



Variability of organic and elemental carbon, water soluble organic carbon, and isotopes in Hong Kong

K. F. Ho, S. C. Lee, J. J. Cao, Y. S. Li, J. C. Chow, J. G. Watson, K. Fung

► To cite this version:

K. F. Ho, S. C. Lee, J. J. Cao, Y. S. Li, J. C. Chow, et al.. Variability of organic and elemental carbon, water soluble organic carbon, and isotopes in Hong Kong. *Atmospheric Chemistry and Physics Discussions*, 2006, 6 (3), pp.4579-4600. hal-00301420

HAL Id: hal-00301420

<https://hal.science/hal-00301420>

Submitted on 18 Jun 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Variability of OC, EC,
WSOC and isotopes
in Hong Kong

K. F. Ho et al.

Variability of organic and elemental carbon, water soluble organic carbon, and isotopes in Hong Kong

K. F. Ho¹, S. C. Lee¹, J. J. Cao², Y. S. Li¹, J. C. Chow³, J. G. Watson³, and K. Fung⁴

¹Research Center for Urban Environmental Technology & Management, Department of Civil & Structural Engineering, The Hong Kong Polytechnic University, Hong Kong, China

²State Key Laboratory of Loess & Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, China

³Division of Atmospheric Sciences, Desert Research Institute, 2215 Raggio Parkway, P.O. Box 60220, Reno, NV 89506, USA

⁴AtmAA Inc., 23917 Craftsman Road, Calabasas, CA 91302, USA

Received: 13 February 2006 – Accepted: 13 March 2006 – Published: 9 June 2006

Correspondence to: S. C. Lee (ceslee@polyu.edu.hk)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

To determine the levels and variations of carbonaceous aerosol in Hong Kong, PM_{2.5} and PM₁₀ samples were collected by high volume (Hi-vol) samplers at three monitoring stations (representing middle-scale roadside, urban-, and regional-scale environments) during winter (November 2000 to February 2001) and summer (June 2001 to August 2001) periods. The highest concentrations of organic carbon (OC), elemental carbon (EC), and water-soluble organic carbon (WSOC) were found at the middle-scale roadside site with the lowest at the regional-scale site. The percentages of WSOC in total carbon at these sites were inversely correlated with their concentrations (i.e., the highest percentages of WSOC were observed at the regional-scale site). A high WSOC fraction may be associated with aged aerosol because of the secondary formation by photochemical oxidation of organic precursors of anthropogenic pollutants during transport. The annual average of isotope abundances ($\delta^{13}\text{C}$) of OC and EC were $-26.9 \pm 0.5\text{‰}$ and $-25.6 \pm 0.1\text{‰}$, respectively. There were no notable differences for seasonal distributions of carbon isotopic composition, consistent with motor vehicle emissions being the main source contributors of carbonaceous aerosol in Hong Kong. OC ^{13}C abundances at the regional-scale site were higher than those at the middle-scale roadside and urban sites, consistent with secondary organic aerosols of biogenic origin.

1 Introduction

In recent years, much research interest has been focused on atmospheric carbonaceous particles due to their influence on climate and adverse health effects (Chameides, 2002; Frazer, 2002). Total carbonaceous aerosol (TC) comprises a complex mixture that is classified mainly in two fractions: elemental carbon (EC, also called black carbon (BC) or soot) and organic carbon (OC). EC is emitted directly from combustion sources and undergoes little chemical transformation. It is a good indicator of primary

ACPD

6, 4579–4600, 2006

Variability of OC, EC, WSOC and isotopes in Hong Kong

K. F. Ho et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

EGU

anthropogenic air pollutants. However, OC can be emitted both from primary emission sources and from chemical reactions of gaseous organic precursors in the atmosphere (Turpin and Huntzicker, 1995). Organic compounds such as polycyclic aromatic hydrocarbon (PAH), oxy-PAH, and nitro-PAH are potential mutagens or carcinogens that have been found in urban particulate matter (PM). In most urban areas, OC and EC constitute ~20 to 50% of fine particle (PM_{2.5}, particles with aerodynamic diameter less than 2.5 μm) mass (Chow et al., 1993).

Urban air pollution in Asia has been increasing and has become recognized at the regional, continental, and global scales (Street et al., 1999). Menon et al. (2002) showed that BC emitted from China and India affects regional climates. Cooke et al. (1999) estimated that ~25% of global anthropogenic BC emissions originate from China. In contrast to other pollutants such as sulfate and nitrate, observations of OC and EC in Asia are insufficient (Cheng et al., 2000; Ho et al., 2003; Yao et al., 2002) for quantitative assessment of their environmental and climatic effects.

Hong Kong, located on the southeastern coast of the Asiatic mainland and on the southern tip of the highly economically developed Pearl River Delta (PRD) region in China, is one of the most densely populated metropolitan areas in Asia. Most of Hong Kong's 7 million inhabitants reside on ~15% of its 1068 km² land area. According to The Census and Statistics Department of Hong Kong, 517 000 registered vehicles traveled on 1904 km of roads in 2000. Diesel trucks with high EC emissions accounted for ~30% of the vehicle fleet. Air pollution in Hong Kong is also influenced by heavy industry, agricultural production, and shipping in the PRD region.

Ambient monitoring of PM_{2.5} and PM₁₀ (particles with aerodynamic diameter less than 10 μm) and PM_{2.5} mass and carbon was conducted during winter (November 2000 to February 2001) and summer (June to August 2001) at three sites in Hong Kong. In addition to OC and EC, water-soluble organic carbon (WSOC) and ¹³C abundances in OC and EC were measured to understand their characteristics in the region. This paper examines the spatial and seasonal variations of OC, EC, WSOC, and carbon isotopes.

Variability of OC, EC, WSOC and isotopes in Hong Kong

K. F. Ho et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

2 Methodology

2.1 Sampling sites

The three sampling sites shown in Fig. 1 include: a vehicle emission dominated middle-scale roadside Hung Hom site (Polytechnic University campus, PU); an urban-scale commercial-residential Kwun Tong (KT) site; and the regional-scale Hok Tsui (HT) site. Detailed site descriptions are given in Table 1.

2.2 Particulate matter collection

Twenty-four-hour sampling (midnight to midnight) was carried out every sixth day at the PU and KT sites, and five PM_{2.5} and PM₁₀ samples each were collected during winter and summer seasons at HT. PM samples were acquired on 20.3 cm×25.4 cm Whatman quartz microfibre filters (QM/A, Whatman Inc., Clifton, NJ, USA) by high volume (hi-vol) samplers (Graseby-Andersen, Atlanta, GA, USA) operated at flow rates of 1130 to 1410 L/min. Two Partisol model 2000 (Rupprecht & Patashnick, Albany, NY) low volume samplers with 10 and 2.5 μm inlets, operated at 16.7 L/min, was used to collect PM_{2.5} and PM₁₀ mass on Teflon-membrane filters (Pall Life Sciences, Ann Arbor, MI). The difference between the hi-volume and the Partisol 2000 samplers was less than 7% for PM_{2.5} and PM₁₀ mass. The quartz-fiber filters were baked before sampling at 900°C for 3 h to remove organic artifacts or impurities. After sampling, samples were stored in a refrigerator at ~4°C prior to chemical analysis to prevent the loss of volatile components. Approximately 5% of field blanks were collected to subtract the positive artifacts that resulted from adsorption of gas-phase organic compounds onto the filter during and/or after sampling. Negative artifacts due to the volatilization of particle-phase organics from particle samples were not quantified in this study.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

2.3 OC, EC, and WSOC analyses

Winter samples were analyzed for OC and EC by selective thermal manganese dioxide oxidation (TMO) with a modified Dohrmann DC-52 carbon analyzer (Fung and Wright, 1990) at AtmAA Inc. of Calabasas, CA, USA. Summer samples were analyzed using a DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA) at the Hong Kong Polytechnic University following the Interagency Monitoring of PROtected Visual Environments (IMPROVE) thermal/optical reflectance (TOR) protocol (Chow et al., 1993). Previous laboratory comparisons between TMO and TOR by Fung et al. (2002) showed comparability for TC (total carbon), OC, and EC. Inter-laboratory comparison between the two methods during this study reported <5% difference for TC and ~10% differences for OC and EC. OC and EC data can be compared with minimal analytical bias.

Several methods have been used to analyze WSOC in particulate samples by using the water extract of a filter sample (Yang et al., 2003). For this study, five punches (0.526 cm²) were removed from a filter and placed into a flat-bottomed screw-capped vial to which 1 ml of distilled de-ionized water (DDW) was added. Sample vials were heated in an oven at ~95°C for ~0.5 h. Samples were cooled to room temperature and stood for ~48 h. About 0.5 ml of the filter extract was transferred to another vial by syringe and 20 µl were taken for WSOC analysis. Triplicate analyses showed that a precision of ±10% can be achieved.

2.4 Stable carbon isotope analyses

Stable isotope analysis (¹³C/¹²C) of TC differs by emission source (Chesselet et al., 1981; Cachier et al., 1986, 1989; Martinelli et al., 2002). Only limited studies have examined isotope abundance (δ¹³C) in atmospheric OC and EC. Variations of δ¹³C in OC and EC may provide a better understanding of the source and fate of carbonaceous aerosol.

OC and EC are operationally defined. Watson et al. (2004) describes more than

ACPD

6, 4579–4600, 2006

Variability of OC, EC, WSOC and isotopes in Hong Kong

K. F. Ho et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

EGU

20 international thermal combustion carbon methods for OC and EC. Different methods compound the uncertainties while evaluating isotope abundances in OC and EC (Reddy et al., 2002).

In the study, $\delta^{13}\text{C}$ was determined from carbon dioxide (CO_2) evolving at two temperatures and detected with a Finnigan MAT-251 mass spectrometer (Thermo Electron Corporation, Burlington, Ontario, Canada). Particulate carbonate was removed with hydrochloric acid prior to isotopic analysis. The remaining carbon was oxidized to CO_2 by heating at 375°C (no oxygen (O_2) under vacuum) for 3 h. The CO_2 was isolated through a series of cold traps and $\delta^{13}\text{C}$ in OC was quantified by manometry. The filter was then combusted at 850°C for 5 h, and the resulting CO_2 was purified in cold traps to determine $\delta^{13}\text{C}$ in EC. $\delta^{13}\text{C}$ is expressed relative to the international standard (PDB) as:

$$\delta^{13}\text{C} = \left({}^{13}\text{C}/{}^{12}\text{C}_{\text{sample}} / {}^{13}\text{C}/{}^{12}\text{C}_{\text{standard}} - 1 \right) \times 1000$$

Samples were analyzed at least in duplicate with a maximum allowable difference of 0.3‰.

3 Meteorological conditions

The climate in Hong Kong (22.12 N, 114.08 E) is sub-tropical, under the influence of the Asian monsoon. Summer and winter are the two longest seasons, each with distinct meteorological characteristics. Prevailing southwesterly wind during summer brings warm and damp air masses from the South China Sea. In winter, prevailing northeasterly wind travels across South China before reaching Hong Kong. Air quality in Hong Kong is poorest in winter due to the influence of local sources and polluted air mass transported from South China. The meteorological information in this study was obtained from Hong Kong Observatory (HKO).

Variability of OC, EC, WSOC and isotopes in Hong Kong

K. F. Ho et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

4 Results and discussion

4.1 Spatial and seasonal distributions of OC and EC

A total of 100 $\text{PM}_{2.5}$ and PM_{10} samples (including field blanks) were collected for this study. Spatial and seasonal distributions of OC and EC are illustrated in Fig. 2, with average concentrations listed in Table 2. $\text{PM}_{2.5}$ mass varied from 10–39 $\mu\text{g m}^{-3}$ during summer and from 42–53 $\mu\text{g m}^{-3}$ during winter. Corresponding PM_{10} concentrations were 15–54 $\mu\text{g m}^{-3}$ during summer and 76–83 $\mu\text{g m}^{-3}$ during winter. $\text{PM}_{2.5}$ accounted for 72–76% of PM_{10} mass during summer, compared to 53–81% during winter. On average, TC (i.e., OC+EC) explains 26% and 32% of $\text{PM}_{2.5}$ mass during winter and summer, respectively. The corresponding TC fractions were 6–7% less in PM_{10} . The average TC in $\text{PM}_{2.5}$ and PM_{10} was $25.5 \pm 8.3\%$ and $18.4 \pm 7.0\%$, respectively, in winter, which is similar to previous observations by Cao et al. (2003). $\text{PM}_{2.5}$ and PM_{10} OC concentrations at the PU and KT sites ranged from 8.8 to 12.1 $\mu\text{g m}^{-3}$ during winter and from 5.9 to 11.1 $\mu\text{g m}^{-3}$ during summer, whereas the corresponding $\text{PM}_{2.5}$ and PM_{10} EC ranged from 4.8 to 7.0 $\mu\text{g m}^{-3}$ during winter and 4.5 to 6.3 $\mu\text{g m}^{-3}$ during summer. The seasonal contrast is only 35–55% for OC and 6–26% for EC at the PU and KT sites. Winter $\text{PM}_{2.5}$ and PM_{10} OC concentrations were 3- to 4-fold and EC concentrations were 3-fold higher than those found during summer at the HT site.

Several factors can affect the carbon concentrations. Dilution due to increased mixing depths (greater convective mixing) (Sequeira and Lai, 1998) and particle washout on rainy days resulted in lower PM and carbon levels in the summer (monthly average rainfall ranged from 318.9 to 1083 mm in summer and from 10.9 to 96.8 mm during winter). Wintertime stagnation decreased the dispersion and transport of pollutants and resulted in an increase in pollution levels. Northeasterly winds during winter carried air pollutants from China to Hong Kong, which elevated PM and carbon concentrations at the regional-scale site.

At the three sites, 78–99% of EC and 79–98% of OC in PM_{10} were found in the $\text{PM}_{2.5}$

Variability of OC, EC, WSOC and isotopes in Hong Kong

K. F. Ho et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

fraction of PM_{10} . Average $\text{PM}_{2.5}$ and PM_{10} OC concentrations at the PU and KT sites were 2–3 times higher and EC concentrations were 4–5 times higher than those at the HT site. Elevated OC and EC concentrations at the urban sites reflect the influence of vehicle exhaust, along with emissions from restaurants and nearby industries.

Ratios of OC to EC have been used to imply the origin of carbonaceous particles (Turpin et al., 1995; Chow et al., 1993). Table 2 shows that the OC/EC ratios at the two urban sites (1.6–1.8) were half of those found at the regional-scale site, with little variation between summer and winter. Low OC/EC ratios are primarily due to the elevated EC concentrations at the urban sites, implying direct emissions from anthropogenic sources. Elevated OC/EC ratios at the regional-scale site suggested the transport of aged aerosol that may have included secondary organic aerosol (SOA).

4.2 Variability of WSOC

The water-soluble fraction of OC (i.e., WSOC) often consists of >30% of $\text{PM}_{2.5}$ or PM_{10} OC, often being associated with polar compounds and correlated with SOA formation (Grosjean et al., 1978; Rogge et al., 1993). WSOC has the potential to modify the hygroscopic properties of particles, including PM size and cloud condensation nuclei activities (Shulman et al., 1996).

A total of 60 samples comprising of five pairs of $\text{PM}_{2.5}$ and PM_{10} samples selected at each site from the summer and winter seasons were analyzed for WSOC. As shown in Table 3, ~80–90% of the PM_{10} WSOC was in the $\text{PM}_{2.5}$ fraction, ranging from 1– $2\ \mu\text{g m}^{-3}$ during summer and 3– $4\ \mu\text{g m}^{-3}$ during winter. Wintertime WSOC was ~1.5–2 times higher than in summer with less spatial variation. Low summertime WSOC (~ $1\ \mu\text{g m}^{-3}$) may be due to clean marine air masses from the South China Sea. The major sources of WSOC include primary emissions from biomass burning and cooking, as well as secondary organic aerosol (Chebbi and Carlier, 1996). Transformation and transport of pollutants from urban areas may be the reason for higher (~ $3\ \mu\text{g m}^{-3}$) wintertime WSOC at the HT site. During the same monitoring period, atmospheric aromatic hydrocarbons such as toluene and xylenes, some of the main precursors

Variability of OC, EC, WSOC and isotopes in Hong Kong

K. F. Ho et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

of SOA (Ho et al., 2004), were determined. Concentrations of aromatic compounds were 2–6 times higher in winter than in summer at the HT site. The formation of SOA occurs both with the oxidation of naturally emitted terpenes and with anthropogenic volatile organic compounds (VOCs), particularly those with high molecular weights. As VOCs or primary organic aerosols react with photochemically derived oxidants (O_3 , $OH\cdot$, $NO_3\cdot$), they generate more polar compounds such as alcohols, carbonyls, carboxylic acids and more complex oxidized compounds (Saxena and Hildemann, 1996). Consequently, it is speculated that a high WSOC fraction is indicative of aged aerosol (e.g. due to photochemical reactions.). This is consistent with the results from Temesi et al. (2003). In addition, previous study has shown that dicarboxylic acids are one of the major identified components of WSOC (Grosjean et al., 1978; Rogge et al., 1993). The spatial-temporal distributions of $PM_{2.5}$ dicarboxylic acids at the three sites reported by Yao et al. (2004) showed similar trends as WSOC in this study.

The relative percentages of $PM_{2.5}$ WSOC, water-insoluble OC ($WIOC=OC-WSOC$), and EC in TC are presented in the ternary diagrams (Fig. 3). The percentages of WSOC in TC were similar at PU (13–20%) and KT (21–24%) in winter and summer as the smallest fraction of $PM_{2.5}$ carbon. In contrast, the regional HT site showed that WSOC was the largest TC fraction (41–54%), with higher summer levels. This is consistent with the notion that regional-scale sites are mostly impacted by aged aerosol. Salma et al. (2001) showed that the mass fraction of WSOC increased from a tunnel to a background area. Meanwhile, the EC concentration is reduced during transport to the background site because of dilution. This explains why WSOC becomes a large fraction (50–70%) of OC at the HT site and accounts for only about one-third of OC at the PU and KT sites for $PM_{2.5}$ and PM_{10} in both seasons.

WSOC constitutes small fractions of $PM_{2.5}$ and PM_{10} mass, ranging from $5.6\pm1.3\%$ to $9.9\pm2.1\%$ for $PM_{2.5}$ and from $4.1\pm1.0\%$ to $8.7\pm0.5\%$ for PM_{10} (Table 3). The WSOC/OC ratios were higher in winter than in summer at the urban sites. Other than primary emissions, transport from the urban area was one of the possible sources of WSOC in winter. However, the WSOC/OC ratios at the regional-scale HT site were

Variability of OC, EC, WSOC and isotopes in Hong Kong

K. F. Ho et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

higher in summer than in winter. Elevated WSOC/EC ratios can be used as indicators for aged aerosol. The average WSOC/EC ratios at the urban PU and KT sites were 0.4–0.6 and 0.5–0.7 (Table 3), respectively, which are similar to the ratio at a high-traffic roadside site in Paris (0.32) (Ruellan and Cachier, 2000). However, the average WSOC/EC ratios at the HT site were ~2.0 for winter and ~2.5 for summer.

4.3 Stable carbon isotopic composition of OC and EC

Twenty-four PM_{2.5} were analyzed for $\delta^{13}\text{C}$ composition of OC and of EC, with the results in Fig. 4.

The average O¹³C abundance (i.e., $\delta^{13}\text{C}$ in OC) was $-26.9 \pm 0.6\text{‰}$, ranging from -26.4‰ to -27.7‰ during winter. A similar average O¹³C abundance ($-26.9 \pm 0.5\text{‰}$) was found in summer, ranging from -26.3 to -28.1‰ . The average E¹³C abundance (i.e., $\delta^{13}\text{C}$ in EC) for both seasons was $-25.6 \pm 0.1\text{‰}$, ranging from -25.4‰ to -25.9‰ . The small difference in carbon isotopic abundance between the two seasons in Hong Kong is consistent with similar source mixtures. Rudolph et al. (2002) also observed little variability in ¹³C abundances for nonmethane hydrocarbons (NMHC) from traffic-related sources in the metropolitan region of Toronto. As shown in Fig. 4, $\delta^{13}\text{C}$ exhibited isotopic variability among the three sites, and these samples can be grouped into two clusters. Given that the ¹³C isotopic fractionation between an aerosol and its fuel is small (Turekian et al., 1998; Currie et al., 1999) and that no apparent isotopic fractionation is occurring during particle production and transport (Cachier et al., 1985), similar isotopic composition of OC and EC at the PU and KT sites (Group I in Fig. 4) are consistent with motor vehicle exhaust as the major contributor. The E¹³C at HT is similar to that found at the PU and KT sites, but the O¹³C at HT (Group II in Fig. 4) is isotopically lighter than those at the PU and KT sites. E¹³C values at the HT site were similar to those at the urban PU and KT sites, suggesting that the majority of the EC originated from motor vehicle emissions. While O¹³C was similar at the PU and KT sites, its abundance was lower at the HT site (-27.2‰ to -28.1‰), implying contributions from non-motor vehicle sources. Cachier et al. (1996) reported that the O¹³C associated

Variability of OC, EC, WSOC and isotopes in Hong Kong

K. F. Ho et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

with sea-salt droplets is $-21 \pm 2\%$. From the O^{13}C difference between the HT and PU sites (Fig. 4), it is unlikely that OC at HT is of direct marine origin. The carbon isotopic signatures of C_3 in bulk plant materials range from -27.7% to -29.2% (Ballentine et al., 1998). Hence, it may be that biogenic sources, through gas-to-particle conversion processes, contribute to regional OC. The distribution of dicarboxylic acids at the HT site is also consistent with biogenic origins (Yao et al., 2004). Kim et al. (2000) showed that local biogenic emissions of OC might be significant during summer at the Kosan ($126^\circ 10' \text{E}$, $33^\circ 17' \text{N}$) background site in Korea.

5 Summary and conclusion

During the study, average OC concentrations in $\text{PM}_{2.5}$ and PM_{10} fractions at the urban sites were higher in winter than in summer. The highest concentration of EC was observed at the micro-scale roadside PU site in both seasons because of the nearby vehicle emissions. Relatively low OC and EC concentrations were found at the HT regional-scale site because it was far from direct emission sources. OC/EC ratios at HT were larger than those at the PU and KT sites owing to the formation of SOA during transport. Average $\text{PM}_{2.5}$ and PM_{10} WSOC concentrations were also higher in winter than in summer. In contrast to the urban PU and KT sites, higher percentages of WSOC in TC were found at the HT site in both seasons. Average WSOC/EC ratios were <1 at the PU and KT sites, and ~ 2.0 to 2.5 at the HT site. These spatial variations suggested that a high WSOC fraction might be associated with aged aerosol. In addition, there were no notable differences for summer/winter distributions of carbon isotopic composition, indicating that motor vehicle sources were the main contributors of carbonaceous particles within the urban areas. Spatial distributions of $\delta^{13}\text{C}$ in EC were uniform, reconfirming the dominant influence of motor vehicle source. However, lighter isotopic compositions in OC found at the HT site, compared with those at the urban sites, indicated the existence of biogenic sources at the regional-scale site. It is apparent that the use of carbon isotope composition in combination with OC and EC

Variability of OC, EC, WSOC and isotopes in Hong Kong

K. F. Ho et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

has considerable potential to allow for a more detailed assessment of source identification. These analyses may provide a rapid and cost-effective technique for conducting source determinations and for quantitatively estimating relative contributions of different sources.

5 *Acknowledgements.* This project is supported by the Research Grants Council of Hong Kong (PolyU5145/03E, PolyU5197/05E) and the Natural Science Funding of China (NSFC40205018, NSFC40121303).

References

10 Ballentine, D. C., Macko, S. A., and Turekian, V. C.: Variability of stable carbon isotopic compositions in individual fatty acids from combustion of C4 and C3 plants: implications for biomass burning, *Chem. Geol.*, 152, 151–161, 1998.

Cachier, H., Buat-Menard, P., Fontugne, M., and Rancher, J.: Source terms and source strengths of the carbonaceous aerosol in the Tropics, *J. Atmos. Chem.*, 3, 469–489, 1985.

15 Cachier, H., Buat-Menard, P., Fontugne, M., and Chesselet, R.: Long-range transport of continentally-derived particulate carbon in the marine atmosphere: evidence from stable carbon isotopes studies, *Tellus*, 38B, 161–177, 1986.

Cachier, H., Bremond, M.-P., and Buat-Menard, P.: Carbonaceous aerosols from different tropical biomass burning sources, *Nature*, 340, 371–373, 1989.

20 Cao, J. J., Lee, S. C., Ho, K. F., Zhang, X. Y., Zou, S. C., Fung, K., Chow, J. C., and Watson, J. G.: Characteristics of Carbonaceous Aerosol in Pearl River Delta Region China during 2001 Winter Period, *Atmos. Environ.*, 37, 1451–1460, 2003.

Chameides, W. L.: Bergin M. Soot Takes Center Stage, *Science*, 297, 2214–2215, 2002.

Chebbi, A. and Carlier, P.: Carboxylic acids in the troposphere, occurrence, sources, and sinks: A review, *Atmos. Environ.*, 30, 4233–4250, 1996.

25 Cheng, Z. L., Lam, K. S., Chan, L. Y., Wang, T., and Cheng, K. K.: Chemical characteristics of aerosols at coastal station in Hong Kong. I. Seasonal variation of major ions halogens and mineral dusts between 1995 and 1996, *Atmos. Environ.*, 34, 2771–2783, 2000.

Chesselet, R., Fontugne, M., Buat-Menard, P., Ezat, U., and Lambert, C. E.: The origin of

Variability of OC, EC, WSOC and isotopes in Hong Kong

K. F. Ho et al.

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
◀	▶
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	

- particulate organic carbon in the marine atmosphere as indicated by its stable carbon isotopic composition, *Geophys. Res. Lett.*, 8, 345–348, 1981.
- Chow, J. C., Watson, J. G., Lowenthal, D. H., Solomon, P. A., Magliano, K. L., Ziman, S. D., and Richards, L. W.: PM₁₀ and PM_{2.5} compositions in California's San Joaquin valley, *Aerosol Sci. Technol.*, 18, 105–128, 1993.
- Cooke, W. F., Lioussse, C., and Cachier, H.: Construction of a 1°×1° fossil fuel data set for carbonaceous aerosol and implementation and radiative impact in the ECHAM4 model, *J. Geophys. Res.*, 104(D18), 22 137–22 162, 1999.
- Currie, L. A., Klouda, G. A., Benner Jr., B. A., Garrity, K., and Eglinton, T. I.: Isotopic and molecular fractionation in combustion three routes to molecular marker validation including direct molecular 'dating' (GC/AMS), *Atmos. Environ.*, 33, 2789–2806, 1999.
- Frazer, L.: Seeing through soot, *Environ. Health Perspect.*, 110, A471–A473, 2002.
- Fung, K. K. and Wright, B.: Particulate Carbon Speciation by MnO₂ Oxidation, *Aerosol Sci. Technol.*, 12, 122–127, 1990.
- Fung, K. K., Chow, J. C., and Watson, J. G.: Evaluation of OC/EC Speciation by Thermal Manganese Dioxide Oxidation and the IMPROVE Method, *JAWMA*, 52, 1333–1341, 2002.
- Grosjean, D., Van Cauwenberghe, K., Schmid, J., Kelley, P., and Pitts, J. N.: Identification of C₃–C₁₀ aliphatic dicarboxylic acids in airborne particulate matter, *Environ. Sci. Technol.*, 12, 313–317, 1978.
- Ho, K. F., Lee, S. C., Chan, C. K., Yu, J. C., Chow, J. C., and Yao, X. H.: Characterization of chemical species in PM_{2.5} and PM₁₀ aerosols in Hong Kong, *Atmos. Environ.*, 37, 31–39, 2003.
- Ho, K. F., Lee, S. C., Guo, H., and Tsai, W. Y.: Seasonal and diurnal variations of volatile organic compounds (VOCs) in the atmosphere of Hong Kong, *Sci. Total Environ.*, 322, 155–166, 2004.
- Kim, Y. P., Moon, K.-C., Shim, S.-G., Lee, J. H., Kim, J. Y., Fung, K., Camichael, G. R., Song, C. H., Kang, C. H., Kim, H.-K., and Lee, C. B.: Carbonaceous species in fine particles at the background sites in Korea between 1994 and 1999, *Atmos. Environ.*, 34, 5053–5060, 2000.
- Martinelli, L. A., Camargo, P. B., Lara, L. B. L. S., Victoria, R. L., and Artaxo, P.: Stable carbon and nitrogen isotopic composition of bulk aerosol particles in a C4 plant landscape of southeast Brazil, *Atmos. Environ.*, 36, 2427–2432, 2002.
- Menon, S., Hansen, J., Nazarenko, L., and Luo, Y. F.: Climate Effects of Black Carbon Aerosols in China and India, *Science*, 297, 2250–2253, 2002.

Variability of OC, EC, WSOC and isotopes in Hong Kong

K. F. Ho et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Reddy, C. M., Pearson, A., Xu, L., Mchichol, A. P., Benner, B. A., Wise, S. A., Klouda, G. A., Currie, L. A., and Eglinton, T. I.: Radiocarbon as a Tool To Apportion the Sources of Polycyclic Aromatic Hydrocarbons and Black Carbon in Environmental Samples, *Environ. Sci. Technol.*, 36, 1774–1782, 2002.

5 Rogge, W. F., Mazurek, M. A., Hildemann, L. M., Cass, G. R., and Simoneit, B. R. T.: Quantification of urban organic aerosols at a molecular level: Identification, abundance and seasonal variation, *Atmos. Environ.*, 27A, 1309–1330, 1993.

Rudolph, J., Czuba, E., Norman, A. L., Huang, L., and Ernst, D.: Stable carbon isotope composition of nonmethane hydrocarbons in emissions from transportation related sources and atmospheric observations in an urban atmosphere, *Atmos. Environ.*, 36, 1173–1181, 2002.

10 Ruellan, S. and Cachier, H.: Characterisation of fresh particulate vehicular exhausts near a Paris high flow road, *Atmos. Environ.*, 35, 453–468, 2000.

Salma, I., Maenhaut, W., Zemplén-Papp, E., and Zaray, G.: Comprehensive characterisation of atmospheric aerosols in Budapest Hungary: physicochemical properties of inorganic species, *Atmos. Environ.*, 35, 4367–4378, 2001.

15 Saxena, P. and Hildemann, L. M.: Water-soluble organics in atmospheric particles: a critical review of the literature and application of thermodynamics to identify candidate compounds, *J. Atmos. Chem.*, 24, 57–109, 1996.

Sequeira, R. and Lai, K.-H.: Small-scale spatial variability in the representative ionic composition of rainwater within urban Hong Kong, *Atmos. Environ.*, 32, 133–144, 1998.

20 Shulman, M. L., Jacobson, M. C., Charlson, R. J., Synovec, R. E., and Young, T. E.: Dissolution behavior and surface tension effects of organic compounds in nucleating cloud droplets, *Geophys. Res. Lett.*, 23, 277–280, 1996.

Streets, D. G., Carmichael, G. R., Amann, M., and Arndt, R. L.: Energy consumption and acid deposition in Northeast Asia, *Ambio*, 28, 135–143, 1999.

25 Temesi, D., Molnar, A., Meszaros, E., and Feczko, T.: Seasonal and diurnal variation in the size distribution of fine carbonaceous particles over rural Hungary, *Atmos. Environ.*, 37, 139–146, 2003.

Turekian, V. C., Macko, S., Ballentine, D., Swap, R. J., and Garstang, M.: Causes of bulk carbon and nitrogen isotopic fractionations in the products of vegetation burns: laboratory studies, *Chem. Geol.*, 152, 181–192, 1998.

30 Turpin, B. J. and Huntzicker, J. J.: Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS, *At-*

**Variability of OC, EC,
WSOC and isotopes
in Hong Kong**

K. F. Ho et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

- mos. Environ., 29, 3257–3544, 1995.
- Watson, J. G., Chow, J. C., and Chen, L.-W. A.: Summary of methods and comparison studies for organic and elemental carbon: Implications for visibility and global warming, in: Proceedings, Regional and Global Perspectives on Haze: Causes, Consequences and Controversies
- 5 Visibility Specialty Conference, edited by: Pitchford, M. and Poirot, R., Air and Waste Management Association, Pittsburgh, PA, p. 55-1–55-38, 2004.
- Yang, H., Li, Q. F., and Yu, J. Z.: Comparison of two methods for the determination of water-soluble organic carbon in atmospheric particles, Atmos. Environ., 37, 865–870, 2003.
- Yao, X. H., Fang, M., and Chan, C. K.: Size distributions and formation of dicarboxylic acids in
- 10 atmospheric particles, Atmos. Environ., 36, 2099–2107, 2002.
- Yao, X. H., Fang, M., Chan, C. K., Ho, K. F., and Lee, S. C.: Characterization of dicarboxylic acids in PM_{2.5} in Hong Kong, Atmos. Environ., 38, 963–970, 2004.

ACPD

6, 4579–4600, 2006

Variability of OC, EC, WSOC and isotopes in Hong Kong

K. F. Ho et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

EGU

Variability of OC, EC, WSOC and isotopes in Hong Kong

K. F. Ho et al.

Table 1. Description of the three monitoring sites in Hong Kong.

Site name (Code) Zone of representation	Site type	Site elevation	Site description
PolyU (PU) Roadside	roadside	~6 m a.s.l.	8 m from a heavily-trafficked roadway that leads to the Cross Harbour Tunnel. Traffic volume 170 000 vehicles per day
Kwun Tong (KT) Urban	urban-residential	~25 m a.s.l.	Near residential buildings with lightly-trafficked streets
Hok Tsui (HT) Background	regional boundary	60 m a.s.l.	Near the coast at 60 m above sea level with 240° of ocean view from northeast to south-west. 10 km away from urban areas and major roads.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Variability of OC, EC, WSOC and isotopes in Hong Kong

K. F. Ho et al.

Table 2. Average (\pm std. deviation) PM_{2.5} and PM₁₀ organic carbon (OC) and elemental carbon (EC) concentrations during the winter and summer at three monitoring sites.

		No. of samples	PM _{2.5}					PM ₁₀				
			Mass	OC	EC	TC/Mass (%)	OC/EC	Mass	OC	EC	TC/Mass (%)	OC/EC
			μg m ⁻³					μg m ⁻³				
PU (urban)	Winter	26	52.5±5.4	11.2±1.8	6.4±1.2	33.3±3.2	1.8	83.0±18.4	12.1±2.2	7.0±1.2	23.5±3.3	1.7
	Summer	10	39.0±9.1	10.2±2.4	5.9±0.3	41.9±4.2	1.7	53.5±12.5	11.1±2.2	6.3±0.3	33.3±4.1	1.8
KT (urban-residential)	Winter	22	61.7±32.0	8.8±1.8	4.8±0.6	24.8±7.1	1.8	76.3±30.2	9.5±1.9	5.1±0.6	20.6±5.4	1.8
	Summer	22	30.1±10.6	5.9±2.5	4.5±0.6	37.1±3.6	1.6	39.8±11.5	6.9±2.5	4.8±0.6	27.3±8.4	1.6
HT (urban back-ground)	Winter	10	42.4±13.3	5.5±1.1	1.4±0.4	16.9±3.1	4.1	80.0±30.4	5.9±1.1	1.6±0.4	9.9 ±2.1	3.8
	Summer	10	10.5±1.8	1.5±0.3	0.4±0.1	18.3±2.2	3.6	14.5±2.8	1.9±0.4	0.5±0.1	16.7±5.3	4.3
Average	Winter	58	52.2±19.8	8.7±2.8	4.3±2.3	25.5±8.3	2.5	80.0±24.7	9.3±3.2	4.7±2.5	18.4±7.0	2.4
	Summer	42	27.4±13.6	5.9±3.8	3.6±2.1	32.4±11.1	2.3	36.9±17.5	6.7±3.9	3.8±2.3	26.1±9.0	2.3

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Variability of OC, EC, WSOC and isotopes in Hong Kong

K. F. Ho et al.

Table 3. Average (\pm std. deviation) $\text{PM}_{2.5}$ and PM_{10} water-soluble organic carbon (WSOC) concentrations during winter and summer at three monitoring sites.

			No. of sam- ples	PM _{2.5}				PM ₁₀			
				WSOC $\mu\text{g m}^{-3}$	WSOC/OC (%)	WSOC/Mass (%)	WSOC/EC	WSOC $\mu\text{g m}^{-3}$	WSOC/OC (%)	WSOC/Mass (%)	WSOC/EC
PU (urban)	Winter	10		3.5±0.5	31.6±5.5	6.6±0.7	0.5	3.9±0.6	32.8±6.2	4.8±0.8	0.6
	Summer	10		2.1±0.3	21.5±6.3	5.6±1.5	0.4	2.4±0.2	22.6±6.5	4.7±1.3	0.4
KT (urban- residential)	Winter	10		3.4±1.0	38.4±7.2	6.1±2.2	0.7	3.7±1.1	39.3±7.4	5.3±2.2	0.7
	Summer	10		2.1±0.9	34.5±10.7	8.1±2.8	0.5	2.3±0.9	32.7±7.6	6.8±2.6	0.5
HT (urban back- ground)	Winter	10		2.8±0.6	51.3±7.4	7.1±2.2	2.0	3.1±0.7	53.1±5.7	4.1 ±1.0	1.9
	Summer	10		1.0±0.3	69.0±8.5	9.9±2.1	2.5	1.2±0.3	62.6±7.7	8.7±.5	2.4
Average	Winter	30		3.2±0.7	39.9±10.5	6.6±1.7	0.7	3.6±0.8	41.2±10.6	4.8±1.4	0.8
	Summer	30		1.7±0.7	42.3±23.1	7.8±2.7	0.5	1.9±0.8	31.4±24.1	5.3±3.8	0.5

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Variability of OC, EC,
WSOC and isotopes
in Hong Kong**

K. F. Ho et al.

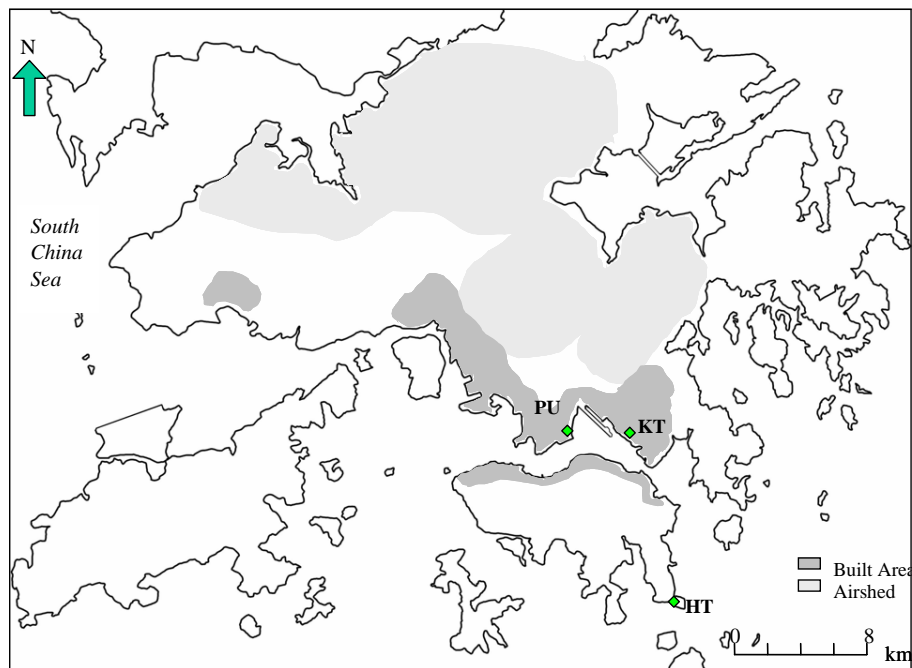


Fig. 1. Location of monitoring sites: middle-scale roadside Hung Hom (Hong Kong Polytechnic University Campus [PU]); urban-scale Kwun Tong (KT); and regional-scale Hok Tsui (HT) in Hong Kong.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Variability of OC, EC, WSOC and isotopes in Hong Kong

K. F. Ho et al.

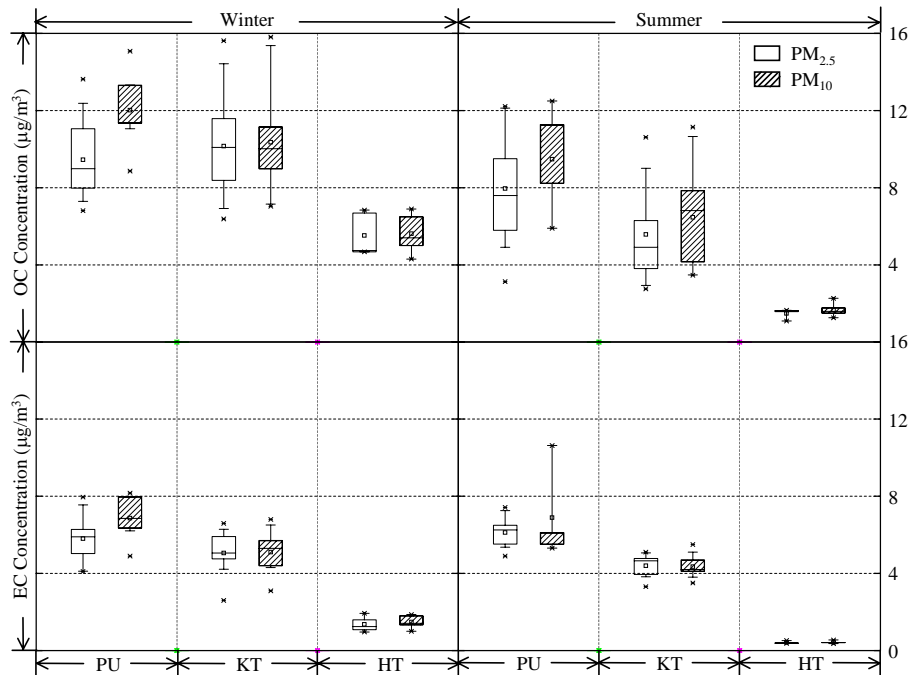


Fig. 2. Box plots of organic carbon (OC) and elemental carbon (EC) concentrations ($\mu\text{g}/\text{m}^3$) in $\text{PM}_{2.5}$ and PM_{10} samples during the winter and summer periods at middle-scale roadside Hung Hom (Hong Kong Polytechnic University Campus [PU]); urban-scale Kwun Tong (KT); and regional-scale Hok Tsui (HT) in Hong Kong.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Variability of OC, EC, WSOC and isotopes in Hong Kong

K. F. Ho et al.

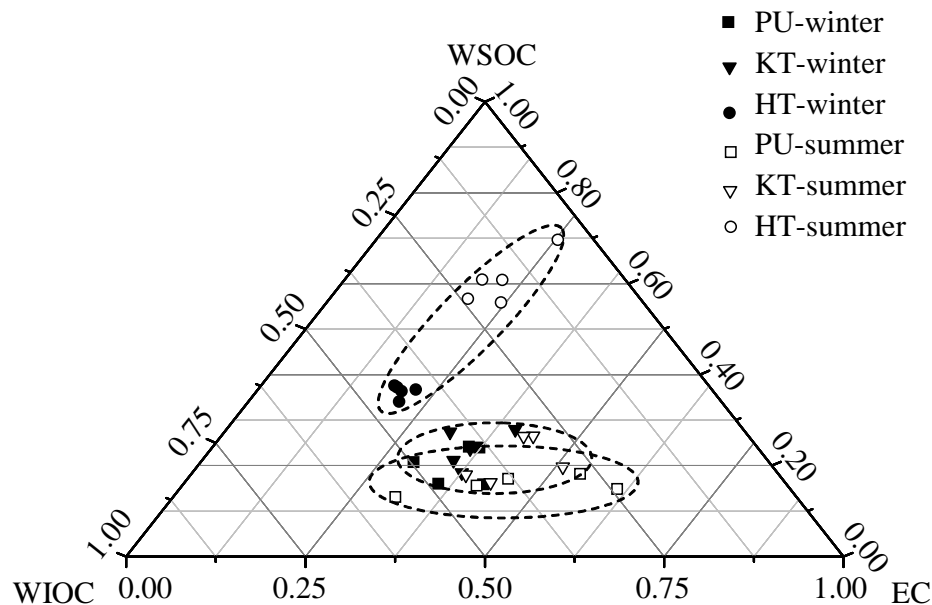


Fig. 3. Compositions of elemental carbon (EC), water-soluble organic carbon (WSOC), and water-insoluble organic carbon (WIOC) (give as fractions of TC) in PM_{2.5} during the winter and summer periods at middle-scale roadside Hung Hom (Hong Kong Polytechnic University Campus [PU]); urban-scale Kwun Tong (KT); and regional-scale Hok Tsui (HT) in Hong Kong.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Variability of OC, EC, WSOC and isotopes in Hong Kong

K. F. Ho et al.

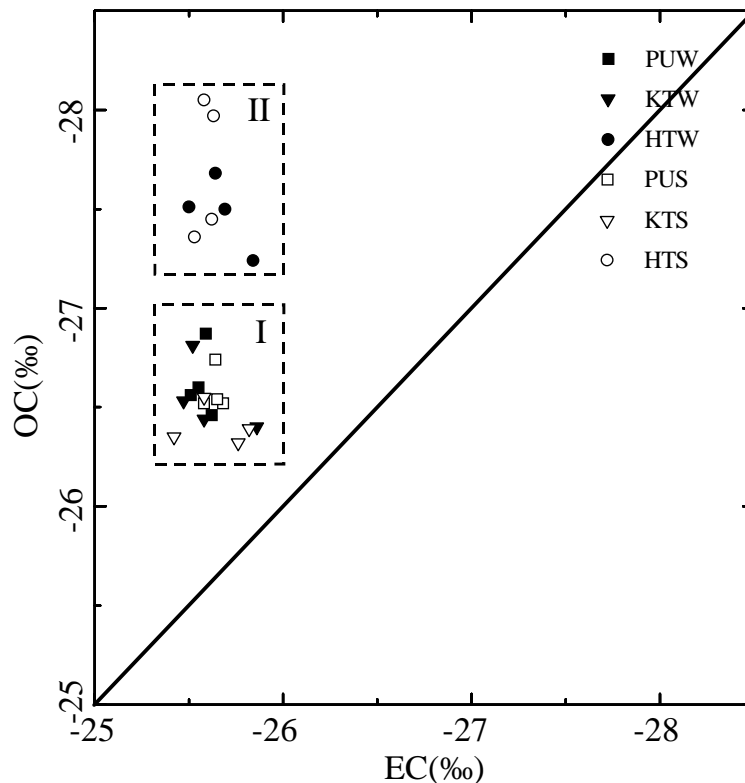


Fig. 4. Isotopic composition ($\delta^{13}\text{C}$) of organic carbon (OC) and elemental carbon (EC) during the winter and summer periods at middle-scale roadside Hung Hom (Hong Kong Polytechnic University Campus [PU]); urban-scale Kwun Tong (KT); and regional-scale Hok Tsui (HT) in Hong Kong.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)