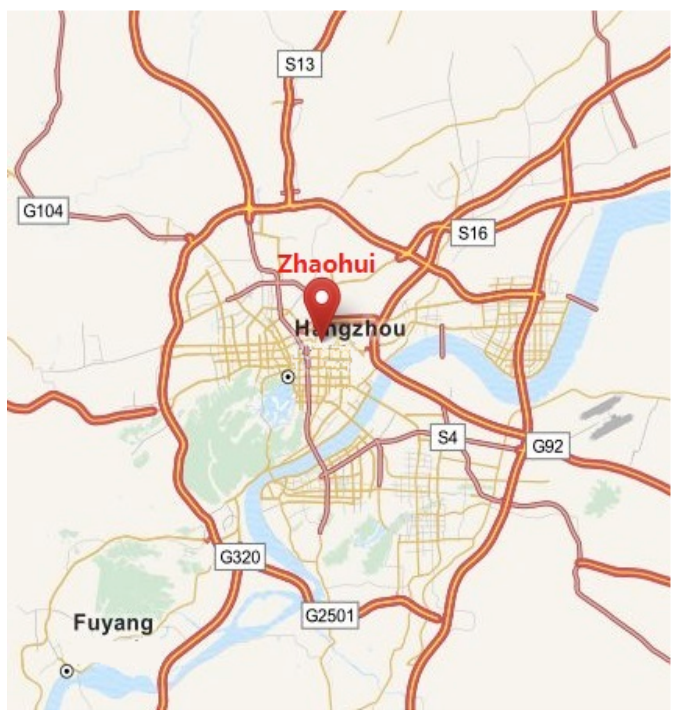

Figure 1. The geological location of the Zhaohui station (© OpenStreetMap contributors. Tiles courtesy of MapQuest).

person inhales on each day. Overall, this study collected a total of PM samples, each fractionated into $PM_{2.5}$, $PM_{2.5-10}$, and PM_{10}. The same number of samples were generated for visibility.

Samplers. For continuous monitoring, $PM_{2.5}$ and $PM_{2.5\sim10}$ sampler is a Thermo Scientific 1405-DF Continuous Dichotomous Ambient Air Monitor. This sampler utilizes two Tapered Element Oscillating Microbalances (TEOM) and two Filter Dynamics Measurement Systems (FDMS), which account for volatile and nonvolatile particulate matter (PM) fractions. Calibrations for temperature, barometric pressure, relative humidity (RH), and volumetric flow measurements were done automatically to guarantee data accuracy. Atmospheric visibility was measured with a visibility sensor (Belfort Model 6000, visual range: 6m-80km).

For $PM_{2.5}$ samples used for chemical analysis, the samplers were the model TH-150C, manufactured by Wuhan Tianhong Instruments Co., Ltd. The operational volume flow rate for $PM_{2.5}$ samplers was set at 100 L min^{-1}, and the size cut was at 2.5 µm. Three TH-150C samplers were used to collect three concurrent $PM_{2.5}$ samples for analyzing inorganic elements, soluble ions, and carbon items, respectively. For elemental analysis, PTEF organic filters (Sumitomo Electric Fine Polymer, Inc.) were used. The pore size was 0.3 µm for the filters, and the collection efficiency at 0.15 µm was 99.97% for organic filters.

Chemical analysis

The bulk masses of PM2.5 samples were weighed with a balance (0.0001 accuracy), and the speciation was conducted for nine ions and two carbon items. Details are elaborated as follows.

Water Soluble Ions. After sampling, a piece of organic filters loaded with $PM_{2.5}$ were put into 25 ml cuvettes. Then, 20.00 ml deionized water was added and bubbles expelled. The cuvettes were placed in a supersonic cleaner running for 20 minutes. After being stilled for a while, clear solution in top layer was drawn and filtered before being analyzed by Ion Chromatography for water-soluble anions (F^-, Cl^-, NO_3^-, SO_4^{2-}; Dionex IC DX600) and cations (NH_4^+, K^+, Na^+, Ca^{2+}, Mg^{2+}; Dionex ICS-90).

Carbon Analysis. After sampling, quartz filters loaded with $PM_{2.5}$ were put on new and clean aluminum foil, and a representative piece was obtained carefully. A second piece with the same area was obtained and processed as follows to remove carbonate. First, the second piece was soaked in concentrated HCl solution in a covered container. Then, the container was placed in a ventilator cabinet for about an hour to remove carbonate in form of CO_2 and for another hour to let remaining HCl evaporate. The sample was then kept at low temperature and saved for subsequent analyses.

The organic, elemental, and total carbon contents of $PM_{2.5}$ samples were determined with a thermo-photometric carbon analyzer (DRI Model 2001A). A piece of processed sample filter (0.495 cm^2) was put in an environment with pure He gas without O_2, and was heated progressively at 120ºC, 250ºC, 450ºC, and 550ºC first to determine organic carbon (OC) contents OC1, OC2, OC3, and OC4, respectively. Then, in an environment with 2% O2 and 98% He, the sample was further heated progressively at 550ºC, 700ºC, and 800ºC to determine elemental carbon (EC) contents EC1, EC2, and EC3. The CO_2 produced within each temperature ladder was reduced into CH4, catalyzed by MnO_2, and detected by Flame Ionization Detector. During heating processes, part of organic carbon was converted into black carbon, which hindered clear distinction between organic carbon and elemental carbon. Hence, the reflection intensity of the He-Ne laser light at 633 nm by a monitoring filter was used to gauge the starting temperature of the oxidation of elemental carbon, to ensure science-based distinction between organic carbon and elemental carbon.

RESULTS AND DISCUSSION

The effect of Particulate Matter on visibility across seasons

In order to study the effect of the size of Particulate Matter (PM) on visibility across seasons, the relationship between visibility and the concentrations of $PM_{2.5}$, $PM_{2.5\sim10}$ and PM_{10} in the four seasons covered were examined. Generally, visibility was reduced as the concentrations of PM increased (**Figure 2** - **Figure 5**). This same pattern was observed for all PM fractions studied.

Summer is the one with the best overall visibility among all four seasons, as most of the data points in summer show a visual range longer than 10 km (**Figure 4**). The least visibility was observed during winter season with most data exhibiting a visual range less than 10 km with an average of ~4 km. Another feature in winter differs from other seasons is the observed maximum concentration of $PM_{2.5}$, which is almost twice larger than the maximum concentration of $PM_{2.5\sim10}$. As a comparison, in the other three seasons, the maximum concentrations

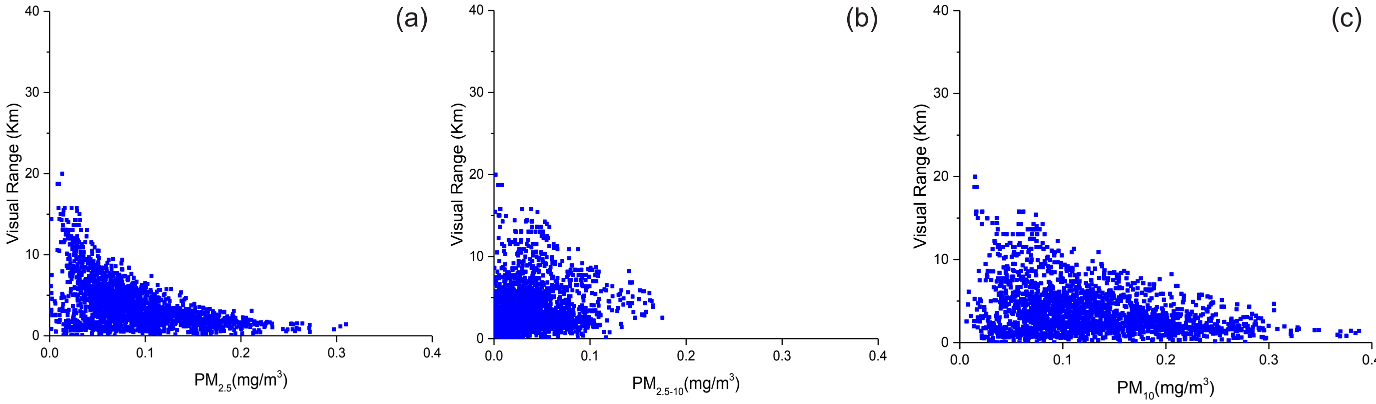

Figure 2. Visual range and concentrations of (a) $PM_{2.5}$, (b) $PM_{2.5\sim10}$, and (c) PM_{10} in winter (From Dec. 1, 2012 to Feb. 30, 2013).

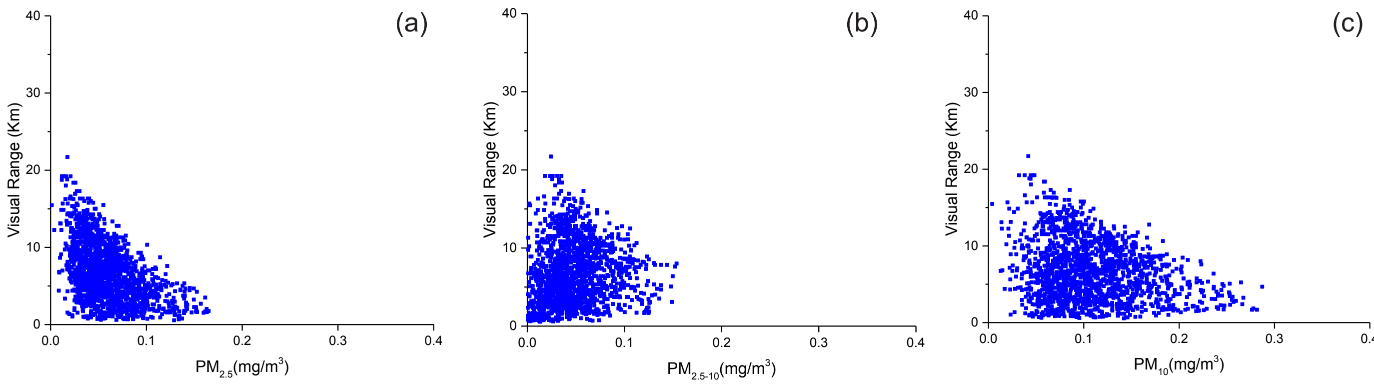

Figure 3. Visual range and concentrations of (a) $PM_{2.5}$, (b) $PM_{2.5\sim10}$, and (c) PM_{10} in spring (From March 1 to May 31, 2013).

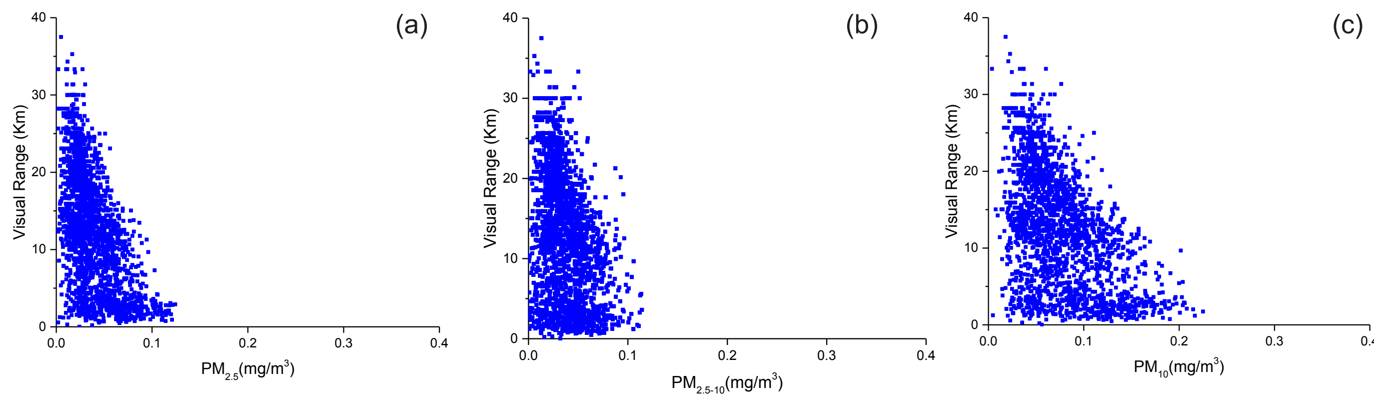

Figure 4. Visual range and concentrations of (a) $PM_{2.5}$, (b) $PM_{2.5\sim10}$, and (c) PM_{10} in summer (From June 1 to August 31, 2013).

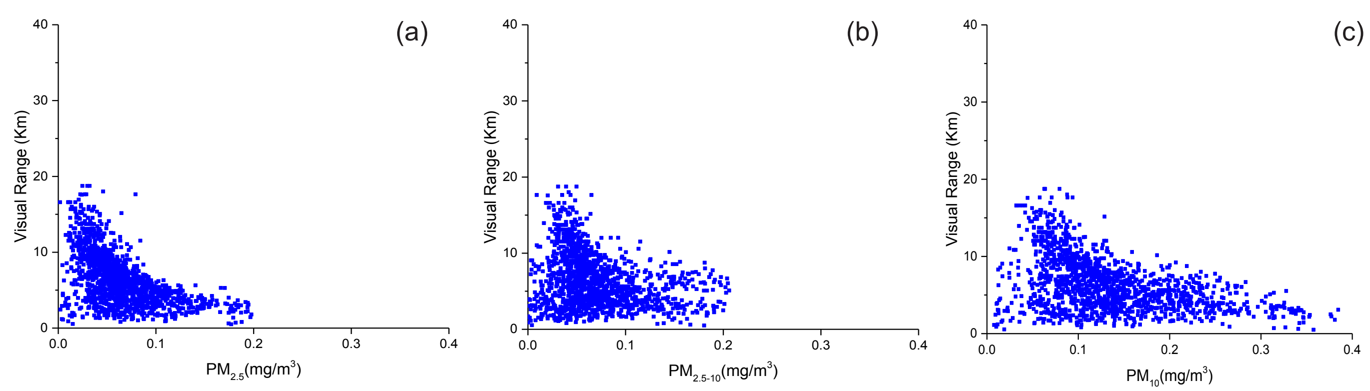

Figure 5. Visual range and concentrations of (a) $PM_{2.5}$, (b) $PM_{2.5\sim10}$, and (c) PM_{10} in autumn (From Sept. 1 to Nov. 30, 2013).

of $PM_{2.5}$ and $PM_{2.5\sim10}$ are very close to each other.

A closer look at the pattern of relationship between $PM_{2.5}$ and $PM_{2.5\sim10}$ and visibility reveals that the relationships may be related to the mass ratio of $PM_{2.5}$/ $PM_{2.5\sim10}$. The ratio is significantly larger in winter than in other seasons, which means more $PM_{2.5}$ fraction was present in the air during winter compared to other seasons, which coincides with lowest visibility among all seasons (**Figure 6** and **7**). This could also be brought about by the prevailing wind from the north during winter bringing along dust to Hangzhou.

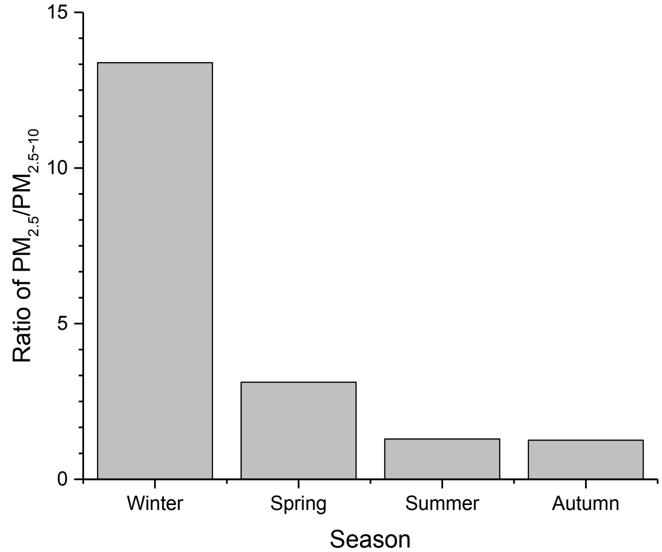

Figure 7. Averaged ratio of $PM_{2.5}/PM_{2.5\sim10}$ for different seasons.

Relationship between visibility and Particulate Matter as affected by Relative Humidity

Comparison of the graphs showed that most visibility data were at a lower visual range during high levels of relative humidity (>90%) (**Figure 8**). In contrast, longer visual range was observed as the levels of relative humidity went lower (e.g., 10 to 20%), which also been reported similarly in other studies in Beijing,(*Chen et al. 2014*) and Guangzhou (China).(*Tao et al. 2012; Tao et al. 2009; Tao et al. 2014*).

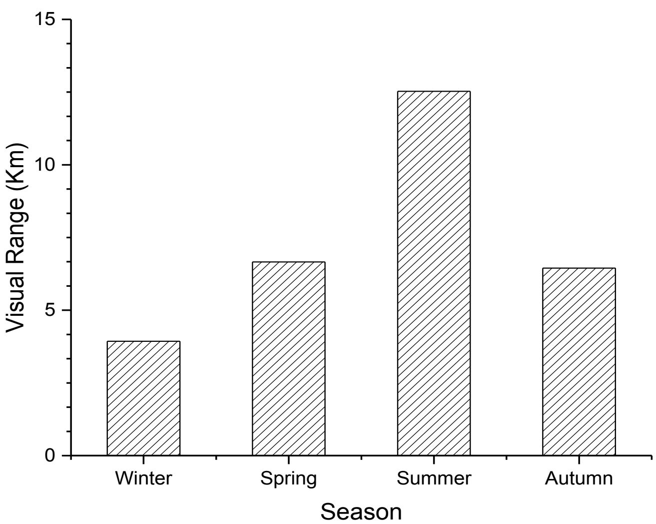

Figure 6. Averaged visual range for different seasons.

In addition, despite the fact that PM10 also correlates well with visibility in a range of RH similar to $PM_{2.5}$, $PM_{2.5\sim10}$ exhibited poor correlations with visual range (**Table 1**). The relationship between visibility and $PM_{2.5\sim10}$ is in general, weaker than that of visibility and $PM_{2.5}$. This indicates that $PM_{2.5}$ is the major constituent in PMs which causes visibility reduction. Most days in Hangzhou has levels of RH higher than 20% (**Figure 8**). As visual range is very sensitive to the concentration of $PM_{2.5}$, a $PM_{2.5}$ control policy for Hangzhou needs to target at a lower level than that for the dry cities in northern part of China.

Relationship between visibility and the chemical composition of PM2.5

Because it is $PM_{2.5}$, not $PM_{2.5\text{-}10}$, which plays a key

Table 1. Regression analysis between visibility and Particulate Matter (PM) in different ranges of Relative Humidity (RH) from Dec 1, 2012 to Nov. 30, 2013.

	$PM_{2.5}$		$PM_{2.5\text{-}10}$		PM_{10}	
	Equation	**R**	**Equation**	**R**	**Equation**	**R**
RH>90	$y=0.3358x^{-0.544}$	0.241	$y=1.486x^{-0.051}$	0.004	$y=0.4191x^{-0.551}$	0.184
80≤RH<90	$y=0.3955x^{-0.784}$	0.677	$y=2.0016x^{-0.187}$	0.054	$y=0.5152x^{-0.844}$	0.539
70≤RH<80	$y=0.5179x^{-0.821}$	0.749	$y=1.7991x^{-0.342}$	0.142	$y=0.6977x^{-0.902}$	0.627
60≤RH<70	$y=0.7983x^{-0.756}$	0.652	$y=1.5433x^{-0.516}$	0.202	$y=0.8901x^{-0.933}$	0.606
50≤RH<60	$y=0.9781x^{-0.75}$	0.703	$y=1.699x^{-0.557}$	0.292	$y=1.1056x^{-0.923}$	0.688
40≤RH<50	$y=0.1237x^{-0.733}$	0.711	$y=1.8806x^{-0.562}$	0.435	$y=1.5028x^{-0.841}$	0.734
30≤RH<40	$y=1.2199x^{-0.714}$	0.622	$y=1.898x^{-0.602}$	0.557	$y=1.7551x^{-0.811}$	0.737
20≤RH<30	$y=3.428x^{-0.363}$	0.306	$y=3.8113x^{-0.359}$	0.383	$y=3.2192x^{-0.538}$	0.518
10≤RH<20	$y = 7.5236x^{-0.146}$	0.208	$y = 9.0531x^{-0.112}$	0.039	$y = 6.9379x^{-0.246}$	0.192

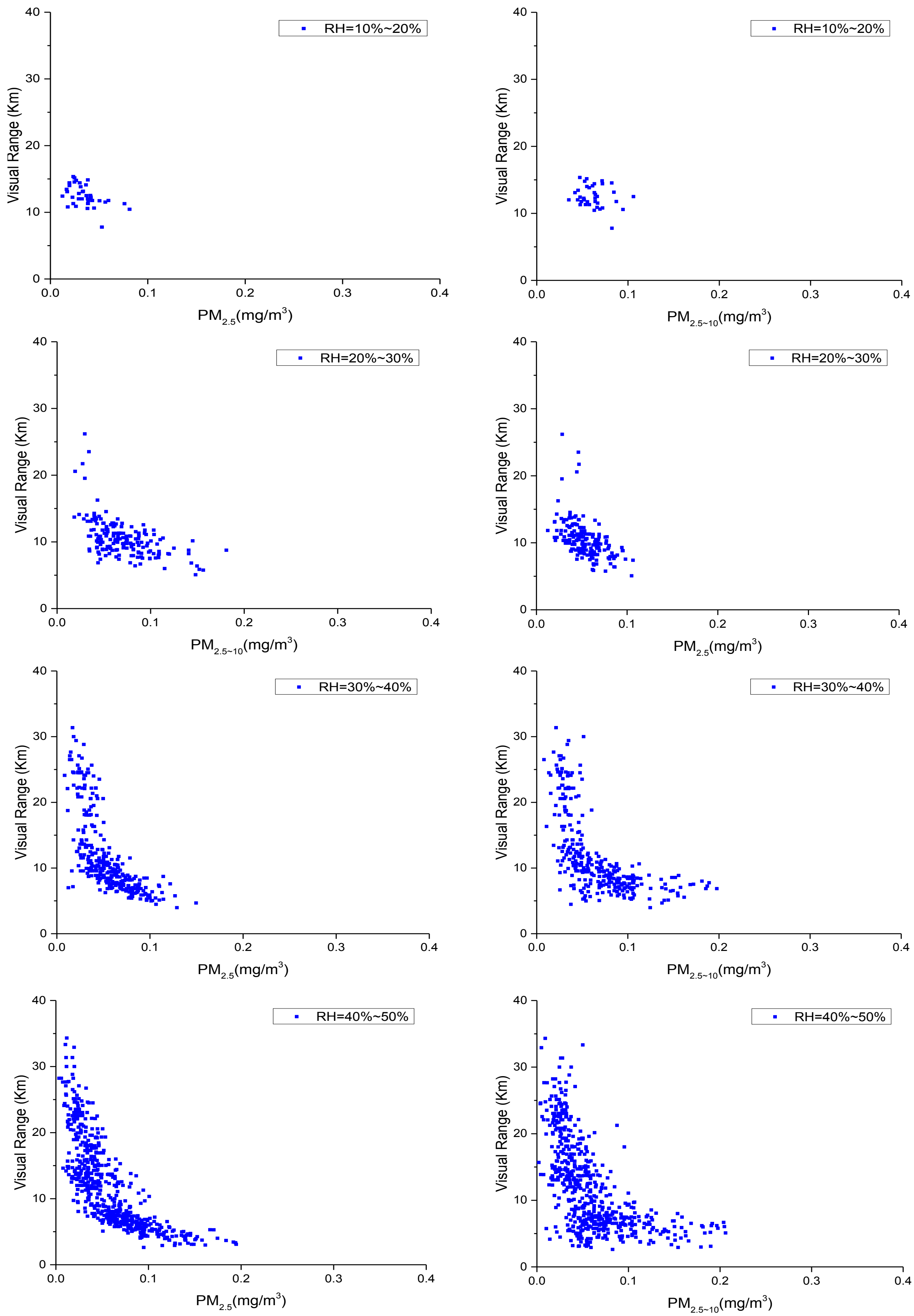

Figure 8. Relationship between visibility and concentrations of $PM_{2.5}$ and $PM_{2.5\sim10}$ at different levels of relative humidity (RH) from Dec 1, 2012 to Nov. 30, 2013.

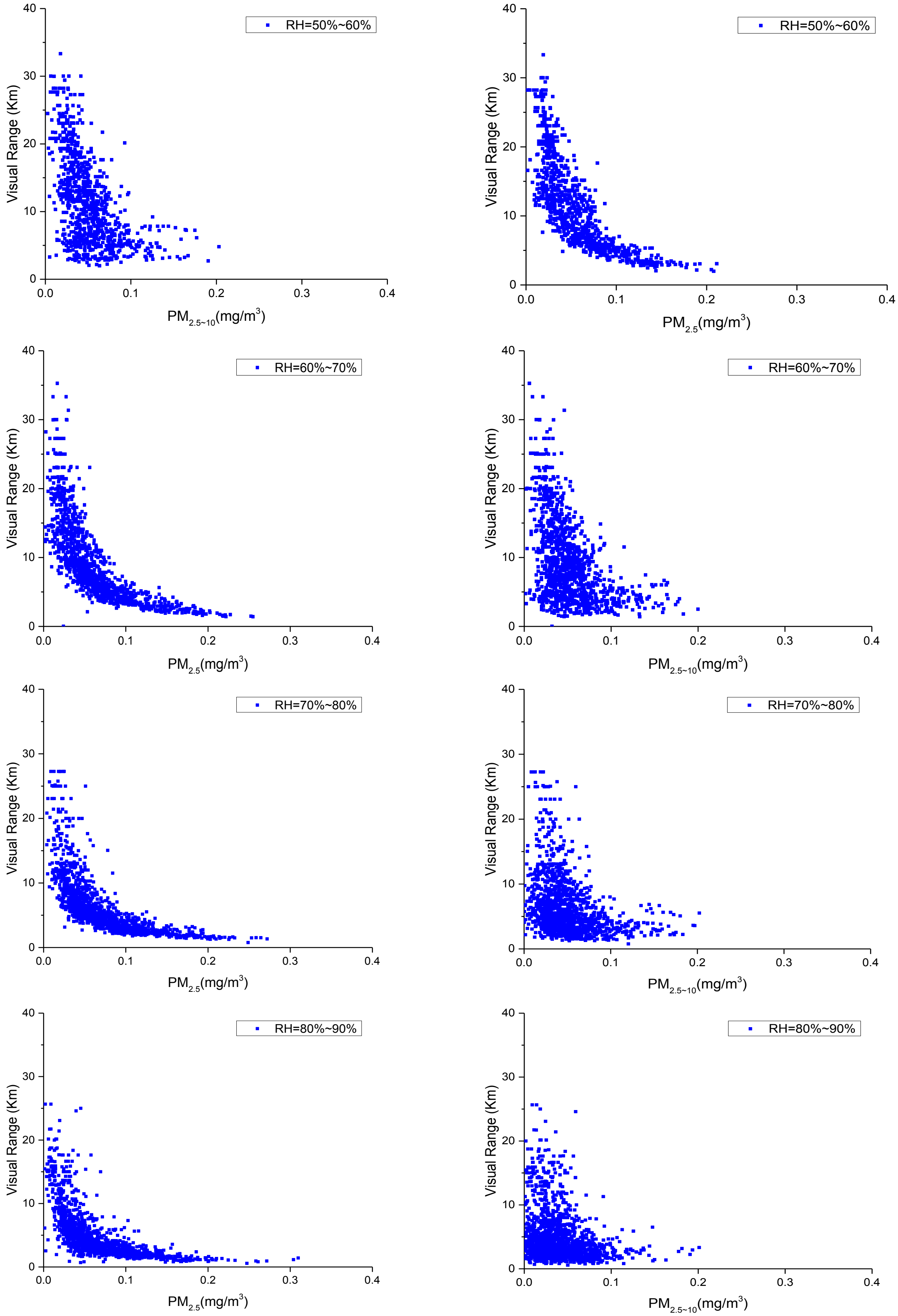

Figure 8. Relationship between visibility and concentrations of $PM_{2.5}$ and $PM_{2.5\sim10}$ at different levels of relative humidity (RH) from Dec 1, 2012 to Nov. 30, 2013 (cont.).

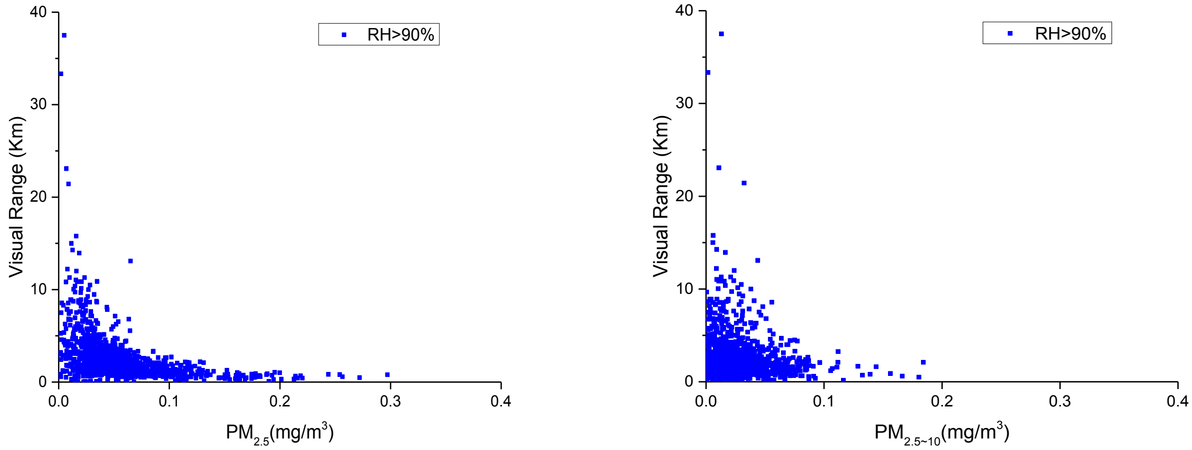

Figure 8. Relationship between visibility and concentrations of $PM_{2.5}$ and $PM_{2.5\sim10}$ at different levels of relative humidity (RH) from Dec 1, 2012 to Nov. 30, 2013 (cont.).

role in visibility reduction, this study further examined the chemical composition of $PM_{2.5}$. The average daily $PM_{2.5}$ concentrations during the sampling period from Oct. 13, 2013 to Nov. 1, 2013 at the Zhaohui station was found to be 78.7±27.9 μg m^{-3}. Meanwhile, the maximum and minimum daily $PM_{2.5}$ concentrations were 121.3 μg m^{-3} and 30.6 μg m^{-3}, respectively. Meanwhile, 60.9% of the $PM_{2.5}$ were water soluble ions (**Table 2**). Among them, NO_3^- and SO_4^{2-} were the two dominant constituents. These secondary constituents were usually considered to be derived from the gaseous precursors SO_2 and NO_x.(*Liu et al. 2014*) Strong solar radiation, high ambient temperature, and high relative humidity enhance photochemical processes.(*Song et al. 2006*) The low concentration of elements, such as Al, Si, Fe, and Ca suggests that road dust has a relatively small impact on air quality during the sampling period.

Water-soluble ions were important fractions of $PM_{2.5}$ which may affect visibility. There were inverse correlations between visibility and secondary inorganic salts (NO_3^-, SO_4^{2-}, and NH_4^+), which suggests that secondary inorganic salts do contribute significantly to the reduction of visibility (**Table 3**). Nitrates and sulfates were found to be the components that contribute most to light scattering which lead to visibility reduction, similar to what was reported by Kuo and his coworkers.(*Kuo et al. 2013*) They observed significant inverse correlations between visibility and NO_3^-, SO_4^{2-} and NH_4^+ at both Taichung and Wuchi stations in Taiwan. In another visibility study,

Farber et. al. (*1994*) reported that sulfate, nitrate, and carbon species were the dominant particulate species during a hazy weather in Los Angeles. Similar results were found in Seoul through the chemical analysis of $PM_{2.5}$ in haze periods (*Geng et al., 2011; Kang et al., 2004*). In Shanghai, secondary inorganic pollution,

Table 2. The mass concentrations of major components in $PM_{2.5}$.

Constituents	Average concentration (μg m^3)	Maximum concentration (μg m^3)	Minimum concentration (μg m^3)
OC	14.5±6.5	27.5	0.0
EC	4.4±2.0	8.6	1.6
F^-	0.1±0.1	0.3	0.0
Cl^-	4.3±1.9	9.9	1.9
NO_3^-	12.6±5.4	20.2	3.6
SO_4^{2-}	18.1±7.1	29.2	7.4
Na^+	1.9±0.7	2.9	0.4
NH_4^+	7.6±3.7	13.3	1.0
K^+	0.8±0.6	1.9	0.0
Mg_2^+	0.2±0.1	0.3	0.1
Ca_2^+	1.5±0.7	2.7	0.0
Al	0.4±0.1	0.6	0.2
Si	0.7±0.2	1.0	0.4
Ca	0.3±0.1	0.4	0.1
Fe	0.6±0.2	1.0	0.3

Table 3. Relationship between visibility and water soluble ions in $PM_{2.5}$.

Soluble Ions	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na_+	NH_4^+	K^+	Mg_2^+	Ca_2^+
Pearson Correlation Coefficients	-0.561	-0.531	-0.782	-0.678	-0.146	-0.783	-0.669	-0.289	-0.219

together with dust and biomass burning, were identified to be three typical haze types (*Du et al., 2011; Huang et al., 2012*).

Organic Carbon (OC) and Elemental Carbon (EC) are important components of $PM_{2.5}$ which also affects visibility (*Turpin and Huntzicker 1995*) The sources of carbonaceous aerosols can be evaluated with the ratio of OC and EC concentrations(C*ao et al., 2007; Zhang et al., 2007*) The OC and EC, as well as TC, have similar negative impact on atmospheric visibility (**Table 4**). However, the effect of these carbonaceous components on visibility is weaker than typical species of secondary inorganic aerosols such as NO_3^-, SO_4^{2-}.

Table 4. Relationship between visibility and carbonaceous component in $PM_{2.5}$.

Component	OC	EC	TC
Pearson Correlation coefficient	-0.492	-0.443	-0.488

CONCLUSION AND RECOMMENDATIONS

This study examined the effect of Particulate Matter (PM) fractions and humidity on atmospheric visibility in Hangzhou, China. It was found that PM negatively affects visibility. Among the PM fractions, $PM_{2.5}$ has the greatest effect on visibility. Furthermore, with lower relative humidity (RH) (e.g., 10 to 20%), visual range was more than 10 km. As the relative humidity levels went up (e.g., >90%), the visual range or visibility was reduced. Summer season exhibited higher visibility, while winter has the least among the four seasons, coinciding with greater $PM_{2.5}$ concentrations during winter. Furthermore, this study found that secondary inorganic salts (NO_3^-, SO_4^{2-} and NH_4^+) does contribute to the reduction of visibility. As Hangzhou is humid subtropical city with levels of RH mostly higher than 20%, a lower target levels for $PM_{2.5}$ is needed for Hangzhou in order to prevent episodes of poor atmospheric visibility.

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