



## Chemical characterization of roadside PM<sub>2.5</sub> and black carbon in Macao during a summer campaign

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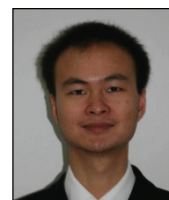
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### ABSTRACT

Air pollution is the leading environmental concern in Macao. The temporal variations of particulate matter (PM) and black carbon (BC) mass concentrations and the size-resolved PM<sub>2.5</sub> chemical compositions, including trace elements and carbonaceous species, were measured in Macao during a near-road summer campaign. The average concentrations for PM<sub>10</sub>, PM<sub>2.5</sub> and BC at a roadside measurement site were 37.8 µg m<sup>-3</sup>, 31.4 µg m<sup>-3</sup> and 5.6 µg m<sup>-3</sup>, respectively. Results showed that local emissions contributed at least 35% to PM<sub>2.5</sub> mass in Macao. Higher BC concentrations were observed in the daytime than at night, consistent with the diurnal variations of traffic flow. Factor analysis classified trace elements into three categories, representing crustal sources (Mg, Si, Al, Na, Fe, Ca and K), road traffic sources (Cu and Co) and secondary inorganic particle formation (S). Crustal elements and road traffic elements were enriched in the size ranges of >1.0 µm and <0.2 µm, respectively. The unimodal distribution pattern with a peak at <0.2 µm for organic carbon (OC) was probably due to secondary organic aerosol formation, whereas about 70% of elemental carbon (EC) was in the size range of 0.2–1.0 µm. Secondary organic aerosols were found to be a strong contributor to PM in the size ranges of <0.2 µm and 1.0–2.5 µm.

**Keywords:** Fine particulate matter, vehicle emission, chemical composition, size distribution



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### 1. Introduction

Macao (22.2°N 113.6°E, also spelled Macau) is one of the two special administrative regions (SAR) in China whose economy is based largely on tourism. It is the world's most densely populated region, with a population density of about 20 000 persons per square kilometer. The motor vehicle population in Macao has exceeded 0.2 million, resulting in one of the highest traffic densities in the world (DSEC, 2011). Air pollution was found to be the leading environmental concern when the Macao SAR government consulted the public regarding the 10-year (2010–2020) planning of environmental protection: 66.4% and 76.5% of the respondents to a phone survey and on-site questionnaire, respectively, thought the government should pay attention to air pollution in this planning (DSPA, 2012). Previous studies have indicated that vehicle emissions are the predominant local source of air pollution in Macao (Wu et al., 2002; Wu et al., 2003).

Particulate matter (PM) is regarded as the principal air pollutant in Macao (Mok and Hoi, 2005; Yang et al., 2010). Yang et al. (2010) calculated daily air pollution indices (API) from the real time monitoring data in 2007–2008 and indicated that PM<sub>10</sub> contributed the highest sub-indices for 92% of “polluted” days with API>50. In recent years, air quality research has begun to focus on fine particulate matter (PM<sub>2.5</sub>) due to its strong effects on human health, environment, global climate, and atmospheric visibility (Zhao et al., 2011; Bond et al., 2013; Rao et al., 2013).

Mass concentration of PM<sub>2.5</sub> is widely used as a metric to evaluate these effects (WHO, 2005), but the chemical composition and size distribution of PM<sub>2.5</sub> can also matter. For example, the long-range transport of aerosol is largely affected by its size distribution (Hussein et al., 2004). Combustion related particles (e.g., polycyclic aromatic hydrocarbons and certain heavy metals) are thought to be more harmful to human health than particles not generated by combustion processes (Chen and Lippmann, 2009; Janssen et al., 2011).

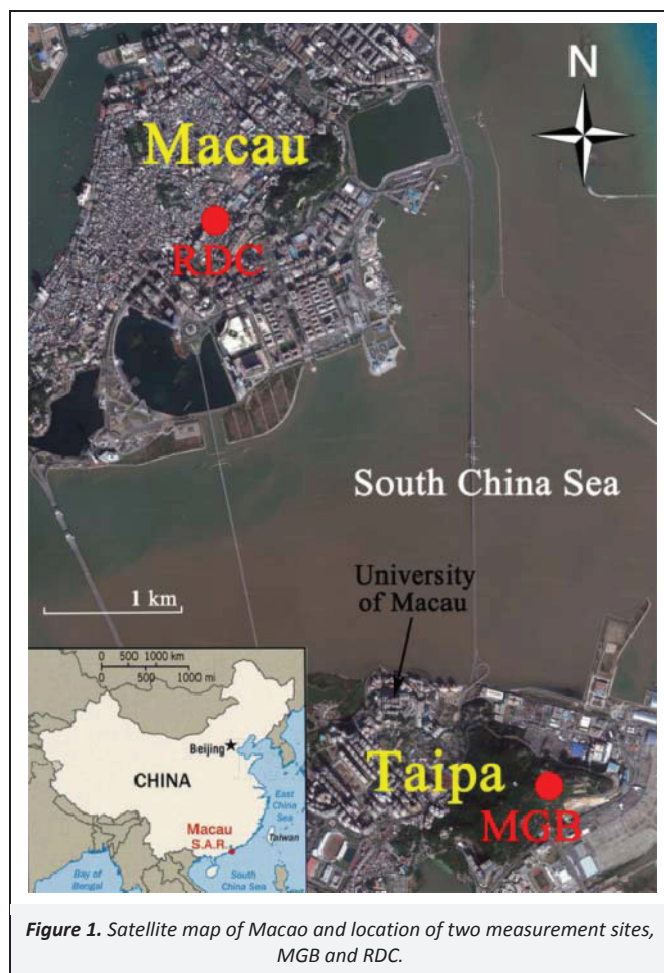
However, only a very few studies have been carried out in Macao on the chemical characteristics of PM<sub>2.5</sub> (e.g., Wu et al., 2003; Zheng et al., 2011). In this paper, we present results from a near-road field campaign in Macao which provides new knowledge of (1) temporal variations of PM<sub>2.5</sub> and black carbon (BC), an indicator of diesel engine vehicle emissions, (2) major sources of trace elements identified by a factor analysis, and (3) chemical compositions of size-resolved PM<sub>2.5</sub>.

### 2. Experiments and Data Analysis

#### 2.1. Field measurements

Macao, located on the western bank of the Pearl River Delta (PRD) region, comprises Macao Peninsula, Taipa, Coloane and Cotai. It has a humid subtropical climate strongly influenced by the monsoons. The summer (May–September) is hot and wet and

experiences about two-thirds of the annual rainfall. As shown in Figure 1, field measurements were performed in early summer (May 1–10, 2010) at two sites: a background site on the roof of the Macao Meteorological and Geophysics Bureau in Taipa (denoted by MGB, 22°09'32" N 113°34'08" E) and a roadside site adjacent to the Rua do Campo Road (about 5 m from the road curb) in Macao Peninsula (denoted by RDC, 22°11'45" N 113°32'41" E). The distance between the two monitoring sites is about 5 km. Meteorological parameters at the MGB site, including temperature, relative humidity, precipitation, and wind direction and speed, are provided by the Macao Meteorological and Geophysics Bureau.

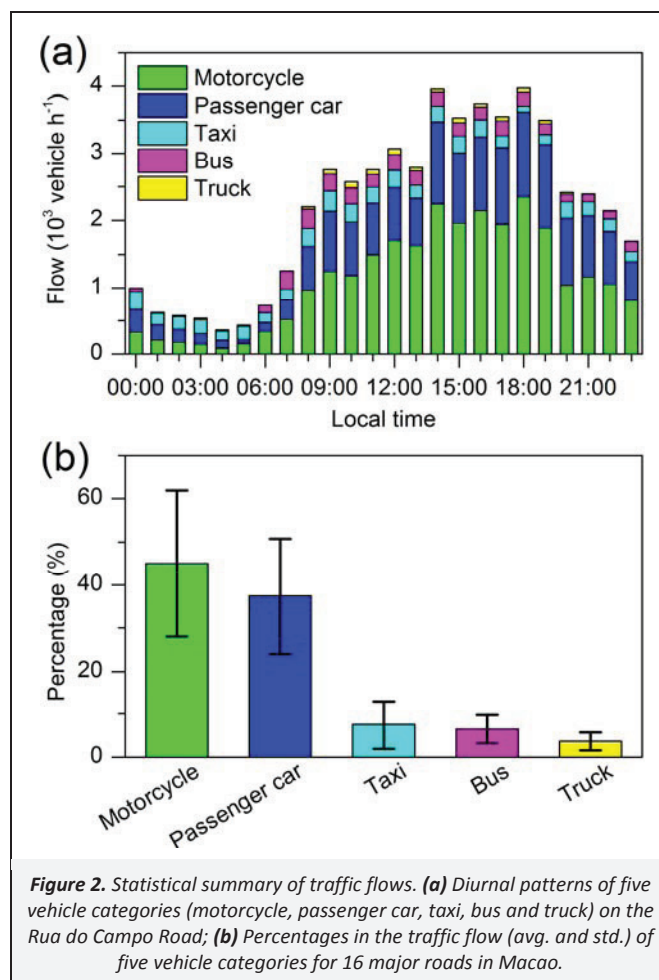


**Figure 1.** Satellite map of Macao and location of two measurement sites, MGB and RDC.

At RDC, two DustTraks (Model 8530, TSI, USA) measured  $PM_{2.5}$  and  $PM_{10}$  mass concentrations, respectively, and a third DustTrak was used to obtain  $PM_{2.5}$  concentrations at MGB. BC mass concentrations were observed at RDC using a single wavelength micro aethalometer ( $\lambda=880$  nm, Model AE-51, Magee Sci., USA). In addition, size-resolved  $PM_{2.5}$  filter samples were collected at RDC using a cascade impactor (DGI Model 1570, Dekati Ltd., Finland) at a flow rate of  $70\text{ L min}^{-1}$  and at 12 hr intervals (7:00–19:00 and 19:00–7:00 in China Standard Time, CST). The four size ranges of this sampler were 0–0.2  $\mu\text{m}$  (I), 0.2–0.5  $\mu\text{m}$  (II), 0.5–1.0  $\mu\text{m}$  (III) and 1.0–2.5  $\mu\text{m}$  (IV). PTFE filters (Timex, Millipore Corp., USA) and quartz filters (Tissuquartz, Pall Corp., USA) were used on alternate days for analyzing trace elements and carbonaceous species, respectively. A total of 48 filter samples (May 3–8, 2010) were obtained (one PTFE sample was contaminated) and additional field blank filters (2 PTFE and 2 quartz filters) were also collected. The inlets of all instruments were placed at a height of  $\sim 2$  m above ground level (AGL).

We also investigated traffic flows on 16 major roads on Macao Peninsula and Taipa, including the Rua do Campo Road. Due to the limitation of personnel, only one day of traffic flow was monitored

for each road. Road traffic was recorded for 20 min in each hour by video camera and the flows of various vehicle categories were counted from the recorded videos. As shown in Figure 2b, the contributions of five vehicle categories (motorcycle, passenger car, taxi, bus and truck) to the total traffic flows were  $45\pm 17\%$ ,  $37\pm 13\%$ ,  $7.5\pm 5.6\%$ ,  $6.5\pm 3.3\%$  and  $3.6\pm 2.1\%$ , respectively.



**Figure 2.** Statistical summary of traffic flows. (a) Diurnal patterns of five vehicle categories (motorcycle, passenger car, taxi, bus and truck) on the Rua do Campo Road; (b) Percentages in the traffic flow (avg. and std.) of five vehicle categories for 16 major roads in Macao.

## 2.2. Chemical analysis

Fourteen trace elements, including sulfur (S), chlorine (Cl), silicon (Si), iron (Fe), potassium (K), sodium (Na), calcium (Ca), aluminum (Al), cobalt (Co), magnesium (Mg), manganese (Mn), scandium (Sc), copper (Cu) and lead (Pb), were determined using a wavelength dispersive X-ray fluorescence spectrometer (RIX 3000, Rigaku Corp., Japan). Organic carbon (OC) and elemental carbon (EC) were analyzed by the thermal optical reflectance method (DRI Model 2001A, Atmoslytic, USA). Data below the detection limit (DL) were represented by half of the DL. All samples were stored in a refrigerator ( $-18\text{ }^{\circ}\text{C}$ ) before further analysis. Field blank filters were treated using the same procedures as ambient filters during sampling, storage and analysis. The concentrations of chemical species were corrected using field blank filters. The concentrations of blank filters were usually very low; for example, OC and EC concentrations of blank filters were only 7.8% and 0.2% of those of ambient filters on average. All chemical analysis procedures were strictly quality-controlled to avoid any possible contamination of the samples.

## 2.3. Correcting DustTrak and aethalometer data

DustTrak uses a light scattering technique where the amount of scattered light is related to aerosol volume concentration. The instrument is factory calibrated using Arizona road dust, and thus

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