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## Aerosol Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/uast20>

### Chemical Mass Closure and Chemical Characteristics of Ambient Ultrafine Particles and other PM Fractions

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Published online: 15 Jul 2010.

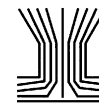
To cite this article: Sheng-Chieh Chen, Chuen-Jinn Tsai, Cheng-Yu Huang, Hong-Dar Chen, Shui-Jen Chen, Chih-Chung Lin, Jen-Hsiung Tsai, Charles C.-K. Chou, S.-C. Candice Lung, Wei-Ru Huang, Gwo-Dong Roam, Wan-Yi Wu, Jiri Smolik & Lucie Dzumbova (2010) Chemical Mass Closure and Chemical Characteristics of Ambient Ultrafine Particles and other PM Fractions, *Aerosol Science and Technology*, 44:9, 713-723, DOI: [10.1080/02786826.2010.486385](https://doi.org/10.1080/02786826.2010.486385)

To link to this article: <http://dx.doi.org/10.1080/02786826.2010.486385>

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# Chemical Mass Closure and Chemical Characteristics of Ambient Ultrafine Particles and other PM Fractions

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Ambient ultrafine particles (UPs or PM<sub>0.1</sub>), PM<sub>2.5</sub> and PM<sub>10</sub> were investigated at the roadside of Syuefu road in Hsinchu city and in the Syueshan highway tunnel in Taipei, Taiwan. A SMPS (TSI Model 3936), three Dichotomous samplers (Andersen Model SA-241), and three MOUDIs (MSP Model 110) were collocated to determine the PM number and mass concentrations simultaneously. The filter samples were further analyzed for organic carbon (OC), element carbon (EC), water-soluble ions, and trace elements. The OC artifact was studied and quantified using the quartz behind quartz (QBQ) method for all PM fractions. Taking into account the OC artifact, chemical mass closure (ratio of the reconstructed chemical mass to the gravimetric mass) of PM<sub>0.1</sub>, PM<sub>2.5</sub>, and PM<sub>10</sub> was then calculated and found to be good. The chemical analysis results of UPs at both sites showed that UPs in the present tunnel was mostly contributed from the vehicle emissions while UPs at the roadside was mainly influenced by urban sources.

## INTRODUCTION

Researchers have found the associations of the exposure to ultrafine particles (UPs) with the adverse health effects due to bounded elemental/organic carbon, sulfate, elements as well as PAH (polycyclic aromatic hydrocarbons) on UPs (Donaldson et al. 2002; Ntziachristos et al. 2007; Oberdörster et al. 2005). UPs are referred to as PM<sub>0.1</sub> in this study and other researches (Arhami et al. 2009; Chow and Watson 2007). Sometimes PM<sub>0.18</sub> was mentioned as UPs in other studies (Geller

et al. 2005; Sardar et al. 2005). It is important to assess the mass and chemical species concentrations of UPs accurately. However, only few researches are able to achieve a good chemical mass closure (ratio of the reconstructed chemical mass to the gravimetric mass) for PM<sub>2.5</sub> (Turpin and Lim 2001). But for smaller particles such as UPs, good mass closure has not been found except in the study of quasi-UP (or PM<sub>0.25</sub>) by Arhami et al. (2009).

Motor vehicles are known to be an important source of ambient UPs and PM<sub>2.5</sub> particles which are continuously evolving both chemically and physically in the atmosphere (Schauer et al. 1996). In order to characterize the motor emissions, several different methods were used, including chassis dynamometer experiments (Cadle et al. 1999; Hildemann et al. 1989; Kleeman et al. 2000; Robert et al. 2007a, b; Schauer et al. 1999, 2002), roadside measurements (Lin et al. 2005; Ntziachristos et al. 2007; Phuleria et al. 2007; Zhu et al. 2002) and tunnel measurements (Allen et al. 2001; Fraser et al. 1998; Grieshop et al. 2006; Geller et al. 2005; Huang et al. 2006; Phuleria et al. 2006; Weingartner et al. 1997). Roadside and tunnel measurements provide more realistic on-road motor emission characteristics and emission factors for PM<sub>2.5</sub> (Allen et al. 2001; Fraser et al. 1998; Grieshop et al. 2006; Phuleria et al. 2006; Weingartner et al. 1997), and for UPs (Geller et al. 2005; Huang et al. 2006; Lin et al. 2005, 2009; Ntziachristos et al. 2007; Phuleria et al. 2007). In these studies, only Geller et al. (2005) investigated chemical mass closure of PM<sub>0.18</sub> in the Caldecott Tunnel, Oakland, CA. However, discrepancy between the chemical reconstructed and gravimetric masses was found, which was suspected due to the adsorption of organic vapor by the quartz filters during sampling. Others studied UPs in the urban areas (Cass et al. 2000; Sardar et al. 2005), but chemical mass closure was not discussed.

Received 27 June 2009; accepted 10 April 2010.

The financial support of the Taiwan EPA (EPA-96-U1U1-02-104 and EPA-97-U1U1-02-106) is gratefully acknowledged.

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The POC (particulate organic carbon) was normally determined by analyzing particle samples collected on quartz filters using the thermal optical reflectance (TOR) or thermal optical transmission (TOT) method. However, sampling with quartz filters may lead to overestimation or underestimation of POC due to the adsorption of gas-phase OC on the quartz filter (positive artifact) or volatilization of POC from the collected PM (negative artifact), respectively. These artifacts were estimated to range from  $-80\%$  for volatilization to  $+50\%$  for adsorption for  $PM_{2.5}$  (Turpin et al. 2000). Subramanian et al. (2004) used the quartz backup filter sampler (TQQQ) to study the positive artifact using a backup quartz filter (QBQ, quartz behind quartz) behind either a main quartz filter (MQ, main quartz) or a Teflon filter (QBT, quartz behind Teflon) in the  $PM_{2.5}$  sampler. Comparison of the POC concentration of the TQQQ sampler with that of a denuder sampler showed that QBQ provided a good estimate of the positive artifact on the MQ when both quartz filters were in equilibrium with the sampled air for OC. But the equilibrium may not always be achieved (Mander and Pankow 2001; Subramanian et al. 2004).

In order to obtain the POM (particulate organic mass) of  $PM_{2.5}$  to achieve a better chemical mass closure, the POC was multiplied by a factor of  $1.6 \pm 0.2$  and  $2.1 \pm 0.2$  (POM/POC) to account for the additional mass of associated H, O, N, and S in the particles in the urban and non-urban locations, respectively (Turpin and Lim 2001). For vehicle emissions, Schauer et al. (1999, 2002) found that the primary emitted  $PM_{1.8}$  from both gasoline vehicles and medium duty diesel trucks had a POM/POC of about 1.2, which was lower than that of the aged urban and non-urban  $PM_{2.5}$ . This factor was used in Kleeman et al. (2000) in the dynamometer study and Huang et al. (2006) in the tunnel study. In Geller et al. (2005), POM/POC of 1.4 was used in the tunnel study for all coarse ( $PM_{2.5-10}$ ), accumulation ( $PM_{0.18-2.5}$ ) and ultrafine ( $PM_{0.18}$ ) particle fractions.

Up to now, both the POC artifact and the chemical mass closure of PM have been studied mainly for  $PM_{2.5}$ . It is of great importance to study these problems for  $PM_{0.1}$ , and other PM fractions, such as  $PM_{10}$ . The influence of the POC artifact on  $PM_{0.1}$  concentrations determined by the filter method is expected to be very large due to low  $PM_{0.1}$  concentrations. In this study,  $PM_{0.1}$ ,  $PM_{2.5}$ , and  $PM_{10}$  in a highway tunnel and at a roadside were studied and the chemical compositions including organic carbon (OC), element carbon (EC), 9 water-soluble ions and 19 trace elements were obtained. The positive POC artifact was studied using the QBQ method proposed by Subramanian et al. (2004) for  $PM_{2.5}$ . Taking into account the positive artifact of OC and by using a reasonable ratio of POC to POM, the chemical mass closure for all PM fractions was examined.

## METHODS

### Site Description

Field samples were collected at the height of 1.5 m at the roadside of Syuefu road in Hsinchu, and the third relay

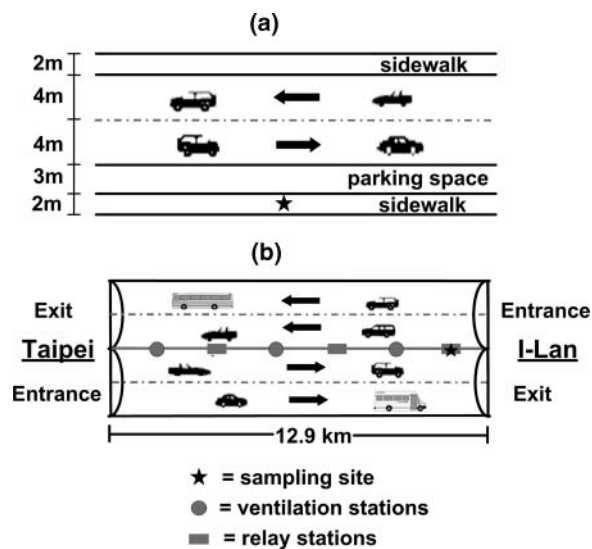


FIG. 1. Schematic diagram of the (a) Syuefu road and (b) Syueshan highway tunnel.

station inside the Syueshan highway tunnel in Yilan, Taiwan. Figure 1a shows the schematic diagram of the roadside sampling site. Syuefu road has two directions with one lane of 4 m in width in each way. There are six schools along this 800 m-long road and it is one of the main roads leading to the Hsinchu Science Park. The traffic flow is heavy during the morning and evening rush hours when commuters as well as the neighborhood residents may expose to high concentration of PM. Sampling was conducted at the sidewalk at the midpoint of the 800 m-long road and about 4 m from the edge of the traffic lane.

The Syueshan highway tunnel is the longest highway tunnel in Taiwan with a total length of 12.9 km in which only shuttle buses, passenger cars and light-duty diesel trucks are allowed. Figure 1b shows the schematic diagram of the tunnel which has two two-lane bores and inclines downward from the west (Pinglin direction, Taipei County) to the east (Toucheng direction, Yilan County) with a slope of 1.3%. There are three ventilation and three relay stations located alternatively with an equal distance of 2 km in between or they are located at 1.5, 3.5, 5.5, 7.5, 9.5, and 11.5 km from the entrance of the tunnel. Sampling was conducted at the third relay stations located 1.4 km from the outlet (Toucheng direction, 11.5 km from the inlet of Pinglin), at a distance of 2 m from the edge of the traffic lane. The tunnel does not have distinct morning and evening rush hours except during the weekend and holidays. In each ventilation station, a huge fan was installed in one vertical well to transport ambient fresh air into the tunnel and while the other fan was installed in another well to exhaust polluted air off the tunnel. However, these fans are seldom activated. The fans in the relay stations, which exchange the air between the two bores, are also normally closed. There are two axial fans mounted on the top of the bores at every 0.5 km along the tunnel. They are activated when the temperature in the tunnel exceeds  $40^{\circ}\text{C}$ . To

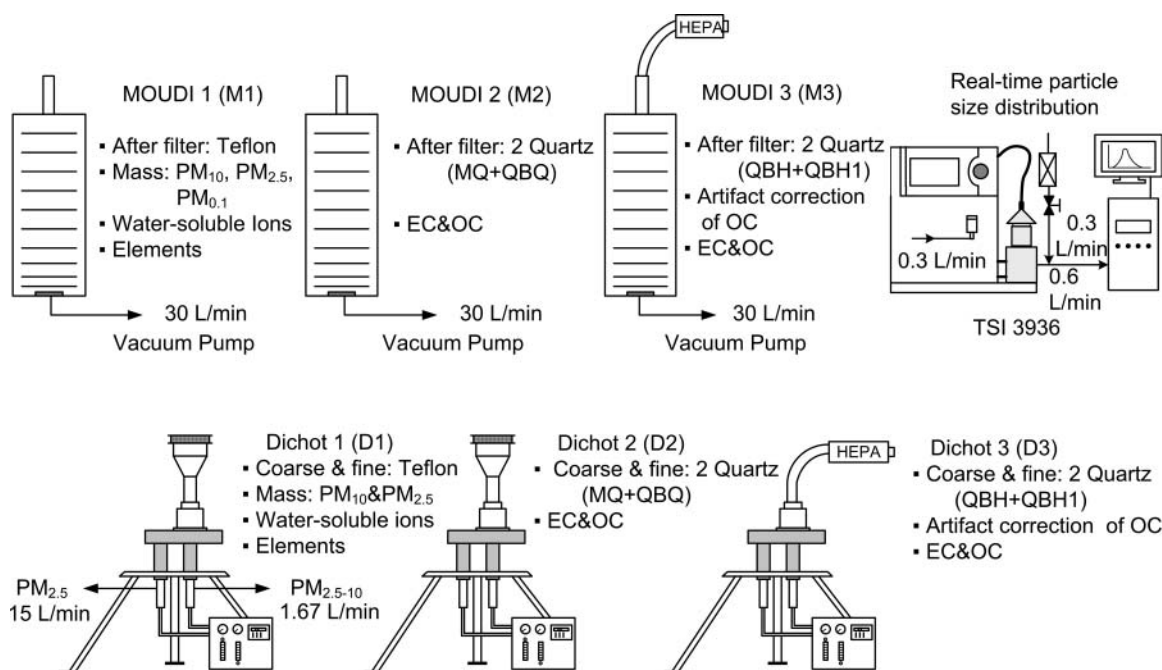


FIG. 2. Schematic diagram of the configurations of the samplers.

avoid sporadic fan operation, these fans were disabled during the sampling periods.

Sampling was conducted from January to December of 2008, during which six 24-h samples were taken at the roadside, sixteen samples were taken in the tunnel, in which ten 3-h samples were taken at daytime (during AM 09:00 to PM 09:00), three 6-h samples were taken at midnight from AM 00:00 to 06:00 and the other three 3-h samples were taken from AM 08:00 to 11:00 on holidays (rush hour).

### Sampling Protocol

$PM_{2.5-10}$  and  $PM_{2.5}$  samples were collected by using three Dichotomous samplers (Model SA-241, Andersen Inc., Georgia, USA). Hereafter they are referred to as Dichots in this study. After obtaining  $PM_{2.5-10}$  and  $PM_{2.5}$ ,  $PM_{10}$  was calculated as the sum of  $PM_{2.5-10}$  and  $PM_{2.5}$ . Figure 2 shows the configurations of the samplers. The  $PM_{0.1}$  samples were collected at the afterfilters of the three 10-stage MOUDIs (Model 110, MSP Corp., MN, USA) operated in parallel. A collocated SMPS (Model 3936, TSI Inc., MN, USA) equipped with NanoDMA (TSI Model 3085) and Ultrafine Water-based Condensation Particle Counter (UWCPC, TSI Model 3786) was used to monitor the number size distributions of ambient  $PM_{0.005-0.2}$  simultaneously. In the MOUDIs, the  $3.2 \mu\text{m}$  cutsize stages were replaced with  $2.5 \mu\text{m}$  cutsize stages and the nozzle plates of the stage 10 with  $56 \text{ nm}$  cutsize was removed since only  $PM_{0.1}$  was studied. Thus, the cutsizes of the MOUDIs were 18, 10, 5.6, 2.5, 1.8, 1.0, 0.56, 0.32, 0.18, and  $0.1 \mu\text{m}$ . In addition, temperature

and relative humidity were recorded and a video camera was used to record the traffic flow at both sites.

In two MOUDIs (M1 and M2), silicone grease (KF-96-SP, Topco Technologies Corp., Taiwan) coated aluminum foils were used as the impaction substrates in 0–9 stages to reduce solid particle bounce (Pak et al. 1992). The samples collected were weighed to determine mass distributions. Teflon (Zefluor P5PJ047, Pall Corp., New York, USA) and quartz filters (Tisquartz 2500QAT-UP, 7201&7202, Pall Corp., New York, USA) were used in M1 and M2, respectively, as the afterfilters for further gravimetric (M1 only) and chemical analysis (both M1 and M2). M2 was used to determine the OC and EC concentrations of  $PM_{0.1}$ , in which two quartz filters (MQ and QBQ) were placed in series at the afterfilter stage of M2. The third MOUDI (M3) was used to determine whether the quartz filters were equilibrium in OC concentration. A HEPA filter (HEPA Capsule 12144, Pall Corp., New York, USA) was installed at its inlet to remove all PMs. The impaction substrates from stage 0 to 9 were not used in M3 while only two quartz filters, QBH (quartz behind HEPA) and QBH1 (quartz behind QBH), were placed in series at the afterfilter stage. This setup, which is called QBH method in this study (detailed description will be shown later), was similar to the QBT method used in Subramanian et al. (2004) who used only one quartz filter after the Teflon filter in the study.

The POC concentration can be calculated based on the OC concentration of the first quartz (MQ) and the second quartz (QBQ) of the M2, when the equilibrium of OC concentration between the two quartz filters and the air stream was achieved

(or when the quartz filters were saturated with gaseous OC) (Subramanian et al. 2004) as:

$$\text{POC} = \text{OC}_{\text{MQ}} - \text{OC}_{\text{QBQ}} \quad [1]$$

where  $\text{OC}_{\text{MQ}}$  and  $\text{OC}_{\text{QBQ}}$  were OC concentrations of MQ and QBQ, respectively. For equilibrium that had not been reached, the POC could be estimated as (Subramanian et al. 2004):

$$\text{POC} = \text{OC}_{\text{MQ}} - \text{OC}_{\text{QBQ}} - 0.68 \quad [2]$$

Similarly, Teflon filters were used in Dichot 1 (D1) while quartz filters were used in both Dichot 2 and 3 (D2 and D3) in fine and coarse particle channels. The QBQ method was again used in D2 (MQ and QBQ in series) to correct for the POC artifact while the QBH method was used in D3 (QBH and QBH1 in series) to check whether the quartz filters were equilibrium in OC concentration. The HEPA capsules installed at the inlet of the M3 and D3 provide high flow rate at a low pressure drop. It was found the two quartz filters, QBH and QBH1, had very close OC concentration (<10% in difference) for all  $\text{PM}_{0.1}$  and  $\text{PM}_{2.5}$  samples at both roadside and tunnel sites due to long sampling time and high face velocity (about 0.4 and 0.8 m/s for Dichot and MOUDI, respectively). Therefore, Equation (1) was used to calculate the POC concentration of  $\text{PM}_{0.1}$  and  $\text{PM}_{2.5}$  for all measurements. On the other hand for coarse particles, it was observed the QBH had a higher OC concentration than the QBH1 for all roadside and tunnel samples due to a relatively lower sampling flow rate ( $\sim 0.04$  m/s of face velocity) of the coarse particle channel in the D3, indicating that the equilibrium was not achieved. Thus, Equation (2) was used to calculate the POC of  $\text{PM}_{2.5-10}$  for all samples. The application of Equation (2) to correct for the positive OC artifact for  $\text{PM}_{2.5-10}$  may lead to a small error. Nevertheless, the error will not affect the present mass closure result of  $\text{PM}_{10}$  because the OC concentration of  $\text{PM}_{2.5-10}$  was much lower than that of  $\text{PM}_{2.5}$  at both sites.

In every sampling run, at least two Teflon filters, two quartz filters and two silicone grease coated aluminum foils (or >10% of sample number) were used as laboratory and field blanks, respectively, to examine the background levels of the gravimetric and chemical analysis. Teflon filters were conditioned at least 24 h in a temperature and relative humidity controlled room ( $22 \pm 1^\circ\text{C}$ ,  $40 \pm 5\%$  RH) before sampling. All quartz filters were pre-baked at  $900^\circ\text{C}$  for 3 h to reduce organic blank level. 0.3 to 0.5 mg of Silicone grease (KF-96-SP, Topco Technologies Corp., Taiwan) was coated uniformly on each aluminum foil of the M1 and M2 stages (Pak et al. 1992). After coating, the foils were baked in an oven at  $65^\circ\text{C}$  for 1.5 h (Marple et al. 1991).

Because the chemical compositions as well as the mass concentration of  $\text{PM}_{0.1}$  were determined from different filter samples of three collocated MOUDIs, mass concentration distributions of the three MOUDIs were compared with each other. The  $\text{PM}_{0.1}$  concentration of MOUDI (M1) was also compared with the calculated  $\text{PM}_{0.1}$  concentration based on the SMPS data and

the apparent particle density determined by using the method of Spencer et al. (2007). Spencer et al. (2007) found the particle effective density increased with decreasing absolute atmospheric water content.

### Sample Analysis

Before chemical analysis, all Teflon samples of M1, D1, and blanks were weighed first to determine the mass concentrations of the PM samples. The electrostatic charge of the filters was eliminated by an ionizing air blower (Model CSD-0911, MEI-SEI, Japan) before weighing. A microbalance (Model CP2P-F, Sartorius, Germany) was used to weigh the filters after they were conditioned at least 24 h in the temperature and relative humidity controlled room ( $22 \pm 1^\circ\text{C}$ ,  $40 \pm 5\%$  RH). After gravimetric analysis, each Teflon filter was cut equally in half using a Teflon coated scissor. One half was analyzed by an ICP-MS (Model 7500 series, Agilent Technologies, Inc., USA) for elements except Si which was analyzed by ICP-AES (Model Optima 2000DV for Si, PerkinElmer, Inc., MA, USA) while the other half was analyzed by an ion chromatograph (IC, Model DX-120, Dionex Corp, Sunnyvale, CA) for ionic species. The analyzed elements included major (crustal) elements (Na, Mg, Al, K, Ca, Fe, and Si) and sub-major (anthropogenic) elements (S, Zn, Ni, Cu, Mn, Sr, Ag, Ba, Pb, V, Cr, and Ti). The analyzed ions were  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$ , and  $\text{Ca}^{+2}$ . Except Si and Na, the detection limit for ionic and elemental species was less than 0.003 and 0.002  $\mu\text{g}/\text{m}^3$ , respectively. The Si and Na had a detection limit of 0.02  $\mu\text{g}/\text{m}^3$  which was an order of magnitude higher than the other species.

Quartz filter samples of D2, D3, M2, M3, and blanks were analyzed by the thermal-optical reflectance (TOR) method for OC and EC concentrations without gravimetric analysis. The quartz samples were stored in a  $-18^\circ\text{C}$  freezer immediately after sampling. The detection limit for OC and EC in this study was 0.06 and 0.01  $\mu\text{g}/\text{m}^3$ , respectively. The EC was estimated from the analyzed results of MQ (Subramanian et al. 2004).

After obtaining the POC, the POM was calculated by multiplying it with a proper POM/POC ratio. Because the tunnel PMs were contributed mainly by vehicle emissions and the POM/POC value of 1.4 was applied for all PM fractions. For the roadside PMs, the value of 1.6 was applied because this site was located in the urban area (Turpin and Lim 2001).

## RESULTS AND DISCUSSION

### PM Concentration and Mass Distribution

The comparison of mass distributions of ambient particles between the three parallel MOUDIs showed a good agreement for all size intervals. Using the method in Spencer et al. (2007), the effective density of  $\text{PM}_{0.1}$  was found to be  $1.25 \pm 0.14$  and  $1.40 \pm 0.10$   $\text{g}/\text{cm}^3$  in the tunnel and at the roadside, respectively, which was then used to convert the SMPS number concentrations to mass concentrations for  $\text{PM}_{0.1}$ . Results showed

TABLE 1  
Comparison of PM concentration ( $\mu\text{g}/\text{m}^3$ ) between MOUDI (M) and Dichot (D) at the roadside and in the tunnel

Site	PM <sub>10</sub>		PM <sub>2.5</sub>		PM <sub>0.1</sub>
	M1	D1	M1	D1	M1
Roadside	54.3 ± 23.6	62.1 ± 27.9	27.5 ± 12.5	30.4 ± 14.7	2.2 ± 0.6
T* daytime**	87.9 ± 9.9	92.8 ± 11.4	78.0 ± 11.2	73.3 ± 10.0	33.2 ± 6.5
T midnight***	54.3 ± 3.8	55.2 ± 4.4	45.7 ± 3.1	47.2 ± 4.5	9.1 ± 1.7
T rush hour****	158 ± 20	177 ± 18	132 ± 16	148 ± 20	46.5 ± 5.2

\*: tunnel; \*\*: during 9 AM–9 PM (mean of ten 3-h measurements); \*\*\*: 0–6 AM (mean of three 6-h measurements); \*\*\*\*: holiday 8 AM–11 AM (mean of three 3-h measurements).

the calculated PM<sub>0.1</sub> concentrations of the SMPS were similar to those of the MOUDIs with a relative difference of less than 30%.

In this study, the average mass concentration and standard deviation of PMs were calculated from pooled samples and shown in Table 1 as “average ± standard deviation.” It is seen the PM<sub>10</sub> and PM<sub>2.5</sub> concentrations of the MOUDI are in agreement with those of the Dichot with a relative deviation of <20%. In the tunnel, the PM concentrations were found to increase with increasing traffic flow rates, which were about 410 ± 70, 1250 ± 280, and 2040 ± 430 vehicles/h during the midnight (mean of all three 6-h measurements), daytime (mean of all ten 3-h measurements), and rush hour (mean of all three 3-h measurements) measurements, respectively. Variation of PMs mass concentration at different sampling days was small because vehicle emission was the most predominant source in the tunnel and the vehicle flow rate and fleet composition remained to be similar. In comparison, although the traffic flow rate of 1130 ± 95 vehicles/h (mean of six 24-h measurements) and fleet composition (to be shown later) were similar during the six roadside

measurements, concentrations of PMs were quite different with a relatively larger standard deviation due to the influence of background sources and meteorological conditions.

The mass concentration of PM<sub>0.1</sub> at the roadside is 2.21 ± 0.59  $\mu\text{g}/\text{m}^3$  (mean of six 24-h measurements), which is comparable to the concentration at the urban areas in LA obtained by Cass et al. (2000) and Sardar et al. (2005), who showed that UP concentrations were 0.55–1.16  $\mu\text{g}/\text{m}^3$  (PM<sub>0.056–0.1</sub>) and 0.86–3.5  $\mu\text{g}/\text{m}^3$  (PM<sub>0.01–0.18</sub>), respectively. Compared to the roadside, significantly higher concentrations of 33.2 ± 6.5 and 46.5 ± 5.2  $\mu\text{g}/\text{m}^3$  were observed in the tunnel during the daytime as well as the rush hour, respectively. Even in the midnight, relatively high PM<sub>0.1</sub> concentration of 9.1 ± 1.7  $\mu\text{g}/\text{m}^3$  was found in the tunnel. High PM<sub>0.1</sub> concentration observed in the 3rd relay station suggests the air quality inside and near the tunnel exit is of serious concern.

Figure 3 shows the comparison of average mass distributions of particles between the roadside and the tunnel in the daytime. It is seen that particles at both sites are bimodal. The saddle point which divides the accumulation and coarse modes is about 0.4 and 1.0  $\mu\text{m}$  at the tunnel and roadside, respectively. In the tunnel, the accumulation mode peaks at 0.1–0.2  $\mu\text{m}$ , which is similar to that found in the dynamometer study for both gasoline and diesel vehicles (Kleeman et al. 2000), while the coarse mode peaks at about 2.5  $\mu\text{m}$ . It is observed that the accumulation mode particles have much higher concentration than the coarse mode particles. In comparison, the concentration of the coarse mode (peaks at 6  $\mu\text{m}$ ) is higher than the accumulation mode (peaks at 0.3  $\mu\text{m}$ ) at the roadside. From Figure 3, it can be concluded that the present tunnel with predominant sources of vehicle emission contains much more UPs and fine particles than coarse particles. In comparison, the background sources contributed larger fraction of coarse particles at the roadside.

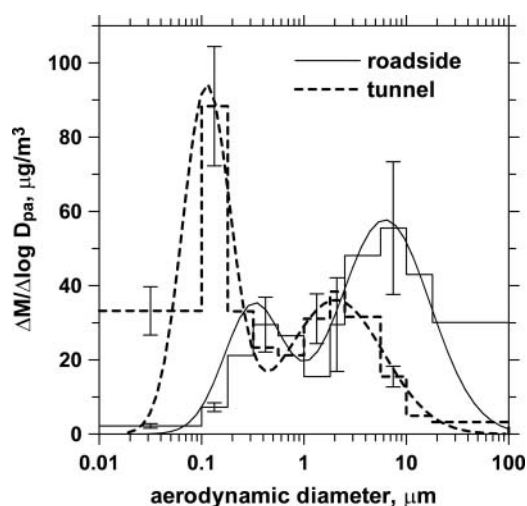


FIG. 3. Comparison of particle mass distributions at the roadside and tunnel. Error bars represent one standard deviation.

### Chemical Mass Closure of PMs

Figure 4 shows the comparison of chemical compositions (%) of all PM fractions in the tunnel (T, mean of all ten daytime measurements) and at the roadside (R, mean of all six measurements). In the figure, good chemical mass closure is seen at both

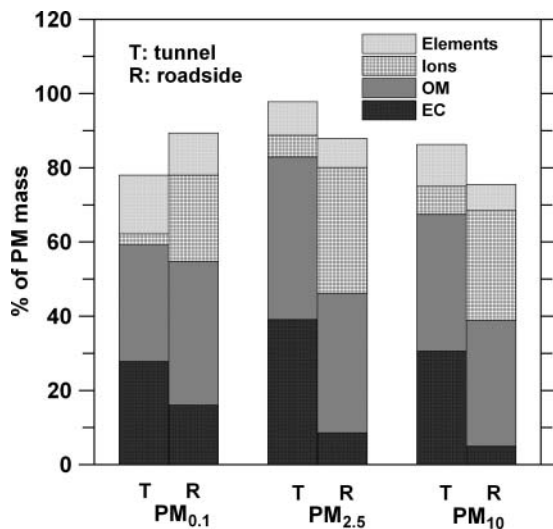


FIG. 4. Average chemical compositions (%) of PMs at Syuefu roadside and in the Syueshan highway tunnel. One standard deviation of each data point ranges from 1.6 to 9.7% depending on the PM fractions and chemical compositions.

sites with unknown compositions of less than 30%. The chemical mass of  $PM_{0.1}$ ,  $PM_{2.5}$ , and  $PM_{10}$  is  $73.8 \pm 5.3$ ,  $97.8 \pm 8.5$ , and  $86.7 \pm 5.0\%$  for the gravimetric mass, respectively, in the tunnel, and it is  $89.4 \pm 9.6$ ,  $87.9 \pm 12.0$ , and  $75.3 \pm 5.7\%$  at the roadside. Better mass closure for  $PM_{0.1}$  was obtained than that in Geller et al. (2005) due to the correction of the OC artifact and use of an appropriate value of POM/POC in the present study.

The OC artifact was found to account for  $51.6 \pm 10.7\%$  and  $20.0 \pm 5.4\%$  of the  $PM_{0.1}$  at the roadside and the tunnel, respectively. For  $PM_{2.5}$  and  $PM_{10}$ , less severe artifact was found at both sites, which was  $7.5 \pm 2.8$  and  $5.8 \pm 1.3\%$  of the particle mass at the roadside while it was  $12.9 \pm 4.1\%$  and  $16.3 \pm 4.3\%$  in the tunnel, respectively. Severe OC artifact in  $PM_{0.1}$  at the roadside is due to the relatively low  $PM_{0.1}$  mass concentration and longer sampling period of 24 h. The achievement of good mass closure for  $PM_{0.1}$ ,  $PM_{2.5}$ , and  $PM_{10}$  indicates the correction of OC artifact proposed by Subramanian et al. (2004) and the use of POC to POM ratio suggested by Turpin and Lim (2001) for  $PM_{2.5}$  (for roadside) and Geller et al. (2005) for  $PM_{2.5-10}$ ,  $PM_{0.18-2.5}$ , and  $PM_{0.18}$  (for tunnel) are reasonable for these two PM fractions. The present mass closure of  $PM_{2.5}$  was compared to the studies of  $PM_{2.5}$  at downtown LA, desert area of Meadview, AZ and Look-Rock, TN which did not correct for the OC artifact (Turpin and Lim 2001). Similar mass closure of 77–100% in this study to those of 70–99% in Turpin and Lim (2001) was found.

### Chemical Characteristics of PMs

#### Contribution of Background Source to the Tunnel and Roadside

The potential contribution of background air to the levels measured in the present two sampling sites was investigated

before discussing the contribution from vehicles. In fact, the present two sites were influenced by urban aerosols rather than the remote background air because the distance from the tunnel entrance to Taipei metropolis is only 20 km and the roadside sampling site is located inside Hsinchu city. The aerosols at the tunnel inlet were expected to have similar concentrations and compositions to the Taipei aerosols which were continuously monitored at the Taipei supersite. Thus, we used the data from the Taipei supersite as the background source of the tunnel and to compare with the results of the present roadside. The supersite is located in a  $10930 \text{ m}^2$  park at the ground level near the center of Taipei metropolis, which is influenced by typical urban aerosols. The daily concentrations of  $PM_{10}$  and  $PM_{2.5}$ , and OC, EC, sulfate, nitrate concentrations of  $PM_{2.5}$  can be found at <http://taqm.epa.gov.tw/taqm/zh-tw/PmIDaily.aspx>. The average  $PM_{2.5}$  concentration at the supersite during the sampling days (ten days during January to December 2008) was  $23.1 \pm 9.6 \mu\text{g}/\text{m}^3$  which was only 1/3 of that at the 3rd relay station. The sum of sulfate and nitrate contributed  $33.4 \pm 6.4\%$  mass to  $PM_{2.5}$  at the supersite, and was expected to contribute 11.1% to the  $PM_{2.5}$  mass at the 3rd relay station in the tunnel assuming water-soluble ions were negligible in fresh vehicle  $PM_{2.5}$  emissions in the tunnel ( $<2\%$ , Robert et al. 2007a). However, the value was much larger than the measured value of 4.5% at the 3rd relay station, indicating the contribution of urban  $PM_{2.5}$  to the tunnel  $PM_{2.5}$  should be much less than 1/3, and was estimated to be about 13.5%.

During the sampling days at the tunnel, the average OC/EC of  $PM_{2.5}$  at the supersite was  $2.9 \pm 0.5$  (2.4–3.9), while the ratio was  $1.0 \pm 0.1$  (0.84–1.17) at the 3rd relay station. Similar to sulfate and nitrate analysis, the OC/EC was found to be 1.22–2.35 considering that 1/3 of  $PM_{2.5}$  was contributed by urban aerosols, 2/3 was contributed by vehicle emissions in the tunnel at the 3rd relay station. The OC/EC of vehicle emissions in the tunnel was calculated based on the fleet compositions, OC/EC and emission factor for gasoline and diesel vehicle emissions proposed by Schauer et al. (1999, 2002) and Weingartner et al. (1997), respectively. The calculated OC/EC, 1.22–2.35, was found to be much higher than the measured data, 0.84–1.17, again indicating that the contribution of urban  $PM_{2.5}$  to the tunnel  $PM_{2.5}$  should be much less than 1/3. Based on the estimated contribution of urban  $PM_{2.5}$  to the tunnel  $PM_{2.5}$ , 13.5%, the OC/EC was found to be 0.88–1.89, which was closer to the measured OC/EC at the 3rd relay station.

Since the  $PM_{10}$  had a similar characteristics as  $PM_{2.5}$  in the aspect of the mass ratio of the urban to tunnel aerosols, OC/EC ratio for diesel and gasoline vehicles emissions (Cadle et al. 1999; Schauer et al. 1999, 2002) and the percentage of OC and ion in the PM mass, it was expected the Taipei urban  $PM_{10}$  also contributed to less than 1/3 of the tunnel  $PM_{10}$ . For the  $PM_{0.1}$  in the tunnel, the background source could be neglected due to a relatively lower urban  $PM_{0.1}$  concentration (normally  $1-3 \mu\text{g}/\text{m}^3$ ) than that in the present 3rd relay station ( $33.2 \pm 6.5 \mu\text{g}/\text{m}^3$ ).

### OM and EC

Figure 4 shows that OM is the most abundant species for all PMs at both sites, which agrees with other urban or roadside measurements (Cass et al. 2000; Phuleria et al. 2007; Sardar et al. 2005; Spencer et al. 2007) and the tunnel or chassis dynamometer studies (Geller et al. 2005; Huang et al. 2006; Kleeman et al. 2000). OM accounted for  $37.2 \pm 5.5$ ,  $43.8 \pm 6.9$ , and  $31.4 \pm 5.1\%$  particle mass in the tunnel while it contributed  $33.7 \pm 6.6$ ,  $37.5 \pm 9.7$ , and  $38.7 \pm 3.3\%$  to particle mass at the roadside for PM<sub>10</sub>, PM<sub>2.5</sub>, and PM<sub>0.1</sub>, respectively. Similar and high mass percentage of OM in all PM fractions was found at both sites, indicating that the fraction of OM in PM was similar for background and vehicle emitted PMs.

EC accounted for  $32.6 \pm 4.5$ ,  $39.1 \pm 5.8$ , and  $27.8 \pm 5.4\%$  in PM<sub>10</sub>, PM<sub>2.5</sub>, and PM<sub>0.1</sub> the tunnel, while it was  $5.0 \pm 1.3$ ,  $8.6 \pm 2.3$ , and  $16.1 \pm 7.5\%$  at the roadside, respectively. The tunnel PMs had a much higher mass percentage of EC than that at the roadside especially for PM<sub>2.5</sub> and PM<sub>10</sub>. The highest percentage of EC in the tunnel PM<sub>2.5</sub> was in agreement with that found in the literature (Huang et al. 2006; Kleeman et al. 2000) in which the MMAD (mass median aerodynamic diameter) of EC was shown to be 0.2–0.4  $\mu\text{m}$  (or mostly outside the range of PM<sub>0.1</sub>). On the other hand, the roadside PM<sub>0.1</sub> had a much higher percentage of EC than that in PM<sub>2.5</sub> and PM<sub>10</sub> because PM<sub>0.1</sub> contained more freshly generated UPs by vehicles (with high EC constituent) while roadside PM<sub>2.5</sub> and PM<sub>10</sub> contained more aged ambient fine and coarse particles (higher ion and OC constituents). The existence of considerable high concentration of OM and EC in the tunnel PM<sub>0.1</sub> and PM<sub>2.5</sub> is of serious environmental and health concerns.

In the tunnel, the video records showed the composition of passenger cars, light-duty diesel trucks and shuttle buses was  $91.6 \pm 3.6$ ,  $6.5 \pm 2.7$ , and  $1.9 \pm 0.4\%$ , respectively, in the daytime when the total vehicle flow rate was  $1250 \pm 280$  vehicles/h. In the passenger cars, there was about 5% of diesel engine. In Table 3 of Weingartner et al. (1997), the emission factor (EF, mg/km) of gasoline and diesel vehicles for PM<sub>1.3</sub>, PM<sub>2.5</sub>, PM<sub>10</sub>, and TSP (total suspended particulate) based on tunnel measurements was compared and the ratio of EF for diesel to that of gasoline vehicles was found to be 45 and 66 for PM<sub>10</sub> and PM<sub>2.5</sub>, respectively. More recently, Robert et al. (2007a, b) found the average emission factor for diesel to gasoline vehicles for PM<sub>0.1</sub> was about 10. Thus, although the ratio of the number of the diesel vehicles to the number of the gasoline vehicles in the present tunnel was low (~8%), more than 45, 80, and 85% of tunnel PM<sub>0.1</sub>, PM<sub>2.5</sub>, and PM<sub>10</sub>, respectively, was contributed from diesel vehicles due to their high emission factors. Besides, Cadle et al. (1999) found the ratio of OC to EC (OC/EC) in PM<sub>10</sub> for the diesel and gasoline vehicles was 0.3–0.9 and >2.0 (without correcting for OC artifact), respectively. For fine particles, Schauer et al. (1999, 2002) found the OC/EC in PM<sub>1.8</sub> for diesel and gasoline vehicles was about 0.6 and 4.3 (without correcting for OC artifact), respectively. In addition, the OC/EC of PM<sub>0.056–0.1</sub> was found to be about 0.3 and 1.2 for

diesel and gasoline vehicles, respectively (Robert et al. 2007a, b). The above OC/EC data show that PM<sub>1.8</sub> and PM<sub>10</sub> have a close OC/EC for diesel and gasoline vehicles, respectively. The average OC/EC of both PM<sub>1.8</sub> and PM<sub>10</sub> was about 0.6 and 3.5 for diesel and gasoline vehicles, respectively. Using the OC/EC values of 0.6 and 3.5 for diesel and gasoline vehicles, respectively, for both PM<sub>2.5</sub> and PM<sub>10</sub>, the present OC/EC of PM<sub>2.5</sub> and PM<sub>10</sub> for the vehicle fleet of the daytime in the Syueshan Tunnel was found to be about 1.2 which is in good agreement with the measured value in the present tunnel of  $1.0 \pm 0.1$  without correcting for the OC artifact. For PM<sub>0.1</sub>, good agreement between the measured OC/EC of  $1.0 \pm 0.1$  and the calculated value of about 0.8 was also found. That is, the measured OC/EC for all PM fractions of this study was reasonable. Taking into account the OC artifact, the OC/EC was  $0.8 \pm 0.1$  for all PM fractions in the present tunnel.

For the roadside, the traffic flow rate was  $1130 \pm 95$  vehicles/h and the average composition of motorcycles, passenger cars, light-duty diesel trucks, and shuttle buses was  $56.3 \pm 6.2$ ,  $40.6 \pm 1.7$ ,  $2.0 \pm 0.8$ , and  $1.2 \pm 0.2\%$  (mean of six 24-h measurements), respectively. Although motorcycles dominated the vehicle number, they only contributed a very low amount to the PMs because their emission factor was relatively low, which was only about 10% of that of the passenger cars (Yang et al. 2005). Based on the fleet compositions, about 25, 75, and 82% of roadside PM<sub>0.1</sub>, PM<sub>2.5</sub>, and PM<sub>10</sub>, respectively, was attributed to diesel vehicle emissions. Since the close percentage of PM<sub>2.5</sub> and PM<sub>10</sub> mass was attributed to diesel vehicle at both sites, the OC/EC should have been close to each other. However, it was observed the roadside had much higher OC/EC values of  $1.5 \pm 0.7$ ,  $2.7 \pm 0.6$ , and  $4.4 \pm 1.3$  for PM<sub>0.1</sub>, PM<sub>2.5</sub>, and PM<sub>10</sub>, respectively, than the value of  $0.8 \pm 0.1$  in the tunnel. Nevertheless, the average OC/EC of the PM<sub>2.5</sub> in the present urban roadside was very close to the average value in 2008 of the Taipei supersite, which was  $2.8 \pm 0.6$ . From the comparison, it showed that the vehicle emission dominated tunnel had a lower OC/EC than the background source dominated roadside for all PM fractions. A closer OC/EC of PM<sub>0.1</sub> than that of PM<sub>2.5</sub> and PM<sub>10</sub> between the two sites indicated that local emissions of vehicles increased the ratio of EC in PM<sub>0.1</sub> much more than that in the other two PM fractions.

### Water-Soluble Ions

The contribution of ionic species to total PM was lower than 10% in the tunnel, while it was greater than 25% at the roadside for all PM fractions. The ion percentages of PM<sub>10</sub>, PM<sub>2.5</sub>, and PM<sub>0.1</sub> for the tunnel and roadside is  $7.5 \pm 3.0$ ,  $5.9 \pm 3.2$ ,  $3.0 \pm 1.6\%$ , and  $32.0 \pm 7.2$ ,  $36.2 \pm 6.5$ ,  $24.8 \pm 9.3\%$ , respectively, as shown in Figure 4. The percentage of the total water-soluble ions to PM<sub>2.5</sub> and PM<sub>10</sub> mass at the roadside was very close to the data at the Taipei supersite and a central monitoring station in Taipei city. The annual average percentage in 2008 of the PM<sub>2.5</sub> and PM<sub>10</sub> at these two stations was  $36.4 \pm 10.2$  and  $33.0 \pm 10.5\%$ , respectively. The high water-soluble ion content



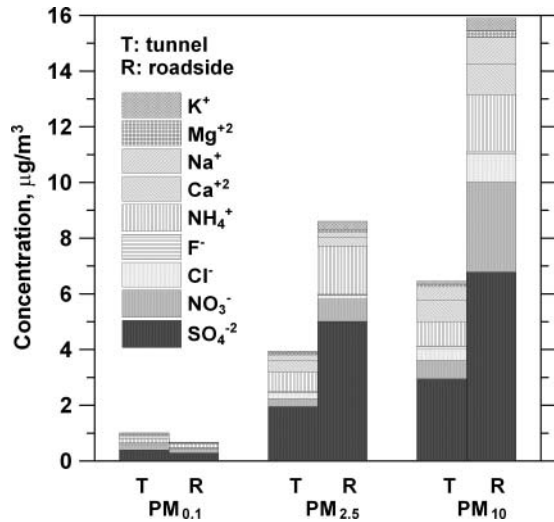


FIG. 5. Comparison of water-soluble ion concentrations ( $\mu\text{g}/\text{m}^3$ ) in all PM fractions between the tunnel and roadside.

in the roadside particles is because they are aged and more secondary sulfates, nitrates, and other inorganic salts are formed (Cass et al. 2000; Sardar et al. 2005; Lin et al. 2009). The sulfates and nitrates are normally produced by photochemical oxidation of gas phase precursors such as  $\text{SO}_2$  and  $\text{NO}_x$  on pre-existing aerosols. This process takes at least several hours. Therefore, the “fresher” tunnel particles were found to have a relatively lower mass percentage of ions (3–7.5%), which agrees with other tunnel and dynamometer studies (Kleeman et al. 2000; Huang et al. 2006; Geller et al. 2005; Robert et al. 2007a).

Figure 5 shows the comparison of water-soluble ion concentration of  $\text{PM}_{0.1}$ ,  $\text{PM}_{2.5}$ , and  $\text{PM}_{10}$  between the tunnel and roadside. It is seen the  $\text{SO}_4^{2-}$  is the most abundant ( $45.3 \pm 13.1\%$  of total ionic species) ionic species in any size fractions at the roadside, followed by  $\text{NH}_4^+$  ( $16.8 \pm 5.5\%$ ),  $\text{NO}_3^-$  ( $15.1 \pm 6.9\%$ ), and  $\text{Ca}^{2+}$  ( $7.5 \pm 2.1\%$ ). The tunnel PMs also showed a similar trend. It was observed that although relatively higher PM concentrations in the tunnel than that

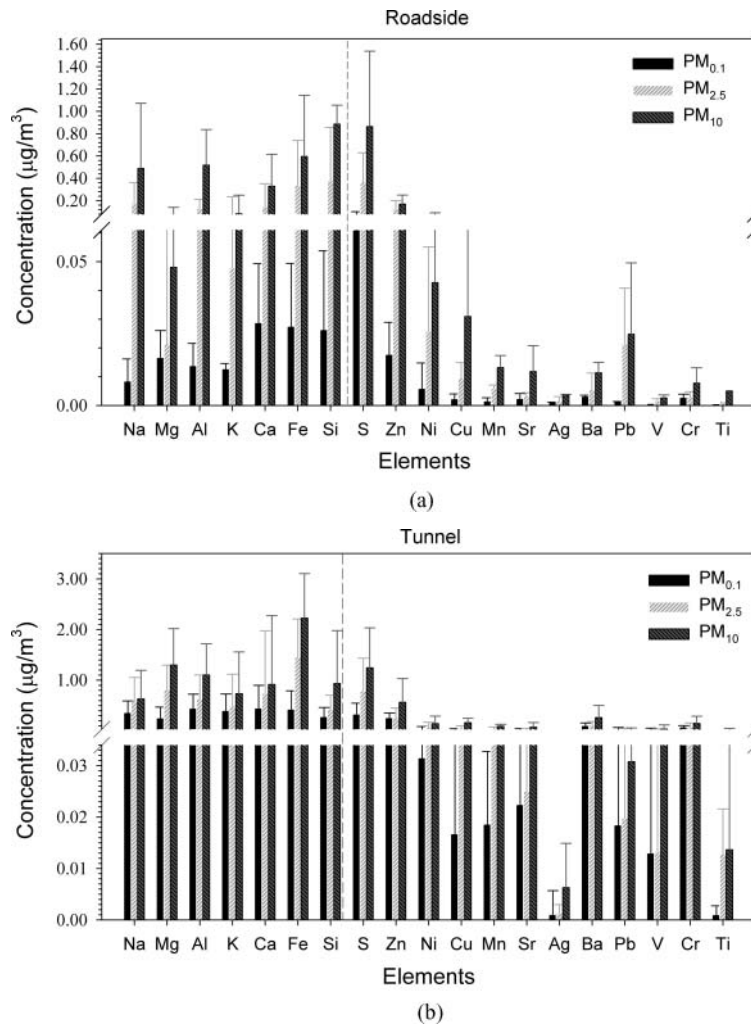


FIG. 6. Concentrations of elements in all PM fractions at the roadside (a) and in the tunnel (b). Error bars represent one standard deviation.

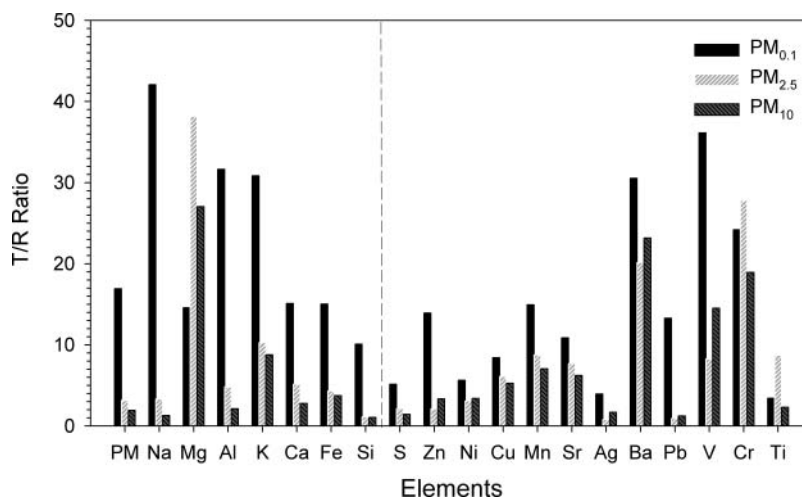


FIG. 7. Ratio of the concentration of the elements in the tunnel to that at the roadside (T/R).

at the roadside, total soluble ion concentrations of the roadside PMs were higher than those in the tunnel for both  $PM_{2.5}$  and  $PM_{10}$ .

#### Elements

The percentage of elements in  $PM_{10}$ ,  $PM_{2.5}$ , and  $PM_{0.1}$  for the tunnel and roadside was  $11.3 \pm 2.6$ ,  $9.1 \pm 2.1$ ,  $11.6 \pm 2.6\%$ ,  $6.9 \pm 1.9$ ,  $7.8 \pm 2.0$ , and  $11.3 \pm 3.3\%$ , respectively. Similar percentage of elements was found for all PM fractions in the tunnel indicating elements were distributed uniformly in every size fractions. This trend was also found for the roadside and tunnel OMs. However, much higher percentage of elements was found for  $PM_{0.1}$  than  $PM_{2.5}$  and  $PM_{10}$  at the roadside, similar to that of EC at the roadside. The finding that OM, EC, and elements had higher percentage of  $PM_{0.1}$  mass than that in  $PM_{2.5}$  and  $PM_{10}$  at the roadside implies that on-road vehicle emissions made a large contribution to the UP mass.

Figures 6a and b show the element concentrations of PMs at the roadside and tunnel, respectively. The elements are divided into two groups: major (crustal) (Na, Mg, Al, K, Ca, Fe, and Si, left-hand side of the figure) and sub-major (anthropogenic) elements (S, Zn, Ni, Cu, Mn, Sr, Ag, Ba, Pb, V, Cr, and Ti, right-hand side of the figure). In the tunnel, the mean concentrations of the major elements in  $PM_{0.1}$ ,  $PM_{2.5}$ , and  $PM_{10}$  were  $2.49 \pm 0.22$ ,  $5.13 \pm 0.49$ , and  $7.85 \pm 1.02 \mu\text{g}/\text{m}^3$ , respectively, and those of sub-major elements were  $0.83 \pm 0.16$ ,  $1.50 \pm 0.23$ , and  $2.78 \pm 0.33 \mu\text{g}/\text{m}^3$ , respectively. In comparison, the mean concentrations of the major elements in roadside  $PM_{0.1}$ ,  $PM_{2.5}$ , and  $PM_{10}$  were  $0.13 \pm 0.04$ ,  $1.23 \pm 0.17$ , and  $2.95 \pm 0.33 \mu\text{g}/\text{m}^3$ , respectively, and those of sub-major elements were  $0.10 \pm 0.02$ ,  $0.57 \pm 0.09$ , and  $1.19 \pm 0.18 \mu\text{g}/\text{m}^3$ , respectively. As opposed to the ions, the tunnel particles had higher total element concentration than that at the roadside. Further analysis showed that  $PM_{2.5}/PM_{10}$  and  $PM_{0.1}/PM_{10}$  of the tunnel sub-major elements were 0.54 and 0.30, respectively, while those

of the roadside were 0.48 and 0.08, respectively. Much lower  $PM_{0.1}/PM_{10}$  value at the roadside than that in the tunnel indicates that the background sources contribute much more sub-major elements to  $PM_{10}$  than  $PM_{0.1}$ .

Figure 7 shows the ratio of the total element concentration of PMs as well as individual element concentration in the tunnel to that of the roadside (T/R). It can be seen that the T/R of  $PM_{0.1}$ ,  $PM_{2.5}$ , and  $PM_{10}$  is 16.9, 3.15, and 1.93, respectively. For comparison, Palmgren et al. (2003) found the emitted particles of gasoline and diesel engines were mostly in the nucleation mode ( $<30 \text{ nm}$ ) and ultrafine mode ( $30\text{--}100 \text{ nm}$ ), which is the main reason why the T/R of  $PM_{0.1}$  in this study is significantly higher than the T/R of  $PM_{10}$  and  $PM_{2.5}$ . It is also seen that the every individual element in  $PM_{10}$  and  $PM_{2.5}$  has a similar T/R value while that of  $PM_{0.1}$  shows a quite different trend. Compared with the T/R value of total elements in  $PM_{0.1}$ , individual element in  $PM_{0.1}$  including Na, Al, K, Cr, V, and Ba has higher T/R. Since V and Ba are the additives of fuel, high T/R values of V and Ba indicate that motor emission is the dominant source for  $PM_{0.1}$  in the tunnel. The present results of higher Pb and Zn T/R values for  $PM_{0.1}$  than  $PM_{2.5}$  and  $PM_{10}$  in the tunnel are also in agreement with Monaci et al. (2000) who found the particle-bound Pb, Zn, Ni, and Ba were produced from the gasoline and diesel engines. Other elements such as Na, Al, K, Ca, V, Fe, and Si also showed higher T/R in  $PM_{0.1}$  than in  $PM_{2.5}$  and  $PM_{10}$ , in which Si, Al, Ca, and Fe were the major bounded elements of diesel engine emission (Wang et al. 2003). This explains why higher T/R value for Si, Al, Ca, and Fe in  $PM_{0.1}$  than that in  $PM_{2.5}$  and  $PM_{10}$  was found in the tunnel in this study.

#### CONCLUSION

Atmospheric  $PM_{0.1}$ ,  $PM_{2.5}$ , and  $PM_{10}$  were sampled at the roadside of Syuefu road in Hsinchu city and in the Syueshan highway tunnel in Taipei, Taiwan using three MOUDIs and three Dichots. The samples of all PM fractions were analyzed for

organic carbon (OC), element carbon (EC), water-soluble ions, and trace elements. By adopting the QBQ methods to account for the positive artifact of OC, it was found the artifact could be as high as  $51.6 \pm 10.7\%$  and  $20.0 \pm 5.4\%$  of the  $PM_{0.1}$  mass for the roadside and tunnel, respectively. Because the PM concentration was larger at larger size fractions, the percentage of artifact was smaller for  $PM_{2.5}$  and  $PM_{10}$ , which was  $7.5 \pm 2.8$  and  $5.6 \pm 1.3\%$  of the particle mass at the roadside while it was  $12.9 \pm 4.1\%$  and  $16.7 \pm 4.4\%$  in the tunnel, respectively. Applying the POC to POM ratio proposed by Turpin and Lim (2001) for  $PM_{2.5}$  and Geller et al. (2005) for  $PM_{0.18}$  to the present roadside and tunnel  $PM_{0.1}$ ,  $PM_{2.5}$ , and  $PM_{10}$  samples, respectively, good chemical mass closure was achieved for all PMs. Therefore in the present study, the OC artifact was corrected accurately and a value of POM/POC was used appropriately in the present study. In the future, it is necessary to determine the OC artifact more accurately for  $PM_{0.1}$  using the VOC denuder method similar to Subramanian et al. (2004) for  $PM_{2.5}$  and Eiguren-Fernandez et al. (2003) for PAH.

The OM is the most abundant species for all PMs at both sites. The roadside and tunnel particles have similar mass fractions of OM in every size fractions. The tunnel particles have much higher mass percentage of EC than that at the roadside especially for the  $PM_{2.5}$  and  $PM_{10}$ . The highest percentage of EC in the tunnel  $PM_{2.5}$  is because that EC is in the accumulation mode and mostly outside the range of  $PM_{0.1}$ . The percentage of ion in all PM fractions is much lower in the tunnel than that at the roadside because particles are aged and formed with more secondary sulfates, nitrates and other inorganic salts at the roadside. Elements of  $PM_{10}$  and  $PM_{2.5}$  have similar T/R values while elements of  $PM_{0.1}$  show higher T/R values. The Pb, Zn, V, and Ba has higher T/R value for  $PM_{0.1}$  than  $PM_{2.5}$  and  $PM_{10}$ , indicating that motor emission is the dominant source for  $PM_{0.1}$  in the tunnel.

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