Final Report

Hong Kong and the Pearl River Delta Pilot Air Monitoring Project: Pilot study on the use of atmospheric measurements to manage air quality in Hong Kong and the Pearl River Delta

Project 2: Fine Particulate Matter ($PM_{2.5}$) in the Pearl River Delta

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1.0 Project Summary

As part of the Pilot Air Monitoring Project, sampling of fine particulate matter (PM2.5) took place at seven stations across the Pearl River Delta from October, 2002 to June, 2003. The sampling consisted of 3 urban locations (Shenzhen, Guangzhou, and Central and Western in Hong Kong), 2 background stations (Tap Mun and Conghua), and 2 receptor sites (Zhongshan and Tung Chung). Sampling involved the collection of filter samples over 24-hr integrated time periods during a month of each season. For a given month samples were collected every sixth day. The filters were used to determine the $PM_{2.5}$ concentration as well as the concentrations of a variety of ions, elemental and organic carbon, specific elements, and solvent extractable organic compounds. The site-to-site variability of various elements and compounds related to specific sources (e.g. coal combustion, wind-blown dust, biomass burning etc.) is used to infer local and sub-regional influences within the PRD. In addition, the relative concentrations of specific organic compounds are used to infer sources and estimate source contributions via a chemical mass balance model (CMB). A summary of the findings is as follows:

- The highest annual mean $PM_{2.5}$ concentration is observed in Guangzhou (71 μgm^{-3}), followed by Shenzhen (47 μgm^{-3}), Zhongshan (46 μgm^{-3}), Conghua (37 μgm^{-3}), Central and Western (34 μgm^{-3}), Tung Chung (32 μgm^{-3}), and Tap Mun (29 μgm^{-3}).
- The annual mean contributions to $PM_{2.5}$ mass are dominated by organic compounds and sulfate, which are responsible for 24-35% and 21-32% of the fine particulate mass across the PRD region, respectively. Lesser contributions are from elemental carbon (3-8%), crustal species (3-13%), ammonium (6-8%), and nitrate (1-6%).
- During the October sampling season surface wind patterns indicate many days are dominated by northerly flow. The highest observed monthly mean $PM_{2.5}$ concentration of 66 μgm^{-3} occurred at Guangzhou, which is nearly two-fold greater than the values measured at Conghua and at the Hong Kong sites.
- During December the highest $PM_{2.5}$ monthly mean concentration is also measured in Guangzhou (72 μgm^{-3}), although the second highest concentration is found at Zhongshan (59 μgm^{-3}). On two of the five sampling days during December, Zhongshan has higher fine particulate concentrations than Guangzhou. On these days surface meteorological data indicate northerly flows throughout the PRD. Taken together, these results suggest that in addition to Guangzhou there is a significant source of $PM_{2.5}$ in Guangdong between Guangzhou and the Zhongshan receptor site.

- Relatively high fine particulate concentrations are observed throughout the PRD in March, with the two highest 24-hr $PM_{2.5}$ concentrations measured during the entire study of ~ 120 μgm^{-3} occurring at Guangzhou. The monthly mean concentration at Conghua is 51 μgm^{-3}, which is 10-15 μgm^{-3} greater than values observed at the Hong Kong sites. On many of the sampling days wind speeds are relatively low (< 4 ms^{-1}) and shifting from both the north and south indicating more regional influences on local air quality.
- During the summer sampling period in June monthly mean concentrations are relatively low at all sites (~25-35 μgm^{-3}) with the exception of Guangzhou with $PM_{2.5}$ of 64 μgm^{-3}. Given the intensity of precipitation scavenging from heavy rains that occurred during the summer monsoon, it is likely that most locations were significantly influenced by local sources.
- The square of the correlation coefficients (r^2) among the Hong Kong stations and Shenzhen for $PM_{2.5}$ are > 0.70, suggesting that these sites are influenced to a large extent by sources outside of their region and to a lesser extent by local sources. The Guangzhou and Conghua sites are not correlated with any other stations, indicating that they are influenced to a large degree by local sources.
- Organic carbon has r^2 values between the Hong Kong and Shenzhen stations that range from 0.61-0.75 suggesting that these sites are influenced both by source regions outside of their region as well as local and perhaps secondary organic aerosol formation.
- Sulfate is highly correlated between the Hong Kong sites, Shenzhen and Zhongshan (r^2 ranges from 0.82-0.93) indicating that these locations are influenced by the same source region. Given the relatively high concentrations of sulfate observed in Guangzhou city, these results suggest a significant source of sulfur, most likely the burning of coal, in the vicinity of Guangzhou.
- The crustal species Silica and Iron have relatively high correlations (r^2 values ranging from 0.76 to 0.97) and nearly identical concentrations at the Hong Kong sites indicating transport of dust into the region. The relatively high concentrations at Guangzhou as well as at Conghua suggest that both long range transport as well as sources in the vicinity of Guangzhou influence regional dust concentrations.
- Comparison of elemental carbon measurements between the sites suggests that all sampling locations are significantly influenced by both local and regional sources of EC.
- Lead concentrations are similar throughout Hong Kong and at Shenzhen (annual means ranging from 0.06 to 0.08 μgm^{-3}) and highly correlated. The annual mean concentration in Guangzhou is nearly three times the concentrations measured in Hong Kong and not correlated with other sites, suggesting local sources dominate. Together, the results suggest a significant regional source of lead in Guangzhou, perhaps from gasoline combustion.

- Concentrations of potassium, an element associated with biomass burning, are nearly identical (annual mean of 0.57 μgm^{-3}) and highly correlated in Hong Kong. A high correlation also exists between the Hong Kong sampling sites and Shenzhen. The concentrations in Guangzhou are nearly three-fold the values in Hong Kong and Shenzhen and are not correlated with these sites. This suggests that Hong Kong and Shenzhen are influenced by similar source regions and that there are significant biomass burning sources throughout Guangdong.
- The ratio of the concentrations of hopanes + steranes (H+S), compounds linked with mobile source emissions, to EC are generally highest in Guangzhou and lowest at the Hong Kong stations. These results when taken together with the relative concentrations of Pb at the sites suggest that Guangzhou is influenced to a greater extent by gasoline vehicles and Hong Kong by diesel vehicles.
- Concentrations of Levoglucosan, a biomass burning tracer, are on average highest in Guangzhou (508 ngm^{-3}), and Conghua (351 ngm^{-3}) and somewhat uniform throughout Hong Kong (110-160 ngm^{-3}). This indicates significant biomass burning sources in Guangdong, and is consistent with the observed concentrations of K.
- Based on Chemical Mass Balance (CMB) modeling, on average across all seasonal samples and all stations the main sources of primary fine particulate OC are mobile sources that are estimated to account for 21±6% of the OC mass (with diesel vehicles contributing 13±6% and gasoline vehicles 8±4%) followed by 18±4% for biomass burning and 12±6% for meat cooking. Although, it should be noted that relative contributions vary with season and site.
- Lesser annual contributions to particulate OC at all sites are attributed by the CMB model to coal combustion (7±4)% and road dust (6±1%). Although, it should be noted that the road dust contribution is an upper limit estimate as dust at many of the sites appears to be from regional and longer range transport and possibly not linked with road dust.
- Caution should be used when interpreting CMB results since key source profiles may not be entirely representative of actual source emissions. This is particularly true for coal burning, which is evident by the high sulfate concentrations observed throughout the PRD. Mobile source profiles of diesel and gasoline vehicles may also vary throughout the PRD. In addition, the meat cooking and biomass burning profiles used may not be representative of the PRD and this again may influence the interpretation of CMB results. It is also possible that we do not account for all significant sources of primary OC (i.e. marine vessels). Hence, it is clear that future studies are needed to assess the emissions profiles of the major sources identified in this study throughout the PRD.
- Despite lack of knowledge of emissions profiles used in the CMB model the results taken collectively suggest that the combined influence of fossil fuel combustion from mobile sources and coal as well as

biomass burning account for on average ~ 40-50% of the primary fine particulate organic carbon mass across the PRD in the samples analyzed during this study.

2.0 Introduction

The Pearl River Delta and adjoining Hong Kong metropolitan area, like virtually all other major urban-industrialized regions of the world, suffers from photochemical smog and the unhealthy concentrations of ozone and fine particles that it engenders. The characteristic of smog that is readily apparent to the unaided observer is the low visibility or haziness caused by the tiny particles or fine particulate matter suspended within the smog. Less readily apparent but equally ubiquitous in smog is the high concentration of ground level ozone (O_3) generated from photochemical reactions between gaseous pollutants. Both fine particles and O_3 are toxic and their presence in photochemical smog represents a health risk to a significant segment of the exposed population, especially the elderly, the young, and the infirm.

To protect the health and to continue to improve the quality of life of its citizens and visitors, officials from the Pearl River Delta region recognize that it must improve its air quality by reducing the severity of photochemical smog. However, the control of photochemical smog is complex and depends on a multitude of factors, including meteorological conditions that foster smog formation (sea-breeze effects, winter monsoon circulations) and the transport and co-mingling of pollutants from distant and local sources.

The subject Pilot Air Monitoring Project was initiated in May, 2002 with a duration of 2 years. The Environmental Protection Department (EPD) project AS:02-011 is part of this larger project being conducted by Civic Exchange. It is intended to build upon the useful work already done by the Hong Kong EPD, the universities in Hong Kong, and their counterparts in South China. The study is designed to explore the use of observation-based methods, analyses, and models based upon new measurements of NO_x, VOC, ozone, and the chemical compositions of the atmospheric fine particles to:

(1) Fill in knowledge gaps in smog and visibility problems in Hong Kong and the PRD region;

(2) Provide insight into policy relevant questions that could assist policy-makers in managing regional air quality in Hong Kong and South China;

(3) Strengthen the ability of public sector agencies, private businesses, and the academic scientific community to develop policies to improve air quality management; and

(4) Build long-term air quality management capacity in Hong Kong and Mainland China.

This report focuses on fine particulate ($PM_{2.5}$) measurements made at seven stations across the PRD over a roughly one year period beginning during October, 2002 and ending during June, 2003. The fine particle mass concentrations a well as specific chemical composition are presented and discussed. The site-to-site variability of the concentrations of specific compounds and elements is used to infer sub-regional sources within the PRD. Also, the concentrations of solvent extractable organic compounds are used to estimate the contributions of a variety of sources to organic carbon concentrations. In addition, surface meteorological data is integrated into the study to gain a better understanding of the impact of meteorology on $PM_{2.5}$ concentrations as well as additional insight into the sub-regional influences of source emissions on concentrations throughout the PRD.

3.0 Background

Anthropogenic fine particles are a growing concern in urban regions worldwide for their immediate and long-term effects on human health and the environment. Fine particles, also known as $PM_{2.5}$, are produced from both natural processes and human activities. The primary source of anthropogenic $PM_{2.5}$ is combustion, which directly emits particles as well as compounds that eventually condense onto existing particles. With lifetimes of days to weeks, elevated levels of fine particles are both a local and regional problem for many urban areas worldwide.

Fine particles have a significant impact on human mortality, associated specifically with short and long-term respiratory distress (13). Not only do the small sizes of the particles allow penetration to the inner depths of the lungs, but a high surface area allows urban pollution contaminants sorbed to the surface of the particles to cause damaging inflammation (4). A recent study by Pope et al. (2002) linked a long-term 10 $\mu g\ m^{-3}$ increase in $PM_{2.5}$ with a 4%, 6%, and 8% increased risk in all-cause, cardiopulmonary, and lung cancer mortality, respectively.

Another important impact of fine particulate matter is its influence on climate. Aerosol particles affect the climate directly by scattering and absorbing solar radiation, and indirectly by serving as nuclei for cloud droplet formation, causing increased cloud lifetimes and albedo (5-7). The net effect of fine particle climate forcing is believed to be a general regional cooling trend (6,7), although soot particles may locally warm the atmosphere through the absorption of solar radiation (32). Side effects of fine particle attenuation of solar radiation include observable reductions in visibility and possible negative impacts on photosynthesis and crop production (8).

The Pearl River Delta region of Guangdong province in southern China, home to nearly 40 million inhabitants, is growing and industrializing at an incredible pace. In fact, the southern city of Shenzhen has grown from a small fishing village to a large city of about 4 million in only the past 20 years. The topography of the region is complex, with mountains bordering the north of the region and each flank of the delta. Hong Kong is located south of the Pearl River Delta, containing a population of nearly 7 million clustered in the small valley regions of its mountainous main peninsula and smaller islands.

Particulate pollution is a recognized problem in the Hong Kong and Pearl River Delta region. While fine particles are currently still unregulated, a broader size class, respirable particulate matter (PM_{10}), is limited in both regions. Daily and annual limits for PM_{10} in Hong Kong are 180 μgm^{-3} and 55 µg/m3, respectively. The Pearl River Delta area has regulations particular to two separate emission classes, nonindustrial regions (150 μgm^{-3} daily, 100 μgm^{-3} annual average) and industrial regions (250 μgm^{-3} daily, 150 μgm^{-3} annual average) (25). Several recent studies have shown that the inhabitants of both regions are regularly exposed to elevated levels of PM_{10}. Lee and Chang (2000) monitored indoor and outdoor levels of PM_{10} for five classrooms in Hong Kong from November 1997 to January 1998. Indoor and outdoor average PM_{10} measurements for all five classrooms exceeded Hong Kong's annual standard, with one site having a maximum outdoor concentration of 617 μgm^{-3}. Although indoor concentrations are also influenced by sources within the measurement environment and not always by outdoor concentrations, such extremely high measurements were attributed to local emissions, such as construction, industrial processes, and vehicle emissions. Chan et al (2002) measured commuter exposure to PM_{10} for various public transportation options in Hong Kong, finding the highest levels of PM_{10} (147 μgm^{-3}) for non-air-conditioned roadway transport and lowest levels (50 μgm^{-3}) for railway transport. Finally, a recent PM_{10} monitoring study was carried out across the PRD region by the environmental engineering company CH2MHill from December 1999 to May 2000. PM_{10} concentrations were found to be highest in the cities of Guangzhou (267 μgm^{-3}) and Shenzhen (114 μgm^{-3}), with values ranging from 50 – 86 μgm^{-3} in Hong Kong.

Increasing interest in the fine particulate subset of PM_{10} has led to several recent studies of $PM_{2.5}$ in the Hong Kong and Pearl River Delta region, with nearly all studies showing fine particle levels far exceeding the current U.S. National Ambient Air Quality Standard (NAAQS) of 15 μgm^{-3} (annual average) and 65 μgm^{-3} (24 hour average). In the Pearl River Delta region, Wei et al. (1999) measured ambient $PM_{2.5}$ for two elementary schools in Guangzhou, one urban and one rural, collecting 15 samples per season for 1995 through 1996. The urban site was found to have an annual mean of 132 μgm^{-3} and 117 μgm^{-3} for 1995 and 1996, respectively. The suburban site had annual means of 68 μgm^{-3} (1995) and 54 μgm^{-3} (1996). The highest daily concentration reported was 506 μgm^{-3}, measured at the urban site in 1995. A more specific study by Chan et al. (2002) measured exposure to $PM_{2.5}$ from various transportation methods in Guangzhou, sampling during 5 consecutive weekdays for May and December 2001. The non-air-conditioned bus had the highest mean $PM_{2.5}$ of 145 μgm^{-3}, followed by non-air-conditioned taxi (106 μgm^{-3}), air-conditioned bus (101 μgm^{-3}), air-conditioned taxi (73 μgm^{-3}), and subway (44 μgm^{-3}).

Chan et al.(2001) measured $PM_{2.5}$ at 11 roadside sites throughout Hong Kong from January 1999 to February 1999, classified as either urban industrial, new town, urban residential, or urban commercial. Mean $PM_{2.5}$ levels ranged from 50 μgm^{-3} to 125 μgm^{-3}. Chao and Wong (2002) compared indoor and outdoor exposure to $PM_{2.5}$ by measuring fine particles at 34 homes in residential areas throughout the Hong Kong region from October 1999 to March 2000. Mean $PM_{2.5}$ indoor and outdoor levels were 45 μgm^{-3} and 47 μgm^{-3}, respectively. A wintertime measurement of $PM_{2.5}$ in Hong Kong was conducted by Ho et al (2003), with samples taken at two urban sites (PolyU and Kwun Tong) and an urban background site (Hok Tsui) from November 2000 to February 2001. The average concentration ranged from 42 to 57 μgm^{-3}, with a high of 117 μgm^{-3} at Kwun Tong. In addition, the Hong Kong Environmental Protection Department (HKEPD) led a recent long-term measurement campaign at three sites in Hong Kong, from November 2000 to October 2001 (30). Annual averages for Hok Tsui (rural), Mong Kok (urban roadside), and Tsuen Wan (urban), were 24, 58, and 34 μgm^{-3}, respectively. Seasonal averages ranged from 15-32 μgm^{-3} (HT), 51-69 μgm^{-3} (MK), and 26-44 μgm^{-3} (TW).

A recent broader field campaign measured particulate matter in both Hong Kong and the Pearl River Delta. Cao et al. (2003, 2004) measured both $PM_{2.5}$ and PM_{10} at 8 sites in the Pearl River Delta region during the winter and summer of 2002. Measurement locations included the cities of Hong Kong, Guangzhou (PRD), Shenzhen (PRD), and Zhuhai (PRD). Peak concentrations were measured in the winter samples, with Guangzhou having the highest average concentration of 106 μgm^{-3}, followed by Shenzhen (61 μgm^{-3}), Zhuhai (59 μgm^{-3}), and Hong Kong (55 μgm^{-3}). These results suggest that at all sites the annual mean concentrations will very likely exceed the U.S. annual NAAQS of 15 μgm^{-3}. With detailed analysis of the carbonaceous fraction, Cao et al (2004) predicted a regional influence on concentrations of organic carbon and observed seasonality in organic carbon and elemental carbon concentrations.

Sources of fine particles are currently poorly understood for this region, complicated by the mountainous topography, sea-land breezes (13-15), urban street canyon effect (16), and complex monsoon meteorology (17-19). Overall, Hong Kong displays maximum fine particulate levels in winter and minimum levels in the summer, usually explained by winter northeasterly winds and summer heavy rains (17-24). The most recent emissions inventory, carried out by CH2MHill, estimated a total PM_{10} production for the region of 258 kilo tonnes/year, with the PRD region producing 95%, and Hong Kong producing the remaining 5%. Specific contributions within each region were energy, industry, and transportation. In Hong Kong the leading source of PM_{10} was estimated to be transportation related sources, while in Guangdong industry is believed to make the largest contribution to PM_{10} (29). Specific emissions inventories for $PM_{2.5}$ have yet to be determined.

Chemical analyses of measured fine particulate matter have yielded important insights about their composition and sources. Several studies have found enrichment of pollutant elements in $PM_{2.5}$ versus PM_{10}, indicating that fine particles are more toxic and more heavily impacted by anthropogenic pollution, including compounds from incomplete combustion and toxics from industrial processes (12, 27, 30, 31, 36). In its year-long study of three sites in Hong Kong, the HKEPD found the most abundant constituents of $PM_{2.5}$ to be ammonium sulfate, organic carbon (OC), and elemental carbon (EC), with crustal material only a small fraction (3-8%) of its total mass (30). At the urban Tsuen Wan site it was found that the contribution of carbonaceous aerosol (organic carbon plus elemental carbon) to seasonal $PM_{2.5}$ concentrations ranged from 39%-50%. Similarly, the study by Cao et al. (2003) found that OC accounted for roughly 40% of the $PM_{2.5}$ mass during the wintertime in the PRD region.

Several early studies targeted particulate organic compounds in the Pearl River Delta region, gleaning information about local and regional sources through the specific organic constituents of the aerosol mass. In 1988, Simoneit (1991) analyzed solvent-extractable organic matter of aerosol samples taken at two sites in Guangzhou, with total extract yields of 5.0 μgm^{-3} and 26.1 μgm^{-3} at the suburban and urban site, respectively. Of these extracts, 3.1 μgm^{-3} and 3.2 μgm^{-3} were characterized as n-alkanes, PAH, diterpenoids, n-alkanoic acids, n-alkanols, and n-alkanones.

Zheng et al (1997) characterized TSP non-volatile solvent-extractable organics at six sites in Hong Kong for December 7-31, 1993. The total extract yield across the six sites ranged from 6.4 to 22.7 μgm^{-3}, with compounds falling into four main categories of n-alkanes, n-fatty acids, n-alkanols, and PAH. The highest yields in PAH (54 ngm^{-3}), UCM (unresolved complex mixture containing branched and cyclic hydrocarbons) (1919 ngm^{-3}), alkanes (550 ngm^{-3}), and alkanoic acids (2104 ngm^{-3}) occurred at the roadside station, Mong Kok. By calculating parameters describing the speciated compounds, anthropogenic, microbial, and biogenic sources were evaluated. Petroleum residues were detected at the three urban sites while the rural sites had a bias towards biogenic and microbial components. Octadecanoic acid was discussed as both a marker for kitchen emissions and as a possible estimation of aged air versus recent biogenesis, as unsaturated fatty acids are known to degrade quickly in the environment. A more detailed study of polycyclic aromatic hydrocarbons (PAH) was performed by Zheng and Fang (1998), analyzing 34 TSP samples from 1993 to 1995 at the same six sites as their previous study. Seasonal variability was identified, with PAH values peaking in autumn and decreasing from winter to summer. Spatially, urban Mong Kok had the highest overall PAH levels and rural sites Hok Tsui and HKUST had the lowest.

A unique study was performed by Fang et al in 1996, where two days of sampling characterized as a dust episode were compared with two non-episodic samples. TSP samples were taken at two sites – western residential Lantau Island and eastern rural HKUST. Organic analyses were performed on all samples and distinct trends were noted. The distribution of n-alkanes in the non-episodic samples showed significant petroleum residues, while the episodic samples showed elevated levels of terrestrial vascular plant wax input, increasing 43% at Lantau and 29% at HKUST. Also, the dust episode samples were determined to have low levels of unsaturated fatty acids, evidence that the air mass was aged and had been advected into the region.

A few recent studies have focused on organic compounds in the fine mode of particulate matter. Xu and Lee (2000) sampled aerosols from May 18-30, 1998 in order to investigate the fraction of nitrated polycyclic aromatic hydrocarbons (NPAHs) adsorbed onto PM_{10} versus fine particles of diameter 0.5 μm or smaller. Although concentrations were within the pgm^{-3} range, fine particles were found to be enriched in NPAHs by 3 to 10 times. A more extensive coverage of solvent-extractable organics in the finer mode was studied by Zheng et al (2000), with 18 24-hour $PM_{2.5}$ samples taken at HKUST for over one year, from October 1996 to September 1997. With a total solvent extract yield of 56.4-233.6 ngm^{-3}, important categories were fatty acids (46-80%), alkanes (10-34%), alkanols (4-21%), and PAHs (1-6%). Sources were determined to be combustion, biogenic, and microbial, with vehicular emissions determined to be characteristic of the Hong Kong region. On average, 79% of alkanes measured were from petroleum residue. The distribution of alkanes shifted seasonally, its peak moving towards lower carbon numbers in fall and winter suggesting a greater relative influence of diesel emissions during these times of the year. Another factor showing the vehicular trait was a strong correlation between total PAH and benzo(ghi)perylene, an organic species associated with mobile emissions. Fatty acids and alkanols both displayed seasonal variability due to microbial activity, with the contribution from microbial sources increasing during the summer season.

The recent year-long $PM_{2.5}$ measurement campaign led by the HKEPD included two types of organic analysis: solvent extractable organic analysis (SEOC) and water soluble organic analysis (WSOC). WSOC is a relatively unexplored region of $PM_{2.5}$ analysis, an important aspect in that it involves compounds most likely to impact visibility due to water uptake. The SEOC analysis, carried out by the Hong Kong Government laboratory found the most abundant solvent extractable organics were UCM (32-71%), fatty acids (23-56%), aliphatic hydrocarbons (5-21%), alkanols (0-5%), and PAHs (1-3%). Overall, SEOC was found to contain 2.4-5.4% of the total carbon and 3.1-10.6% of total organic carbon. Of the three sites measured, urban Mong Kok displayed the highest overall values but little seasonal variation. Oppositely, rural Hok Tsui had the lowest concentrations but displayed elevated levels in winter and low levels in the summer. Dominant sources were noted to be microbial activities, vascular plant wax, vehicular exhaust, and kitchen emissions.

Water soluble organic compounds were measured to contribute 14-64% of the organic carbon mass. Analyses of water soluble organic compounds identified 12-29% as organic anions (4-14%), amino acids (3-8%), aliphatic amines in free and combined form (0.3-0.6%), and carbohydrates (2-7%). Aromatic acids, hydroxy acids, oxo-acids, and dicarbonyls together formed 0.7-3.2% of the WSOC mass. The annual mean ratio of WSOC to total aerosol carbon at remote Hok Tsui, Tsuen Wan, and Mong Kok was 40%, 20%, and 9%, respectively. Since the oxidation of organic compounds in the atmosphere generally leads to greater water solubility, these results suggest that secondary production of particulate organic compounds significantly influence fine particulate concentrations in Hong Kong.

Several studies indicate that secondary aerosols, particularly sulfate particles, are transported during winter to Hong Kong from mainland China (11, 18, 22). Ho et al. (2003) found high levels of non-sea-salt sulfate at a rural coastal site (Hok Tsui), evidence that the sulfate species must have been advected into the region. The lack of variability of sulfate particles among a wide range of monitoring sites in Hong Kong also shows the regional nature of the sulfate aerosols (11, 18, 30). In one study, air masses moving to Hong Kong via continental China were correlated with increases in sulfate and ammonium concentrations by ~ 40-400% and 30-300% respectively (22). The presence of sulfate in Hong Kong particulate matter indicates that secondary formation of aerosols play an important role in $PM_{2.5}$ levels in the region.

Overall, past studies show that the concentrations of particulate matter across the Pearl River Delta are extremely high during the fall and winter seasons. Levels of $PM_{2.5}$ have been found to often exceed the U.S. NAAQS 24 hour standard at many locations, as well as the annual average systematically throughout the region. Measurements of the chemical composition of $PM_{2.5}$ indicates that sulfate, produced primarily from the burning of coal, as well as carbonaceous species which originate from a variety of combustion processes are the primary sources of fine particulate matter. Prior work also indicates that meteorology plays an important role in defining $PM_{2.5}$ concentrations throughout the region.

4.0 Field Measurements

4.1 Sampling Sites and Schedule

Sampling sites were carefully chosen to represent background, urban, and urban influenced sites throughout the region. The 7 sites dedicated to aerosol sampling are presented in Figure 1 and can be summarized as follows:

- 2 Background sites located at Tap Mun and Conghua;
- 2 Receptor sites located at the cities of Zhongshan and at Tung Chung; and
- 3 Urban sites located at Shenzhen, Guangzhou, and Central and Western.

At each of these 7 sites, $PM_{2.5}$ mass and chemical composition are measured on selected days (five 24-hour integrated samples every 6th day) for one month during each season of the year using integrating filters and subsequent laboratory analysis. Sampling was conducted during the months of October and

December, 2002 and March and June of 2003. The criteria used in the selection of each of the sites, as well as descriptions of their characteristics, the general measurement strategy and project timetable are given in Appendix A. Table 1 shows the completeness of sampling over the 24-hr measurement periods at each location. In general, 133 24-hr samples were obtained on schedule (out of a possible 140 samples) yielding a sample completion of 95%. It should be pointed out that the stations operated by the Hong Kong EPD had a 100% sample success rate.

In addition to the daily sampling during each season, Hi-volume samples collected by the Hong Kong EPD in coordination with Dr. Jianzhen Yu of HKUST at two locations in Hong Kong (urban Yuen Long and Tung Chung) have been analyzed for solvent extractable organic compounds for four specific events. The filters were collected over 24-hours on the following dates: 10/20/02, 12/13/02, 12/19/02, 03/25/03.

4.2 Sampling Methodology and Analyses

At 3 sites in Hong Kong and 2 sites in Guangdong ThermoAndersen RAAS $PM_{2.5}$ chemical speciation samplers were used to collect aerosol samples. The samplers are designed with 4 separate channels. Two of the channels were operated at 16.7 $lmin^{-1}$ with quartz filters that were analyzed for organic (OC) and elemental carbon (EC), and specific water soluble and solvent extractable organic compounds (SEOC) that are used as tracers for specific sources (i.e. mobile sources, biomass burning, coal combustion, etc.). The other two sampling lines collected aerosol particles on Teflon filters at a flowrate of 7.3 $lmin^{-1}$ that were then used to determine the $PM_{2.5}$ mass concentration as well as the concentrations of major ions and elements. At two additional sites in Guangdong 2 prototype samplers designed and fabricated at Caltech operated under similar conditions as described above. A detailed description of the samplers, analytical techniques, as was as quality assurance-quality control procedures (QA/QC) is given in Appendix B.

In order to insure that the samplers as well as field and laboratory handling procedures did not add significant uncertainty to $PM_{2.5}$ measurements at each of the sites, field intercomparisons were conducted as part of this study. Logistical considerations made it difficult to compare all samplers simultaneously at one location and hence two separate intercomparisons were conducted during the field study. The first intercomparison took place in Shenzhen between the four samplers that were subsequently deployed in Guangdong on September 9, 2002 in Shenzhen. An intercomparison was also conducted with the three Hong Kong samplers and the Shenzhen ThermoAndersen sampler at HKUST on September 11-12, 2003. In this way the Shenzhen sampler served as the reference sampler for $PM_{2.5}$ mass concentrations. As shown in Tables 2 and 3, all samplers are within ~5% of the reference sampler $PM_{2.5}$ mass concentration. The results suggest that differences in samplers as well as the sample handling, shipping and analysis procedures did not significantly add to measurement uncertainties. In particular, slight differences in the cyclone cut-points due to the designs of the samplers and operational flowrates appear to have a negligible (5% or less) influence on fine particulate concentrations.

5.0 Results and Discussion

5.1 $PM_{2.5}$ Mass Concentration and General Chemical Composition

In the following section results are presented for the $PM_{2.5}$ mass concentration as well as the concentrations of the major ions, elemental and organic carbon (EC and OC), and elements which are used to determine the crustal and trace elemental contributions to the $PM_{2.5}$ mass. We begin by presenting annual mean concentrations for the field sampling study and follow with the daily concentrations during each month of sampling. The daily samples are discussed in terms of surface meteorological measurements (wind speed, direction, and precipitation).

5.1.1 Annual Mean $PM_{2.5}$ Concentrations

The annual mean concentrations of specific $PM_{2.5}$ associated species are shown in Figure 3 as well as Table 4. It should be pointed out that the values do not necessarily represent the actual annual mean concentrations since samples were collected only for several days during a month of each season. The highest $PM_{2.5}$ concentrations are observed in Guangzhou, which has an annual mean value of 71 μgm^{-3}. The concentrations at all of the sites in Guangdong, including the background Conghua site, are greater than $PM_{2.5}$ concentrations measured in Hong Kong. There is a roughly two-fold increase in $PM_{2.5}$ concentrations between the Conghua and the urban Guangzhou site. The Hong Kong sites have $PM_{2.5}$ concentrations that are within ~ 20% of one another, ranging from 29 – 34 μgm^{-3}. This relative uniformity of concentrations across Hong Kong suggests that the city is influenced to some extent by more distant sources, outside of Hong Kong. Overall these general results suggest that Guangdong, and in particular Guangzhou city, is a significant source of $PM_{2.5}$ in the PRD.

The chemical composition throughout the PRD is dominated by organic compounds and sulfate which account for 24 - 35%, and 21 – 32% of the $PM_{2.5}$ mass, respectively. Lesser contributions to $PM_{2.5}$, as presented in Table 4, are from crustal species (3 –13%), ammonium (6 – 8%), and nitrate (1 - 6%). Nitrate is generally low at all sites. This is due in part to the fact that the sulfate to ammonium equivalence ratio is nearly always greater than one for all daily samples at all sites. In fact, the sulfate to ammonium equivalence ratio for all samples is 1.43±0.29. This suggests that the aerosols are not neutralized by ammonium and hence the formation of aerosol nitrate is not favored. The portion of the pie charts labeled as 'trace' contains the contribution of other measured elements and ions not included as their own categories. A fraction of the 'trace' concentrations is due to seasalt aerosol. Generally speaking the 'trace' contribution is less than 4% of the fine particle mass at all sites. The annual mean contribution of seasalt aerosol (taken as the contribution from sodium and chloride) is less than 2% of the $PM_{2.5}$ mass at all sites, indicating that seasalt, which is typically associated with the coarse mode, is not a significant fraction of the fine particulate mass. It should be pointed out that the unaccounted for $PM_{2.5}$ mass, labeled as 'other', ranges from 10 – 21%. This fraction of the fine particulate mass may be due to several reasons including water mass associated with the deposited particulate matter, underestimation of the crustal mass from elemental concentrations, as well as the underestimation of the mass of organic compounds. We have used a multiplication factor of 1.4 times the measured organic carbon concentration to estimate the concentration of particulate organic compounds and it could be that this value represents a lower limit estimate, although this cannot be determined without knowledge of the full speciation of organic compounds.

In the following sections (5.1.2 – 5.1.5) we present the daily measurements during each month, and discuss the influence of meteorology (local wind speed and direction as well as precipitation) on the relative concentrations at each of the sites. We also present and discuss the monthly mean concentrations at each of the sites and link these concentrations with observed surface meteorology. We do not have meteorological data for several of the specific aerosol sampling stations (CH, CW, and ZS) and have chosen stations that in general represent flow throughout the region. The location of the met stations is indicated on Figure 1. It should be noted that the surface meteorological data should be taken with some caution with respect to discussions on source regions since surface flow patterns are not always indicative of upper level winds that also influence air pollutant concentrations at the surface. Another important consideration is that the complex topographic structure in the Hong Kong region results in surface winds that are often not indicative more regional flow patterns. As discussed above we have attempted to choose meteorological stations that to a large extent are not influenced by local meteorological effects, such as surface topography, but represent more regional flow patterns. Although, it is apparent that the topography of the region results in a relatively complex relationship between surface winds and regional transport. Nonetheless, we use the meteorological data for qualitative discussions on source regions and meteorological influences. The results clearly indicate that surface winds yield important insights into source regions within the PRD.

5.1.2 Daily Concentrations During October, 2002

Figure 8 shows the daily $PM_{2.5}$ mass concentrations for the sampling days during October 2002. During the first sampling day of the month (October 2), Guangzhou (GZ) experienced the highest $PM_{2.5}$ concentrations with lowest concentrations of nearly three-fold less occurring at the background Tap Mun (TM) and Conghua (CH) sites. The concentrations across the sites in Hong Kong are only ~ 30% greater than the concentrations at the background sites. Shenzhen experiences $PM_{2.5}$ concentrations that are relatively high compared to the Hong Kong sites. Wind speeds and directions throughout the PRD region for October 1-2 (Figure 12) indicate that for the day prior to sampling, winds in the region are primarily northerly. During the day of sampling nearly all sites experienced relatively moderate wind speeds (2- 4 m s^{-1}) with both northerly and southerly components suggesting a land-sea breeze effect throughout the region.

During October 8th winds are moderate to high and from the north throughout the PRD region as shown in Figure 13. During this day Zhongshan (ZS) experiences the highest $PM._{2.5}$ concentrations, with a 24-hr average concentration of ~ 80 μg m^{-3} (Figure 8). The concentrations at TM, CW and TC are the highest observed in Hong Kong during the sampling month with values that are ~ 45 μg m^{-3}. The fact that CH has the lowest observed $PM_{2.5}$ concentration and that ZS and SZ experience higher concentrations than GZ during north-northeasterly flow conditions, combined with the uniformly high concentrations in Hong Kong indicate strong sources of $PM_{2.5}$ within the Guangdong region most likely in the vicinity of Guangzhou. Furthermore, it does seem likely that there is a significant source of fine particulate matter located in Guangdong south of Guangzhou, north of Shenzhen and Zhongshan, since the concentrations increase as winds traverse south through the region.

In contrast to the northerly flow conditions of October 8, October 14 had light winds (< 2 m s^{-1}) with a southerly flow component in addition to a northerly component (Figure 14). On this day the concentrations throughout Hong Kong are uniformly low (~20 μg m^{-3}) with the highest concentration of ~ 100 μg m^{-3} occurring at Guangzhou. The background CH site has a $PM_{2.5}$ concentration that is more than a factor of 2 greater than the Hong Kong stations. These results also suggest that sources in and around

Guangzhou city are responsible for a significant fraction of the regional $PM_{2.5}$ concentration, as demonstrated by the ~ 30 μg m^{-3} increase in fine particle mass from the Hong Kong stations to the background CH site. It should also be pointed out that the extremely high concentrations in GZ are also in part due to the low wind speeds that result in relatively lower mixing heights during the sampling day.

On October 20, precipitation occurred at the Guangdong sampling sites as shown in Figure 15. On this day winds are moderate (2 – 4 m s^{-1}) and from the south. The relative $PM_{2.5}$ concentrations are similar to October 14, when surface flows are also from the south, with the Hong Kong sites having the lowest concentrations and GZ the highest $PM_{2.5}$. The $PM_{2.5}$ concentration at CH of 40 μg m^{-3} is nearly a factor of 4 greater than the HK sites. As with October 14, a ~ 30 μg m^{-3} increase in $PM_{2.5}$ occurs as airmasses travel from Hong Kong across the PRD region to CH. These results are another indication that aerosol sources in and around Guangzhou city are responsible for a significant fraction of the $PM_{2.5}$ in the PRD area.

On October 26 surface meteorological data (Figure 16) from the Guangdong stations suggest northerly flow in Guangdong province. Guangzhou experiences the highest $PM_{2.5}$ concentrations (~50 μg m^{-3}). The concentration in Guangzhou is the lowest measured at that station during the month of October. This is very likely due to the high windspeeds (4-8 ms^{-1}) in Guangzhou that occurred over much of the sampling day which resulted in greater atmospheric mixing and dilution of surface concentrations. As is typical of cases of northerly flow, the CH site has lowest $PM_{2.5}$ concentration, with uniformly high (~35 μg m^{-3}) concentrations throughout Hong Kong.

The monthly mean $PM_{2.5}$ chemical composition across the PRD is shown in Figure 4. Fine particulate mass is dominated by organic compounds and sulfate which account for from 30-41% and 21-32% of the fine particulate mass, respectively. The combined mass fraction of organic compounds and sulfate ranges from 57-67%. Crustal material also has a significant contribution to fine particle mass, accounting for 10-15% of the $PM_{2.5}$. Lesser mass contributions are from nitrate (1-3%), ammonium(5-8%), and trace elements(2-4%).

5.1.3 Daily Concentrations During December, 2002

Figure 9 shows $PM_{2.5}$ concentrations during the month of December 2002. The first sampling day of the month (December 1) is characterized by moderate to low winds from the east-southeast throughout much of the PRD. Surface winds at Guangzhou are low and northerly (Figure 17). Surface meteorological data indicates that on the prior day (November 30) wind speeds are low and generally from the north. On both days (November 30 and December 1) moderate precipitation occurred throughout the PRD region, with somewhat high amounts of rain (~30 mm) in northern Guangdong. On this day Guangzhou experiences the highest concentration (~100 μg m^{-3}) of any of the PRD sites, and the highest concentration observed at any location during the month of December. This is probably due to the low wind speeds in Guangzhou resulting in less atmospheric mixing and less advection of local pollution out of the city. CH has the lowest concentrations, in part due to the relatively high precipitation observed in northern Guangdong. The concentrations at the Hong Kong sites and Shenzhen are relatively uniform at ~ 30 μg m^{-3}. It is difficult to assess the source areas of the $PM_{2.5}$ concentrations on December 1 due to the shifting winds prior to the sampling day, the relatively low wind speeds, and the precipitation occurring throughout the region.

On December 6 and 7 winds in the PRD are generally moderate and from the south, as shown in Figure 18. Although, there is also a northerly component to airflow patterns, suggesting shifting winds at many of the meteorological sites. Light rain occurred at several of the stations. $PM_{2.5}$ concentrations at GZ are nearly three-fold higher than at the other stations. Concentrations at the background TM station are lower than at CH, likely due to the southerly flow component bringing somewhat cleaner air to TM, and more polluted air from upwind source regions to CH. Concentrations are somewhat uniform at the other sampling sites, with the exception of TC that has the lowest observed concentrations. It is not clear why TC experienced the lowest concentrations, although it may be due to the spatial distribution of rainfall in Hong Kong. As with the case of December 1, shifting winds prevent a clear case to be made for source regions based on upwind-downwind relations. Nonetheless, it is apparent that the Guangzhou area is a dominant source of $PM_{2.5}$ and related precursors.

On December 13 the lowest $PM_{2.5}$ concentration occurs at the background CH site, with the highest observed concentrations at ZS (Figure 9). The concentrations are uniformly high (~35 μgm^{-3}) in Hong Kong. Figure 19 indicates that winds are moderate and from the north on the day prior to sampling, and predominantly from the north on the day of sampling. There are several hours at the end of the sampling day during which the flow shifted to the east for several of the sampling sites. The ~ 20 μgm^{-3} increase in $PM_{2.5}$ concentration from GZ to ZS suggests significant sources of fine particulate matter south of Guangzhou city in Guangdong province.

The highest $PM_{2.5}$ concentrations observed at the Hong Kong stations during the sampling month occur on December 19, with values ranging from 43 – 52 μgm^{-3}. Guangzhou has the highest $PM_{2.5}$ concentration of ~ 100 μgm^{-3}, followed by Zhongshan with a value of ~ 80 μgm^{-3}. Meteorological data indicates that surface winds are relatively low at most sites on the day of sampling with shifting winds from the north and south. The CH site experiences relatively high concentrations (~50 μgm^{-3}) suggesting an impact from sources to the south. The elevated concentrations throughout the region are likely from the low wind speeds linked with minimal atmospheric mixing, as well as a shifting wind pattern distributing fine particulate mass from the sources throughout the region.

On December 25, the lowest concentrations are observed at the background CH site. The concentrations are nearly two-fold lower at CH as compared to the Hong Kong sites and Shenzhen. Concentrations increase from CH to the background TM station by ~ 15 μgm^{-3}. The $PM_{2.5}$ concentration in Guangzhou is not significantly different than the values in Hong Kong and Shenzhen (~ 35 μgm^{-3}). The highest $PM_{2.5}$ concentration occurs at Zhongshan. The winds on December 25 are generally strong (> 4 ms^{-1}) and from the north (Figure 21). As is often the case for northerly flow, the concentrations at CH are low with relatively high $PM_{2.5}$ values in Hong Kong, Shenzhen, and Zhongshan. Once again for a northerly flow case, measurements suggest a significant source of fine particulate matter in Guangdong, between Guangzhou and Shenzhen. The surprisingly low concentrations in Guangzhou are probably due to the extremely high wind speeds, which reach 8 ms^{-1}, resulting in greater than normal atmospheric mixing.

Figure 5 presents the monthly mean $PM_{2.5}$ mass and chemical concentrations for December, 2002. As shown in the figure, the lowest $PM_{2.5}$ concentration is at CH (28 μgm^{-3}), with the highest concentration of 72 μgm^{-3} at Guangzhou. The next highest concentration is observed at Zhongshan (59 μgm^{-3}). The concentrations across Hong Kong range from 31 – 38 μgm^{-3}. The tendency of surface winds on the sampling days, as discussed above, is from the north. Although, winds are often from the south for parts of the sampling days. Overall the spatial distribution of $PM_{2.5}$ concentrations suggests that Guangzhou is a significant regional source of $PM_{2.5}$. As also discussed above there would appear to be a significant source of $PM_{2.5}$ and associated precursors between the Guangzhou and Zhongshan stations as is evidenced by the relatively high fine particulate concentrations observed at the Zhongshan receptor site. As with the month of December, sulfate and organic compounds are the dominant fine particulate chemical components accounting for 24-39% and 19-35% of the $PM_{2.5}$ mass, respectively.

5.1.4 Daily Concentrations During March, 2003

Figure 10 shows the daily $PM_{2.5}$ concentrations for the five 24-hr integrated filter samples during the month of March, 2003. Surface wind speeds and directions as well as precipitation for the month of March are given in Figures 22-26.

Surface meteorological data (Figure 22) indicates relatively light winds with both a northerly and southerly component for the first half of the sampling day on March 1, with pronounced moderate winds from the south for the second half of the day. The concentrations in Hong Kong are relatively high (30 – 40 μgm^{-3}), with the highest concentration occuring at Guangzhou (85 μgm^{-3}). The second highest concentration observed throughout the sampling domain is at Conghua, which has a concentration of nearly 70 μgm^{-3}. The concentration at CH is nearly two-fold higher than values measured in Hong Kong. Overall, the light and shifting winds suggest that the sites are influenced by both local pollution as well as regional sources. The location of the regional influences cannot be directly inferred due to the dynamic nature of the surface winds observed on the sampling day. Although, the dramatic increase in fine particulate concentrations between Hong Kong and CH suggests sources in and around Guangzhou contribute to $PM_{2.5}$ in CH.

On March 7, $PM_{2.5}$ concentrations are relatively low throughout the entire PRD region as is seen in Figure 10. The fine particle concentration in Guangzhou is 40 μgm^{-3}, which is nearly identical to values observed at SZ and ZS as well as at TC. Concentrations at the background CH and TM sites are the lowest values observed over the sampling domain and are ~ 35 μgm^{-3}. The low concentrations are linked with the strong (> 4 ms^{-1}) northerly flow that was observed throughout the region for both the entire sampling day and the day prior to sampling. In addition, light precipitation is observed at both Shenzhen and HKUST on March 6, indicating that precipitation scavenging may also play a role in the relatively low $PM_{2.5}$ concentrations observed on March 7 at the sampling sites.

The distribution of $PM_{2.5}$ concentrations at the stations on March 13 is similar to the concentrations observed at the stations on March 1. Concentrations across the Hong Kong sites are uniform at 30 μgm^{-3}, with a roughly 10 – 20 μgm^{-3} increase at SZ and ZS. The highest concentration of 120 μgm^{-3} is the second highest value observed at any site during the entire study. On this sampling day CH once again experiences the second highest concentration of any of the sampling sites (70 μgm^{-3}). Surface winds (Figure 24) are low and from the north for the first part of the sampling day, and from the south-southeast for the second half of the day. The increase in $PM_{2.5}$ from the Hong Kong Stations to CH is nearly two-fold. Combined with the extremely high concentrations observed in Guangzhou this suggests significant sources in and around GZ. It should be noted that the hypothesized sources of fine particulate matter south of Guangzhou in Guangdong that may be responsible for the high concentrations of $PM_{2.5}$ observed in ZS during northerly flow conditions, may also be influencing Guangzhou $PM_{2.5}$ concentrations on March 13.

On the March 19 sampling day light precipitation is observed at both Fogang and HKUST (Figure 25). On March 18 several of the stations experience east-northeast flow, while all stations are under the influence moderate northerly flow on March 19. On this day, Zhongshan experiences the highest concentration of any site (~ 60 μgm^{-3}). The fine particulate concentration in Guangzhou is uncharacteristically low at 35 μgm^{-3}. Both TC and SZ have fine particulate matter concentrations that are higher than GZ. It is not apparent why this is the case, although it is possible that scattered precipitation plays a role in the regional fine particulate matter concentrations on March 19.

On the March 25 sampling day all stations experience high $PM_{2.5}$ concentrations. At GZ, the $PM_{2.5}$ concentration is ~ 125 μgm^{-3} which is the highest measured value during the field study. Concentrations across Hong Kong are uniformly high and range from 40-50 μgm^{-3}. Conghua has the lowest concentration of 30 μgm^{-3}. As shown in Figure 26, wind speeds are relatively low (< $4ms^{-1}$) and variable on the day prior to and the day of sampling. In fact, at many of the sites winds are less than 1 ms^{-1} for a significant fraction of the sampling day. The meteorological data indicates relatively stagnant conditions in the PRD for much of the sampling period. Combined with the shifting nature of winds this suggests that there is not a great deal of vertical atmospheric mixing, and that advection of clean background air into the region is at a minimal.

The monthly mean chemical composition of $PM_{2.5}$ at each sampling site is presented in Figure 6. Once again organic compounds and sulfate dominate the fine particulate mass accounting for 20-33% and 20-31% of the fine particle mass, respectively. Perhaps one of the most striking observations is the high monthly mean concentration at Conghua (51 μgm^{-3}), which is ~10 μgm^{-3} greater than the concentrations observed across Hong Kong and similar to the concentrations at Shenzhen and Zhongshan. This is due to transport of air from south of CH, resulting from shifting winds from more southerly flow conditions as compared to the prior two sampling months. Guangzhou experiences the highest mean monthly concentration observed at any of the stations of ~ 80 μgm^{-3}. The concentration in Guangzhou is roughly double the fine particle mass concentrations in Hong Kong. The high concentrations observed in

Guangzhou, and throughout the region, are due in part to the meteorology which was marked by low and shifting winds. The dramatic increase in $PM_{2.5}$ from the stations south of Guangzhou to Guangzhou city suggests that local sources and very likely sources just south of the city impact concentrations.

Another fact to point out is that the contribution of 'other', unidentified compounds to the total fine particulate mass concentration is on average 21±5% across all sites. This is in comparison to values of 8±3% and 11±4% for October and December. It is not entirely clear what is responsible for this roughly two-fold increase in unidentified fraction. The most likely reason for the change in the 'other' contribution for March is a shift in the OC correction factor. A factor of 1.4 is applied to all OC measurements to determine the organic compound concentrations, although it cannot be ruled out that the factor varies with season and location. In order to determine the actual correction factor it would be necessary to measure the concentrations of all organic compounds, of which there are several hundreds to thousands. It cannot be absolutely verified at this time that the assumption of a constant OC correction factor is responsible for the increase in the contribution of unidentified compounds to fine particulate mass during March (as well as June which will be discussed below). If it is indeed the reason then the OC concentrations presented during March can be considered as lower limit estimates.

5.1.5 Daily Concentrations During June, 2003

On the first day of the sampling month, June 5, concentrations are relatively high throughout the PRD (Figure 11). The lowest observed concentration is at the Hong Kong background site, Tap Mun, with the highest concentration being nearly two-fold (80 μgm^{-3}) at Conghua. Surface winds are generally from the south across the PRD, although there are times of extremely low wind speeds (< $1ms^{-1}$) as well as periods of light northerly flow (Figure 27). Given the dramatic increase in concentration of roughly two-fold from TM to CH, it is not surprising that winds are primarily from the south during June 5. Given that the winds have both a northerly and southerly component does suggest that multiple source areas influence concentrations across the PRD during the sampling day.

During June 10-11 strong rains occurred throughout the PRD, as shown in Figure 28. Surface wind patterns were generally from south, although several sites also had northerly flow components. As shown in Figure 11, the concentrations at all sites, with the exception of Guangzhou, are low due to precipitation scavenging of particulate matter. Once again the concentration at CH (30 μgm^{-3}) is more than twice that at TM, which is linked with more polluted air from the south being advected into the region. The relatively high concentration in Guangzhou is likely due to local sources as well as transport from the hypothesized source region in Guangdong to the south of Guangzhou.

On June 17, The lowest fine particle concentrations are measured at the CH site (~30 µgm^{-3}). The concentrations at all other sites, besides Guangzhou, are somewhat uniform ranging from 50-60 µgm^{-3}. The PM$_{2.5}$ concentration in Guangzhou is 100 µgm^{-3}, which is the highest value measured at any of the sites for the month of June. In general the concentrations at the Hong Kong sites, Zhongshan and Shenzhen are ~ 30 µgm^{-3} higher than at CH. According to the surface meteorological data (Figure 29) precipitation occurred at several of the sites on the day prior to sampling. Surface wind patterns were primarily from the north on the day of sampling which is not surprising given the differences in concentrations between CH and the more southerly sampling sites.

The last two sampling periods (June 23 and June 29) are characterized by very similar spatial distributions of fine particulate concentrations (Figure 11) as well as surface meteorology (Figures 30 and 31). On both days moderate southerly winds dominate surface meteorology, with rain throughout the PRD region. Concentrations are low and similar (10-15 µgm^{-3}) at all Hong Kong sites as well as at Zhongshan and Shenzhen. The concentration at CH is nearly two times the values at these sites, with Guangzhou experiencing the highest fine particulate concentrations of any of the monitoring sites. Once again, results indicate a significant source of fine particulate mass in Guangdong between the sites south of Guangzhou and Conghua. The relatively low concentrations observed throughout the region are due to precipitation scavenging.

Figure 7 presents the monthly mean PM$_{2.5}$ mass and chemical composition for the month of June, 2003. The Tap Mun station has the lowest observed concentrations, with CH being ~12 µgm^{-3} higher. Concentrations at the other Hong Kong sites as well as Zhongshan and Shenzhen are somewhat similar ranging from 29^{-}35 µgm^{-3}. The monthly mean concentration in Guangzhou is nearly twice that of the more southerly stations. As with the previous sampling months, the chemical composition of fine particulate matter is dominated by organic compounds and sulfate which account for 19-30% and 22-32% of the PM$_{2.5}$ mass, respectively. Overall, the increase in fine particulate matter seen from the more southerly stations (CW, TC, TM, SZ, and ZS) to Guangzhou and Conghua once again suggests significant sources of fine particulate matter in the vicinity of Guangzhou.

5.2 Sub-regional Sources within the PRD

In this section we explore the site-to-site relationships between the concentrations of specific compounds and elements from various sources in order to gain an understanding of how sub-regions within the PRD affect one another. This is accomplished by determining the squares of the correlation coefficients (r^2) for a given tracer between all sites for the entire sampling period. Thus r^2 values are based on linear regressions of 20 data points, representing five 24-hr samples collected during each of the four seasons. Based on r^2 values, the relative contributions from local and distant sources is inferred. High r^2 values (>0.9) between sites suggest that concentrations are not significantly influenced by local sources, while low values (<0.3) suggest local sources dominate. Values that are in the range from 0.5-0.9 indicate a combination of local and more regional sources for a specific compound. It should be pointed out that a site can have a relatively low correlation coefficient with another site and still be influenced by emissions from that site. This is due to the fact that the measurement site in the vicinity of a source will generally be influenced by local emissions while sites further away will be influenced by the particular source (when meteorological conditions are favorable) as well as local sources and other upwind sources when transport is not from the emission source area in question. Hence the combination of sites that have high correlation coefficients for specific species as well as those that have low r^2 values, taken together with chemical concentrations and meteorological factors can be used to infer source regions within the sampling network. Table 14 shows the means and standard deviations for the compounds and elements used in the analyses below. Elemental enrichment factors (EF) are presented in Table 15, with values less than five indicating that soil is the main source of the particular element. This is done to rule out windblown dust as the main source of several trace elements.

5.2.1. $PM_{2.5}$ and Organic Carbon

Correlation coefficient values for $PM_{2.5}$ between all sites are shown in Table 5. An alternative view of correlation between sites is a matrix of scatterplots, each plot linearly fitted via the least-squares method. It should be noted that the scatterplots have varying axis ranges to best show each pairing of sites. The $PM_{2.5}$ scatterplot matrix is shown in Figure 32. The r^2 values for $PM_{2.5}$ among the Hong Kong stations range from 0.71 to 0.94. Within Hong Kong, Tung Chung is the site having the lowest correlation with the other sites. This suggests that TC is more influenced by local sources than the other Hong Kong sites. Nonetheless, the relatively high r^2 values (>0.70) among the sites in Hong Kong is an indication that local $PM_{2.5}$ has much less of a contribution to fine particle contributions as do sources outside of the region.

Shenzhen $PM_{2.5}$ concentrations are also highly correlated with the Hong Kong stations (r^2 values range from 0.74 to 0.83), suggesting that these sites have similar sources. Zhongshan r^2 values with the Hong Kong sites and Shenzhen range from 0.56 to 0.77, suggesting that similar sources influence Zhongshan. It is interesting to point out that both Guangzhou and the background CH site have very low r^2 values (0.22) with all other stations. This suggests that both of these stations are impacted by local sources. In the case of Guangzhou, which has the highest $PM_{2.5}$ concentrations measured throughout the sampling network, it is perhaps obvious that local sources impact $PM_{2.5}$ concentrations. For CH, the lack of strong correlations with other sites may be due to the fact that northerly flow often brings relatively clean background air to the station, with local sources adding to background concentrations.

Although organic compounds make up a significant portion of the $PM_{2.5}$ mass at each site, their correlation coefficients are lower than those calculated for the overall mass, indicating increased local contribution for this specific portion of mass. The OC correlations between sites is shown in Table 6 as well as more visually in Figure 33. Among the Hong Kong sites, r^2 values range from 0.67 to 0.75, with the lowest correlation ($r^2 = 0.67$) between Tung Chung and Central/Western. The pairing of Tap Mun and Central/Western has an r^2 of 0.75, significantly lower than the r^2 value of 0.94 for overall $PM_{2.5}$ mass. Local contributions of organic compounds are expected to be the cause of this increased variability between the sites in Hong Kong. The formation of secondary organic aerosol also may contribute to decreasing the correlation between the stations. The Guangdong sites in close proximity to Hong Kong, Zhongshan and Shenzhen, also have lower correlation coefficients with the Hong Kong sites for organic compounds, in comparison with r^2 values for fine particulate mass. Zhongshan's pairing with the Hong Kong sites yields r^2 values ranging from 0.36-0.46, while the pairing of Shenzhen with the Hong Kong sites results in r^2 values of 0.61-0.72. Further north, sites Conghua and Guangzhou show very low correlation overall (average $r^2 = 0.05$), indicating local sources and perhaps the formation of secondary organic aerosol are the dominating cause of variability at these sites.

5.2.2. Sulfate

Sulfate is a species found in fine particles that is typically associated with the burning of coal and other high sulfur fuels. Although sulfur emissions inventories are not definitively known in the PRD, a recent study conducted by CH2M Hill (29) found that the combination of the energy and industrial sectors accounted for ~ 93% of all SO_2 emissions. A relatively small contribution was found to be due to transportation related sources although it is not entirely clear what role marine vessels, potentially important sources of SO_2, play in the PRD. Taken on face value the CH2M Hill report suggests that marine sources are responsible for roughly a few percent of total SO_2 emissions in the PRD. Among the sampling sites in this study sulfate contributes 21-32% of the fine particulate mass on an annual average. Correlations performed between sites in the Hong Kong region, shown in Table 7 and Figure 34, demonstrate low variability (r^2 = 0.76-0.93). Zhongshan and Shenzhen also show high correlation with the Hong Kong sites and when paired with each other, with r^2 values ranging between 0.82 and 0.90. This high sulfate r^2 values for the southern five sites in the Pearl River Delta suggest that these locations are influenced by the same source region, with only a modest contributions from localized sources with respect to each station. In comparison, the two northernmost sites, Guangzhou and Conghua, have very low correlations with the five southern sites (average r^2 = 0.16) while a higher correlation (r^2 = 0.48) is seen between the Guangzhou and Conghua sites. This shows that local sources have strong influences on the sulfate concentrations at the two sites, and both sites at Conghua and Guangzhou may be receiving sulfate emissions from some of the same sources. These results are consistent with the interpretation that source regions within Guangdong, in particular the Guangzhou area, have a significant influence on air quality in southern Guangdong and Hong Kong.

5.2.3. Crustal Species

Silica atoms are second only to oxygen in terms of average mass concentration in the Earth's crust. Found in abundance across the globe, silica is commonly used to determine crustal contribution to fine particle concentrations. In Table 8 and scatterplot matrix 35, a very high correlation is seen among the three sites in Hong Kong, with r^2 values ranging from 0.93 to 0.97. Such high r^2 values among Tap Mun, Tung Chung, and Central/Western indicate a regional advection of crustal materials to the Hong Kong sites rather than contribution from local sources. Extending comparison to Shenzhen and Zhongshan, moderate correlation (average r^2 = 0.77) is seen between the two and in pairing with the Hong Kong sites. It appears that Shenzhen and Zhongshan may have independent sources of crustal material influencing concentrations at their respective locations. This may be the reason that concentrations at these sites (Table 14) are nearly twice the values in Hong Kong. With the highest silica concentrations on nearly every sampling day, Guangzhou shows no correlation with the six other sampling sites (average r^2 = 0.05). Such high variability indicates that local sources dominate crustal material found in fine particles at the Guangzhou site. The source of elevated silica in Guangzhou is not entirely clear, although possibilities include construction and changes in land use due to urban development. Though further north than Guangzhou, measured silica concentrations in Conghua have slightly higher correlation with the

Hong Kong sites, Shenzhen, and Zhongshan, with r^2 values ranging from 0.36 to 0.49. It can be concluded that large-scale transport of crustal material may strongly contribute to background concentrations across the Pearl River Delta region. In looking at the daily concentrations of silica, sampling date October 8th is of note for a near quadrupling of measured silica levels at all sites except for Guangzhou. This date is shown to have no rainfall and moderately high winds from the north.

Iron is a second mineral element that is commonly used as a tracer for crustal material in $PM_{2.5}$. Table 15 indicates enrichment factors for both iron and silica that clearly indicate they are crustal in nature. Like silica, regressions performed on iron concentrations yielded very high r^2 values among the three Hong Kong sites ($r^2 = 0.91$ to 0.96), with lower correlation seen in combination with sites Shenzhen and Zhongshan ($r^2 = 0.53$ to 0.79). Guangzhou is again seen to have no correlation with the Hong Kong sites, Shenzhen, and Zhongshan (average $r^2 = 0.02$) though a low correlation ($r^2 = 0.23$) is seen between Guangzhou and Conghua. Conghua has low correlations with the Hong Kong sites, though slightly higher correlations (average $r^2 = 0.23$) with the four sites in Guangdong. As with silica, a spike in iron concentrations is seen again on October 8th. Again, the results suggest a source of crustal material in the vicinity of Guangzhou.

5.2.4. Mobile Sources

The concentration of elemental carbon (EC) in fine particles is associated with combustion, in particular of diesel fuel. It should also be noted that EC in PM_{10} at specific sites in Hong Kong has also been attributed to harbor emissions from shipping (Yu et al., 2004). It can be seen in Table 10 and Figure 37 that elemental carbon varies significantly from one site to the next, with a peak correlation for the region of $r^2 = 0.66$ for the pairing of Tung Chung and Central/Western. Correlation is moderate for the Hong Kong sites, Shenzhen, and Zhongshan, with an average r^2 of 0.38. This signifies a strong local influence of mobile sources on elemental carbon at sites in the Hong Kong region. Conghua has virtually no correlation with any other site, with r^2 values ranging from 0.00 to 0.06. Guangzhou, with nearly double the amount of elemental carbon compared with the other measured sites (Table 14), has a moderate correlation with Zhongshan ($r^2 = 0.39$), though very low correlation with any other site. Overall, local sources appear to be the significant cause of concentrations of EC at each site.

Though lead can be found naturally in the earth's crust, the use of lead-containing gasoline can cause significantly higher lead concentrations in fine particles. While our crustal tracers, silica and iron, both show a significant peak on the October 8th measuring day, the lead species does not. In addition, the enrichment factor for lead shown in Table 15 is ~6000. Combined with the observation of unnaturally high lead levels across the region, this indicates that anthropogenic sources, presumably combustion of leaded gasoline, dominate lead concentrations. Although, it is possible that other sources, such as lead smelting, may be the cause of the relatively high lead concentrations observed throughout the region. It is important to point out that the high concentrations of lead may not be only due to current lead emissions but also from re-suspension of Pb deposited to the surface. Given the relatively minor role that dust plays in fine particulate concentrations in the PRD it is not clear to what extent re-suspension of anthropogenic Pb contributes to observed lead concentrations. It is shown in Table 11 and Figure 38 that the correlation of lead among the seven sites is very different from the linear regression results of elemental carbon. Though EC has relatively high variability at each site, lead has quite low variability among the three sites in Hong Kong and Shenzhen, with a range of r^2 values from 0.73 to 0.96. For these four sites, it is evident that regional transport of anthropogenic lead dominates the local concentrations. Although it should be noted that the annual concentration of Pb at Shenzhen is ~ 30% greater than at the Hong Kong sites indicating the Shenzhen may also contain sources of Pb. Zhongshan has moderate correlation with the Hong Kong sites and Shenzhen (average $r^2 = 0.45$) and very low correlation with Guangzhou and Conghua (average $r^2 = 0.06$), pointing towards a combination of local and regional sources at this site. Guangzhou and Conghua have very low correlations with all other sites (average $r^2 = 0.08$), indicating that local sources strongly influence lead concentrations at each site. It is important to point out that the concentrations of lead at Guangzhou (Table 14) are nearly four times higher than at Hong Kong/Shenzhen indicating that this area is a significant source of lead throughout the region.

5.2.5. Biomass Burning

Found in tissues of plants and animals, potassium is an element often used to trace emissions from biomass burning. Potassium is also found in the earth's crust, but as with lead, has been measured to be at much higher levels than if the element was coming from crustal material alone (Table 15). High correlation is seen of potassium concentrations measured at the three Hong Kong sites and Shenzhen (average $r^2 = 0.88$), shown in Table 12 and Figure 40. With such high correlation, it is expected that emissions of potassium from outside of the region encompassed by these four sites dominates the concentrations. Zhongshan shows lower r^2 values when paired with the Hong Kong sites and Shenzhen (average $r^2 = 0.60$) and no correlation with Guangzhou and Conghua (average $r^2 = 0.03$). Guangzhou and Conghua have a lack of correlation with the other sites and with each other, yielding r^2 values ranging from 0.00 to 0.21. Local sources are expected to be partially influencing concentrations at Zhongshan and strongly influencing concentrations at Conghua and Guangzhou. It should be noted that the annual mean potassium concentrations at both Conghua and Guangzhou are similar at 1.6 μgm^{-3} (Table 14), roughly 2-3 times higher than the Hong Kong sites, suggesting that biomass burning in northern Guangdong is prevalent.

Rubidium (Rb) is a second element that is also found in plant and animal tissues, but in much smaller concentrations in comparison with potassium. Due to detection limits in chemical analysis, rubidium has not been commonly used as a source tracer element. For the Pearl River Delta region, however, rubidium concentrations were high enough for detection and proved to be very highly correlated with potassium measurements, when the two were paired at a specific site (average $r^2 = 0.91$). Although it cannot be verified at this time, it is possible that rubidium is also a tracer for biomass burning given that it is incorporated in plant tissues in a similar fashion as potassium. Rubidium may be present in soils in the PRD and/or present in fertilizer that also contains potassium and hence incorporated into plants along with potassium. Nonetheless, here we suggest that rubidium is a tracer for biomass burning and use it along with potassium concentrations to infer sub-regional source areas. As with potassium, Table 13 and Figure 39 show the high correlation of rubidium concentrations within the three Hong Kong sites and Shenzhen, with r^2 values ranging from 0.79 to 0.93. Zhongshan shows lower r^2 values when paired with the four previous sites, with r^2 ranging from 0.39 to 0.46. Guangzhou and Conghua have very low correlation, with an average r^2 value of 0.12. Again, the trend is seen of regional influence at Tap Mun, Tung Chung, Central/Western, and Shenzhen, partial local influence at Zhongshan, and strong local influences at Guangzhou and Conghua.

5.3. Concentrations of Organic Tracer Compounds and CMB Modeling

In this section the concentrations of a variety of solvent extractable organic compounds are presented and discussed. The compounds are shown in Table 16 and represent a variety of sources including biomass burning, gasoline and diesel combustion, coal combustion, cooking, and road dust. Figure 41 shows measured source profiles of specific solvent extractable organic compounds, indicating that sources have unique organic tracers as well as compounds that have several sources in common. The concentrations presented and discussed below are monthly mean values based on composited daily samples for each month. The relative concentrations of specific compounds and classes of compounds are used to infer differences in sources of primary organic particulate matter across the PRD. Primary organic carbon source apportionment is utilized through a chemical mass balance (CMB) model (37). In addition, Hi-volume filter samples collected over 24-hour sampling times during 4 separate days at Yuen Long and Tung Chung are analyzed and discussed. More detailed information on sample preparation, handling and analyses can be found in Appendix B. More on the technique of identifying specific solvent extractable organic compounds, the sources of these compounds, and the application of CMB modeling is described by Schauer et al. (1996).

5.3.1 Organic Carbon and Elemental Carbon

Before presenting the concentrations of solvent extractable organic compounds, the concentrations of OC and EC both seasonally and spatially in the PRD will be discussed. The seasonal and spatial distributions of OC and EC are shown in Figure 42**,** and the ratios of EC to OC are shown in Figure 43. As can be seen in Figure 42, Guangzhou has the highest average OC concentration (17.6 μgm^{-3}), followed by ZS (10.6 μgm^{-3}), SZ (10.1 μgm^{-3}) and CH (9.3 μgm^{-3}). The samples collected from the three Hong Kong sites had the lowest OC concentrations (CW 6.6 μgm^{-3}, TC 6.3 μgm^{-3}, and TM 4.9 μgm^{-3} on average). The highest EC annual average concentrations occur at GZ (4.4 μgm^{-3}), followed by SZ (3.6 μgm^{-3}), ZS (2.5 μgm^{-3}), TC (2.0 μgm^{-3}), and CW (1.9 μgm^{-3}). The samples from the background sites CH (1.4 μgm^{-3}) and TM (0.8 μgm^{-3}) have the lowest EC concentrations. The relatively low concentrations of EC at the background sites, high concentrations at urban sites and general variability of EC throughout the sampling region supports the notion discussed previously that EC to a large extent is influenced by local sources. Generally speaking EC and OC concentrations are lowest in summer due to increased precipitation and scavenging of particulate matter.

It is worthwhile to note that the EC concentrations are generally lower during the present study than measured during November 2000 to October 2001 as part of the 'Twelve-month particulate matter study in Hong Kong' funded by the Hong Kong EPD. As part of the pilot study annual mean concentrations for the rural Hok Tsui site were 1.3 μgm^{-3}, for urban Tsuen Wan 5.9 μgm^{-3}, and for the roadside Mong Kok site 19.7 μgm^{-3}. There is not a site similar to Mong Kok in the present study so a direct comparison cannot be made. The Tap Mun site has an annual mean concentration of 0.8 μgm^{-3}, significantly less than the value previously measured at Hok Tsui. Both CW and TC have EC concentrations in the present study more than a factor of two lower than measured at Tsuen Wan for the pilot study. There are several potential reasons for the apparent discrepancy. First, it is possible that the current stations are influenced by a different distribution of sources. Indeed the relatively high EC concentrations at Tsuen Wan suggest the dominant influence of diesel vehicles. It is also possible that EC concentrations are different due to subtle differences in analytical techniques. Although, measurements were made using a similar thermal evolution technique for both studies. Another possibility is that EC is lower in Hong Kong during the present study, perhaps due to a decrease in diesel emissions.

The EC/OC ratio provides information on the source of OC with higher ratios (>1) typically associated with diesel exhaust, although the burning of fuel oil also has relatively high EC/OC (Figure 44). As will be discussed later in the report, the EC/OC ratio for the coal source profile which represents residential coal burning in Beijing, may not be representative of coal burning emissions in the PRD. Hence, caution must be used when inferring general sources based on EC/OC ratios since it is possible that this ratio is either higher or lower for the coal burning taking place across the PRD. Generally speaking the EC/OC ratio is able to implicate the importance of diesel exhaust to the total organics in fine particulate matter only when the contribution from other EC sources (e.g. fuel oil, biomass burning and coal combustion) is insignificant. It should also be noted that the formation of secondary organic aerosol may also decrease the ratio through the formation of OC. The highest annual average EC/OC ratios are found at the SZ (0.35), TC (0.32), and CW (0.29) sites. The GZ and ZS samples have slightly lower EC/OC ratios (0.25 for GZ and 0.23 for ZS). The results generally suggest that the relative importance of diesel exhaust to fine OC is higher at the SZ, TC and CW than at GZ.

5.3.2 Organic Tracers in Monthly Aggregate $PM_{2.5}$ Samples

The organic tracers including *n*-alkanes, PAHs, steranes, hopanes, resin acids, and levoglucosan were identified and quantified in the PM2.5 samples collected form the HKEPD monitoring network including TM, TC, CW, CH, ZS, SZ, and GZ. The concentrations of these organic species are listed in Table 17. In the following section, results are presented for hopanes and steranes which are abundant in lubricating oils used in both diesel and gasoline powered vehicles (38). They can be used as molecular tracers for the fine particulate matter emitted from motor vehicles (39). Levoglucosan is a major constituent of the fine particle emissions from cellulose during biomass burning and has been widely accepted as a major tracer for biomass burning (40). PAHs are the products of incomplete combustion from variable sources, such as fossil fuel combustion and biomass burning. Important sources for PAHs include automobile emissions, coal combustion, biomass burning, and natural gas combustion (Figures 41a, c). Picene, a PAH with molecular weight of 278, is a unique emissions product from the burning of coal (Figure 41c) and thus has been selected as a tracer of coal combustion (41).

5.3.2.1 Hopane and Sterane (H+S) Concentrations

The concentrations of H+S were found the highest in the samples collected from GZ (17.1-20.7 ngm^{-3}), ZS (1.2-15.1 ngm^{-3}), and SZ (4.8-8.7 ngm^{-3}). Lower concentrations are observed at CH (1.1-2.5 ngm^{-3}), TM (0.2-1.4 ngm^{-3}), TC (1.0-3.6 ngm^{-3}), and CW (1.4-4.5 ngm^{-3}) (Figure 45). Concentrations of hopanes and steranes are lowest during the summer, which is not surprising given the frequency and amount of precipitation. It should be noted that the ZS fall sample showed extremely high concentration of H+S (15.1 ngm^{-3}), most likely due to transport from the Guangzhou area that readily occurred during the fall month. At the urban Guangzhou site, hopanes and steranes were uniformly high throughout the year suggesting intense local mobile source emissions.

Figure 46a shows the ratios of H+S to fine OC concentrations. Since H+S are mainly from motor vehicles, the normalization of H+S to OC can indicate the relative importance of motor vehicle emissions to OC concentrations, with high values indicating that mobile sources play a relatively important role. The highest annual average ratios are found at GZ (~1.0 e^{-3}) and Shenzhen (0.7 e^{-3}) as well as during October in Zhongshan (1.2 e^{-3}). Thus results suggest that mobile sources significantly contribute to OC at GZ and SZ as well as during fall in ZS.

The ratio of H+S to elemental carbon (EC) can be used to infer the relative contributions of diesel and gasoline emissions to OC at a particular location with diesel vehicles emitting relatively more EC and hence having lower H+S to EC ratios. Although, it should again be pointed out that coal burning also potentially emits both hopanes and steranes, and can thus influence H+S/EC ratios. An assumption in attributing hopanes and steranes to mobile sources in the present case assumes that contributions from coal burning are negligible. Given the current lack of knowledge of the coal burning source profiles in the PRD this assumption can not be verified. Figure 46b shows the previous emission test studies for H+S to EC ratios from four emission sources (42, 43, 44) . The (H+S)/EC ratios are 4.6 e^{-4} and 0.15 for the diesel- and gasoline-powered vehicle exhausts, respectively. In the present study, the average H+S to EC ratios (in ascending order) are 8 e^{-4} at TM (4 e^{-4} – 2 e^{-3}), 1.2 e^{-3} at CH (9 e^{-4} - 2 e^{-3}), 1.3 e^{-3} at TC (8 e^{-4} - 2 e^{-3}), 2 e^{-3} at CW (1 e^{-3} – 2 e^{-3}), at SZ 2 e^{-3}, 3 e^{-3} at ZS (9 e^{-4} – 7 e^{-3}), and 4.4 e^{-3} at GZ (3.7e^{-3} - 6.e^{-3}) (Figure 46c). All of the H+S to EC ratios were smaller than 0.15 but larger than 4.6e^{-4}. Overall, the results indicate that mobile source emissions of primary organic carbon in Guangzhou are very likely dominated by gasoline vehicles as compared to diesel exhaust. This inference is also supported by the relatively high Pb concentrations observed in Guangzhou relative to the other sampling sites.

5.3.2.2 Levoglucosan Concentrations

Figure 47 shows the distribution of levoglucosan concentrations among the seven sites. At five of the seven sites the highest concentrations of levoglucosan are found in the winter samples (from 207 to 813 ng m^{-3}). At Tung Chung, the highest concentration is observed during the fall, while at CH the second highest concentration observed across all stations occurs in spring. It is unclear why the Tung Chung concentration is so high in the fall as compared to the other Hong Kong sites. With the exception of the fall levoglucosan concentration, the concentrations across Hong Kong are similar during each season. This is in agreement with the observed K and Rb concentrations at the sites, and generally supports the notion that biomass burning from outside of Hong Kong is responsible for biomass related PM in the area.

The highest annual average concentration of levoglucosan occurs at GZ (508 ngm^{-3}), followed by CH (351 ngm^{-3} on average), ZS (321 ngm^{-3}) SZ (216 ngm^{-3}), TC (159 ngm^{-3}), CW (125 ngm^{-3}), with the lowest concentration at Tap Mun (110 ngm^{-3}). The relative relationship between the annual mean concentrations between the sites is generally similar to that observed for K and Rb suggesting that these elements are from the same sources as levoglucosan. The relatively high concentrations in both CH and GZ indicate that Guangdong province is a significant source of biomass burning aerosol.

The annual mean concentrations of levoglucosan during the previous Hong Kong pilot study were 51 ngm^{-3}, 81 ngm^{-3} and 213 ngm^{-3}, at Hok Tsui, Tsuen Wan and Mong Kong, respectively. Values during the present study are within this range of values. Although it is worthwhile to note that concentrations at Mong Kok were significantly higher compared to the other sites during the Pilot Study, and the reason was attributed to possible local sources. Leaving out the roadside Mong Kok site, it would appear that concentrations of levoglucosan measured during this study are higher than values reported for the previous study, possibly indicating that biomass burning played a more significant role in fine particulate concentrations during the current study. It is not entirely clear why levoglucosan concentrations perhaps increased during the present study although it could be due to changes in meteorology as well as in emissions throughout the PRD.

5.3.2.3 PAH Concentrations

Figure 48 shows the spatial and seasonal distributions of specific PAH concentrations. The samples collected from the sites in Guangdong (CH, ZS, SZ and GZ) have much higher PAH concentrations than the Hong Kong samples (TM, TC and CW). The highest annual mean concentration of total PAHs is at GZ (49 ngm^{-3}), followed by ZS (42 ngm^{-3}), SZ (30 ngm^{-3}), CH (21 ngm^{-3}), TC (9 ngm^{-3}), CW (9 ngm^{-3}), and TM (6.0 ngm^{-3}). Generally speaking, at all seven sites PAH concentrations are lowest in summer, with winter samples typically having highest concentrations. An exception to this is the concentration in Zhongshan during the fall which has the highest measured PAH concentration of any of the measurements. The reason for this is unclear, but may include transport of air from the Guangzhou area as well as the influence from more localized sources of the specific PAHs.

The PAH concentrations were grouped by their molecular weights and normalized to the total PAH concentration (Figure 49). Two groups of PAHs are further classified based as low molecular weight PAHs (PAHs with molecular weight less than 252) and high molecular weight PAHs (PAHs with molecular weight equal to or higher than 252). As can be seen in Figure 49, the samples have obvious regional characteristics with regards to relative PAH fractions. The proportion of the low molecular weight PAHs (e.g., PAHs with molecular weight 202, 226 & 228 and their methyl substitutions) is higher for the Hong Kong samples than for the PRD samples. Similarly, the high molecular weight PAHs (e.g., PAHs with molecular weight 252, 276 and 300) account for a smaller proportion of the total PAHs in the Hong Kong samples. The relative differences may be due to several reasons, including transformation of higher molecular weight compounds to lower molecular weights during transport as well as differences in the distribution of PAHs emitted from the sources impacting the concentrations at the sites.

5.3.3 Organic Tracers in Episodic High Volume Samples

Four specific sampling events were chosen and high volume filter samples were obtained over 24-hour integrated sampling periods at Tung Chung and Yuen Long, an urban site in the northern new territory. The dates were chosen to represent time periods of relatively high particulate matter concentrations in Hong Kong (December 13 and 19, 2002; March 25, 2003) as well as a day having extremely low concentrations (October 20, 2002). The overall objective of the high volume sampling is to evaluate the extent to which daily samples represent monthly composite samples, and to determine the spatial variability of specific organic tracer compounds across Hong Kong for specific events. The high volume samples have an advantage in that they collect enough particulate carbon mass during a 24-hr period to allow for the characterization of single event organic compound concentrations. Comparing side-by-side high volume and low volume samples at Tung Chung reveals high volume OC concentrations that are nearly 60% greater than low volume values. In addition, an extremely large organic compound spike is found in the high volume samples that is not present in the low volume samples. The compound appears to be impactor oil used in the high volume sampler impactor. The contaminant clearly interferes with several organic tracer compounds and further analyses are needed to determine the extent to which the contaminant influences the tracer compound concentrations identified in the present study. The concentrations of the high volume organic compounds as well as a report discussing the differences in the concentrations between the sites for the sampling days is presented in Appendix F. Although, it should be noted that at the present time it is not possible to draw conclusions from the data based on the presence of contamination. It should be pointed out that additional studies are needed to assess the source of the contaminant and extent to which the samples can be used to infer sources based on the analyses of organic compounds.

5.3.4 Source Apportionment of Primary Fine Particulate Organic Carbon

The source profiles used for CMB model, including diesel exhaust, gasoline exhaust, vegetative detritus, biomass burning, cigarette smoke, road dust, meat cooking and natural gas combustion, were obtained from previous studies in North America and applied to this study (33, 42, 43, 45, 46, 47, 48) . The coal source profile was obtained from the analysis of fine particulate matter emitted from the burning of Datong coal in China (44) . For the biomass burning source, the source profile for wood combustion (33) is used in the present study. The eight source profiles used in the present study are shown in Figures 41a-c. Given that source profiles have not been directly measured in Hong Kong, the model inputs served as the best estimates of the actual emission profiles based on available data.

The results of the CMB source apportionment are shown in Figure 50 and in Table 18. Up to eight emission sources including diesel exhaust, gasoline exhaust, meat cooking, cigarette smoke, biomass burning, road dust, vegetative detritus, and coal combustion are identified. The contribution from cigarette smoke should be regarded as an upper limit estimate since the major tracers (iso-nonacosane, anteiso-triacontane, and iso-hentriacontane) could be influenced by local vegetative detritus. As discussed in the previous section, significant sources of dust exist in Guangdong in addition to dust that is transported into the PRD region as well as generated locally due to the re-entrainment of road dust. It is not clear that the dust measured at the site is associated with anthropogenic organic compounds as is the case with road dust. Despite this point, it is assumed that elemental tracers for dust are associated with organic compounds present in road dust. Therefore, estimates of the contributions of road dust to primary organic carbon can be considered as upper limit estimates. It should also be pointed out that there are potentially important sources of direct emissions of organic carbon that are not included in the CMB modeling due to lack of adequate source profile information. An example of one such source are marine sources related to shipping and transportation. Although it is not entirely clear that marine sources influence the concentrations of organic carbon in the PRD, the relatively heavy marine traffic in the area may be a source of both primary PM as well as compounds that contribute to secondary PM.

5.3.4.1 Biomass Burning

The highest annual mean concentrations of primary fine particulate OC estimated by the CMB for biomass burning is at the GZ site (3.74 μgm^{-3}), followed by CH (2.47 μgm^{-3}), ZS (2.24 μgm^{-3}), SZ (1.61 μgm^{-3}), TC (1.18 μgm^{-3}), CW (0.98 μgm^{-3}), and TM (0.81 μgm^{-3}). The high concentrations of particulate OC from biomass burning estimated at the CH site is in accordance with high levels of levoglucosan found in the CH samples. The elevated concentrations of biomass burning aerosol in Guangdong, which are in agreement with K and Rb concentrations relative to the other sampling sites as previously discussed, indicate that Guangdong is a significant source of these aerosols in the PRD. It should be pointed out that for the seven measured sites in the PRD, biomass burning is estimated to account for on average 18% of the measured fine particulate OC mass, ranging from 27% at Conghua to ~14% at Shenzhen and CW as shown in Table 19. At 5 of the 7 sites biomass burning is the most pronounced source of annual fine particulate OC based on CMB model results.

It is apparent that biomass burning is estimated to be a much more significant fraction of primary fine particulate OC during the present study as compared to the Pilot Study. As pointed out earlier, with the exception of the Mong Kok roadside site, levoglucosan concentrations are higher during the present study. Although, it should be noted that it is difficult to make direct comparisons of the concentrations measured during the two separate studies since the sampling sites are not the same, indicating that they may be influenced by different sources. Nonetheless, given that the same source profiles are used for both studies, the results indicate an increase in the biomass burning contribution for the current study.

5.3.4.2 Meat Cooking

Meat cooking exhaust was found the highest (annual mean) at the CH rural site (2.20 μgm^{-3}), followed by GZ (2.14 μgm^{-3}), SZ (1.25 μgm^{-3}), CW (1.00 μgm^{-3}), ZS (0.81 μgm^{-3}), TC (0.64 μgm^{-3}), and TM (0.38 μgm^{-3}). The urban sites (GZ, SZ and CW) had generally higher meat cooking exhaust than the receptor (ZS and TC) and rural (TM) sites. CH had the highest contribution from meat cooking very likely due to local sources in the vicinity of the sampling site. The CMB results for meat cooking at CH correspond well with the concentrations of nonanal (the tracer used for meat cooking), with the highest mean value in the CH samples (11.38 ngm^{-3}). The results are similar to values measured during the previous Pilot Study, with annual means of 1.45, 0.78 and 0.26 μgm^{-3} at MK, TW and HT, respectively. However, it should be noted that the style of meat cooking in the PRD is different than in the United States and therefore the source profile may not sufficiently estimate the actual contributions of cooking to primary OC mass. Given the fact that meat cooking contributes significantly to fine OC mass at several of the stations in the PRD suggests the importance of future studies to determine source profiles for the region.

5.3.4.3 Diesel Exhaust

The highest yield for diesel exhaust is obtained from the SZ site (2.06 μgm^{-3}), GZ (1.71 μgm^{-3}), CW (1.36 μgm^{-3}), TC (1.23 μgm^{-3}), ZS (0.86 μgm^{-3}), TM (0.43 μgm^{-3}), and CH (0.31 μgm^{-3}). The highest EC/OC ratios were also found in the SZ samples. Diesel exhaust at the SZ site is expected to be significant due to the large number of diesel-powered container trucks commuting between Hong Kong and Shenzhen. The relatively high variability between sites suggests local sources influence most of the sampling sites, as has been already inferred based on the spatial distribution of EC concentrations. The estimated contribution of diesel exhaust to annual mean measured OC concentrations ranges from 4% and 8% at the urban CH and TM stations to ~ 20% at TC, CW, and SZ. Across Hong Kong the annual mean contributions range from 9-20%. These values are much lower than mean contributions of 25% at the background Hok Tsui site to 60% at the urban Tsuen Wan location estimated for the Pilot Study. The primary reason for the difference is the much lower EC concentrations measured in Hong Kong during the current study, which are used in the CMB model to estimate the contribution of diesel exhaust. As discussed earlier this may be due to several factors including subtle differences in EC measurement techniques between the two studies (although this is unlikely), shifts in emissions, site differences, and changes in meteorology during the studies. Nonetheless, it should be pointed out that in the current study the EC concentrations were measured using the same laboratory and instrumental setup as for the source profile samples used in the CMB model and therefore a bias should not exist in the present CMB estimates based on EC measurement techniques. Overall the results suggest that diesel emissions have a significant influence on fine particulate OC concentrations, particularly at the urban and receptor sites.

5.3.4.4 Gasoline Exhaust

Unlike diesel exhaust, the contribution of gasoline exhaust to fine particulate OC is the highest at the GZ site (2.82 µgm^{-3}), followed by ZS (1.30 µgm^{-3}), SZ (0.83 µgm^{-3}), CH (0.51 µgm^{-3}), CW (0.48 µgm^{-3}), TC (0.35 µgm^{-3}), and TM (0.25 µgm^{-3}). The sites in Guangdong appear to be more influenced by gasoline exhaust than those in Hong Kong. Even at the rural site in the PRD area (CH), the level of gasoline exhaust is as high as in urban Hong Kong (CW). On average gasoline exhaust accounts for 5-7% of the measured fine particulate organic carbon at the Hong Kong stations, which is a factor of 2-4 less than the % contribution from diesel exhaust. Hence the results suggest that among mobile sources, diesel emissions are more prominent than that of gasoline vehicles in Hong Kong. The contribution of gasoline vehicles at Guangzhou to annual measured OC concentrations is 16%, as compared to 10% for diesel vehicles. These results suggest that Guangzhou is a significant source of gasoline vehicle related pollutants. It is possible that the relative increase in the amount of OC attributed to gasoline vehicles is linked with differences in the profiles of mobile sources emissions in Guangzhou. For example, if diesel vehicles in Guangzhou emit a great proportion of H+S as compared to the Hong Kong sites a bias would exist in estimated that is not related to actual emissions. It should be pointed out that the CMB attribution of a significant fraction of primary OC to gasoline vehicles is in line with the relatively high concentrations of Pb measured in Guangzhou, and it is interesting to point out that Pb concentrations are roughly a factor of 5 higher in Guangzhou than in Central/Western, which is roughly the ratio of estimated gasoline vehicle organic carbon at the two sites. These results generally suggest that gasoline vehicle emissions in the Guangzhou area influence fine particle OC concentrations regionally throughout the PRD.

The results of the current study are in general agreement with the Pilot Study that found relatively insignificant (< 5%) contributions of gasoline vehicles to fine particulate organic carbon at Hok Tsui and Tsuen Wan. At the roadside Mong Kok station the annual mean concentration of OC estimated to be from gasoline vehicles was 1.12 µgm^{-3}, which accounted for 8% of the measured OC at that site. It is worthwhile to point out that the Guangzhou estimated annual mean concentration attributed to gasoline vehicles is more than a factor of 2 greater than that measured at Mong Kok. This is somewhat surprising given that the site in Guangzhou is urban but not located directly at roadside. This underscores the impact of mobile sources, and in particular gasoline vehicles, on fine particulate OC in Guangzhou.

5.3.4.5 Incomplete Combustion of Coal

The contribution of coal combustion to primary OC is estimated to be relatively minor (< 5%) in Hong Kong. In Guangdong the contribution of the incomplete combustion of coal is estimated to account for from 8% of the measured OC at Conghua to 12% at Zhongshan. It is interesting to note that the highest contribution of coal to primary OC at ZS may be due to the apparent source region of particulate matter that is suggested to exist in Guangdong between Guangzhou and the location. It was also estimated in the Pilot Study that coal combustion had a minor contribution (<5%) to measured fine particulate OC. As previously discussed, it is not clear that the coal source profile for Beijing coal well represents the actual burning of coal that takes place across the PRD. Hence, caution must be used in attributing coal combustion to primary organic carbon concentrations. It should be noted that an SO_2 emission inventory has been generated for the PRD, and roughly 40% of SO_2 emissions were attributed to electricity generation with ~60% due to industrial purposes. Based on the emissions inventories it not possible to infer a general source profile for the region given that the methodologies of coal combustion as well as type of coal being burned is not known. The lack of knowledge of the actual coal source profile influences not only the CMB estimate of the coal contribution, but also that of mobile sources since coal burning can generate hopanes and steranes as well as EC both of which are used as tracers for these sources.

It should be pointed out that although coal does not appear to significantly influence OC concentrations it does indeed impact sulfate contributions, which are relatively high (annual mean values at monitoring sites ranging from ~ 9 μgm^{-3} at the Hong Kong sites to μgm^{-3} at Guangzhou). Therefore, the CMB results should not be interpreted to mean that coal burning does not contribute to overall fine particulate matter in the PRD, given that through sulfate, coal burning accounts for a significant fraction of the PRD's $PM_{2.5}$.

5.3.4.6 Road Dust

As pointed out earlier, road dust contributions should be considered to be absolute upper limit estimates since it is not clear that the elements associated with dust are accompanied by organic compounds. Particularly given the fact that Guangzhou appears to be a tremendous source of dust related elements, and that other locations are likely influenced by transport from the Guangzhou area and not necessarily locally emitted road dust. The estimated contributions of road dust to fine particulate organic carbon for the seven sites are estimated to be 0.91 (GZ), 0.75 (ZS), 0.64 (SZ), 0.53 (CH), 0.40 (TM), 0.38 (CW), and 0.33 μgm^{-3} (TC). The concentrations of road dust are uniform across Hong Kong, which relates to the similar uniformity in concentrations of the dust tracers Si and Fe measured in Hong Kong. Overall, road dust is estimated to account for on average an upper limit of 5 – 8% of fine particulate organic carbon in the PRD.

5.3.4.7 Cigarette Smoke

The contribution of cigarette smoke to OC concentrations is highest at GZ (0.72 μgm^{-3}), followed by ZS (0.24 μgm^{-3}), SZ (0.23 μgm^{-3}), CW (0.19 μgm^{-3}), TC (0.14 μgm^{-3}), CH (0.13 μgm^{-3}), and TM (0.05 μgm^{-3}). The contribution of cigarette smoke to fine particulate OC across all sites is on average 2% (with a range of from 1-4%). As stated earlier, concentrations of cigarette smoke tracers can be influenced by the presence of vegetative detritus, which are found in samples at all sites, and therefore the contributions from cigarette smoking should be taken as upper limit estimates. Regardless, these results suggest that cigarette smoke has a negligible influence on OC concentrations measured at sampling sites within the PRD during the present study.

5.3.4.8 Vegetative Detritus

The estimated contribution of contribution from vegetative detritus to fine OC is the lowest among the eight identified emission sources, with the highest annual mean (~0.21 μgm^{-3}) located at both CH and GZ, followed by ZS (0.13 μgm^{-3}), and SZ (0.09 μgm^{-3}). Similar low levels of vegetative detritus are found at the three Hong Kong sites (0.07 μgm^{-3} each). Overall CMB results indicate that vegetative detritus plays a minor role in fine OC in the Pearl River Delta.

5.3.4.9 Organic Carbon Not Accounted For by CMB and Water Soluble Organic Carbon (WCOC)

The difference between the measured organic carbon and the OC concentration estimated from the sum of the identified sources using CMB modeling is given in Figure 50 and classified as ‘other OC’. This other OC can be due to a variety of factors including unidentified sources, uncertainties in the CMB modeling, and potential artifacts in sampling carbonaceous particulate matter. Another possible explanation is secondary organic aerosol, which is not attributed to primary emissions in the CMB model. Dr. Jian Yu of HKUST conducted a variety of analyses as part of the PRD project including water soluble organic carbon (WSOC) concentrations (Appendix G). In general, oxidation of organic compounds in the gas-phase as well as heterogeneously on existing particulate matter will lead to more polar water soluble compounds. Figure 51 shows the relationship between % 'other' organic carbon defined as OC not identified by the CMB Model, and the% WSOC, both presented as a fraction of the measured OC concentration. The results are annual averages for all sampling sites. Interestingly, there is a clear relationship between other organic carbon and WSOC. In general the Tap Mun site has the highest fraction of both 'other' OC and WSOC, with lowest relative values at GZ. This may be due to a greater fraction of secondary organic aerosol present at the remote TM site, generated during transport from source regions, and less of a fraction at GZ due to the prominence of primary OC emissions. The differences seen for the sites could also be due to differences in the sources influencing the OC concentrations at each location.

6.0 Acknowledgements

This report arose out of the Hong Kong and Pearl River Delta Pilot Air Monitoring Project (the Project). The Project was split into two focus areas with Project 1 gaining further understanding on the characteristics of Ozone in Hong Kong and Project 2 focusing on the characteristics of fine particulates in the Pear River Delta region. This report is the main publication arising from Project 2.

Organizational Collaborators

The Project has required and enabled the collaboration between regional authorities, regulators, industry, civic organizations and the scientific community. It is the first time a cross-section of local and international stakeholders, led by a Hong Kong-based think tank, have teamed up to work on regional air quality issues.

Listed alphabetically the Project collaborators include: Argonne National Laboratory USA, California Institute of Technology USA, Castle Peak Power Co. Ltd. HK, Civic Exchange HK, Conghua Environmental Monitoring Centre PRC, Georgia Institute of Technology USA, Guangdong Environmental Protection Bureau PRC, Guangzhou Environmental Monitoring Station PRC, Hong Kong Environmental Protection Department, Hong Kong Jockey Club Charities Trust, Hong Kong Observatory,

Hong Kong Polytechnic University, Hong Kong University of Science and Technology, NOAA Aeronomy Laboratory USA, Peking University PRC, Shell Hong Kong Ltd., Shenzhen Environmental Monitoring Centre PRC and Zhongshan Environmental Monitoring Centre PRC.

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Personnel

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Table 1. 24-hr Sample Completeness During Field Study

Site	*Complete*	*Partial*	*No Sample*
Tap Mun (TM1)	**20**	**--**	**--**
Tung Chung (TC2)	**20**	**--**	**--**
C&W (CW3)	**20**	**--**	**--**
Shenzhen (SZ4)	**17**	**3**	**--**
Guangzhou (GZ5)	**19**	**1**	**--**
Conghua (CH6)	**18**	**1**	**1**
Zongshan (ZS7)	**19**	**--**	**1**

Table 2. Intercomparison results for Caltech (CT) and ThermoAndersen (TA) Samplers Conducted at Shenzhen on September 9, 2002

Sampler	**Type**	**PM2.5 (μg m^{-3})** **mean**	 **std. dev.**	**% Difference from SZ4**
Shenzhen (SZ4)	**TA**	**73.0**	**1.8**	**--**
Guangzhou (GZ5)	**TA**	**72.6**	**0.1**	**-0.5**
Conghua (CH6)	**Caltech**	**70.5**	**2.8**	**-3.4**
Zhongshan (ZS7)	**Caltech**	**69.9**	**1.4**	**-4.2**

Table 3. Intercomparison results for Hong Kong ThermoAndersen Samplers on Sept. 11, 12 2003

Sampler	**Type**	**PM2.5 (μg m^{-3})** **mean**	 **std. dev.**	**% Difference from SZ4**
		September 11, 2003		
Shenzhen (SZ4)	**TA**	**52.8**	**3.4**	**--**
Tap Mun (TM1)	**TA**	**50.5**	**1.6**	**-4.4**
Tung Chung (TC2)	**TA**	**50.2**	**2.7**	**-4.9**
C & W (CW3)	**TA**	**50.7**	**0.4**	**-4.0**
		September 12, 2003		
Shenzhen (SZ4)	**TA**	**41.2**	**0.1**	**--**
Tap Mun (TM1)	**TA**	**41.6**	**0.6**	**1.0**
Tung Chung (TC2)	**TA**	**39.4**	**1.9**	**-4.4**
C & W (CW3)	**TA**	**40.1**	**0.3**	**-2.7**

Table 4. Seasonal and annual mean concentrations across the PRD

		Mean Concentration (µg/m^3)[a]															
	Site	PM$_{2.5}$		OC[b]		EC		Nitrate		Sulfate		Ammonia		Crustal		Trace	
October, 2002	TM	25.8	(14.6)	8.0	(5.3)	0.9	(0.6)	0.4	(0.3)	8.2	(3.4)	2.1	(1.0)	3.1	(2.8)	1.0	(0.6)
	TC	29.1	(13.9)	10.6	(5.6)	2.0	(1.2)	0.5	(0.4)	7.9	(3.1)	2.3	(1.1)	2.9	(2.6)	1.0	(0.3)
	CW	30.1	(13.8)	9.0	(5.6)	2.0	(1.4)	0.7	(0.5)	8.2	(2.5)	2.2	(1.0)	3.1	(2.7)	0.9	(0.8)
	SZ	42.7	(21.2)	17.3	(10.5)	4.1	(1.4)	1.0	(0.9)	8.8	(3.3)	2.5	(1.3)	4.9	(3.1)	1.3	(0.6)
	GZ	66.2	(26.1)	28.3	(14.0)	4.6	(0.9)	1.9	(1.8)	14.2	(5.1)	3.6	(0.7)	6.8	(3.4)	1.6	(0.7)
	CH	35.3	(9.5)	12.4	(3.5)	1.5	(0.4)	0.3	(0.1)	9.8	(2.8)	2.2	(0.4)	5.4	(1.6)	1.6	(0.5)
	ZS	42.4	(27.7)	16.3	(11.9)	2.1	(1.0)	0.7	(0.6)	11.7	(5.4)	2.5	(0.7)	6.1	(6.7)	0.9	(0.8)
December, 2002	TM	32.3	(7.8)	7.8	(2.5)	1.1	(0.5)	0.5	(0.2)	11.2	(3.5)	2.5	(0.8)	2.4	(1.2)	1.1	(0.1)
	TC	31.1	(9.4)	9.5	(4.3)	2.6	(0.8)	1.0	(0.5)	9.1	(3.8)	2.5	(0.9)	2.3	(1.2)	0.7	(0.4)
	CW	37.7	(7.8)	11.0	(1.8)	2.4	(0.7)	1.6	(0.6)	10.9	(3.1)	2.8	(0.8)	2.5	(1.1)	1.0	(1.9)
	SZ	54.7	(24.8)	18.1	(8.4)	4.9	(3.2)	3.5	(2.1)	11.8	(6.3)	4.0	(1.7)	4.9	(2.4)	2.2	(1.5)
	GZ	72.4	(30.7)	27.0	(13.0)	5.3	(1.9)	4.8	(3.4)	14.0	(5.4)	4.5	(2.4)	7.3	(3.6)	3.1	(0.2)
	CH	28.3	(11.7)	10.9	(5.1)	1.5	(0.5)	0.2	(0.1)	7.7	(3.6)	1.7	(0.8)	3.6	(1.5)	1.1	(0.5)
	ZS	58.5	(18.5)	21.2	(8.3)	4.0	(0.9)	2.9	(1.6)	13.7	(4.2)	4.0	(1.2)	5.9	(2.5)	2.2	(0.7)
March, 2003	TM	32.9	(12.6)	6.7	(2.8)	0.7	(0.3)	0.7	(0.4)	10.1	(4.3)	2.9	(1.4)	2.1	(0.9)	0.8	(0.7_
	TC	39.9	(5.7)	9.6	(2.2)	2.1	(0.5)	1.4	(1.2)	10.6	(2.0)	3.1	(0.7)	2.1	(0.7)	1.4	(0.2)
	CW	39.4	(9.7)	10.5	(1.7)	1.9	(0.9)	1.6	(0.4)	9.9	(2.8)	2.9	(0.5)	2.1	(0.7)	1.1	(0.8)
	SZ	54.6	(11.8)	17.0	(3.3)	4.0	(1.5)	3.6	(0.6)	10.6	(3.3)	3.9	(0.5)	4.0	(0.8)	1.6	(0.4)
	GZ	79.4	(41.3)	23.8	(12.5)	4.5	(2.4)	7.1	(4.9)	16.3	(7.7)	5.8	(2.5)	5.8	(2.9)	2.7	(0.3)
	CH	50.6	(22.8)	16.9	(7.8)	1.5	(0.8)	0.6	(0.3)	14.6	(6.6)	3.1	(1.4)	5.7	(3.8)	1.8	(0.2)
	ZS	55.4	(15.7)	15.8	(4.7)	2.5	(1.0)	3.0	(2.1)	13.1	(2.4)	3.8	(0.9)	4.1	(0.3)	1.8	(0.7)
June, 2003	TM	24.0	(19.9)	4.9	(4.9)	0.6	(0.5)	0.3	(0.1)	7.2	(7.2)	1.7	(1.6)	1.6	(1.4)	0.7	(0.3)
	TC	29.7	(25.0)	5.7	(5.6)	1.2	(1.0)	0.2	(0.1)	8.6	(9.6)	1.9	(2.0)	1.7	(1.5)	0.9	(0.3)
	CW	30.0	(22.4)	6.6	(6.1)	1.4	(0.8)	0.3	(0.1)	8.1	(8.1)	2.0	(2.0)	1.9	(1.5)	1.0	(1.1)
	SZ	35.0	(23.1)	9.3	(6.2)	2.5	(2.2)	0.9	(0.4)	8.3	(7.7)	2.2	(2.0)	2.3	(1.5)	1.1	(0.3)
	GZ	64.3	(28.9)	19.4	(7.9)	3.1	(1.2)	2.2	(2.1)	14.4	(7.5)	4.0	(2.5)	6.7	(3.5)	2.4	(0.1)
	CH	35.8	(25.2)	11.4	(8.4)	1.2	(0.5)	0.3	(0.2)	10.5	(7.1)	2.5	(1.8)	4.0	(2.2)	1.0	(0.2)
	ZS	28.8	(23.1)	5.8	(4.5)	1.4	(0.4)	0.3	(0.2)	9.1	(9.1)	2.5	(2.6)	2.0	(1.4)	0.7	(0.4)
Annual	TM	28.7	(13.8)	6.9	(3.9)	0.8	(0.5)	0.5	(0.3)	9.2	(4.7)	2.3	(1.2)	2.3	(1.7)	0.9	(0.4)
	TC	32.5	(14.8)	8.8	(4.7)	2.0	(1.0)	0.8	(0.8)	9.0	(5.1)	2.5	(1.3)	2.2	(1.6)	1.0	(0.4)
	CW	34.3	(14.1)	9.3	(4.3)	1.9	(1.0)	1.0	(0.7)	9.3	(4.5)	2.5	(1.2)	2.4	(1.6)	1.0	(0.3)
	SZ	47.1	(21.3)	15.6	(7.9)	3.9	(2.3)	2.3	(1.8)	10.0	(5.3)	3.2	(1.6)	4.1	(2.3)	1.6	(0.9)
	GZ	70.6	(30.2)	24.6	(11.6)	4.4	(1.8)	4.0	(3.7)	14.7	(6.1)	4.5	(2.2)	6.6	(3.1)	2.5	(1.3)
	CH	36.8	(18.5)	12.7	(6.3)	1.4	(0.5)	0.3	(0.2)	10.4	(5.4)	2.4	(1.2)	4.6	(2.3)	1.4	(0.5)
	ZS	46.5	(23.0)	14.7	(9.1)	2.5	(1.2)	1.8	(1.8)	11.9	(5.7)	3.3	(1.6)	4.5	(3.5)	1.4	(0.9)

[a] Values in parentheses represent standard deviation

[b] OC (organic compounds) is calculated by multiplying the measured organic carbon by 1.4

Table 5. r^2 values calculated from a least-squares fit of $PM_{2.5}$ mass at a pair of sites.

$PM_{2.5}$	TM1	TC2	CW3	SZ4	ZS7	GZ5	CH6
TM1	1.00	0.71	0.94	0.82	0.77	0.19	0.08
TC2	0.71	1.00	0.78	0.74	0.56	0.02	0.12
CW3	0.94	0.78	1.00	0.83	0.68	0.20	0.11
SZ4	0.82	0.74	0.83	1.00	0.77	0.18	0.15
ZS7	0.77	0.56	0.68	0.77	1.00	0.17	0.04
GZ5	0.19	0.02	0.20	0.18	0.17	1.00	0.22
CH6	0.08	0.12	0.11	0.15	0.04	0.22	1.00

Table 6. r^2 values from a least-squares fit of organic carbon concentrations at a pair of sites.

OC	TM1	TC2	CW3	SZ4	ZS7	GZ5	CH6
TM1	1.00	0.75	0.75	0.65	0.42	0.02	0.00
TC2	0.75	1.00	0.67	0.72	0.46	0.02	0.01
CW3	0.75	0.67	1.00	0.61	0.36	0.04	0.03
SZ4	0.65	0.72	0.61	1.00	0.50	0.10	0.03
ZS7	0.42	0.46	0.36	0.50	1.00	0.23	0.02
GZ5	0.02	0.02	0.04	0.10	0.23	1.00	0.08
CH6	0.00	0.01	0.03	0.03	0.02	0.08	1.00

Table 7. r^2 values from a least-squares fit of sulfate concentrations at a pair of sites.

Sulfate	**TM1**	**TC2**	**CW3**	**SZ4**	**ZS7**	**GZ5**	**CH6**
TM1	1.00	0.76	0.93	0.88	0.87	0.27	0.06
TC2	0.76	1.00	0.86	0.86	0.82	0.15	0.10
CW3	0.93	0.86	1.00	0.89	0.85	0.26	0.09
SZ4	0.88	0.86	0.89	1.00	0.90	0.29	0.12
ZS7	0.87	0.82	0.85	0.90	1.00	0.21	0.04
GZ5	0.27	0.15	0.26	0.29	0.21	1.00	0.48
CH6	0.06	0.10	0.09	0.12	0.04	0.48	1.00

Table 8. r^2 values from a least-squares fit of silica concentrations at a pair of sites.

Si	**TM1**	**TC2**	**CW3**	**SZ4**	**ZS7**	**GZ5**	**CH6**
TM1	1.00	0.93	0.97	0.83	0.75	0.03	0.28
TC2	0.93	1.00	0.94	0.76	0.73	0.01	0.26
CW3	0.97	0.94	1.00	0.81	0.73	0.04	0.27
SZ4	0.83	0.76	0.81	1.00	0.77	0.03	0.49
ZS7	0.75	0.73	0.73	0.77	1.00	0.04	0.31
GZ5	0.03	0.01	0.04	0.03	0.04	1.00	0.13
CH6	0.28	0.26	0.27	0.49	0.31	0.13	1.00

Table 9. r^2 values from a least-squares fit of iron concentrations at a pair of sites.

Fe	TM1	TC2	CW3	SZ4	ZS7	GZ5	CH6
TM1	1.00	0.93	0.91	0.73	0.53	0.01	0.04
TC2	0.93	1.00	0.96	0.70	0.61	0.01	0.07
CW3	0.91	0.96	1.00	0.79	0.65	0.00	0.08
SZ4	0.73	0.70	0.79	1.00	0.59	0.05	0.26
ZS7	0.53	0.61	0.65	0.59	1.00	0.03	0.20
GZ5	0.01	0.01	0.00	0.05	0.03	1.00	0.23
CH6	0.04	0.07	0.08	0.26	0.20	0.23	1.00

Table 10. r^2 values from a least-squares fit of elemental carbon concentrations at a pair of sites.

EC	TM1	TC2	CW3	SZ4	ZS7	GZ5	CH6
TM1	1.00	0.53	0.22	0.30	0.44	0.14	0.06
TC2	0.53	1.00	0.66	0.49	0.37	0.06	0.05
CW3	0.22	0.66	1.00	0.22	0.26	0.05	0.00
SZ4	0.30	0.49	0.22	1.00	0.27	0.19	0.00
ZS7	0.44	0.37	0.26	0.27	1.00	0.39	0.03
GZ5	0.14	0.06	0.05	0.19	0.39	1.00	0.01
CH6	0.06	0.05	0.00	0.00	0.03	0.01	1.00

Table 11. r^2 values from a least-squares fit of lead concentrations at a pair of sites.

Pb	TM1	TC2	CW3	SZ4	ZS7	GZ5	CH6
TM1	1.00	0.73	0.96	0.81	0.40	0.05	0.01
TC2	0.73	1.00	0.79	0.80	0.44	0.18	0.04
CW3	0.96	0.79	1.00	0.79	0.40	0.05	0.01
SZ4	0.81	0.80	0.79	1.00	0.57	0.15	0.00
ZS7	0.40	0.44	0.40	0.57	1.00	0.09	0.03
GZ5	0.05	0.18	0.05	0.15	0.09	1.00	0.16
CH6	0.01	0.04	0.01	0.00	0.03	0.16	1.00

Table 12. r^2 values from a least-squares fit of potassium concentrations at a pair of sites.

K	TM1	TC2	CW3	SZ4	ZS7	GZ5	CH6
TM1	1.00	0.86	0.95	0.92	0.64	0.02	0.10
TC2	0.86	1.00	0.86	0.82	0.58	0.02	0.08
CW3	0.95	0.86	1.00	0.85	0.58	0.02	0.08
SZ4	0.92	0.82	0.85	1.00	0.61	0.01	0.02
ZS7	0.64	0.58	0.58	0.61	1.00	0.00	0.05
GZ5	0.02	0.02	0.02	0.01	0.00	1.00	0.21
CH6	0.10	0.08	0.08	0.02	0.05	0.21	1.00

Table 13. r^2 values from a least-squares fit of rubidium concentrations at a pair of sites.

Rb	TM1	TC2	CW3	SZ4	ZS7	GZ5	CH6
TM1	1.00	0.82	0.93	0.81	0.42	0.06	0.22
TC2	0.82	1.00	0.84	0.79	0.46	0.05	0.18
CW3	0.93	0.84	1.00	0.81	0.39	0.04	0.21
SZ4	0.81	0.79	0.81	1.00	0.41	0.10	0.13
ZS7	0.42	0.46	0.39	0.41	1.00	0.02	0.15
GZ5	0.06	0.05	0.04	0.10	0.02	1.00	0.12
CH6	0.22	0.18	0.21	0.13	0.15	0.12	1.00

Table 14. Mean annual concentrations of species at each site

	Mean annual concentrations at each site ($\mu g/m^3$)[a]						
	TM1	**TC2**	**CW3**	**SZ4**	**GZ5**	**CH6**	**ZS7**
PM2.5	28.7 (13.8)	32.5 (14.8)	34.3 (14.1)	47.1 (21.3)	70.6 (30.2)	36.8 (18.5)	46.5 (23.0)
OC	6.9 (3.9)	8.8 (4.7)	9.3 (4.3)	15.6 (7.9)	24.6 (11.6)	12.7 (6.3)	14.7 (9.1)
Sulfate	9.2 (4.7)	9.0 (5.1)	9.3 (4.5)	10.0 (5.3)	14.7 (6.1)	10.4 (5.4)	11.9 (5.7)
Si	0.35 (0.28)	0.31 (0.25)	0.35 (0.26)	0.61 (0.35)	0.88 (0.42)	0.51 (0.31)	0.68 (0.49)
Fe	0.14 (0.10)	0.16 (0.11)	0.17 (0.10)	0.29 (0.14)	0.53 (0.40)	0.27 (0.17)	0.30 (0.19)
EC	0.8 (0.5)	2.0 (1.0)	1.9 (1.0)	3.9 (2.3)	4.4 (1.8)	1.4 (0.5)	2.5 (1.2)
Pb	0.06 (0.05)	0.06 (0.05)	0.05 (0.04)	0.10 (0.08)	0.27 (0.11)	0.16 (0.10)	0.14 (0.12)
K	0.57 (0.43)	0.56 (0.41)	0.56 (0.42)	0.86 (0.55)	1.67 (0.88)	1.44 (0.82)	1.03 (1.01)
Rb	0.004 (0.004)	0.004 (0.003)	0.004 (0.003)	0.007 (0.005)	0.016 (0.009)	0.014 (0.009)	0.009 (0.010)

[a] Standard deviations are shown in parentheses

Table 15. Enrichment factors (EF) of elements in PM2.5 samples. Values represent a grouping of all measurements made at the seven sampling sites.

Compound	Mean ($\mu g/m^3$)	S.D. ($\mu g/m^3$)	EF
Silica	0.52	0.38	1.2
Iron	0.25	0.17	3.1
Lead	0.12	0.11	5965.8
Potassium	0.93	0.77	29.3
Rubidium	0.0081	0.0079	57.9

* Calculation of EF: $EF = (C_{Element}/C_{Aluminum})_{air}/(C_{Element}/C_{Aluminum})_{crust}$

Table 16. Molecular Markers for Major Sources

Molecular Markers	Major Urban Sources
n-pentacosane [b]	gasoline vehicles, diesel vehicles
n-hexacosane [b]	gasoline vehicles, diesel vehicles
n-heptacosane [b]	gasoline vehicles, diesel vehicles
n-octacosane [a]	gasoline vehicles, diesel vehicles
n-nonacosane [b]	vegetative detritus
n-triacontane [b]	variety
n-hentriacontane [b]	vegetative detritus, cigarette smoke
n-dotriacontane [a]	variety
n-triatriacontane [c]	vegetative detritus, cigarette smoke
20 S&R-5α(H), 14β(H), 17β(H)-cholestanes [a]	gasoline vehicles, diesel vehicles
20R-5α(H), 14α(H), 17 α (H)-cholestane [a]	gasoline vehicles, diesel vehicles
20 S&R-5α(H), 14β(H), 17β(H)-ergostanes [a]	gasoline vehicles, diesel vehicles
20 S&R-5α(H), 14β(H), 17β(H)-sitostanes [a]	gasoline vehicles, diesel vehicles
22,29,30-trisnorneohopane [b]	gasoline vehicles, diesel vehicles
17α(H), 21 β(H)-29-norhopane [b]	gasoline vehicles, diesel vehicles
17α(H), 21 β(H)-hopane [a]	gasoline vehicles, diesel vehicles
22S-17α(H), 21 β(H)-homohopane [b]	gasoline vehicles, diesel vehicles
22R-17α(H), 21 β(H)-homohopane [b]	gasoline vehicles, diesel vehicles
22S-17α(H), 21 β(H)-bishomohopane [b]	gasoline vehicles, diesel vehicles
22R-17α(H), 21 β(H)-bishomohopane [b]	gasoline vehicles, diesel vehicles
cholesterol [a]	meat cooking
levoglucosan [a]	biomass burning
8,15-pimaredienoic acid [c]	softwood burning
pimaric acid [a]	softwood burning
isopimaric acid [a]	softwood burning
propionylsyringol [c]	hardwood burning
benzo(b)fluoranthene [a]	natural gas, coal combustion and gasoline vehicle
benzo(k)fluoranthene [a]	natural gas, coal combustion and gasoline vehicle
benzo(e)pyrene [c]	natural gas, coal combustion and gasoline vehicle
indeno(1,2,3-cd)fluoranthene [c]	natural gas, coal combustion and gasoline vehicle
indeno(1,2,3-cd)pyrene [c]	natural gas, coal combustion and gasoline vehicle
benzo(ghi)perylene [c]	natural gas, coal combustion and gasoline vehicle
coronene [a]	noncatalyst cars
picene [c]	coal combustion
iso-nonacosane [c]	cigarette smoke
anteiso-triacontane [c]	cigarette smoke
iso-hentriacontane [c]	cigarette smoke
elemental carbon	diesel exhaust
aluminum	crustal material
silicon	crustal material

[a] Identified and quantified by using authentic standard (PMSTD standard and internal standard 1, 2);

[b] Identified by using mass spectra and quantified using authentic standard with similar structure and volatility;

[c] Identified by using secondary standard (picene standard, wood smoke standard, wax extraction, etc) and quantified using authentic standard with similar structure and volatility.

Table 17. Concentrations of Organic Compounds, OC and EC in PM2.5 (ng /m^3)

Compounds	TM-03	TM-06	TM-10	TM-12	TC-03	TC-06	TC-10	TC-12	CW-03	CW-06	CW-10	CW-12	CH-03	CH-06	CH-10	CH-12	ZS-03	ZS-06	ZS-10	ZS-12	SZ-03	SZ-06	SZ-10	SZ-12	GZ-03	GZ-06	GZ-10	GZ-12
heptadecane			0.08				0.22	0.25		0.03	0.38	0.22			0.14	0.15			0.31	0.16		0.06	0.20	0.34		0.15	0.21	0.50
octadecane			0.08	0.05		0.10	0.07	0.25		0.11	0.31	0.31			0.25	0.01			0.32	0.33		0.14	0.23	0.40		0.40	0.36	0.75
nonadecane		0.07	0.13	0.11		0.37	0.32	0.33		0.36	0.33	0.41	0.58	0.32	0.19	0.20		0.33	0.57	0.41		0.59	0.54	0.64	0.96	0.93	0.61	1.30
eicosane	0.06	0.08	0.21	0.13	0.33	0.46	0.41	0.43	0.19	0.42	0.38	0.48	0.99	0.24	0.31	0.20	0.24	0.40	1.66	1.22	0.18	0.75	0.64	0.85	2.04	1.18	0.83	2.27
heneicosane	0.31	0.01	0.28	0.26	0.88	0.32	0.53	0.45	0.93	0.24	0.55	0.91	1.29	0.12	0.47	0.35	1.22	0.18	1.94	0.63	1.20	0.69	1.02	1.32	3.77	1.71	1.14	3.02
docosane	0.32	0.08	0.33	0.30	1.31	0.29	0.62	0.74	1.27	0.33	0.82	0.91	1.10	0.27	0.71	0.90	2.50	0.26	3.00	1.60	1.98	0.80	1.39	2.40	5.54	2.31	1.95	6.08
tricosane	0.62	0.20	0.66	0.48	2.96	0.44	1.08	1.86	3.11	0.62	1.17	1.44	3.25	1.75	1.65	1.70	5.48	0.75	6.02	2.91	5.00	2.37	2.62	4.49	11.32	6.17	3.64	11.69
tetracosane	0.88	0.19	0.85	0.77	3.96	0.44	0.96	3.45	3.59	0.55	1.38	2.90	2.39	0.78	2.10	2.31	6.26	0.96	10.60	5.11	5.66	1.03	3.61	5.92	11.20	3.94	4.74	15.05
pentacosane	1.52	0.35	1.64	1.33	4.77	0.63	1.53	5.04	4.76	0.79	1.85	3.46	4.67	1.70	3.07	3.10	8.33	1.53	14.20	7.66	7.71	1.33	5.53	6.65	13.80	5.43	7.59	17.11
hexacosane	1.68	0.37	2.04	1.42	3.68	0.44	1.74	4.68	4.17	0.56	1.86	3.20	5.28	1.58	3.61	2.61	8.22	1.63	13.81	8.01	6.70	1.42	5.57	5.46	11.35	6.02	7.75	12.36
heptacosane	1.49	0.64	2.57	2.16	2.70	0.76	2.75	4.55	2.88	1.05	2.51	3.64	6.46	2.12	4.56	3.56	6.17	2.02	13.62	7.72	5.12	1.77	6.18	5.17	9.40	6.26	9.52	11.96
octacosane	1.09	0.37	1.70	1.70	1.60	0.37	1.84	3.43	1.71	0.46	1.74	2.28	4.44	1.25	2.96	2.37	4.58	1.48	10.11	6.11	3.42	1.15	4.63	3.50	6.12	4.75	6.90	7.26
nonacosane	1.78	0.96	2.76	2.64	2.23	1.36	2.89	4.37	2.78	1.45	3.05	3.52	9.58	2.22	4.15	4.27	5.33	2.08	10.07	6.60	4.42	2.19	5.45	4.66	8.09	6.40	9.99	9.17
triacontane	0.80	0.23	0.99	1.04	0.95	0.26	1.21	1.84	1.12	0.40	1.00	1.39	3.55	0.86	1.64	1.36	3.46	0.88	5.92	3.33	2.69	0.79	2.88	2.30	4.65	3.84	4.61	4.96
hentriacontane	2.67	0.76	3.41	3.38	3.01	1.08	4.63	4.61	3.87	1.60	4.50	5.83	19.44	2.45	6.45	5.89	6.81	1.58	11.80	7.07	6.61	2.06	7.40	7.18	14.96	7.46	14.76	17.03
dotriacontane	0.69	0.18	0.82	1.06	0.88	0.25	1.31	1.77	0.82	0.32	1.14	1.58	3.07	0.67	1.60	1.37	2.36	0.55	5.25	2.88	2.10	0.56	2.93	2.69	3.98	2.80	5.44	5.88
tritriacontane	0.91	0.27	1.41	1.35	1.06	0.41	2.29	1.82	1.49	0.58	1.75	2.13	4.86	0.87	2.29	1.63	2.31	0.61	4.84	3.32	2.46	0.72	3.42	2.70	5.17	3.23	7.54	7.87
tetratriacontane	0.39	0.10	0.34	0.41	0.76	0.10	0.61	0.93	0.48	0.17	0.30	0.70	1.33	0.39	0.45	0.43	1.62	0.31	3.01	1.33	1.60	0.40	1.71	1.55	3.11	2.02	3.19	4.46
pentatriacontane	0.35	0.21	0.36	0.34	0.46	0.26	0.42	0.75	0.38	0.40	0.50	0.48	1.09	0.31	0.55		1.09	0.54	2.02	1.19	1.38		1.76	0.87	2.04	1.61	1.92	2.57
hexatriacontane	0.22	0.10	0.18		0.21			0.39					0.66	0.28			0.66	0.31	1.49	0.65	0.98		0.87	0.58	1.29	1.01	1.32	0.90
iso-nonacosane	0.09	0.12	0.55	0.46			0.85	1.07		0.24	0.84	0.91	0.38		0.57	0.52	0.33		2.22	1.09	0.50	0.35	1.33	1.22	0.66	0.62	2.23	2.61
anteiso-triacontane	0.08		0.15		0.42		0.19	0.55	0.51	0.14	0.34	0.60	0.60	0.16	0.24	0.31	0.42		1.76	0.64	0.64	0.31	0.58	0.60	1.70	1.01	1.36	2.49
iso-hentriacontane	0.11	0.02	0.41	0.36	0.55	0.12	0.50	1.26	0.79	0.30	0.59		1.00	0.26	0.31	0.20	0.55	0.14	1.73	1.15	0.88	0.47	1.07	1.13	1.87	1.79	2.70	3.22
tetradecanoic acid	2.01	0.42	0.44	0.16	1.92	0.40	0.57	0.64	4.21	0.91	1.34	0.94	9.23	1.39	1.98	1.06	3.71	0.96	1.98	1.46	3.91	2.16	1.28	1.42	6.12	4.66	1.39	1.61
pentadecanoic acid	1.49	0.41	0.19	0.06	1.14	0.30	0.25	0.23	2.60	0.65	0.71	0.39	6.06	1.02	0.93	0.60	1.99	0.64	1.18	0.84	2.69	1.48	0.58	0.65	4.49	3.64	0.78	0.98
hexadecanoic acid	10.91	2.04	2.81	2.47	18.44	3.31	6.34	12.38	34.60	6.95	9.65	15.59	71.02	31.49	18.43	21.40	45.61	9.31	47.71	21.60	48.47	22.12	25.40	28.14	78.06	50.39	30.85	58.43
heptadecanoic acid	0.47	0.12	0.21	0.16	0.52	0.14	0.30	0.39	1.08	0.23	0.43	0.51	2.33	0.62	0.67	0.63	1.13	0.25	1.51	0.83	1.26	0.61	0.69	0.74	2.27	1.53	1.08	1.56
octadecanoic acid	3.53	0.43	0.06		6.81	1.36	2.71	4.10	11.38	2.15	2.96	5.82	19.17	6.21	4.75	3.90	15.86	2.04	20.70	7.02	17.94	6.81	11.45	9.23	27.55	17.37	15.87	21.50
nonadecanoic acid	0.21	0.09	0.17	0.15	0.25	0.10	0.20	0.21	0.33	0.11	0.18	0.23	0.93	0.25	0.32	0.32	0.53	0.17	0.57	0.35	0.47	0.21	0.36	0.33	0.87	0.52	0.50	0.56
eicosanoic acid	0.92	0.37	0.85	0.83	1.06	0.44	0.98	1.00	1.69	0.58	0.97	1.35	6.19	1.57	2.19	2.55	2.26	0.57	2.75	1.67	2.09	1.00	1.84	1.90	4.30	2.71	3.16	3.68
heneicosanoic acid	0.32	0.17	0.47	0.43	0.33	0.19	0.47	0.43	0.46	0.22	0.42	0.51	1.77	0.39	0.75	0.72	0.70	0.25	0.91	0.66	0.57	0.31	0.66	0.55	1.10	0.68	1.04	0.93
docosanoic acid	1.54	1.06	2.21	2.01	1.58	1.18	2.30	1.96	2.30	1.27	1.98	2.44	9.75	2.71	4.57	4.58	2.93	1.31	4.55	3.16	2.52	1.74	3.21	3.22	5.56	4.02	5.63	5.47
tricosanoic acid	1.04	0.43	1.54	1.33	1.01	0.49	1.39	1.16	1.30	0.51	1.28	1.38	6.08	1.02	2.33	2.10	1.87	0.57	2.43	1.90	1.63	0.75	1.92	1.61	3.25	1.75	2.91	2.44
tetracosanoic acid	3.09	1.39	3.64	3.41	2.75	1.41	3.32	3.02	3.67	1.48	2.94	3.32	16.26	3.81	6.65	6.12	4.78	1.75	6.33	4.57	4.34	2.25	4.69	4.46	8.66	4.94	7.50	6.99
pentacosanoic acid	0.72	0.31	0.82	0.66	0.64	0.32	0.74	0.63	0.91	0.33	0.62	0.69	3.28	0.61	1.20	0.79	1.04	0.36	1.16	0.98	1.00	0.46	1.03	0.81	1.84	1.05	1.56	1.19
hexacosanoic acid	1.96	0.76	1.80	1.67	1.72	0.82	1.94	1.63	2.28	0.85	1.44	1.73	9.22	1.95	3.35	2.79	3.07	1.04	3.60	2.64	2.68	1.21	2.47	2.45	5.08	2.63	3.92	3.37
heptacosanoic acid	0.46	0.21	0.69	0.61	0.42	0.24	0.82	0.62	0.57	0.24	0.59	0.62	1.80	0.39	0.91	0.59	0.65	0.24	0.88	1.12	0.63	0.29	0.95	0.69	1.17	0.66	1.35	0.89
octacosanoic acid	1.76	0.75	3.77	3.15	1.67	0.82	4.58	2.95	2.29	0.87	3.21	3.38	9.62	1.66	6.20	4.51	2.60	0.84	5.34	4.23	2.32	1.03	4.49	4.01	4.87	2.08	7.05	5.68
nonacosanoic acid	0.35	0.14	0.78	0.64	0.31	0.14	0.92	0.54	0.38	0.13	0.64	0.58	1.62	0.27	1.06	0.55	0.46	0.13	0.85	0.97	0.52	0.18	0.94	0.75	0.94	0.42	1.56	1.02
triacontanoic acid	1.45	0.47	5.82	4.94	1.24	0.50	7.94	4.34	1.38	0.50	4.55	4.64	8.16	1.29	8.65	6.86	1.94	0.50	7.76	6.29	1.85	0.64	5.96	5.76	4.04	1.56	10.71	8.09
9-hexadecenoic acid	1.75		0.26	0.33	0.83	0.05	0.32		2.52	0.07	0.47		5.71	0.29			0.84	0.03			2.82	0.93			4.22	3.31		
9,12-octadecanedienoic acid	0.31		0.06	0.08	0.69		0.12	0.20	2.40		0.16	2.69	0.86		0.23	0.49	0.60		2.87	0.64	1.67	0.07	1.34	2.40	3.58	3.27	1.47	18.78
9-octadecenoic acid	1.78				2.69	0.01		0.09	5.85	0.36	0.23	2.77	5.96	0.51	0.07	0.27	2.67		4.77	1.24	5.91	1.10	3.31	4.54	11.42	9.07	2.67	23.86
17α(H)-21β(H)-29-norhopane	0.18	0.03			0.49	0.14	0.32	0.49	0.50	0.17	0.21	0.51	0.38	0.17	0.30	0.38	0.71	0.18	1.84	0.80	0.96	0.52	1.01	1.09	2.05	2.03	1.85	2.61
17α(H)-21β(H)-hopane	0.41	0.04	0.20	0.30	0.61	0.17	0.50	0.75	0.73	0.22	0.40	0.78	0.68	0.32	0.48	0.78	1.39	0.36	3.94	1.77	2.12	1.07	1.90	1.88	4.46	4.37	4.45	5.25
22,29,30-trisnorneohopane				0.14	0.12	0.04	0.27	0.38	0.21	0.06	0.21	0.34	0.20		0.40	0.35	0.23	0.07	0.74	0.61	0.24	0.18	0.52	0.46	0.46	0.46	0.80	0.88
22,29,30-trisnorhopane	0.08				0.12	0.06		0.18	0.21	0.06		0.17				0.25	0.18	0.05	0.54	0.33	0.27	0.27	0.34	0.44	0.52	0.62	0.46	0.82
20S,R-5α(H),14β(H),17β(H)-cholestanes					0.30	0.05	0.14		0.28	0.09	0.19	0.36		0.09			0.21		0.59	0.43	0.31	0.18	0.30	0.35	0.62	0.55	0.47	0.85
20R-5α(H),14α(H),17α(H)-cholestane		0.01			0.18	0.05		0.05	0.24	0.09		0.14			0.12	0.15	0.28		0.95	0.26	0.35	0.16	0.25	0.22	0.75	0.72	0.50	0.81
20S,R-5α(H),14β(H),17β(H)-ergostanes					0.20	0.04	0.16	0.20	0.27	0.09		0.25					0.20		0.69		0.38	0.19	0.26	0.39	1.05	1.14	0.67	1.03
20S,R-5α(H),14β(H),17β(H)-sitostanes		0.02			0.29	0.10	0.26	0.34	0.39	0.13	0.21	0.42					0.43		1.09	0.48	0.71	0.39	0.74	0.61	1.23	1.59	1.28	1.83
22S,17α(H),21β(H)-homohopane	0.18	0.03	0.12		0.29	0.10	0.23	0.32	0.36	0.14	0.21	0.35	0.27	0.11		0.15	0.47	0.13	1.24	0.61	0.69	0.42	0.71	0.70	1.51	1.72	1.68	1.65
22R,17α(H),21β(H)-homohopane	0.11	0.02			0.26	0.07	0.25	0.26	0.30	0.14	0.24	0.42	0.26	0.10		0.21	0.42	0.13	0.94	0.64	0.64	0.35	0.63	0.59	1.35	1.55	1.49	1.40
22S,17α(H),21β(H)-bishomohopane	0.13	0.02			0.19	0.07	0.36	0.27	0.20	0.10	0.16	0.30	0.25	0.16		0.16	0.34	0.11	0.83	0.48	0.53	0.35	0.48	0.61	1.07	1.20	1.13	1.15
22R,17α(H),21β(H)-bishomohopane	0.11	0.02			0.16	0.04		0.16	0.19	0.04	0.14	0.20	0.26	0.09			0.25	0.08	0.74	0.37	0.43	0.27	0.41	0.46	0.82	0.93	0.94	1.03
22S,17α(H),21β(H)-trishomohopane	0.14	0.02			0.11	0.05		0.22	0.18	0.06		0.25	0.20	0.05			0.26	0.07	0.59	0.28	0.33	0.23	0.36	0.50	0.73	0.81	0.87	0.88

Table 17. (Cont'd)

Compounds	TM-03	TM-06	TM-10	TM-12	TC-03	TC-06	TC-10	TC-12	CW-03	CW-06	CW-10	CW-12	CH-03	CH-06	CH-10	CH-12	ZS-03	ZS-06	ZS-10	ZS-12	SZ-03	SZ-06	SZ-10	SZ-12	GZ-03	GZ-06	GZ-10	GZ-12
22R,17α(H),21β(H)-trishomohopane	0.07	0.02			0.07	0.01			0.12	0.04							0.17	0.06	0.37	0.29	0.21	0.23	0.33	0.37	0.49	0.70	0.57	0.50
nonanal	0.99	0.31	3.44	2.36	2.23	0.34	5.99	4.34	4.37	0.67	8.01	4.95	12.53	5.51	11.37	16.12	11.31	0.38	5.41	5.59	4.95	4.23	10.46	5.28	11.68	4.83	24.17	5.51
sinapyl aldehyde													8.01															
acetonylsyringol	1.78		3.07	2.49			5.09	5.18			3.23	5.19	9.39	2.28	14.69	23.98	9.69	0.54	25.15	20.47	2.61	1.79	13.05	21.01	6.55	2.02	22.26	33.23
coniferyl aldehyde			0.35													0.62			1.71									0.66
propionylsyringol			4.63	4.81			10.64	5.61			5.09	7.76			15.35	17.87			29.85	20.89			14.83	16.32			24.99	34.03
benz(de)anthracen-7-one	5.46	0.41	10.17	10.33	9.62	0.74	14.58	16.58	6.20	1.00	7.69	12.77	24.57	6.48	15.07	27.09	120.90	4.79	118.77	52.61	45.20	9.28	59.80	60.50	57.28	17.43	69.69	102.02
cholesterol	2.32	0.47	0.19	0.58	1.03	1.55	0.31	0.92	1.99	1.22	1.25	2.81	3.75	0.42	0.47	0.38	1.74	0.42	1.37		3.68	1.81	3.22	3.44	7.90	10.65	1.70	3.80
levoglucosan	109	7	115	207	75	10	299	250	92	24	129	255	543.1	67.6	322.7	470.1	199	21	521	541	146	54	315	350	430	255	534	814
8,15-pimaredienoic acid														0.40				0.34										
pimaric acid	0.05		0.07	0.07	0.07		0.07	0.14	0.12	0.02	0.10	0.15	0.23	0.06	0.16	0.49	0.16	0.04	1.53	0.51	0.25	0.05	0.80	1.78	0.23	0.26	0.59	2.09
sandaracopimaric acid	0.11	0.05	0.07	0.08	0.18			0.04	0.17	0.05	0.08		0.44	0.15	0.12	0.25	0.77	0.07	0.31	0.10	1.25	0.15	0.19	0.47	1.19	0.63	0.13	0.54
isopimaric acid	0.18		0.29	0.28	0.61					0.12			1.47						1.84		0.88	0.30	0.96	1.49	1.38	1.05	0.53	2.49
dehydroabietic acid	1.29	0.11	1.01	0.99	2.02	0.19	1.05	1.75	1.96	0.40	1.07	1.38	8.97	2.20	2.48	5.19	9.85	1.31	16.65	6.31	15.08	4.11	10.26	11.79	14.06	7.11	9.50	16.19
abietic acid			0.22		0.10			0.13		0.02	0.09		0.24	0.05	0.13	0.35	0.21		0.73	0.38	0.46	0.06	0.49	1.18	0.43	0.15	0.29	1.28
abieta-6,8,11,13,15-pentae-18-oic acid	0.11	0.01	0.27	0.35	0.09	0.01	0.27	0.36	0.11	0.01	0.26	0.30	0.49	0.09	0.40	0.66	0.33	0.08	1.05	0.75	0.28	0.09	0.75	0.71	0.48	0.24	1.20	1.25
abieta-8,11,13,15-tetraen-18-oic acid	0.04		0.14	0.15	0.03		0.13	0.17	0.03	0.01	0.12	0.12	0.16	0.04	0.21	0.35	0.12	0.02	0.71	0.36	0.13	0.04	0.50	0.52	0.23	0.09	0.54	0.89
7-oxodehydroabietic acid	0.93	0.11	0.81	0.81	0.91	0.11	0.70	0.84	1.00	0.19	0.59	0.84	5.20	1.60	1.35	2.24	3.63	1.13	4.10	2.26	3.85	1.85	2.89	2.57	5.05	3.16	3.85	4.17
1,2-benzenedicarboxylic acid	7.21	1.74	4.63	11.16	3.98	2.26	6.38	9.70	6.52	1.37	4.28	10.28	15.51	3.93	5.92	7.64	21.56	1.91	19.35	14.16	4.39	1.74	6.59	8.86	10.67	5.53	10.06	9.11
1,4-benzenedicarboxylic acid	6.31	0.90	4.61	7.38	4.09	1.32	7.86	6.85	6.27	1.29	5.02	8.01	17.38	5.51	5.08	6.06	43.44	3.28	21.17	17.19	13.72	2.77	19.57	13.47	21.54	10.87	27.48	28.90
1,3-benzenedicarboxylic acid	0.50	0.14	0.66	0.81	0.49	0.22	0.68	0.93	0.86	0.27	0.69	1.00	1.21	0.37	0.58	0.50	2.75	0.26	1.37	0.95	0.87	0.42	1.16	0.99	1.93	0.94	1.63	1.66
fluoranthene	0.37	0.05	0.32	0.45	0.47	0.09	0.38	0.49	0.41	0.10	0.35	0.46	1.60	0.19	0.48	0.79	0.89	0.10	1.41	0.71	0.71	0.13	0.70	0.84	1.09	0.31	0.91	1.11
acephenanthrylene	0.09	0.01	0.07	0.08	0.10	0.01	0.09	0.10	0.08	0.01	0.07	0.08	0.23	0.05	0.11	0.15	0.26	0.03	0.44	0.18	0.21	0.04	0.20	0.24	0.30	0.09	0.23	0.31
pyrene	0.36	0.04	0.33	0.44	0.52	0.09	0.40	0.49	0.43	0.10	0.34	0.49	1.58	0.21	0.50	0.85	1.07	0.13	1.73	0.81	0.83	0.13	0.86	0.99	1.27	0.35	1.05	1.32
retene			0.01	0.02	0.02	0.01	0.03	0.03	0.02				0.06		0.01	0.04	0.09		0.14	0.06	0.06	0.02	0.08	0.08	0.11	0.03	0.07	0.13
methyl substituted MW 202 PAH	0.37	0.06	0.35	0.36	0.45	0.10	0.42	0.48	0.43	0.11	0.25	0.51	1.16	0.33	0.45	0.76	1.16	0.20	1.71	0.81	0.80	0.21	0.84	1.18	1.42	0.50	0.90	1.24
benzo(ghi)fluoranthene	0.16	0.02	0.17	0.20	0.32	0.04	0.21	0.28	0.22	0.05	0.15	0.25	0.63	0.15	0.25	0.44	0.87	0.12	1.46	0.69	0.65	0.09	0.63	0.67	0.96	0.27	0.65	1.16
cyclopenta(cd)pyrene	1.50	0.11	2.20	2.18	2.28	0.22	2.89	2.87	1.55	0.22	1.51	2.50	5.21	1.42	2.99	5.28	7.53	0.95	26.56	9.34	6.84	1.20	9.05	11.67	9.51	2.85	10.04	20.29
benz(a)anthracene	0.18	0.02	0.16	0.18	0.30	0.04	0.19	0.26	0.22	0.05	0.15	0.22	0.65	0.14	0.27	0.46	1.11	0.14	1.72	0.81	0.81	0.11	0.65	0.85	1.20	0.33	0.74	1.56
chrysene/triphenylene	0.35	0.05	0.35	0.38	0.61	0.09	0.44	0.57	0.46	0.11	0.37	0.48	2.11	0.28	0.60	1.29	1.91	0.27	2.92	1.39	1.42	0.22	1.28	1.58	2.13	0.63	1.48	2.54
methyl substituted MW 228 PAH	0.20	0.03	0.25	0.41	0.41	0.05	0.40	0.55	0.35	0.09	0.28	0.49	0.83	0.22	0.53	0.99	1.07	0.28	2.71	1.27	1.03	0.23	1.29	1.51	1.82	0.69	1.66	2.78
methyl substituted MW 226 PAH	0.16	0.02	0.26	0.22	0.24	0.04	0.25	0.35	0.18	0.03	0.13	0.25	0.57	0.19	0.46	0.63	0.97	0.15	2.46	0.94	0.82	0.24	0.96	1.12	1.34	0.45	0.83	1.73
benzo(b)fluoranthene	0.39	0.04	0.43	0.42	0.62	0.06	0.66	0.76	0.51	0.08	0.43	0.72	2.99	0.45	1.17	3.22	3.09	0.44	5.34	2.33	2.40	0.52	2.44	3.25	3.54	1.52	3.44	4.96
benzo(k)fluoranthene	0.31	0.03	0.34	0.42	0.63	0.06	0.58	0.76	0.39	0.06	0.38	0.58	1.75	0.37	0.77	2.08	2.47	0.36	5.61	2.53	2.23	0.52	2.46	2.74	3.10	1.38	3.39	5.26
benzo(j)fluoranthene	0.07		0.08	0.08	0.11	0.01	0.13	0.13	0.06	0.01	0.06	0.11	0.25	0.08	0.16	0.35	0.42	0.06	1.16	0.56	0.35	0.06	0.51	0.64	0.53	0.25	0.54	1.22
benzo(e)pyrene	0.37	0.04	0.40	0.49	0.62	0.07	0.66	0.77	0.43	0.07	0.45	0.70	2.45	0.46	1.27	3.34	2.40	0.37	5.45	2.64	2.35	0.57	2.63	2.74	3.43	1.67	3.91	5.43
benzo(a)pyrene	0.28	0.03	0.33	0.31	0.50	0.05	0.48	0.54	0.31	0.04	0.33	0.46	1.37	0.30	0.70	1.43	1.86	0.24	4.54	2.17	1.58	0.29	1.92	2.26	2.35	1.11	2.23	4.87
perylene	0.05		0.06	0.08	0.07	0.01	0.11	0.13	0.03	0.01	0.07	0.12	0.20	0.06	0.17	0.31	0.32	0.08	0.80	0.40	0.28	0.05	0.39	0.43	0.44	0.23	0.42	0.94
indeno(cd)fluoranthene	0.22	0.02	0.23	0.30	0.27	0.02	0.27	0.37	0.19	0.04	0.19	0.31	0.94	0.31	0.43	0.91	1.08	0.22	2.41	1.14	1.12	0.36	1.22	1.20	1.50	0.81	1.77	2.13
indeno(cd)pyrene	0.53	0.06	0.54	0.61	0.75	0.08	0.85	0.84	0.47	0.08	0.45	0.62	2.86	0.70	1.23	2.35	3.20	0.55	7.25	2.95	2.99	0.83	3.42	3.14	4.48	2.45	4.80	5.80
picene	0.07	0.01	0.06	0.04	0.10	0.01	0.08	0.06	0.06	0.01			0.46	0.10	0.10	0.21	0.40	0.07	0.66	0.28	0.32	0.10	0.29	0.32	0.47	0.27	0.46	0.59
benzo(ghi)perylene	0.47	0.06	0.44	0.55	0.75	0.08	0.80	0.89	0.52	0.09	0.47	0.64	2.70	0.80	1.28	2.62	3.24	0.52	7.23	3.11	3.12	0.87	3.46	3.19	4.97	2.89	5.45	6.81
coronene	0.30	0.04	0.33	0.35	0.54	0.05	0.56	0.54	0.31	0.06	0.24	0.34	1.92	0.70	0.66	1.14	2.43	0.35	4.11	1.66	2.06	0.64	2.06	1.82	3.87	2.40	3.10	3.39
propanedioic acid	15.59	2.50	15.96	20.16	5.60	4.11	18.57	16.82	4.92		17.60	18.78	14.90	3.14	24.65	12.43	5.46	0.67	14.34	20.94	5.09	1.38	24.94	17.07	22.14	10.88	26.37	14.59
methylpropanedioic acid	0.30	0.06	0.31	0.34			0.25	0.26	0.15		0.27	0.31	0.43	0.09	0.34	0.25	0.24	0.09	0.25	0.37	0.19		0.29	0.30		0.23	0.37	0.30
butanedioic acid	19.55	2.85	6.18	15.83	7.75	3.65	6.61	10.38	15.14	3.95	5.65	12.53	24.91	4.45	8.43	10.18	15.58	2.59	12.69	10.34	10.85	3.48	9.45	14.97	22.10	8.91	9.84	16.17
methylbutanedioic acid	2.37	0.29	0.59	1.44	1.13	0.36	0.56	1.03	1.88	0.42	0.48	1.04	4.80	0.76	0.90	1.36	2.52	0.41	1.57	1.01	1.72	0.44	0.97	1.33	2.86	0.87	1.04	1.95
pentanedioic acid	5.46	0.96	2.37	4.51	3.08	0.87	1.81	2.80	5.56	1.24	1.39	3.31	7.17	1.33	2.33	2.98	4.03	0.71	3.80	2.93	4.06	1.82	3.11	3.67	4.93	1.66	2.60	3.54
hexanedioic acid	1.42	0.25	0.95	1.72	1.01	0.33	1.19	1.43	1.71	0.38	1.13	1.67	3.43	1.29	2.40	1.82	1.94	0.47	2.37	1.84	1.59	0.56	1.83	2.06	2.48	0.92	1.97	1.93
heptanedioic acid	0.43	0.10	0.33	0.47	0.40	0.13	0.41	0.39	0.67	0.17	0.32	0.63	1.81	0.64	0.78	0.57	1.15	0.21	0.65	0.57	0.81	0.37	0.49	0.46	1.65	0.62	0.72	0.61
octanedioic acid	0.46	0.11	0.47	0.49	0.48	0.18	0.61	0.68	1.01	0.32	0.63	0.98	3.16	1.13	1.20	1.12	1.17	0.40	1.14	0.88	0.95	0.72	0.90	0.92	1.89	0.95	1.21	1.15
nonanedioic acid	1.23	0.29	1.35	1.49	2.31	0.78	2.38	3.32	5.56	1.47	3.12	5.29	12.27	5.06	5.07	5.50	4.76	1.15	5.72	4.08	5.14	3.62	4.49	4.29	11.26	4.58	6.76	6.14
OC	4847	3518	5710	5534	6873	4057	7504	6716	7479	4683	6407	7833	12541	8119	8840	7762	11293	4149	12019	15116	12155	6640	12321	9390	16961	13789	20446	19235
EC	698	597	890	1118	2137	1233	2023	2560	1854	1346	2001	2432	1585	1163	1513	1481	2474	1401	2121	3948	3958	2493	4059	3743	4495	3047	4672	5294

Note: TM: Tap Mun, TC: Tung Chung, CW: Central and Western, CH: Conghua, ZS: Zhongshan, SZ: Shenzhen, GZ: Guangzhou

Table 18. Source Contributions to Organic Carbon in PM2.5 (μg /m^3)

Site	Season	Diesel Exhaust	Gasoline Exhaust	Meat Cooking	Cigarette Smoke	Biomass Burning	Road Dust	Vegetative Detritus	Coal Combustion	Other OC	Measured Organic Carbon	R^2	χ^2	% Mass	DF
TM	Spring	0.38±0.13	0.37±0.09	0.22±0.06	0.03±0.006	0.78±0.23	0.36±0.02	0.07±0.01	0.19±0.03	2.45	4.85±0.39	0.97	2.07	50	16
	Summer	0.29±0.04	-	0.07±0.02	-	0.05±0.02	0.32±0.01	0.03±0.005	0.02±0.004	2.73	3.52±0.35	0.95	2.32	23	19
	Fall	0.48±0.15	0.25±0.10	0.74±0.21	0.08±0.02	0.86±0.25	0.54±0.02	0.10±0.02	0.20±0.03	2.46	5.71±0.47	0.98	2.5	57	14
	Winter	0.58±0.15	0.38±0.10	0.50±0.14	0.08±0.02	1.53±0.43	0.38±0.02	0.08±0.02	0.18±0.03	1.79	5.50±0.42	0.98	1.35	68	13
	Mean	0.43±0.13	0.25±0.18	0.38±0.30	0.05±0.04	0.81±0.61	0.40±0.10	0.07±0.03	0.15±0.09	2.36	4.90±0.99	0.97	2.06	49	16
TC	Spring	1.40±0.20	0.50±0.09	0.22±0.08	0.16±0.03	0.55±0.16	0.28±0.02	0.05±0.02	0.30±0.04	3.40	6.87±0.49	0.95	2.34	50	21
	Summer	0.68±0.11	0.07±0.03	0.07±0.02	0.03±0.008	0.08±0.02	0.29±0.02	0.03±0.007	0.03±0.005	2.77	4.06±0.38	0.96	1.66	32	21
	Fall	1.14±0.20	0.38±0.08	1.31±0.36	0.10±0.02	2.20±0.62	0.44±0.02	0.12±0.02	0.27±0.04	1.55	7.50±0.56	0.98	1.22	79	19
	Winter	1.70±0.24	0.43±0.10	0.94±0.26	0.26±0.05	1.90±0.54	0.30±0.02	0.07±0.03	0.34±0.05	0.79	6.72±0.50	0.96	2.59	88	18
	Mean	1.23±0.43	0.35±0.19	0.64±0.59	0.14±0.10	1.18±1.03	0.33±0.08	0.07±0.04	0.24±0.14	2.13	6.29±1.52	0.96	1.95	62	20
CW	Spring	1.29±0.20	0.78±0.10	0.89±0.20	0.21±0.04	0.69±0.20	0.31±0.02	0.06±0.02	0.19±0.03	3.06	7.48±0.53	0.97	1.58	59	22
	Summer	0.77±0.12	0.15±0.04	0.14±0.04	0.07±0.01	0.18±0.05	0.34±0.01	0.03±0.009	0.03±0.005	2.97	4.68±0.43	0.97	1.66	37	22
	Fall	1.36±0.20	0.32±0.09	1.87±0.50	0.15±0.03	1.04±0.29	0.51±0.02	0.11±0.02	-	1.04	6.40±0.50	0.98	2.51	84	13
	Winter	2.03±0.38	0.68±0.13	1.10±0.30	0.34±0.09	2.01±0.57	0.35±0.02	0.09±0.04	-	1.23	7.83±0.55	0.97	2.25	84	14
	Mean	1.36±0.52	0.48±0.30	1.00±0.71	0.19±0.11	0.98±0.77	0.38±0.09	0.07±0.04	0.06±0.09	2.08	6.60±1.42	0.97	1.99	66	18
CH	Spring	-	0.60±0.14	2.12±0.51	0.29±0.05	3.42±1.00	0.42±0.04	0.44±0.08	1.23±0.13	4.01	12.54±0.85	0.95	2.01	68	19
	Summer	0.66±0.15	0.17±0.06	1.30±0.35	0.07±0.01	0.50±0.15	0.47±0.02	0.06±0.01	0.29±0.03	4.60	8.12±0.64	0.98	2.2	43	17
	Fall	0.56±0.19	0.54±0.11	1.66±0.45	0.08±0.02	2.46±0.69	0.81±0.03	0.18±0.03	0.46±0.06	2.09	8.84±0.63	0.97	2.7	76	18
	Winter	-	0.72±0.14	3.70±0.99	0.06±0.02	3.49±0.97	0.41±0.02	0.14±0.03	1.16±0.12	NV	7.76±0.58	0.96	2.32	125	20
	Mean	0.31±0.35	0.51±0.24	2.20±1.06	0.13±0.11	2.47±1.39	0.53±0.19	0.21±0.16	0.79±0.48	2.68	9.32±2.20	0.97	2.31	78	19
ZS	Spring	0.64±0.25	0.77±0.11	0.85±0.24	0.15±0.03	1.27±0.36	0.68±0.02	0.13±0.03	1.48±0.16	5.32	11.29±0.76	0.98	1.78	53	18
	Summer	1.08±0.13	-	0.11±0.03	0.03±0.009	0.20±0.06	0.37±0.01	0.04±0.01	0.25±0.03	2.07	4.15±0.37	0.98	1.96	50	16
	Fall	-	3.16±0.34	1.11±0.32	0.51±0.11	3.37±1.05	0.96±0.04	0.20±0.07	2.30±0.22	0.03	11.65±0.86	0.98	2.38	100	20
	Winter	1.73±0.33	1.27±0.19	1.18±0.33	0.27±0.06	4.11±1.17	0.98±0.03	0.15±0.04	1.25±0.15	4.19	15.12±1.00	0.99	1.83	72	18
	Mean	0.86±0.73	1.30±1.35	0.81±0.49	0.24±0.20	2.24±1.81	0.75±0.29	0.13±0.07	1.32±0.84	2.90	10.56±4.61	0.98	1.99	69	18
SZ	Spring	2.13±0.34	0.94±0.15	0.70±0.21	0.24±0.05	0.92±0.27	0.61±0.03	0.11±0.03	1.24±0.14	5.27	12.16±0.81	0.97	2.14	57	21
	Summer	1.48±0.22	0.42±0.08	0.90±0.25	0.16±0.02	0.41±0.12	0.37±0.02	-	0.32±0.04	2.59	6.64±0.53	0.97	1.59	61	22
	Fall	1.96±0.34	1.00±0.13	2.28±0.63	0.25±0.05	2.41±0.69	0.85±0.03	0.14±0.04	1.39±0.15	2.05	12.33±0.89	0.99	1.48	83	20
	Winter	2.68±0.47	0.95±0.17	1.11±0.31	0.28±0.06.	2.70±0.77	0.71±0.04	0.11±0.04	1.47±0.16	1.65	11.65±0.92	0.98	1.13	86	21
	Mean	2.06±0.50	0.83±0.27	1.25±0.71	0.23±0.05	1.61±1.12	0.64±0.20	0.09±0.06	1.11±0.53	2.89	10.70±2.72	0.98	1.59	72	21
GZ	Spring	1.95±0.38	2.69±0.32	1.32±0.41	0.69±0.11	3.14±0.94	0.69±0.04	0.22±0.07	1.71±0.20	4.55	16.96±1.15	0.96	2.79	73	23
	Summer	1.49±0.28	2.60±0.30	0.74±0.22	0.52±0.09	1.83±0.54	1.05±0.03	0.10±0.05	0.79±0.10	4.68	13.79±0.92	0.98	2.29	66	22
	Fall	1.81±0.38	2.28±0.29	5.37±1.47	0.62±0.12	4.00±1.16	0.94±0.04	0.29±0.08	1.92±0.22	3.23	20.45±1.33	0.98	1.72	84	20
	Winter	1.57±0.44	3.72±0.43	1.13±0.32	1.04±0.19	5.97±1.75	0.97±0.05	0.23±0.09	2.63±0.30	1.99	19.24±1.27	0.97	2.75	90	22
	Mean	1.71±0.20	2.82±0.62	2.14±2.17	0.72±0.23	3.74±1.74	0.91±0.16	0.21±0.08	1.76±0.76	3.61	17.61±2.93	0.97	2.39	78	22

Note: -, the contribution to OC is not significantly different from zero; NV, negative value.

Table 19. Percentage of Source Contributions to measured OC in PM2.5 (%)

Site	Season	Diesel Exhaust	Gasoline Exhaust	Meat Cooking	Cigarette Smoke	Biomass Burning	Road Dust	Vegetative Detritus	Coal Combustion	Other OC
TM	Spring	7.8	7.6	4.5	0.6	16.1	7.4	1.4	3.9	50.5
	Summer	8.2	-	2.0	-	1.4	9.1	0.9	0.6	77.6
	Fall	8.4	4.4	13.0	1.4	15.1	9.5	1.8	3.5	43.1
	Winter	10.5	6.9	9.1	1.5	27.8	6.9	1.5	3.3	32.5
	Mean	8.8	4.7	7.1	0.9	15.1	8.2	1.4	2.8	50.9
TC	Spring	20.4	7.3	3.2	2.3	8.0	4.1	0.7	4.4	49.5
	Summer	16.7	1.7	1.7	0.7	2.0	7.1	0.7	0.7	68.2
	Fall	15.2	5.1	17.5	1.3	29.3	5.9	1.6	3.6	20.7
	Winter	25.3	6.4	14.0	3.9	28.3	4.5	1.0	5.1	11.8
	Mean	19.4	5.1	9.1	2.1	16.9	5.4	1.0	3.4	37.5
CW	Spring	17.2	10.4	11.9	2.8	9.2	4.1	0.8	2.5	40.9
	Summer	16.5	3.2	3.0	1.5	3.8	7.3	0.6	0.6	63.5
	Fall	21.3	5.0	29.2	2.3	16.3	8.0	1.7	-	16.3
	Winter	25.9	8.7	14.0	4.3	25.7	4.5	1.1	-	15.7
	Mean	20.2	6.8	14.5	2.7	13.7	6.0	1.1	0.8	34.1
CH	Spring	-	4.8	16.9	2.3	27.3	3.3	3.5	9.8	32.0
	Summer	8.1	2.1	16.0	0.9	6.2	5.8	0.7	3.6	56.7
	Fall	6.3	6.1	18.8	0.9	27.8	9.2	2.0	5.2	23.6
	Winter	-	9.3	47.7	0.8	45.0	5.3	1.8	14.9	NV
	Mean	3.6	5.6	24.8	1.2	26.6	5.9	2.0	8.4	28.1
ZS	Spring	5.7	6.8	7.5	1.3	11.2	6.0	1.2	13.1	47.1
	Summer	26.0	-	2.7	0.7	4.8	8.9	1.0	6.0	49.9
	Fall	-	27.1	9.5	4.4	28.9	8.2	1.7	19.7	0.3
	Winter	11.4	8.4	7.8	1.8	27.1	6.5	1.0	8.3	27.7
	Mean	10.8	10.6	6.9	2.1	18.0	7.4	1.2	11.8	31.2
SZ	Spring	17.5	7.7	5.8	2.0	7.6	5.0	0.9	10.2	43.3
	Summer	22.3	6.3	13.6	2.4	6.2	5.6	-	4.8	39.0
	Fall	15.9	8.1	18.5	2.0	19.5	6.9	1.1	11.3	16.6
	Winter	23.0	8.2	9.5	2.4	23.2	6.1	0.9	12.6	14.2
	Mean	19.7	7.6	11.8	2.2	14.1	5.9	0.7	9.7	28.3
GZ	Spring	11.5	15.9	7.8	4.1	18.5	4.1	1.3	10.1	26.8
	Summer	10.8	18.9	5.4	3.8	13.3	7.6	0.7	5.7	33.9
	Fall	8.9	11.1	26.3	3.0	19.6	4.6	1.4	9.4	15.8
	Winter	8.2	19.3	5.9	5.4	31.0	5.0	1.2	13.7	10.3
	Mean	9.8	16.3	11.3	4.1	20.6	5.3	1.2	9.7	21.7

Note: -, the contribution to OC is not significantly different from zero; NV, negative value.

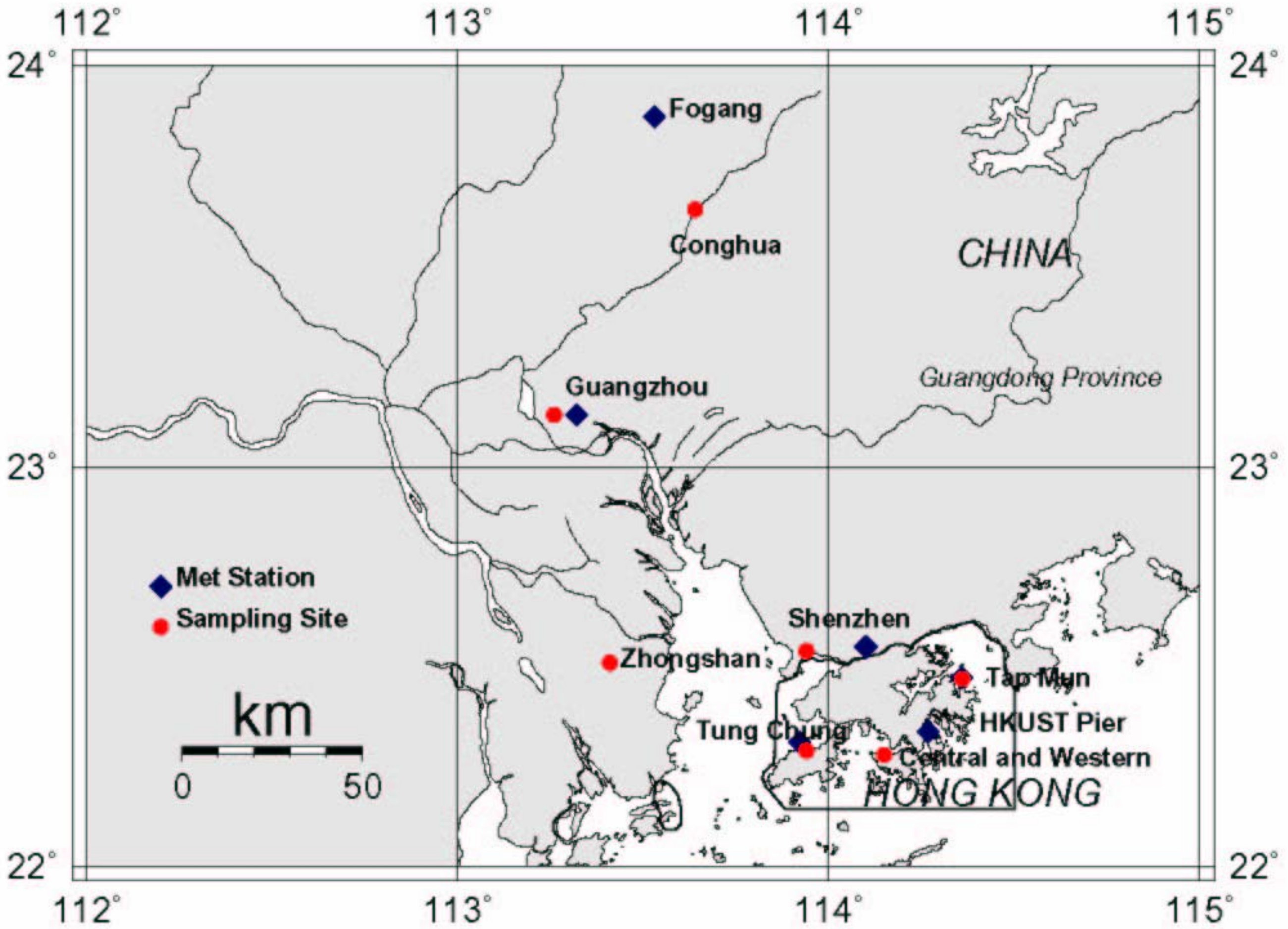
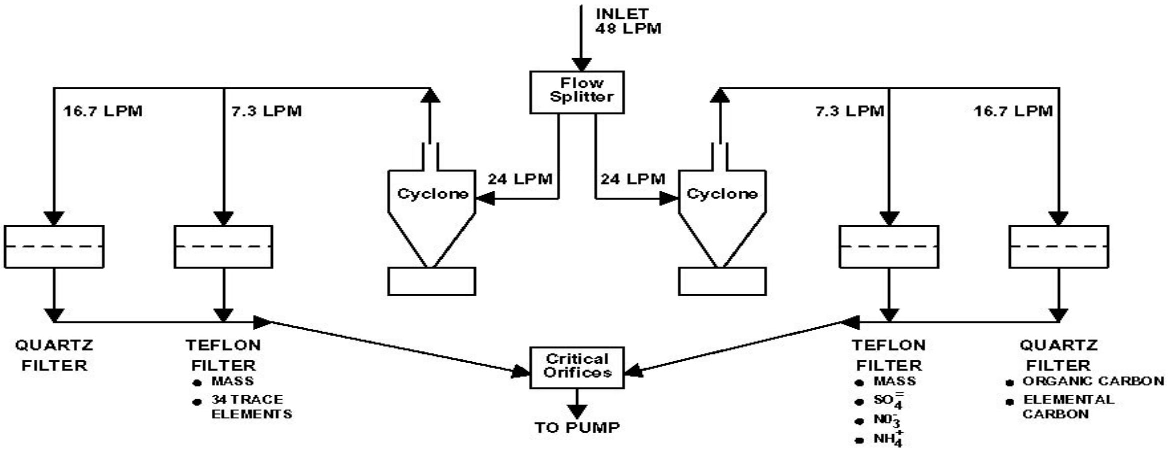
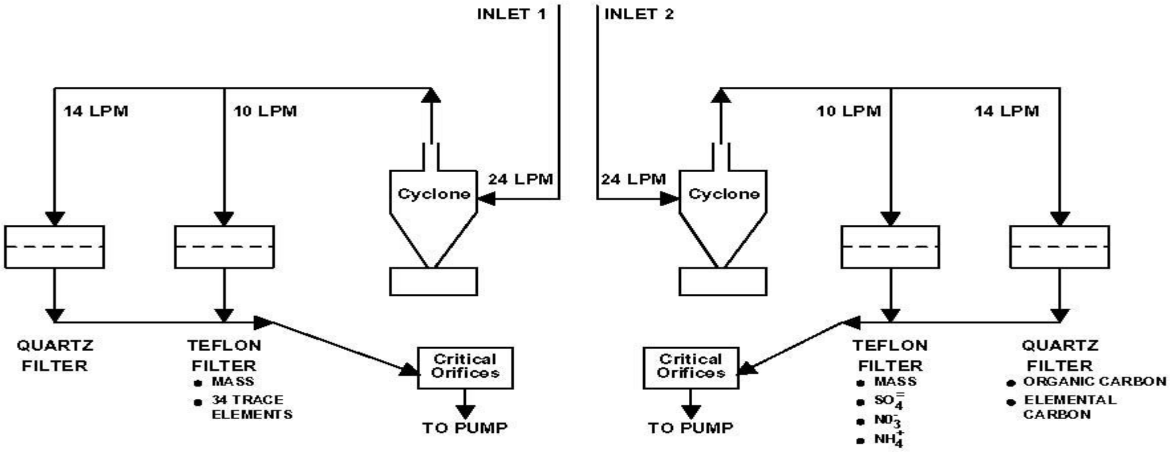


Figure 1. Sampling and Meteorological Measurement Sites in the PRD



(a) Andersen Sampler



(b) Caltech Sampler

Figure 2. Schematic Diagrams of both the ThermoAndersen and Caltech samplers used to collect daily 24-hr filter samples

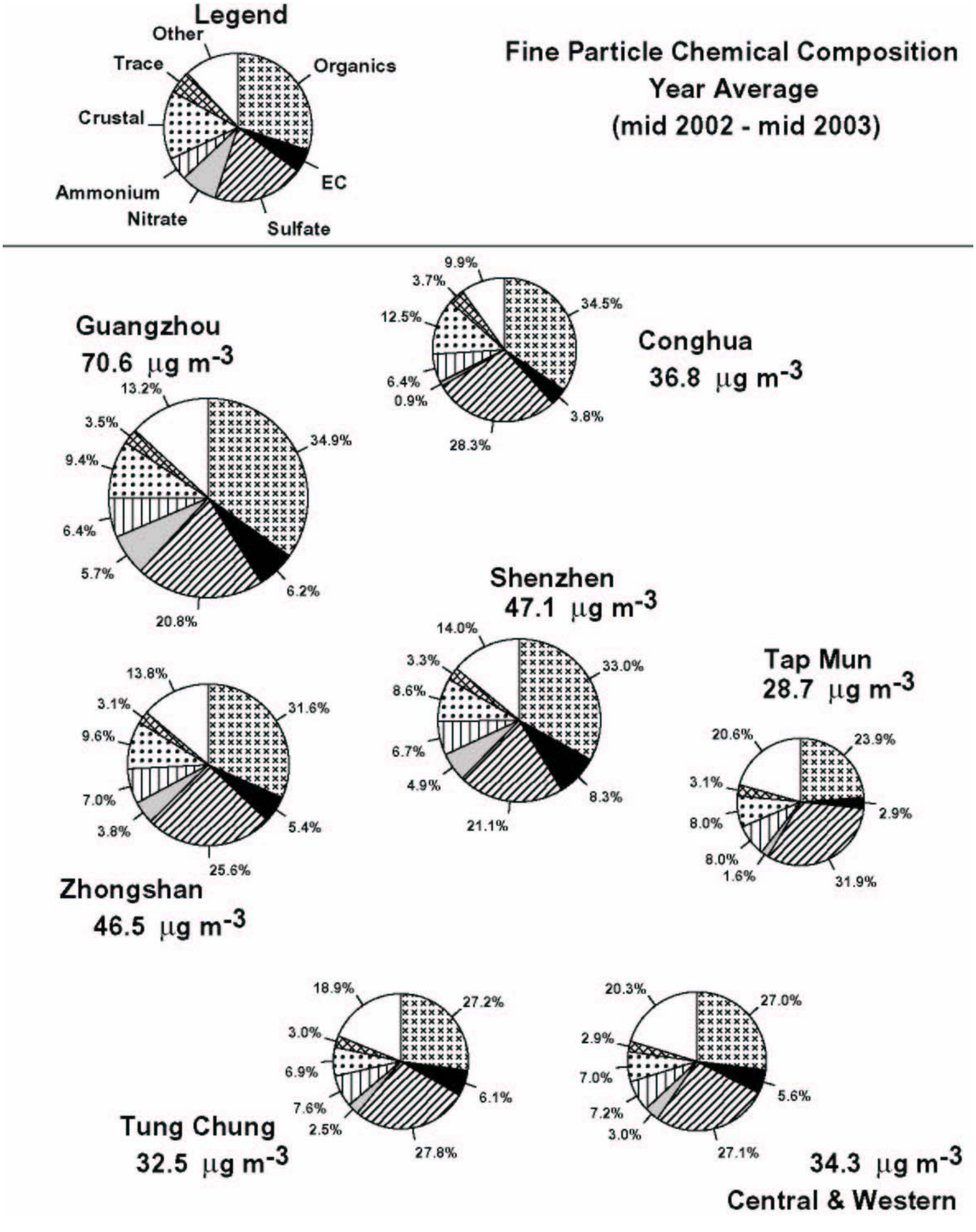


Figure 3. Annual Mean Concentrations Across the Pearl River Delta Region

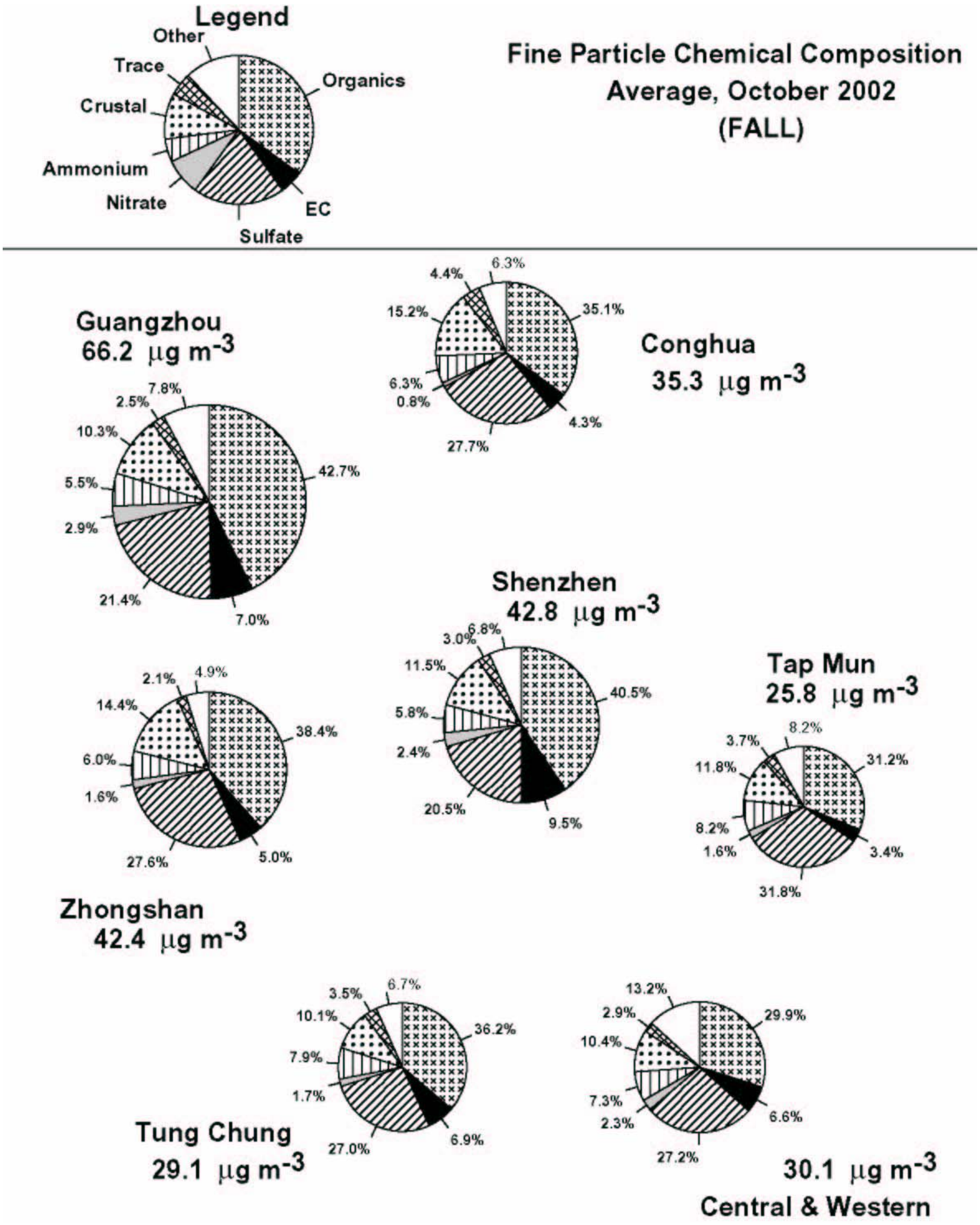


Figure 4. Monthly Mean Concentrations During October 2002

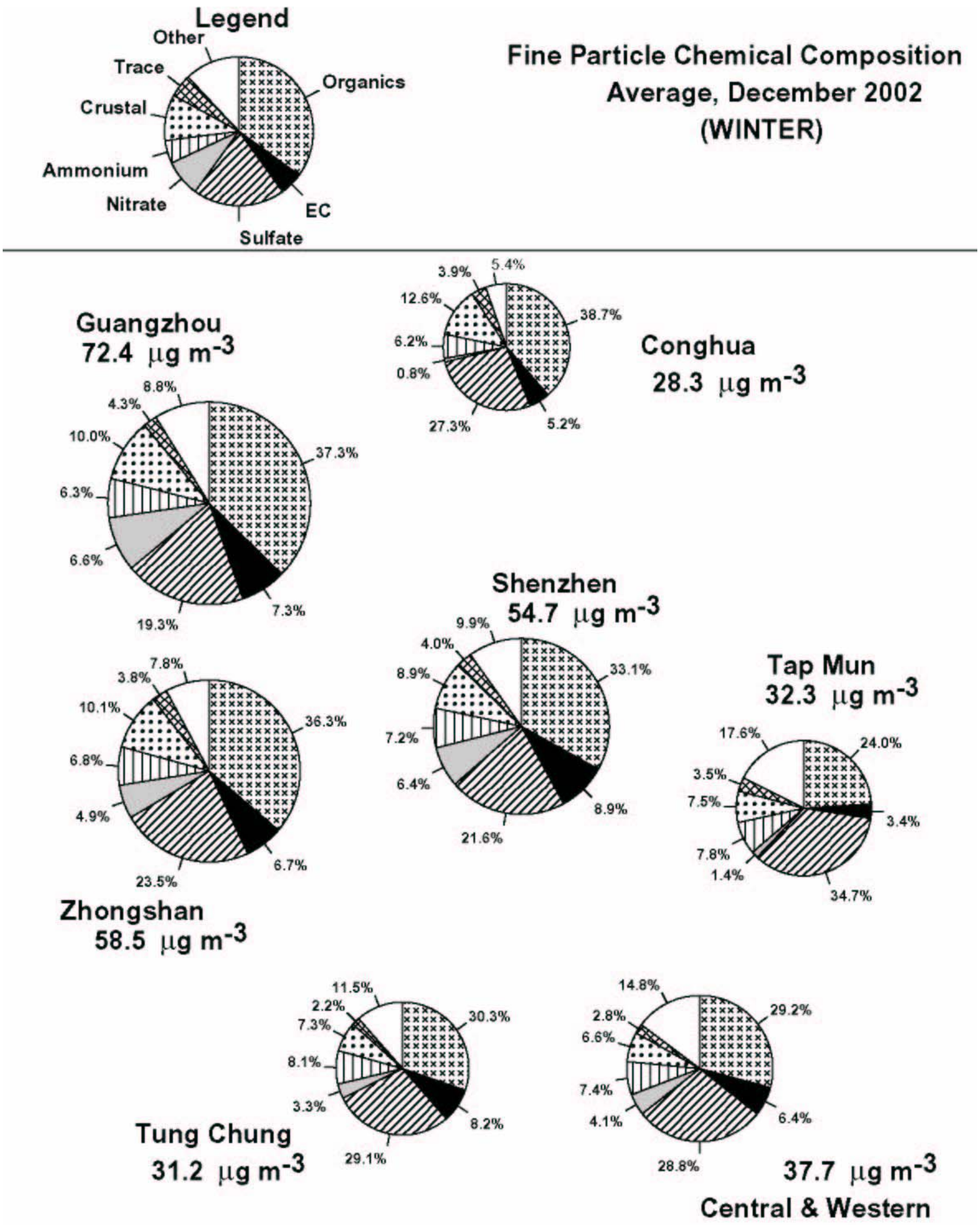


Figure 5. Monthly Mean Concentrations During December 2002

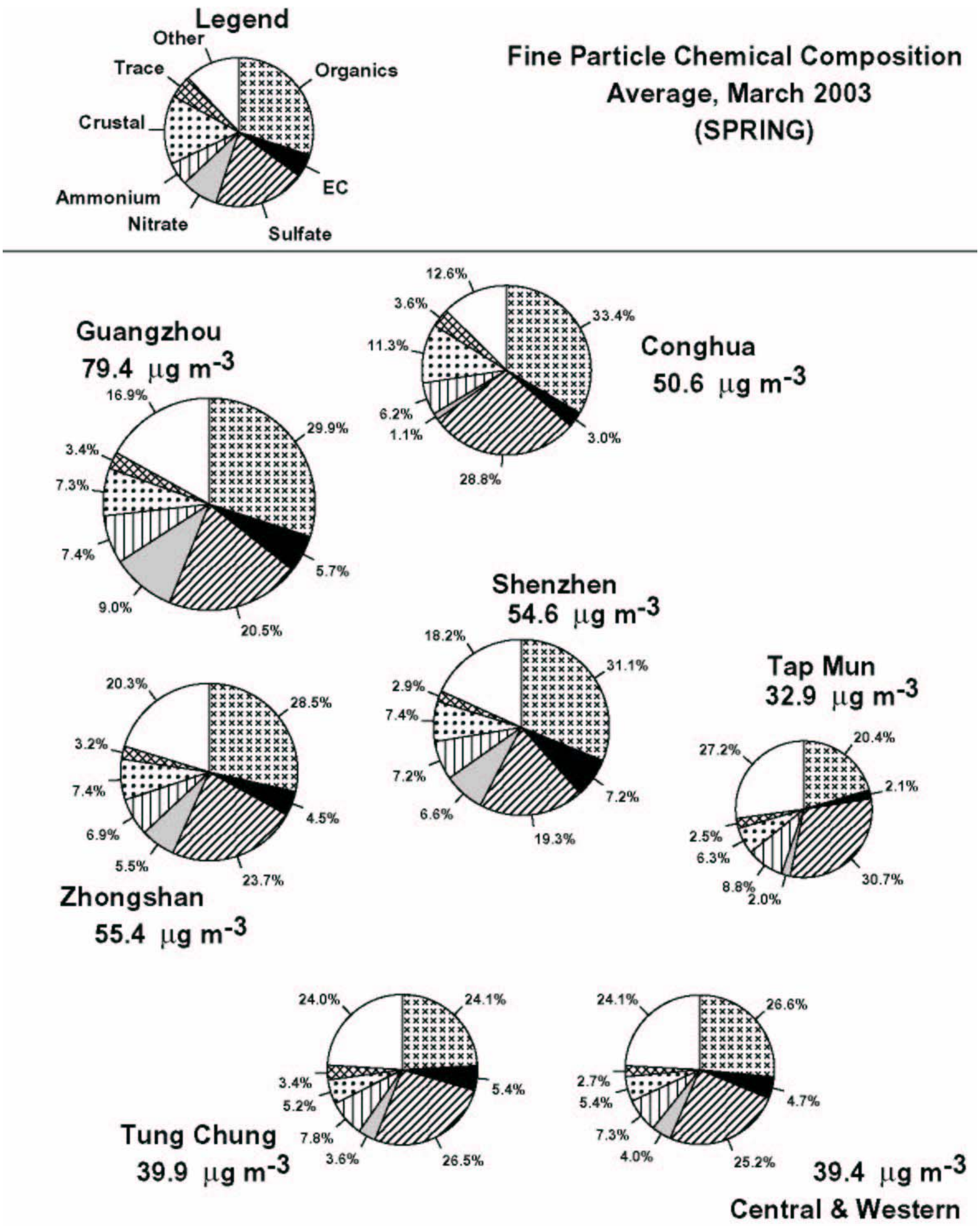


Figure 6. Monthly Mean Concentrations During March 2003

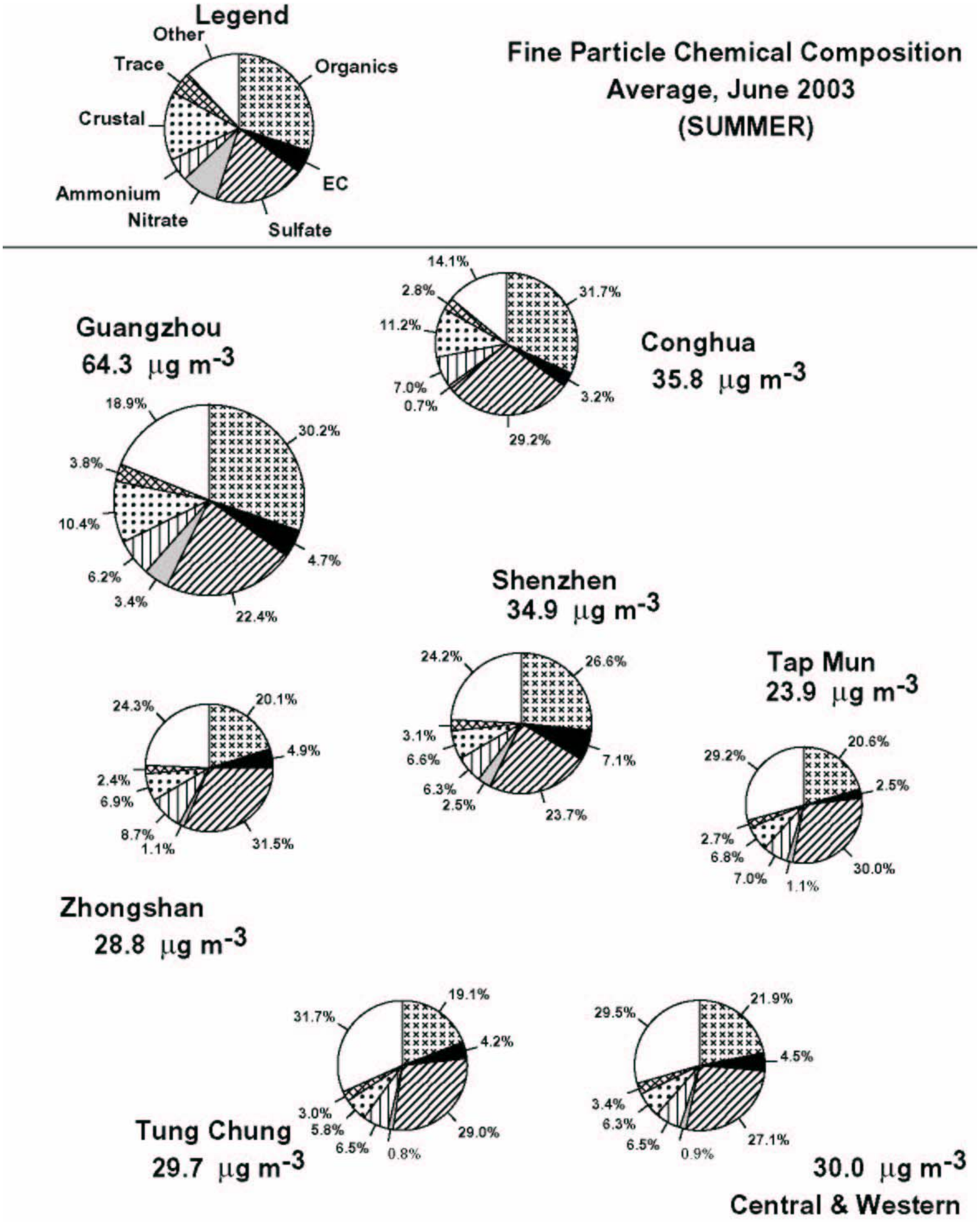


Figure 7. Monthly Mean Concentrations During June 2003

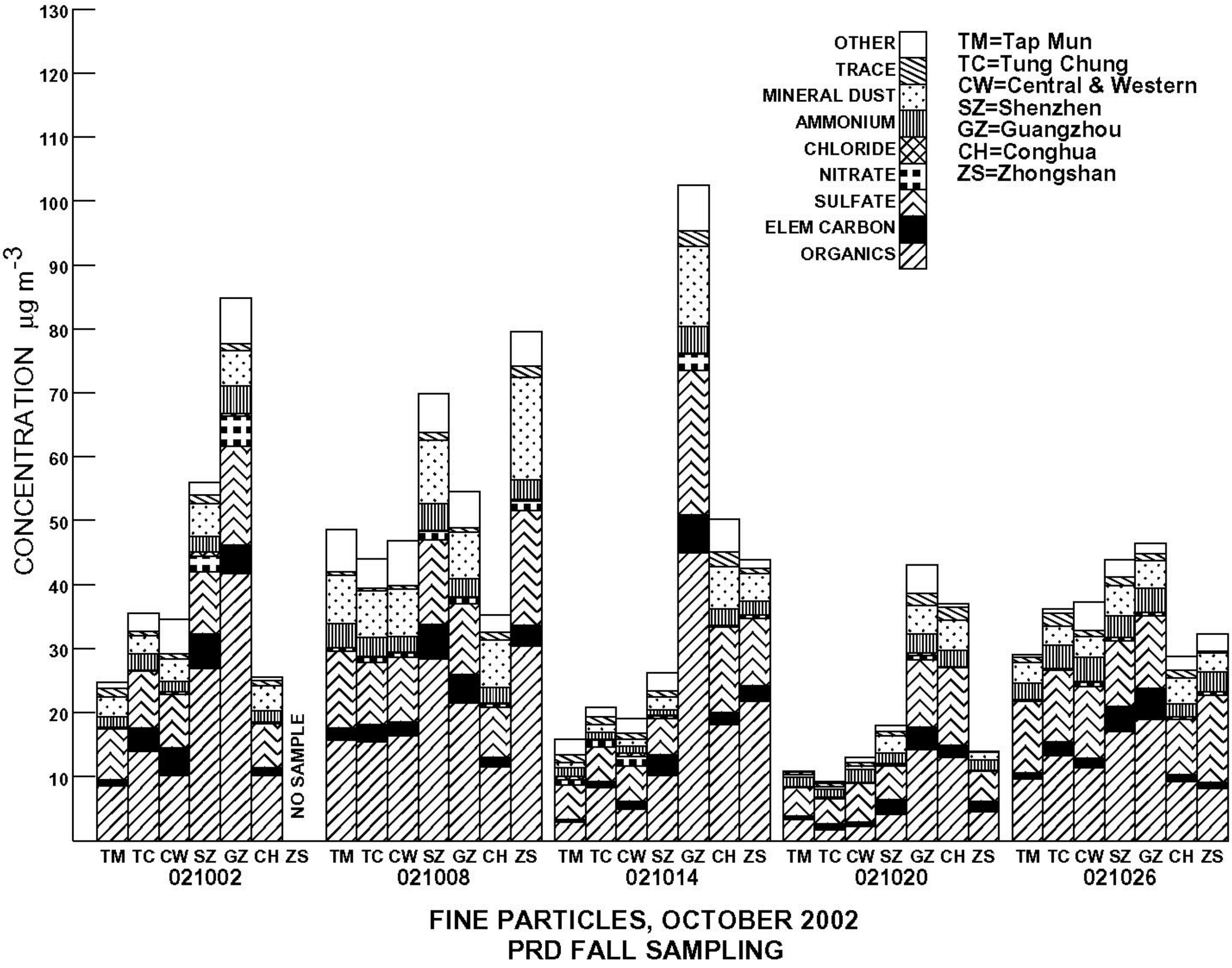


Figure 8. Daily Concentrations During October 2002

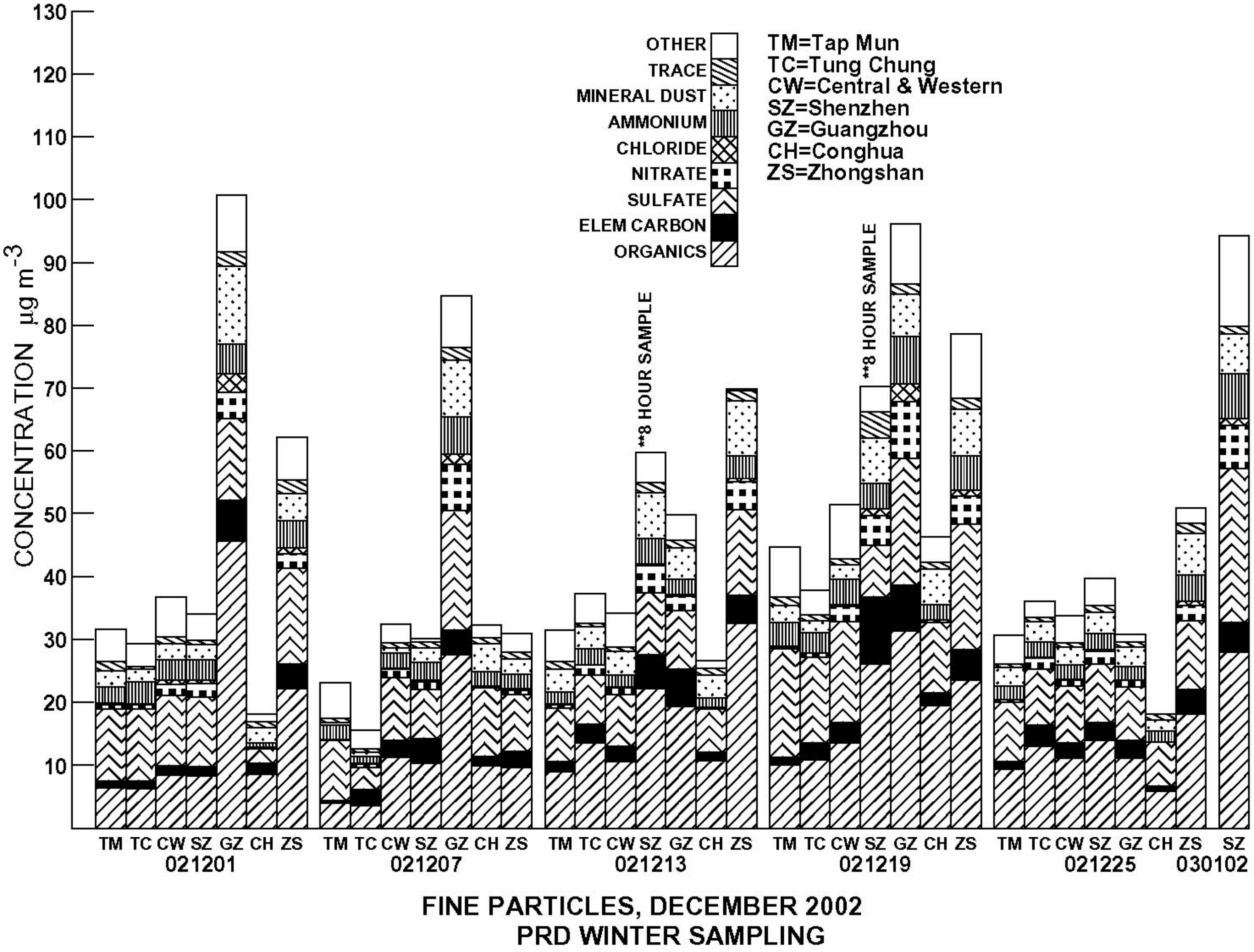


Figure 9. Daily Concentrations During December 2002

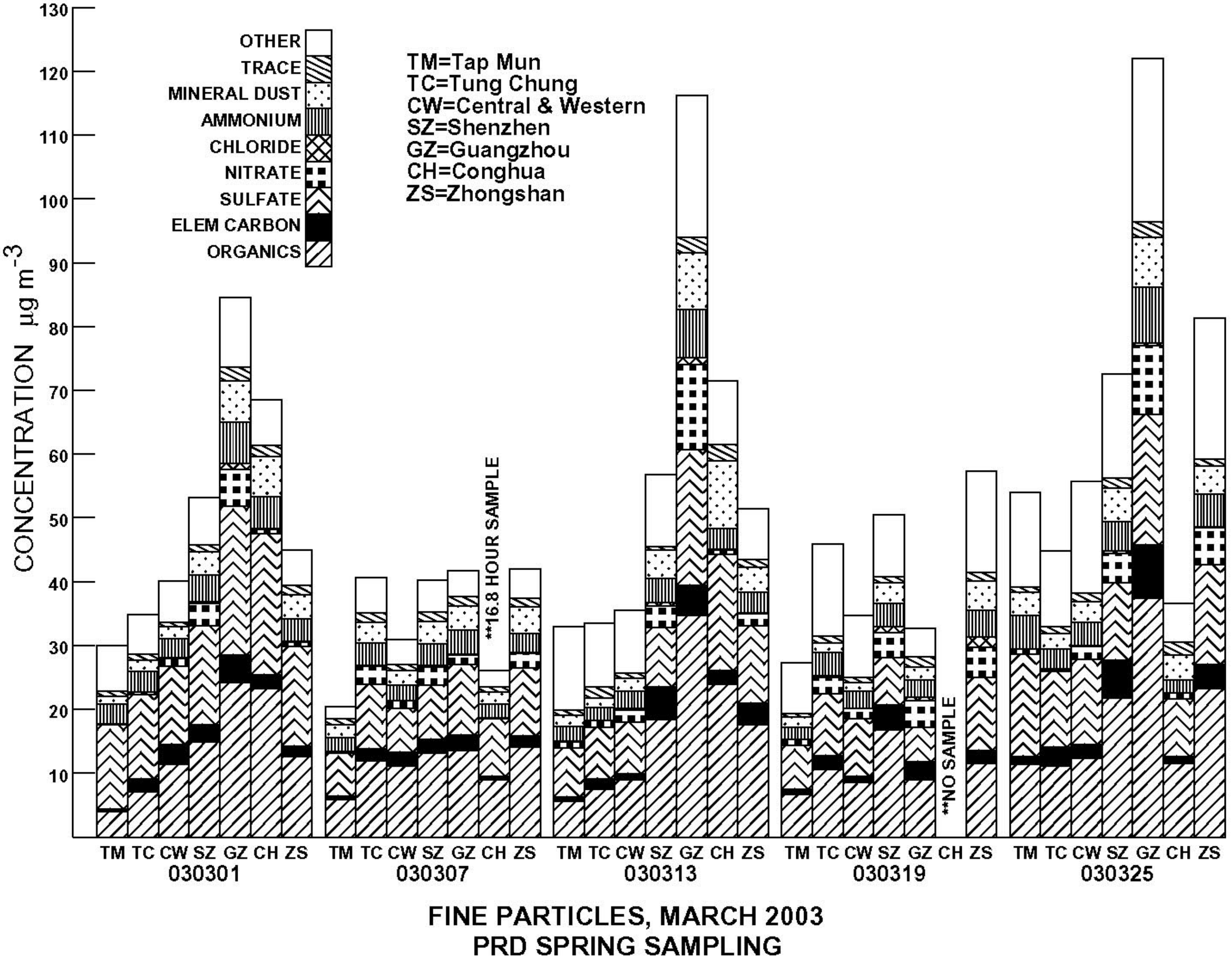


Figure 10. Daily Concentrations During March 2003

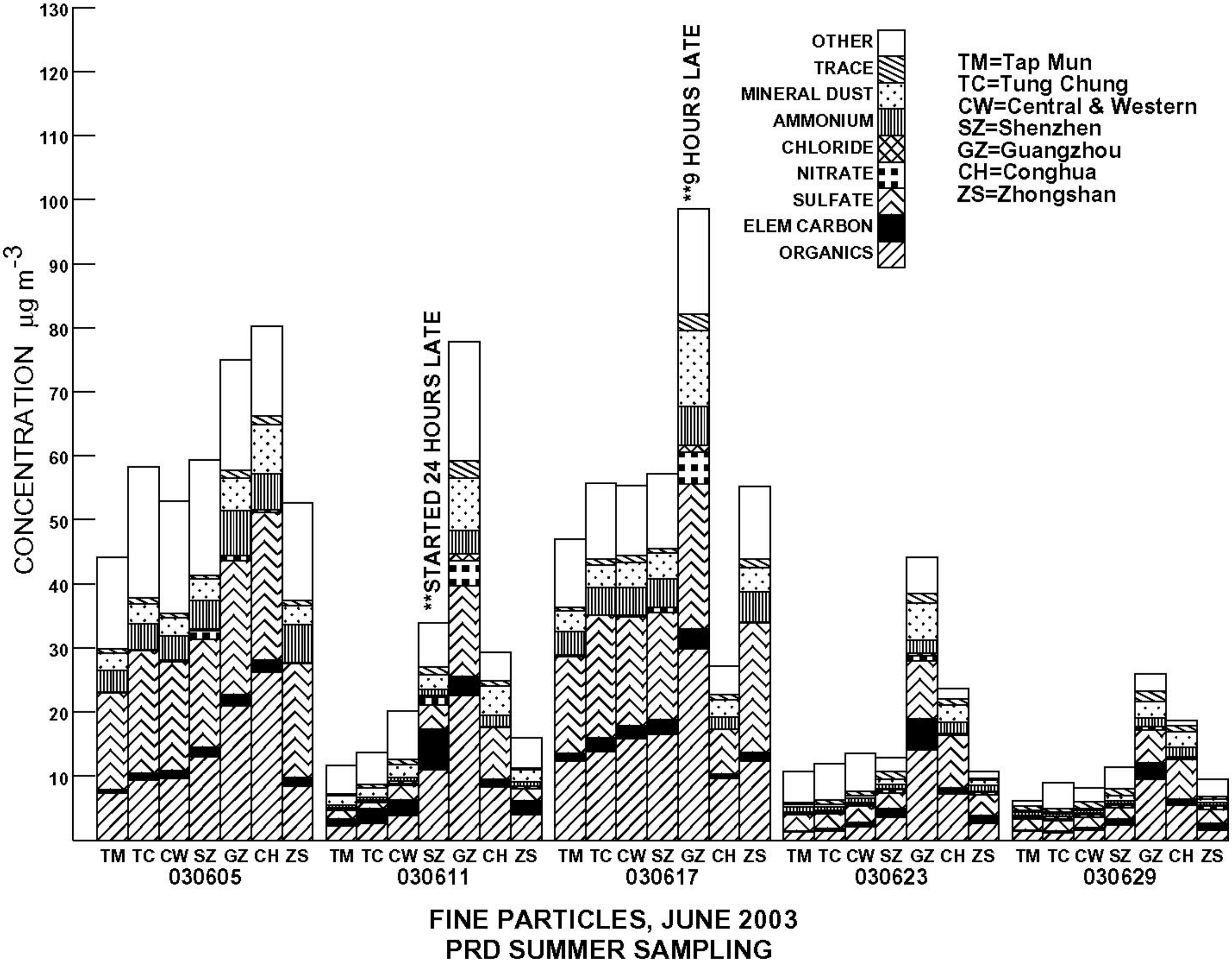


Figure 11. Daily Concentrations During June 2003

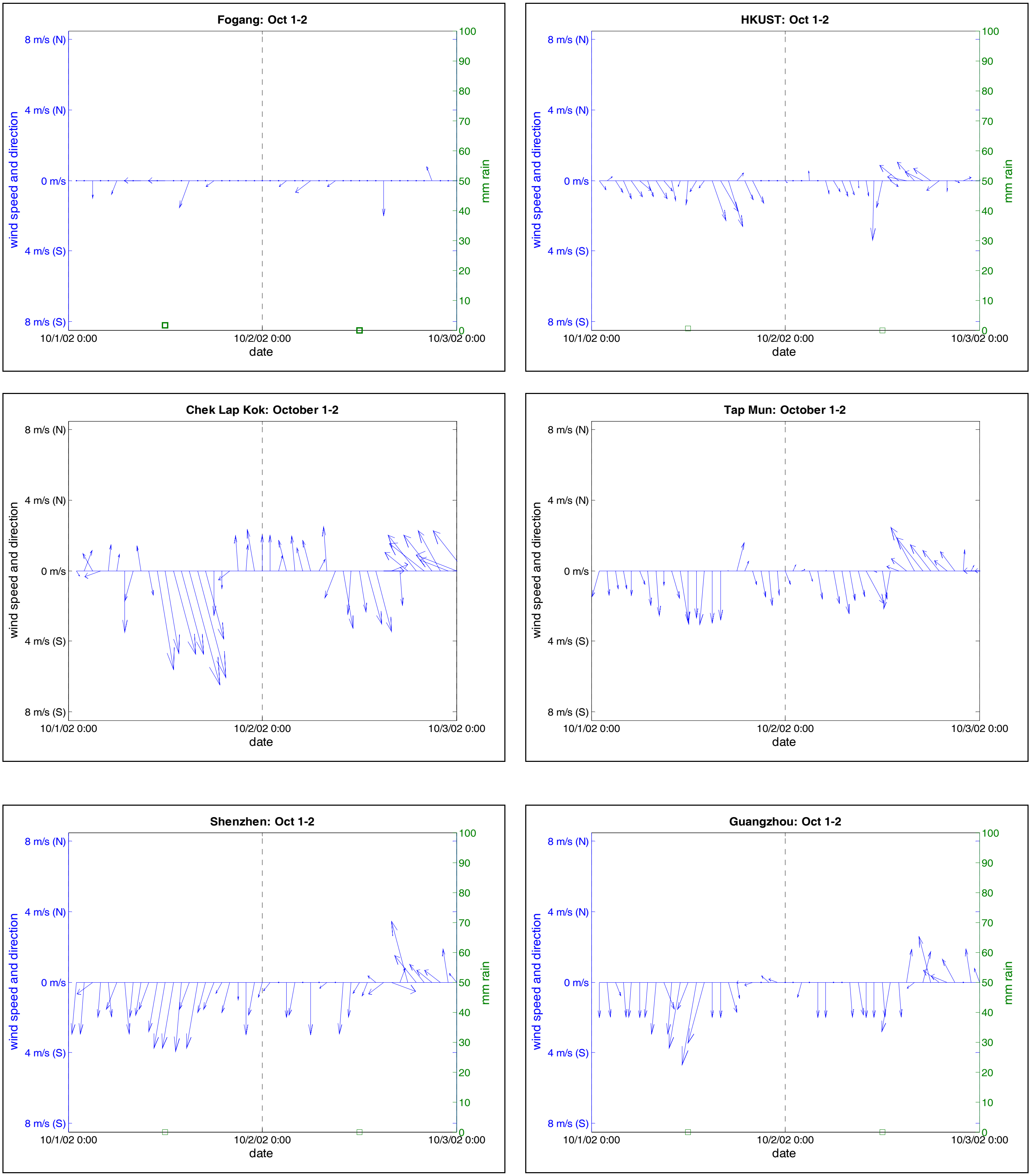


Figure 12. Wind Speed, Direction and Precipitation During October 1-2, 2002

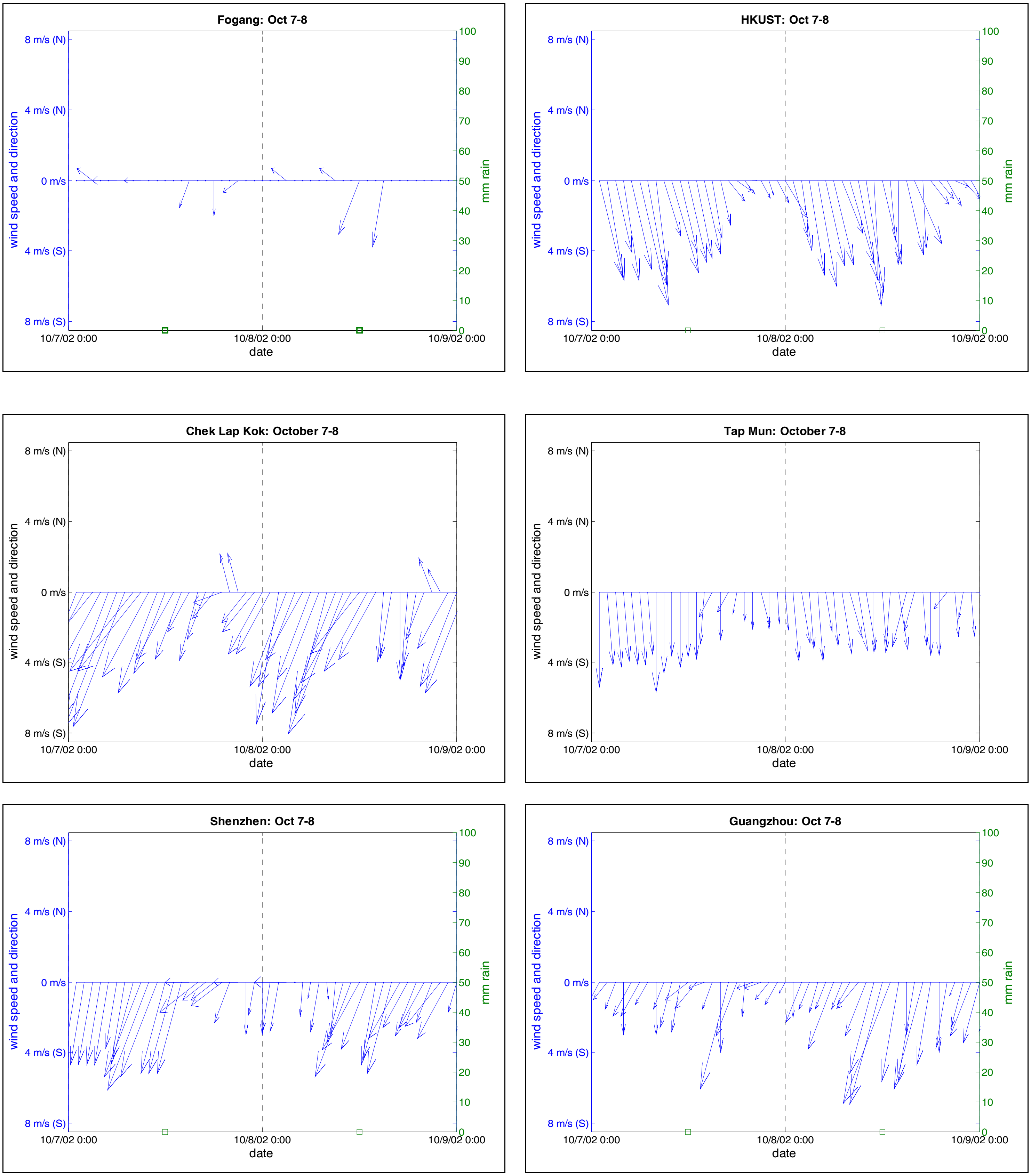


Figure 13. Wind Speed, Direction and Precipitation During October 7-8, 2002

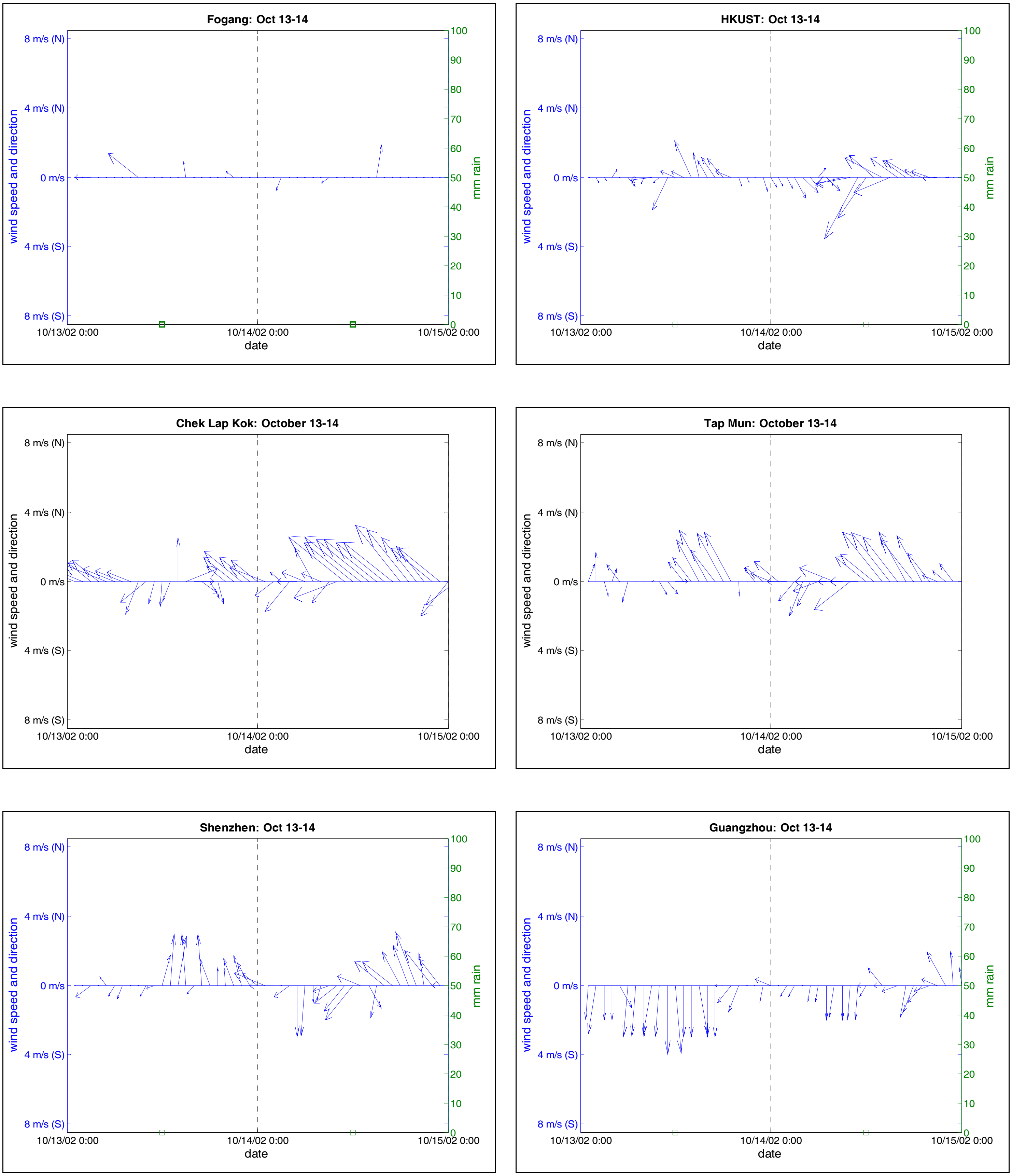


Figure 14. Wind Speed, Direction and Precipitation During October 13-14, 2002

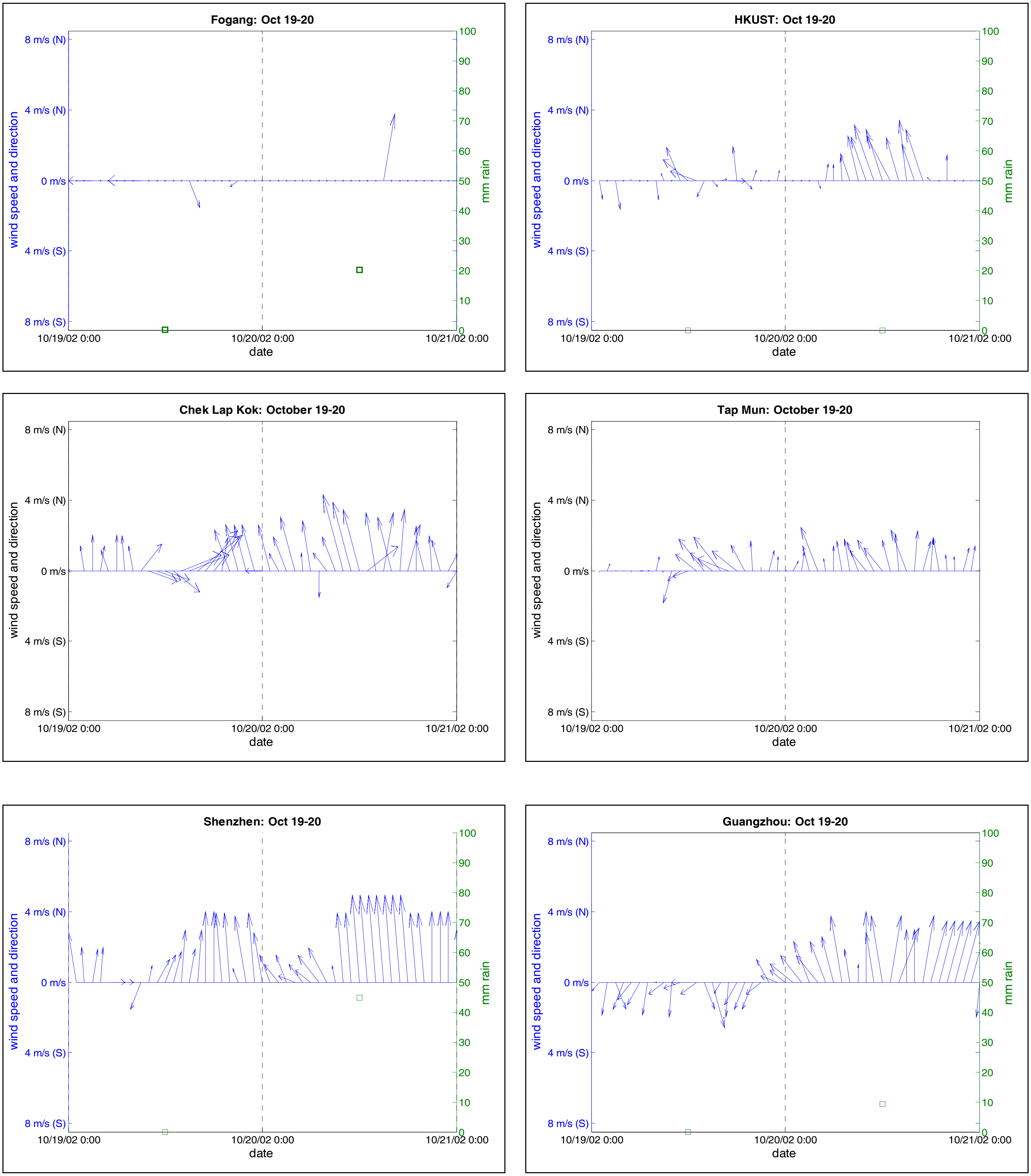


Figure 15. Wind Speed, Direction and Precipitation During October 19-20, 2002

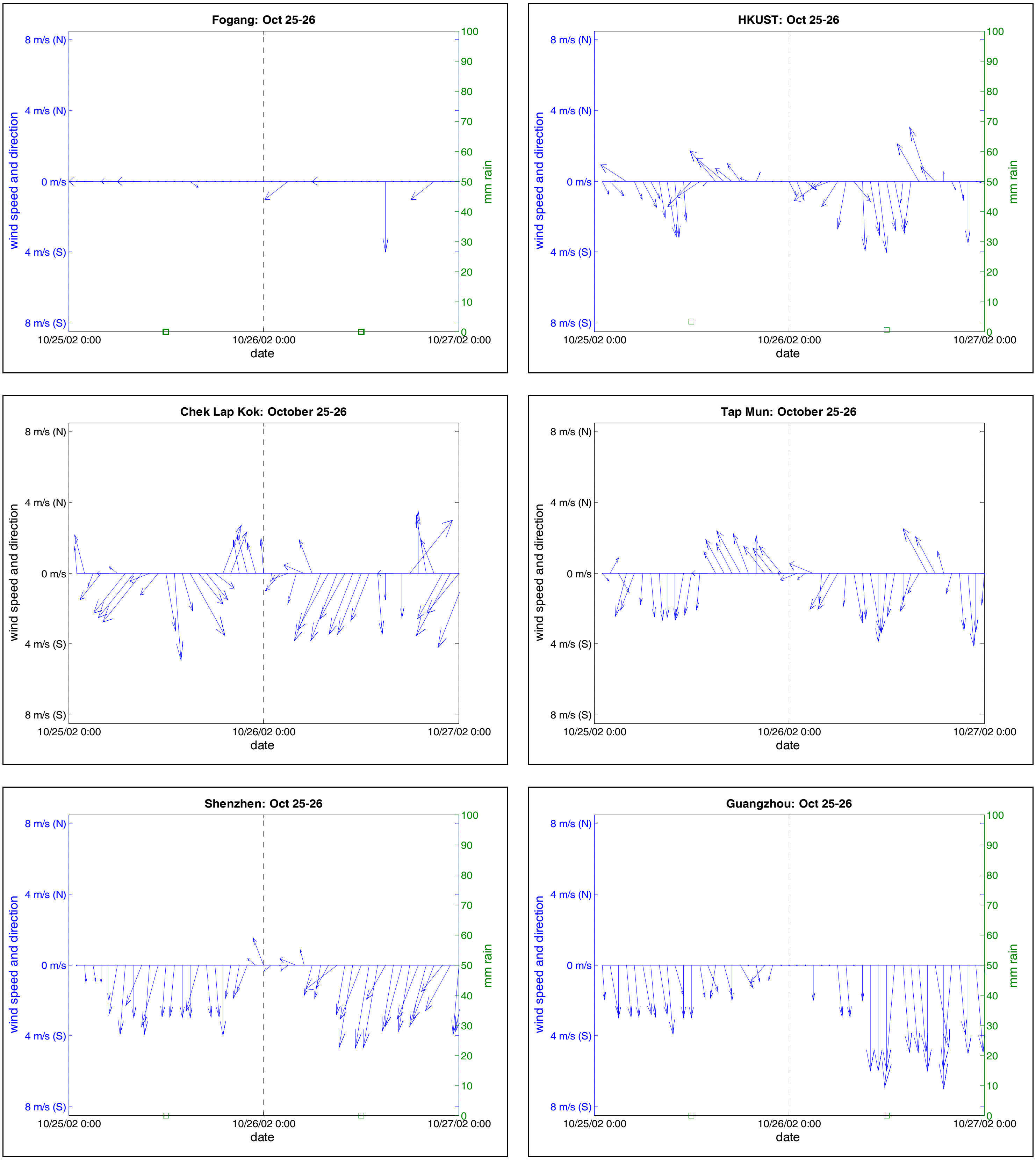


Figure 16. Wind Speed, Direction and Precipitation During October 25-26, 2002

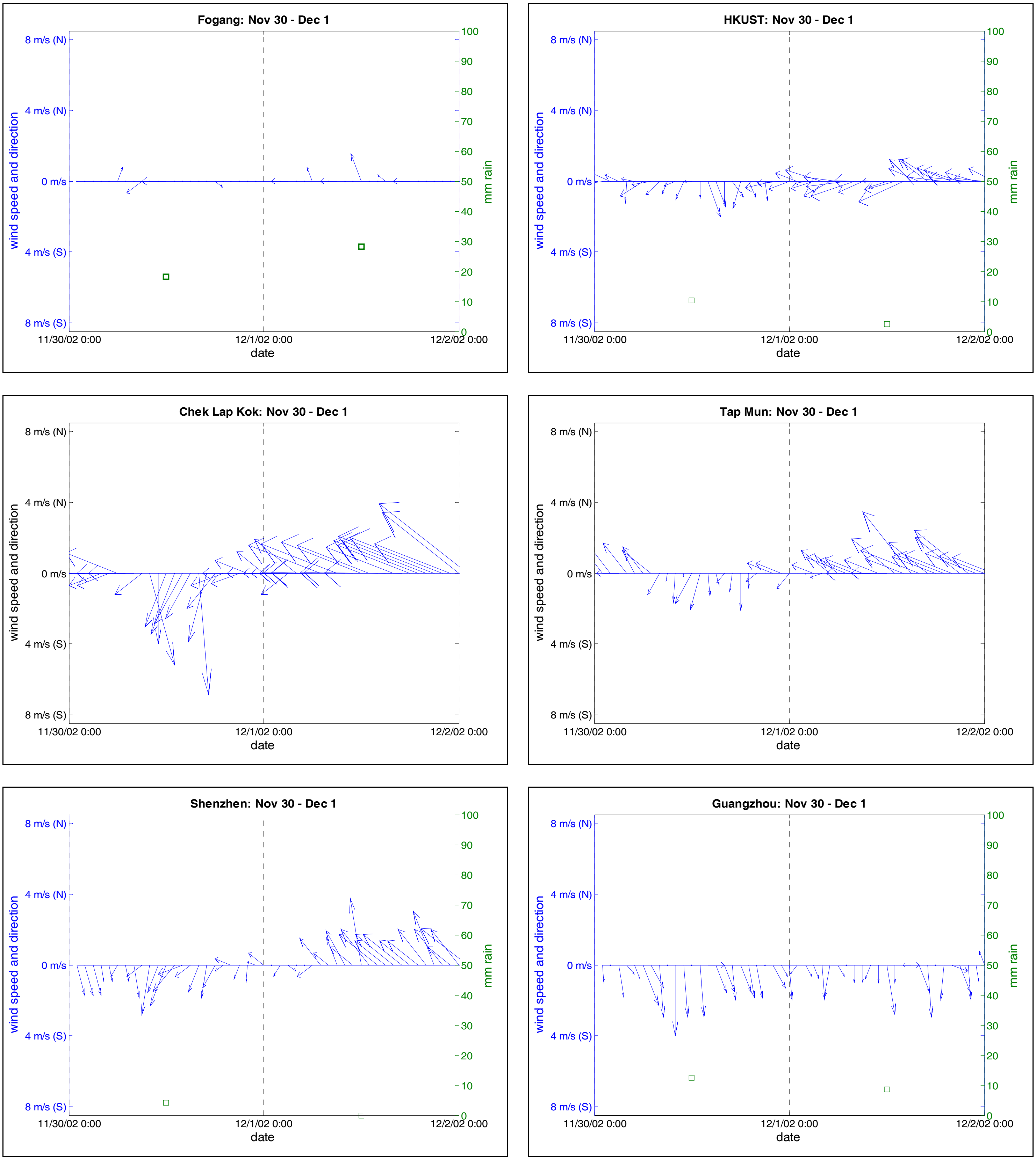


Figure 17. Wind Speed, Direction and Precipitation During Nov. 30 – Dec. 1, 2002

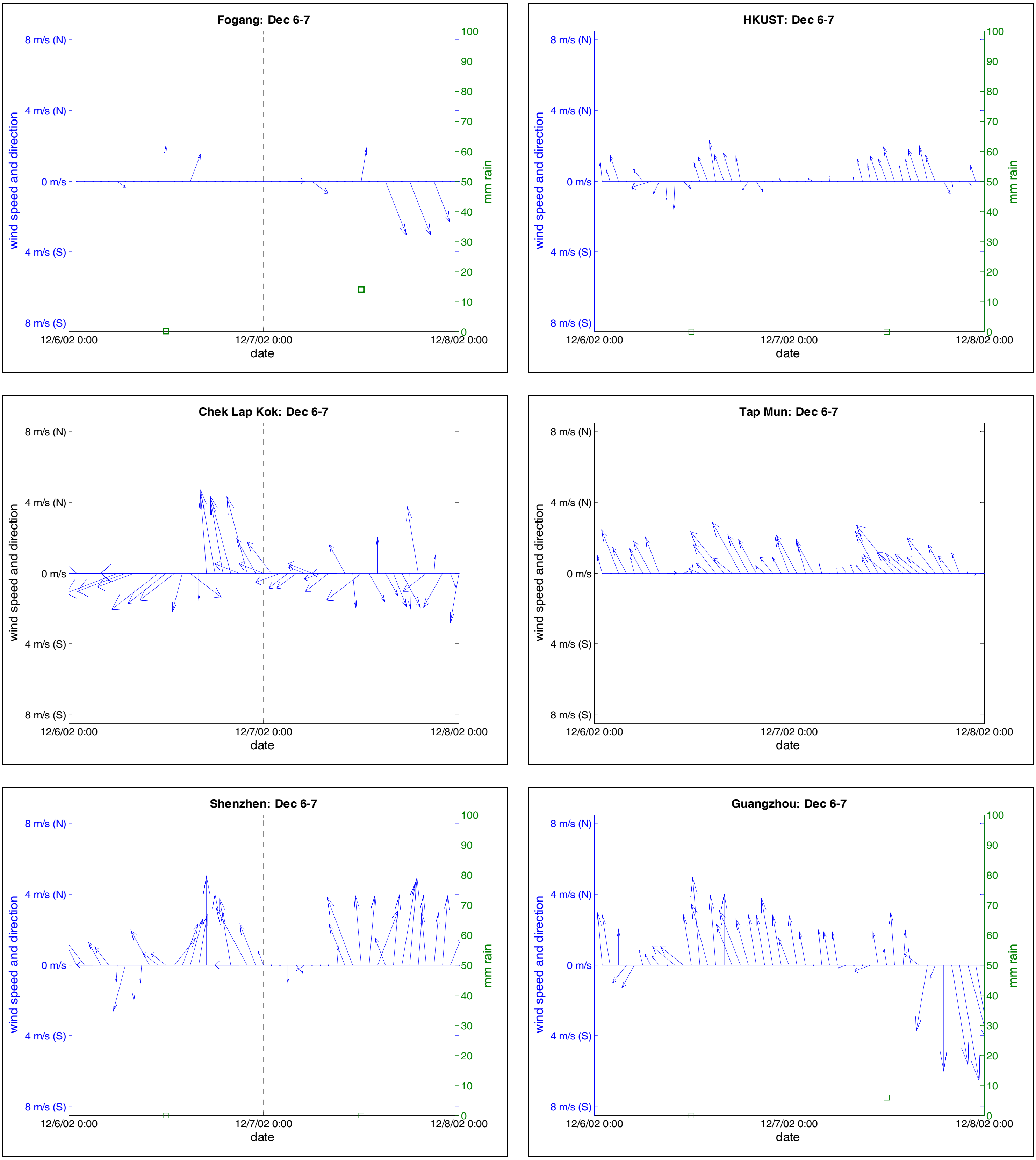


Figure 18. Wind Speed, Direction and Precipitation During December 6-7, 2002

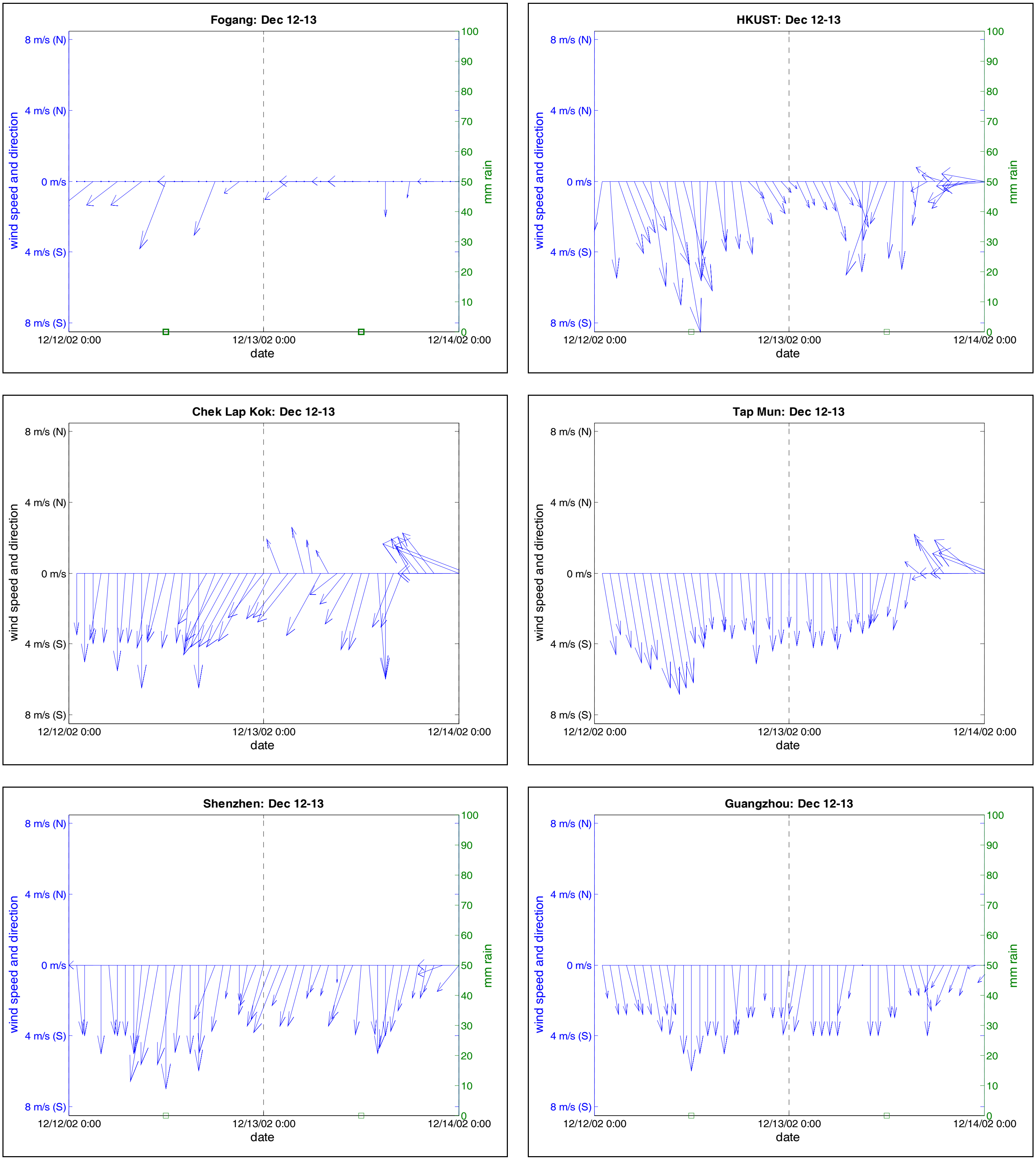


Figure 19. Wind Speed, Direction and Precipitation During December 12-13, 2002

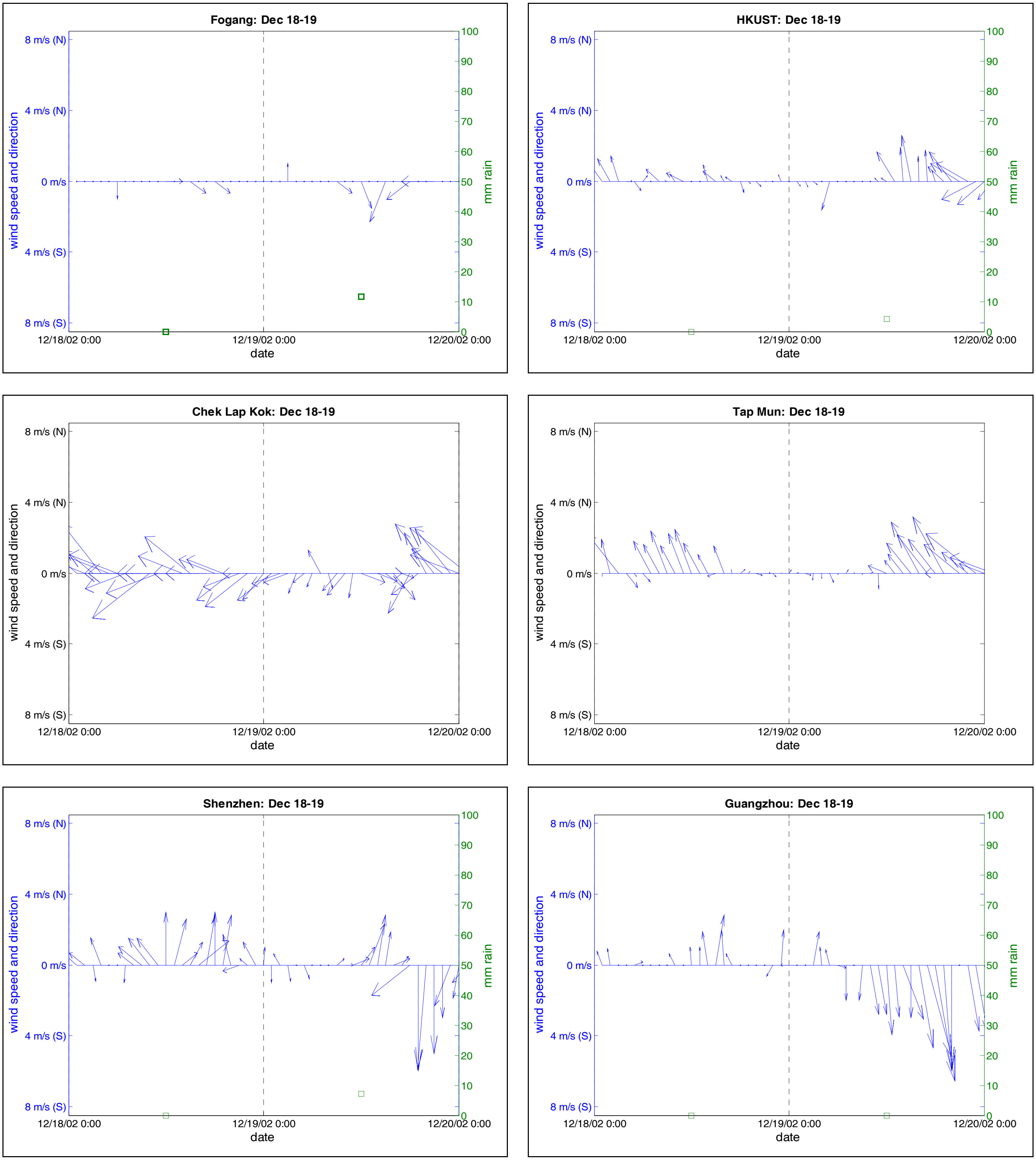


Figure 20. Wind Speed, Direction and Precipitation During December 18-19, 2002

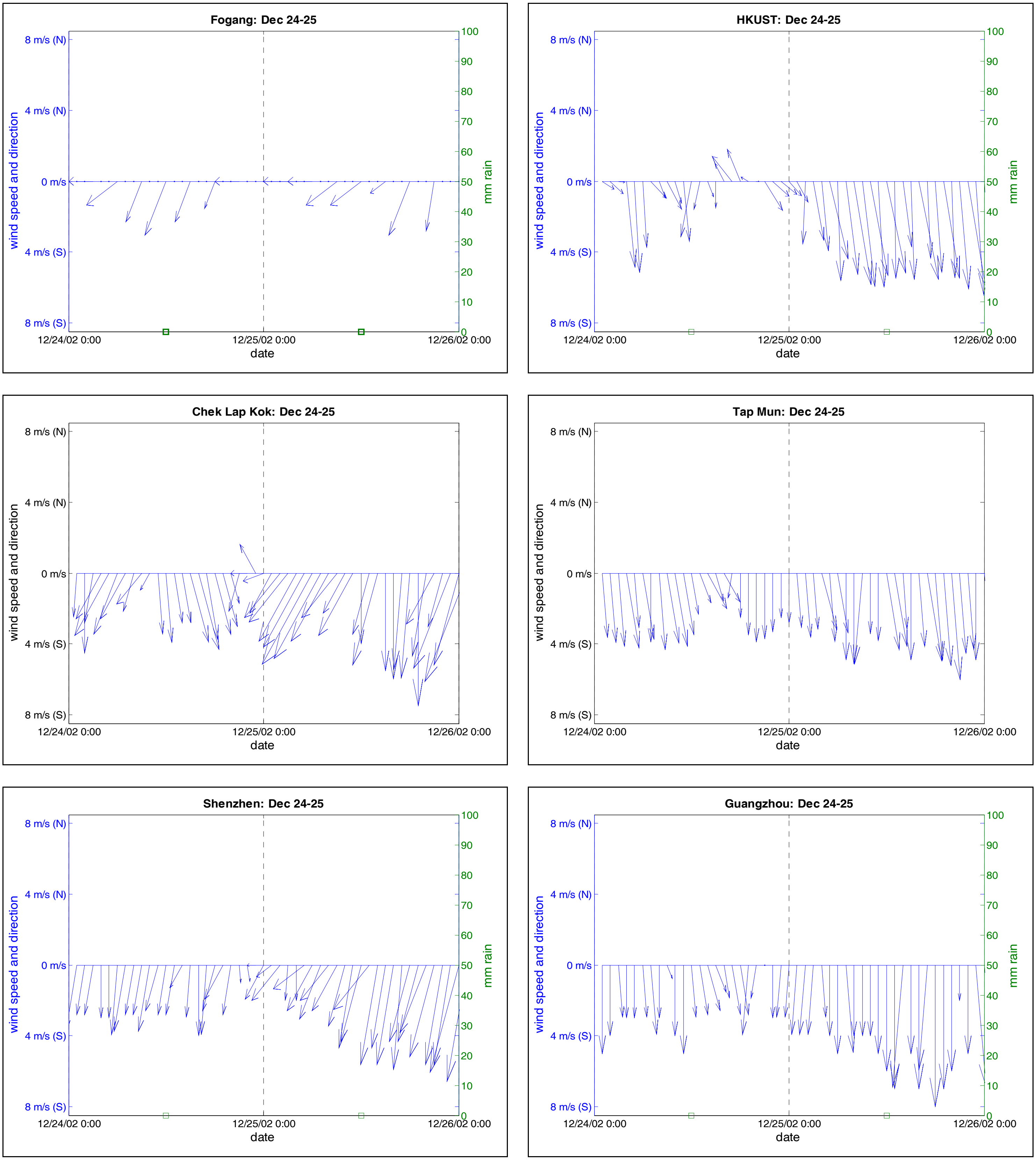


Figure 21. Wind Speed, Direction and Precipitation During December 24-25, 2002

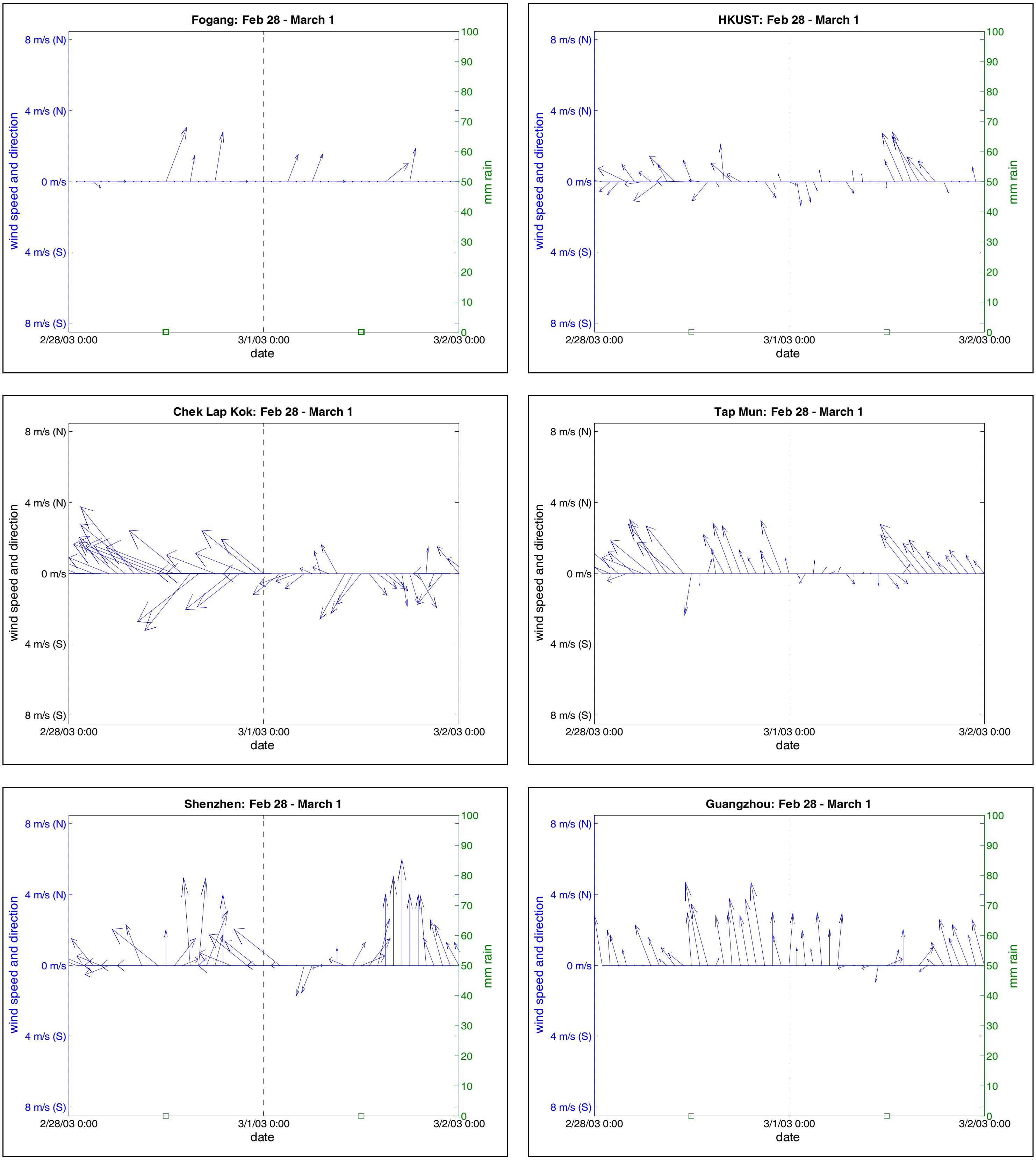


Figure 22. Wind Speed, Direction and Precipitation During Feb. 28 – March 1, 2003

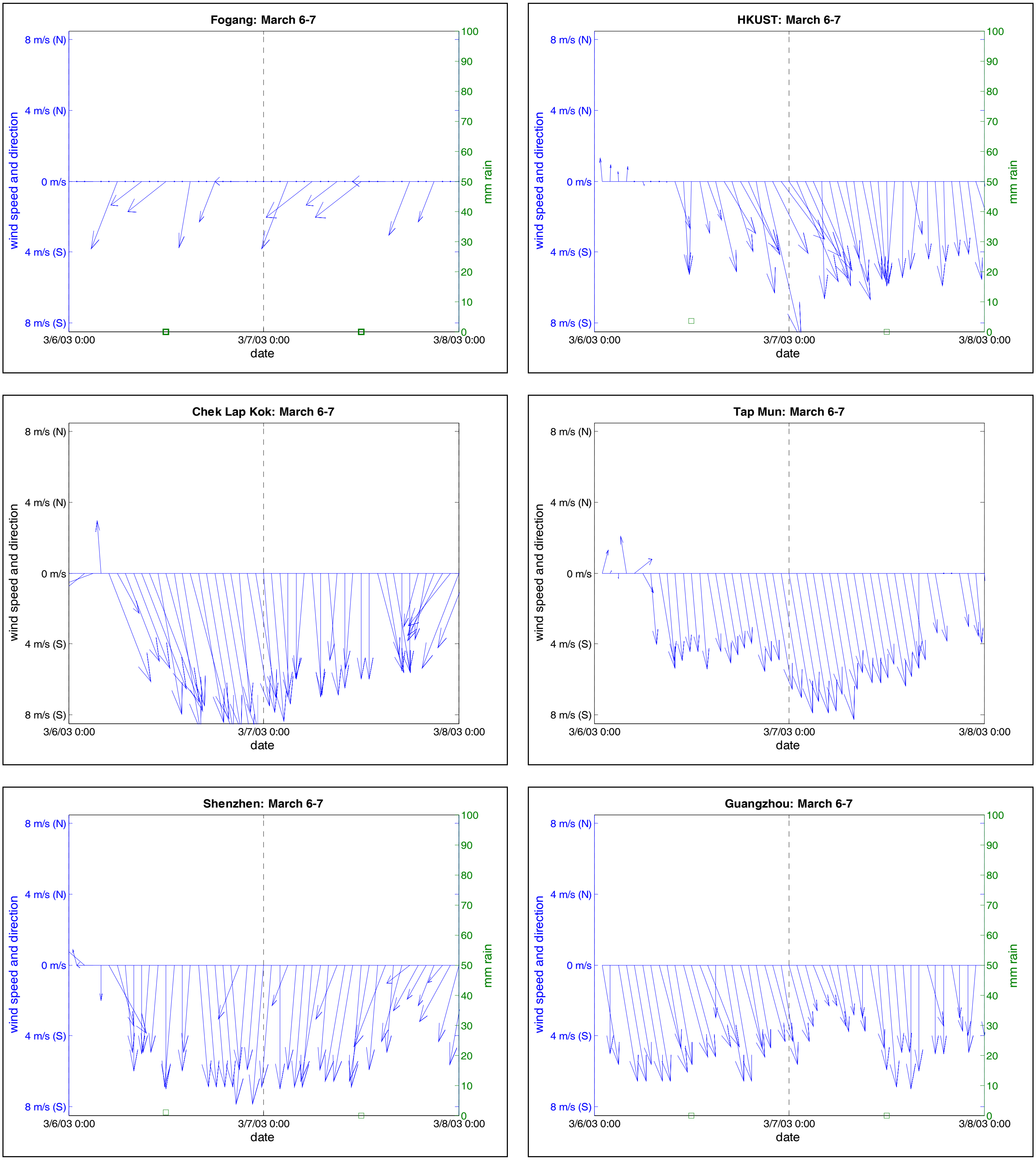


Figure 23. Wind Speed, Direction and Precipitation During March 6 – March 7, 2003

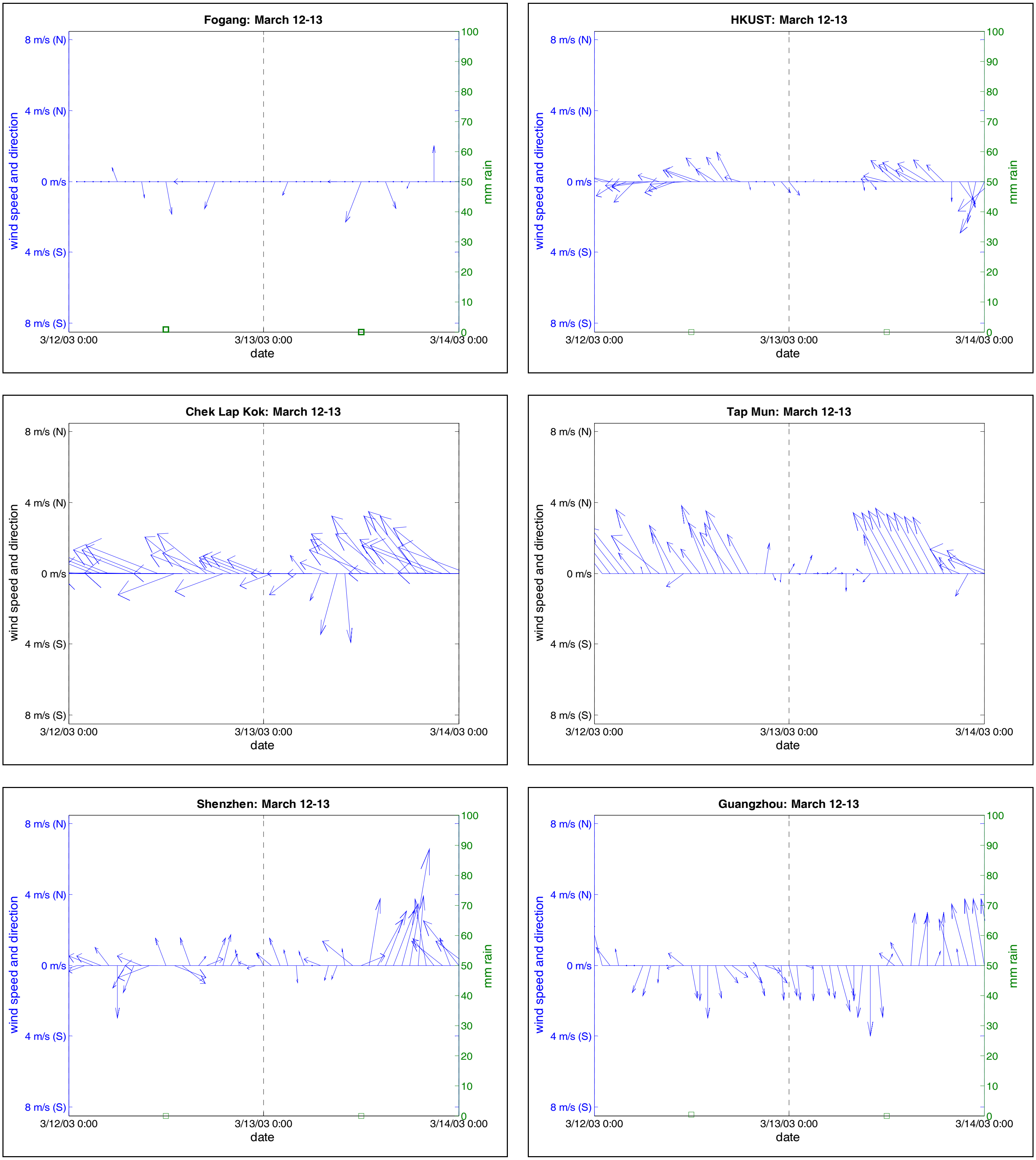


Figure 24. Wind Speed, Direction and Precipitation During March 12 – March 13, 2003

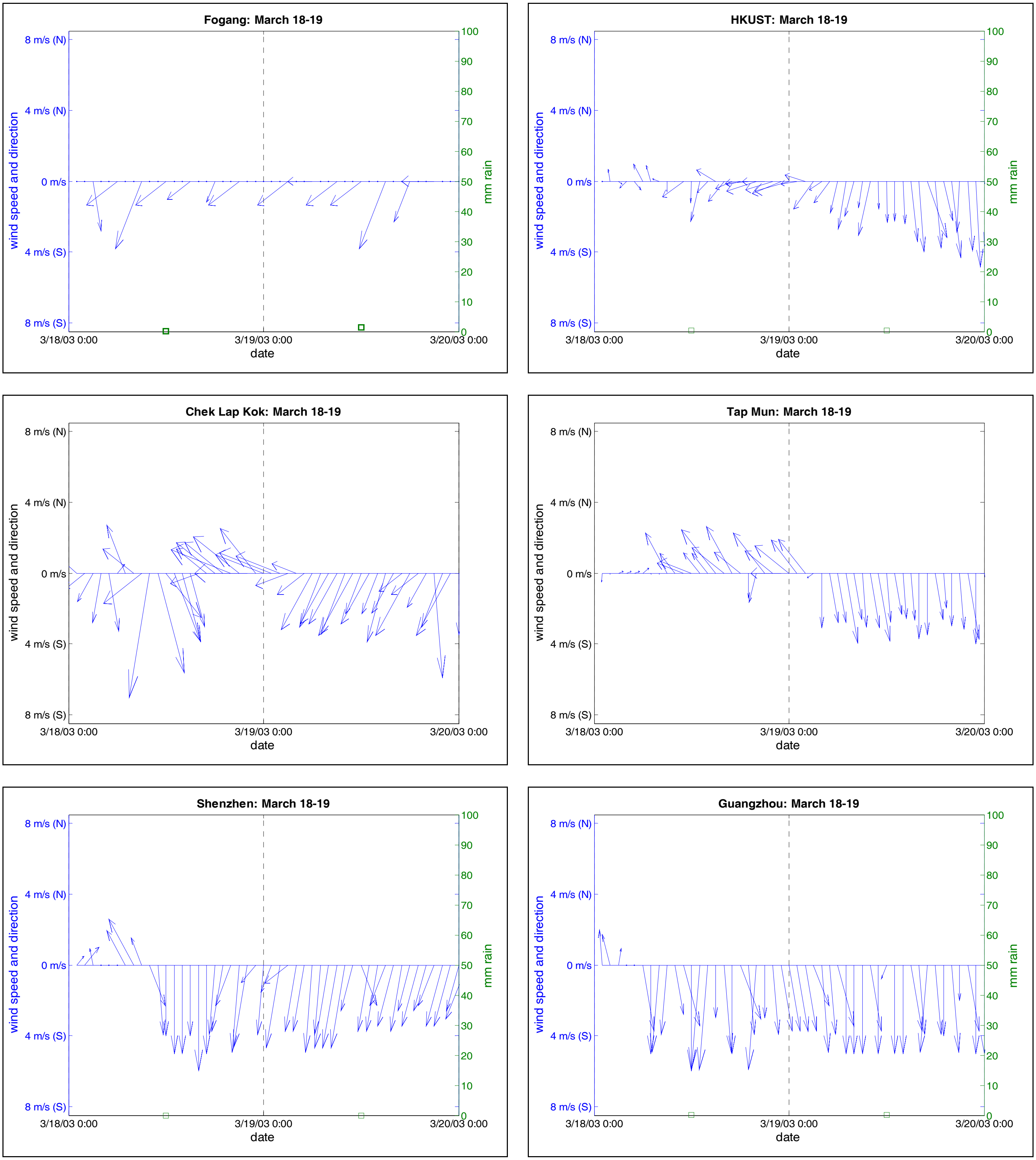


Figure 25. Wind Speed, Direction and Precipitation During March 18 – March 19, 2003

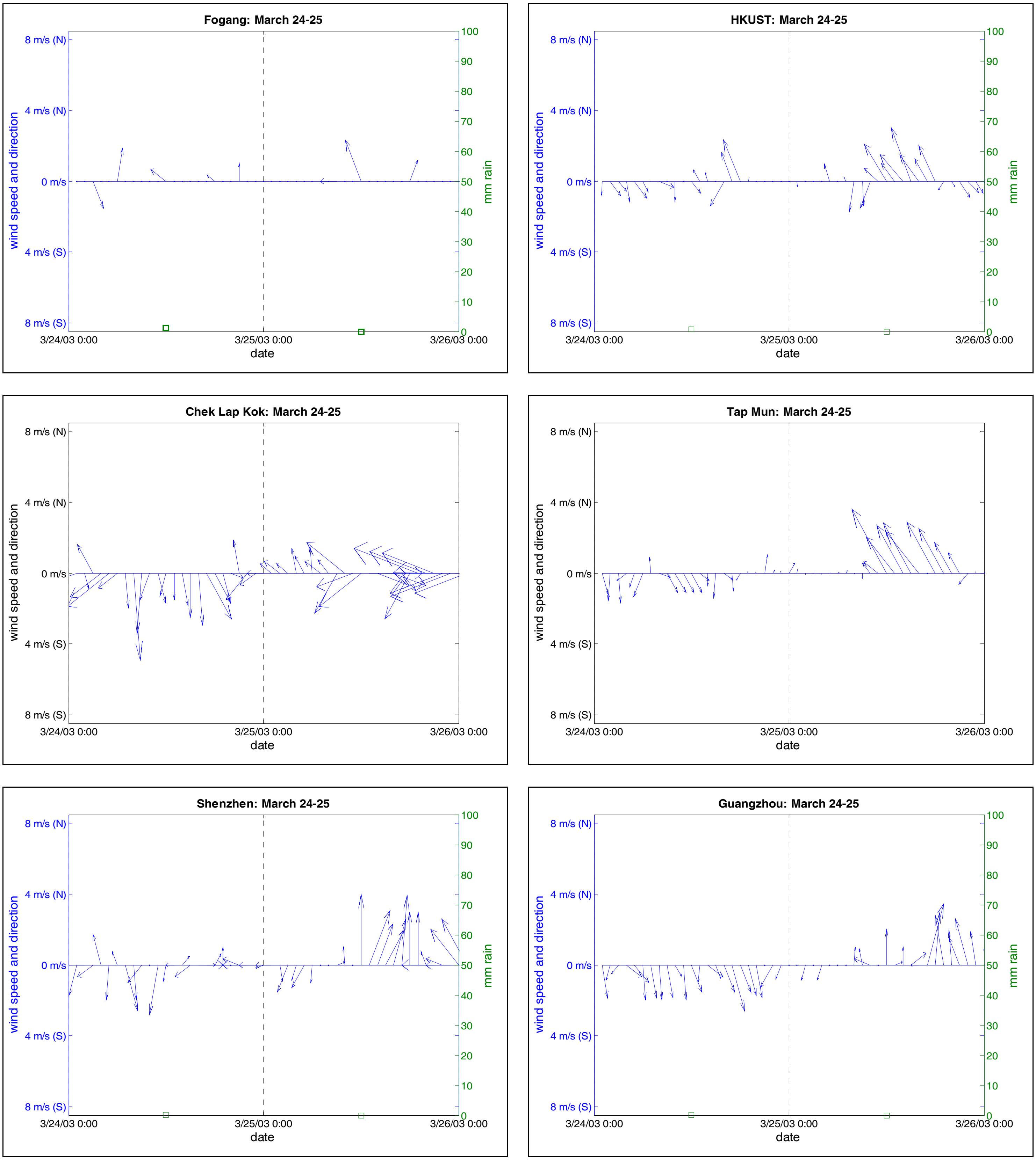


Figure 26. Wind Speed, Direction and Precipitation During March 24 – March 25, 2003

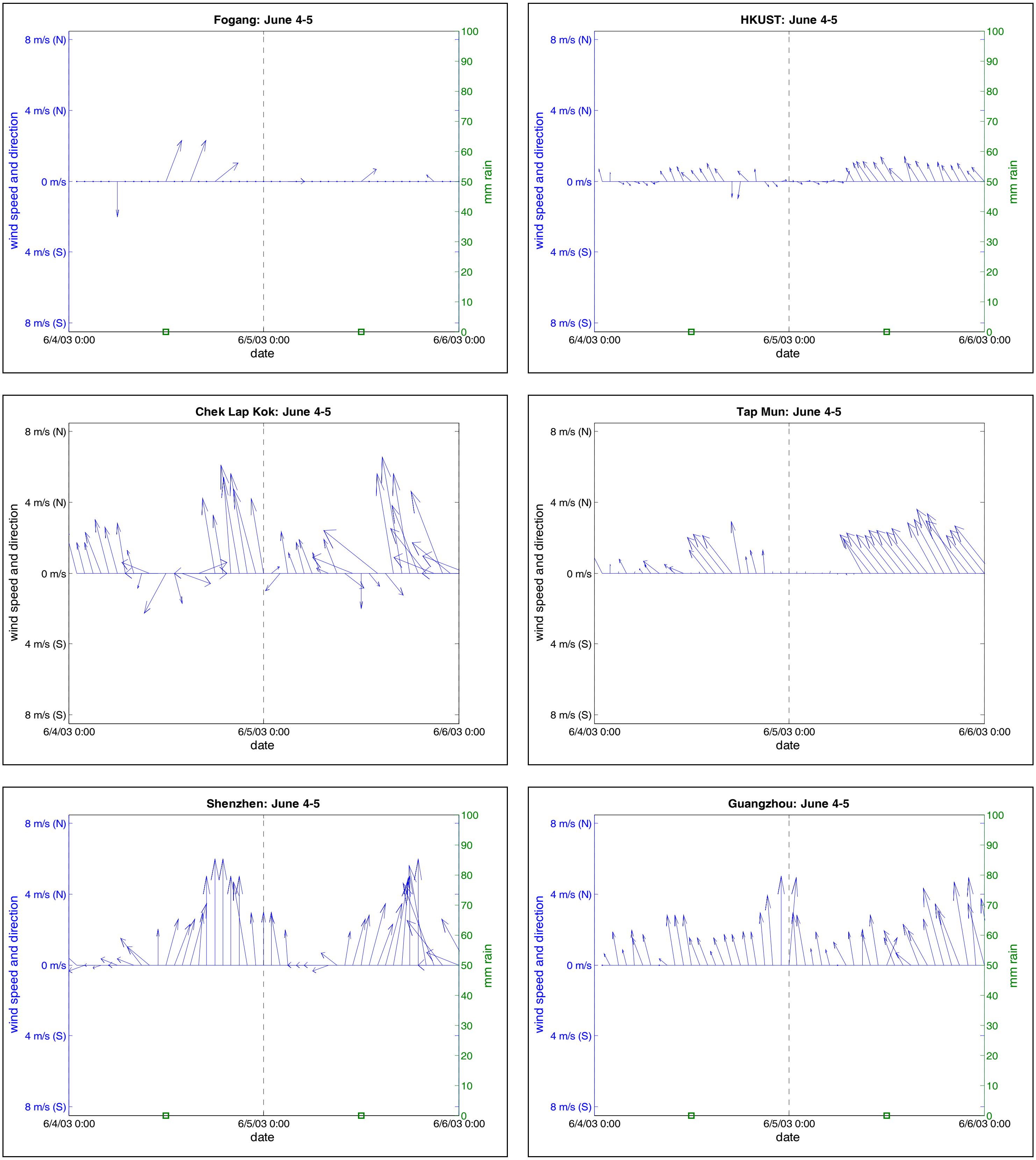


Figure 27. Wind Speed, Direction and Precipitation During June 4 – June 5, 2003

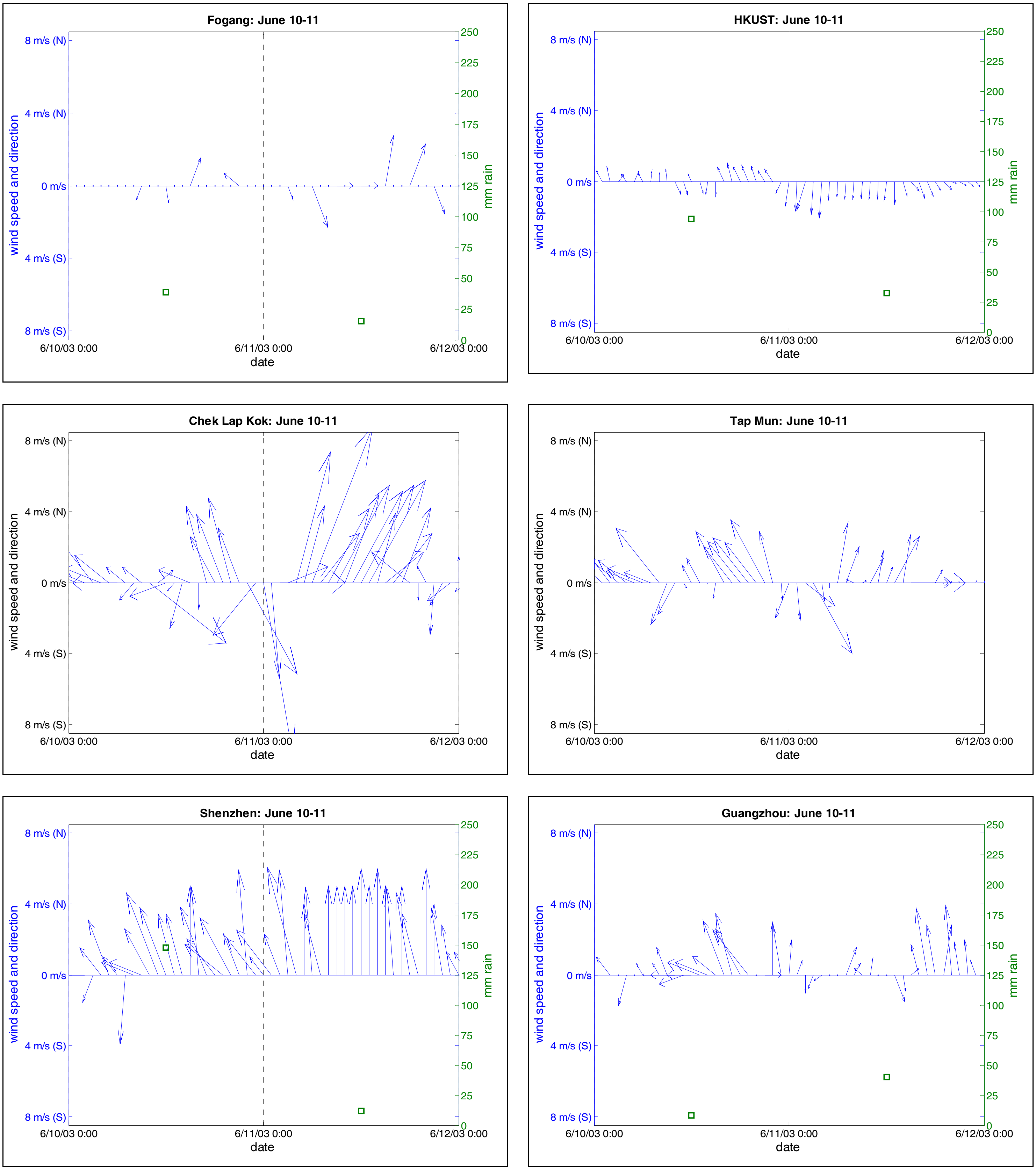


Figure 28. Wind Speed, Direction and Precipitation During June 10 – June 11, 2003

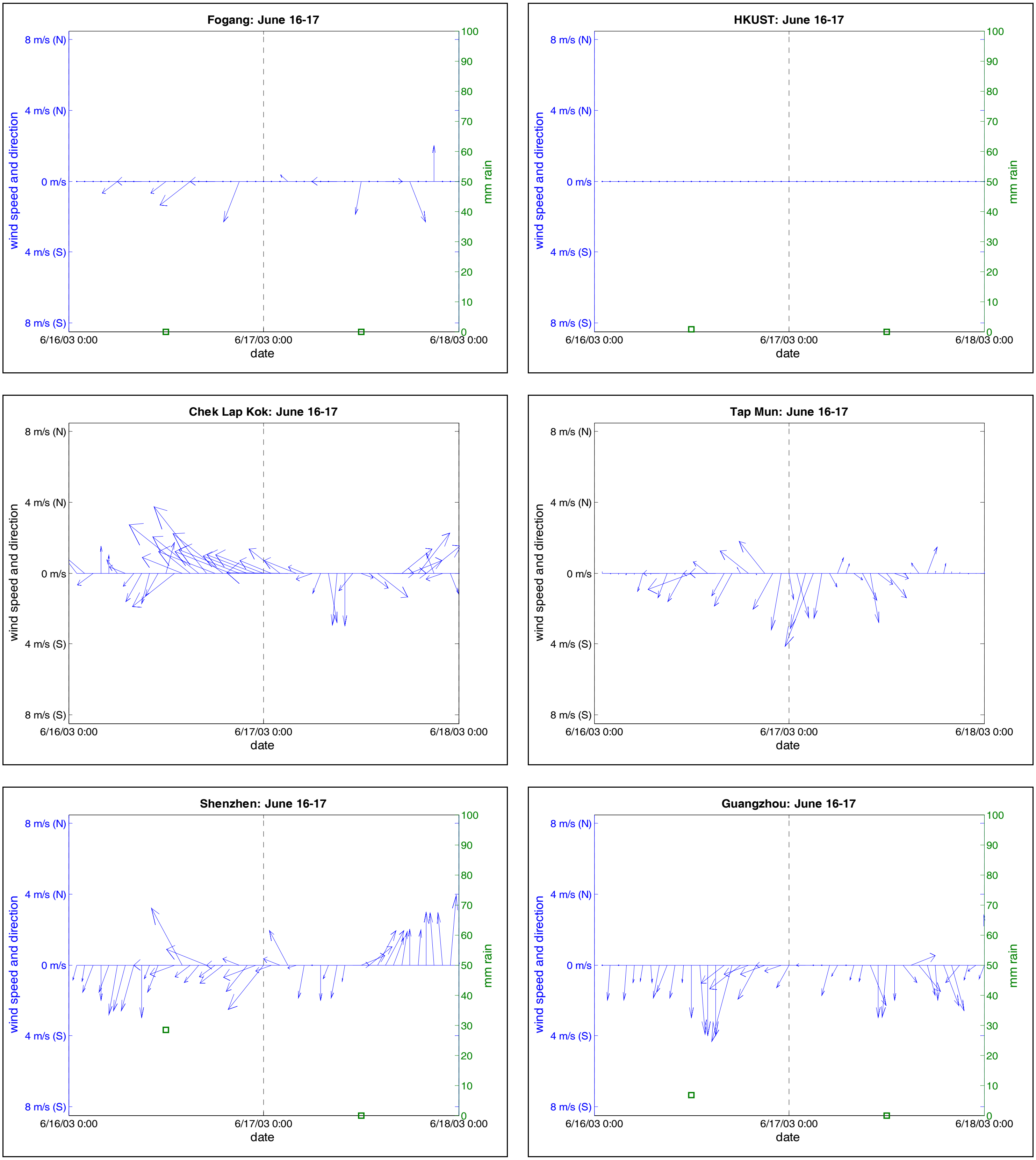


Figure 29. Wind Speed, Direction and Precipitation During June 16 – June 17, 2003

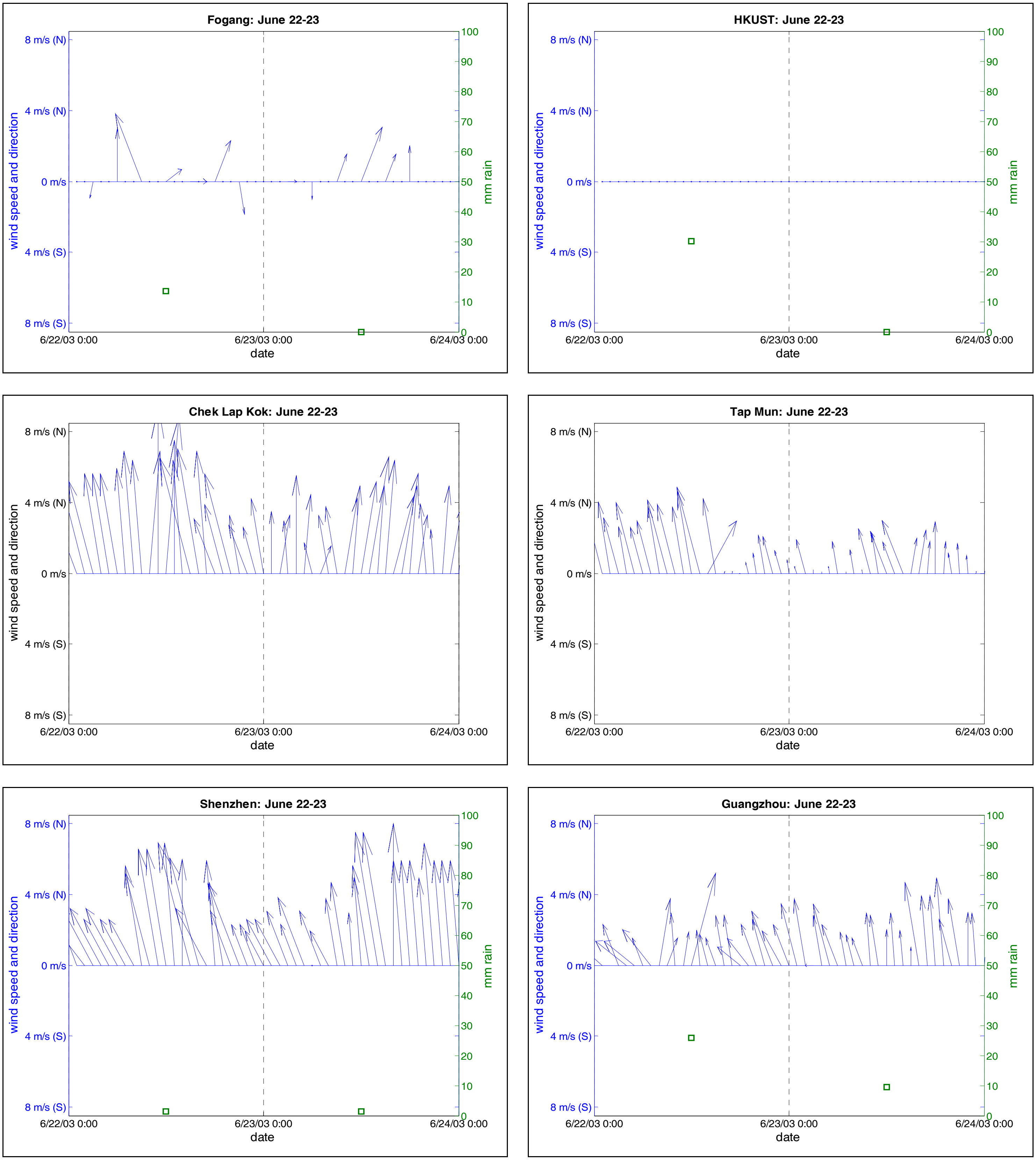


Figure 30. Wind Speed, Direction and Precipitation During June 22 – June 23, 2003

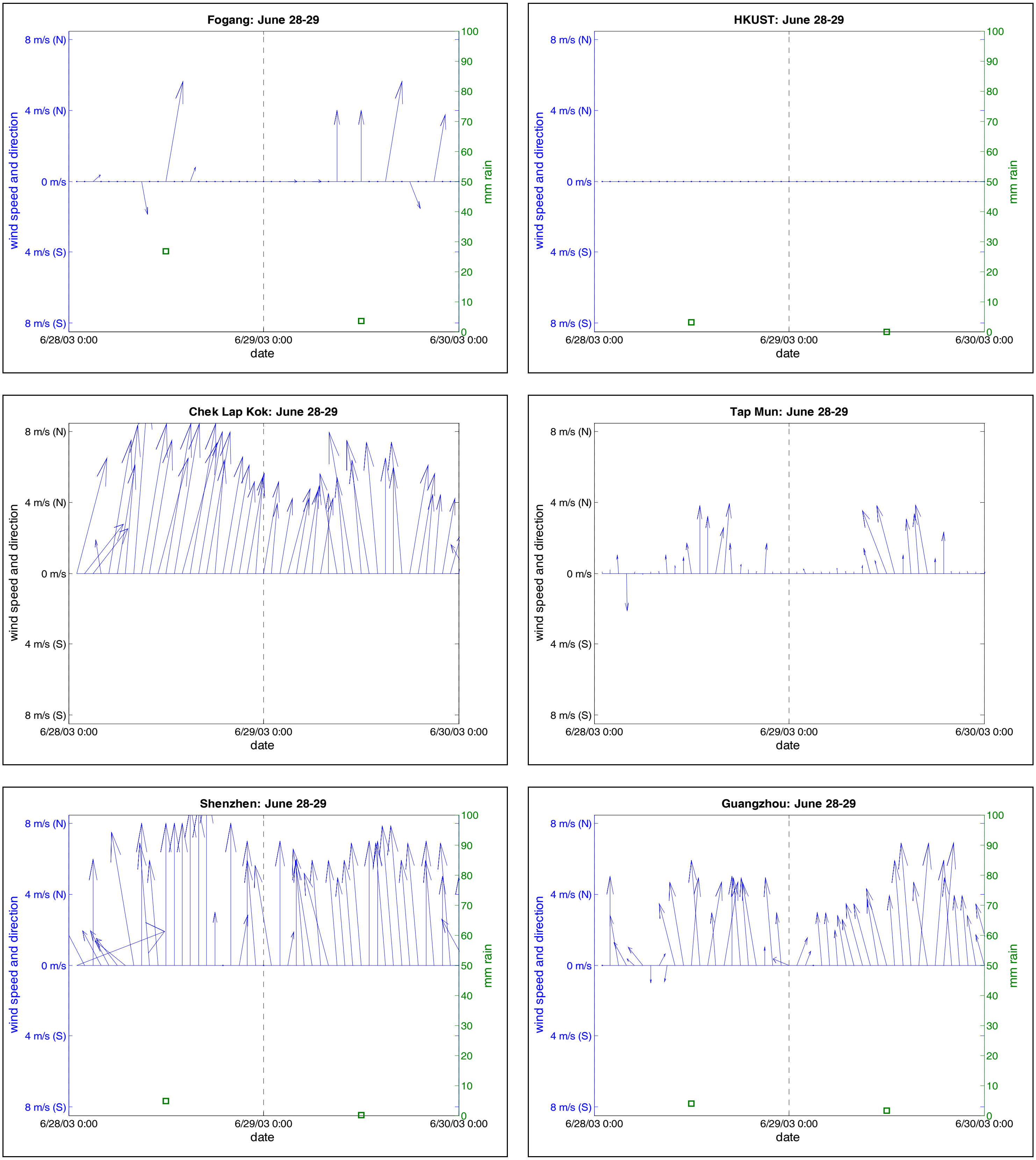


Figure 31. Wind Speed, Direction and Precipitation During June 28 – June 29, 2003

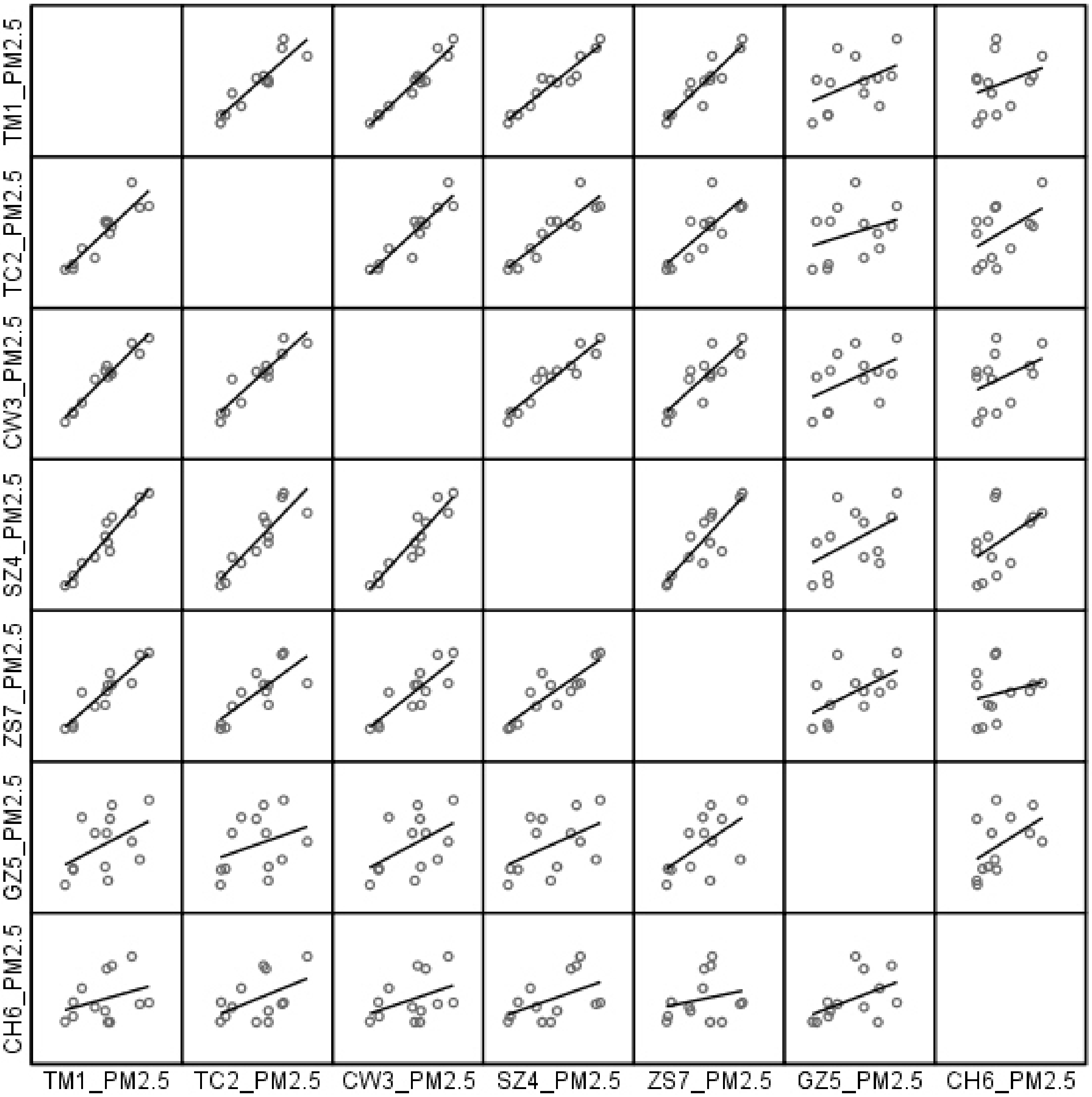


Figure 32. A matrix of least-squares linear fit of PM2.5 measurements paired by site. Note that the axes for each pair of sites have been scaled to best show the data points.

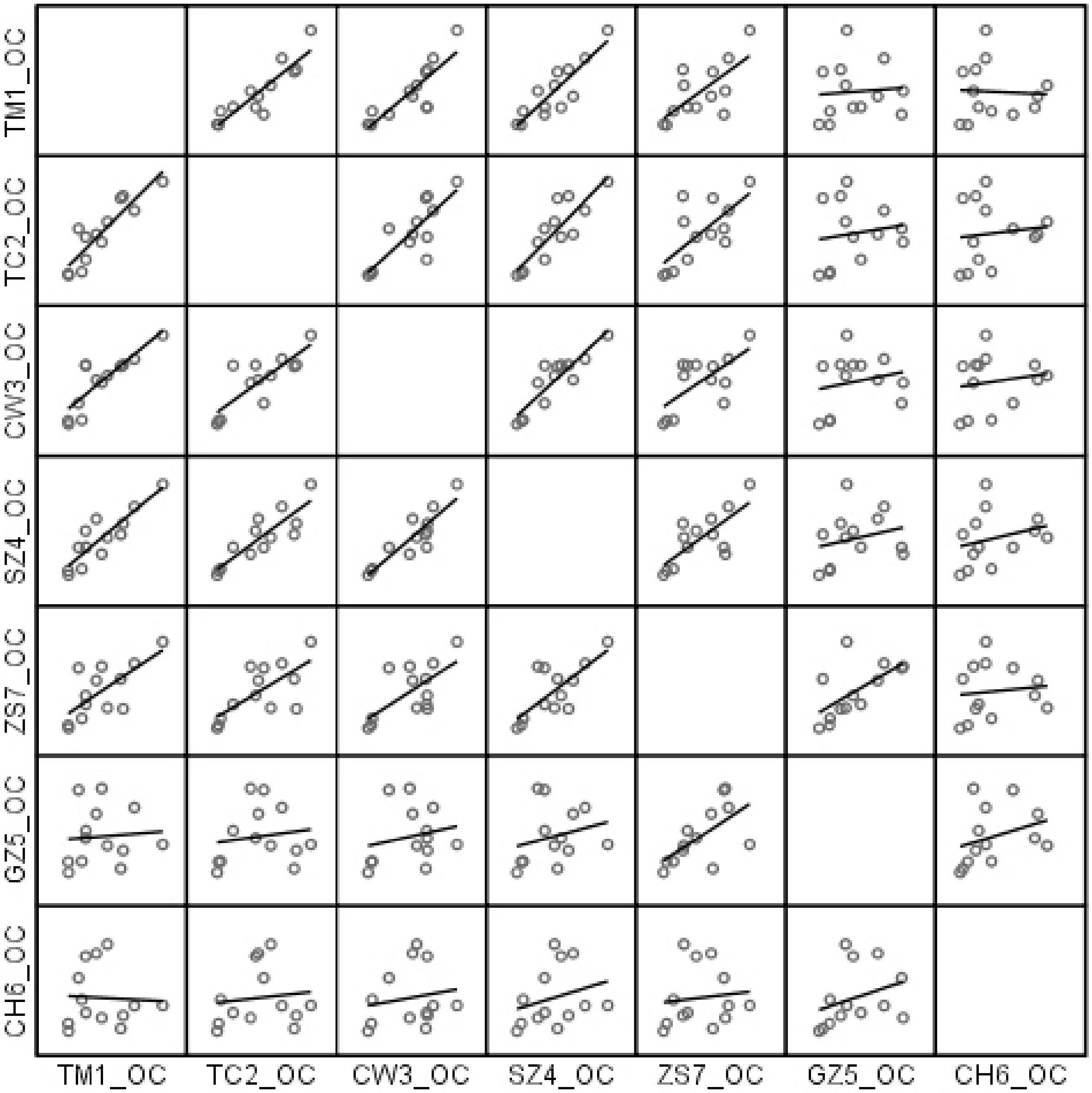


Figure 33. A matrix of least-squares linear fit of organic carbon measurements paired by site. Note that the axes for each pair of sites have been scaled to best show the data points.

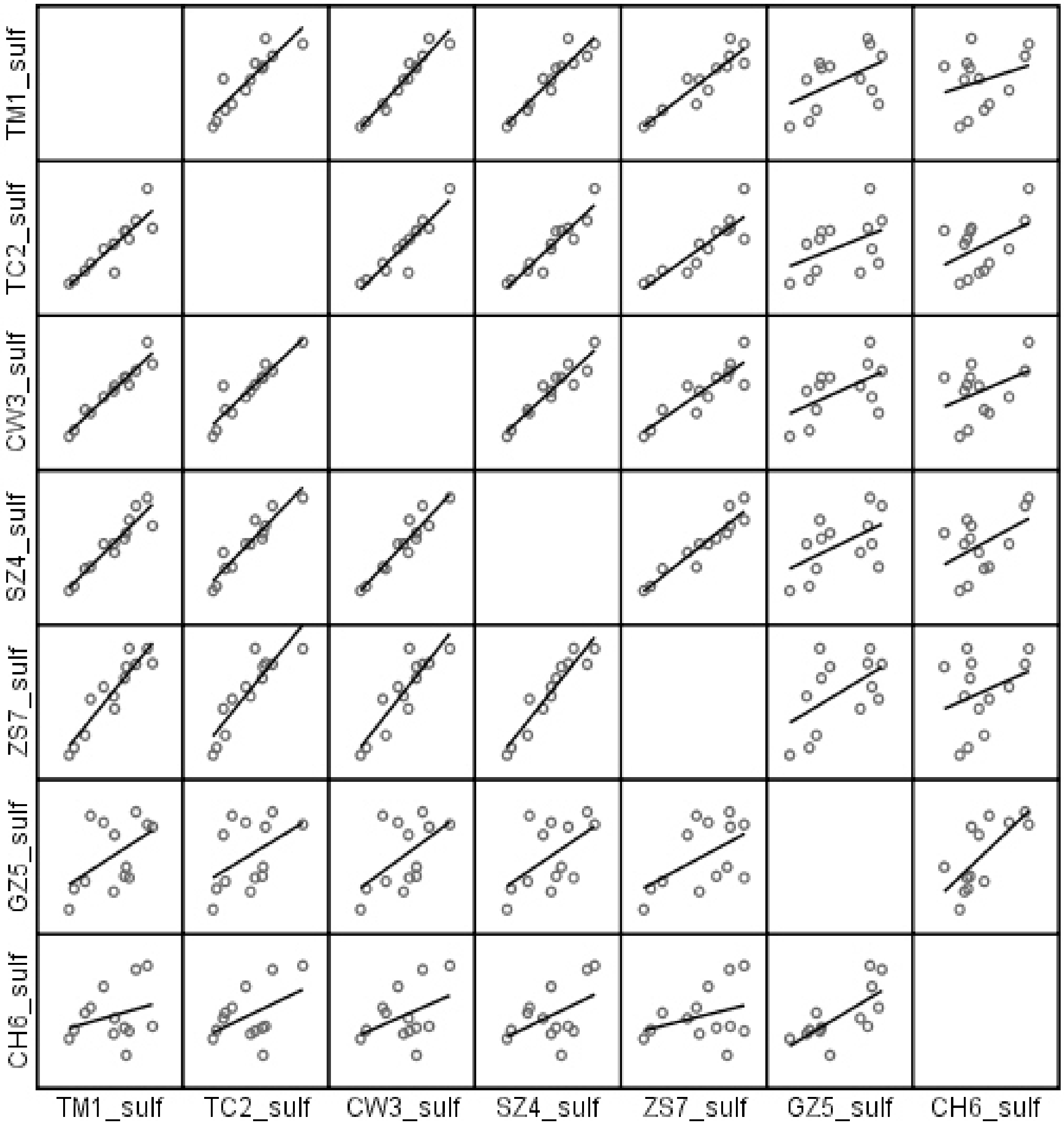


Figure 34. A matrix of least-squares linear fit of sulfate measurements paired by site. Note that the axes for each pair of sites have been scaled to best show the data points.

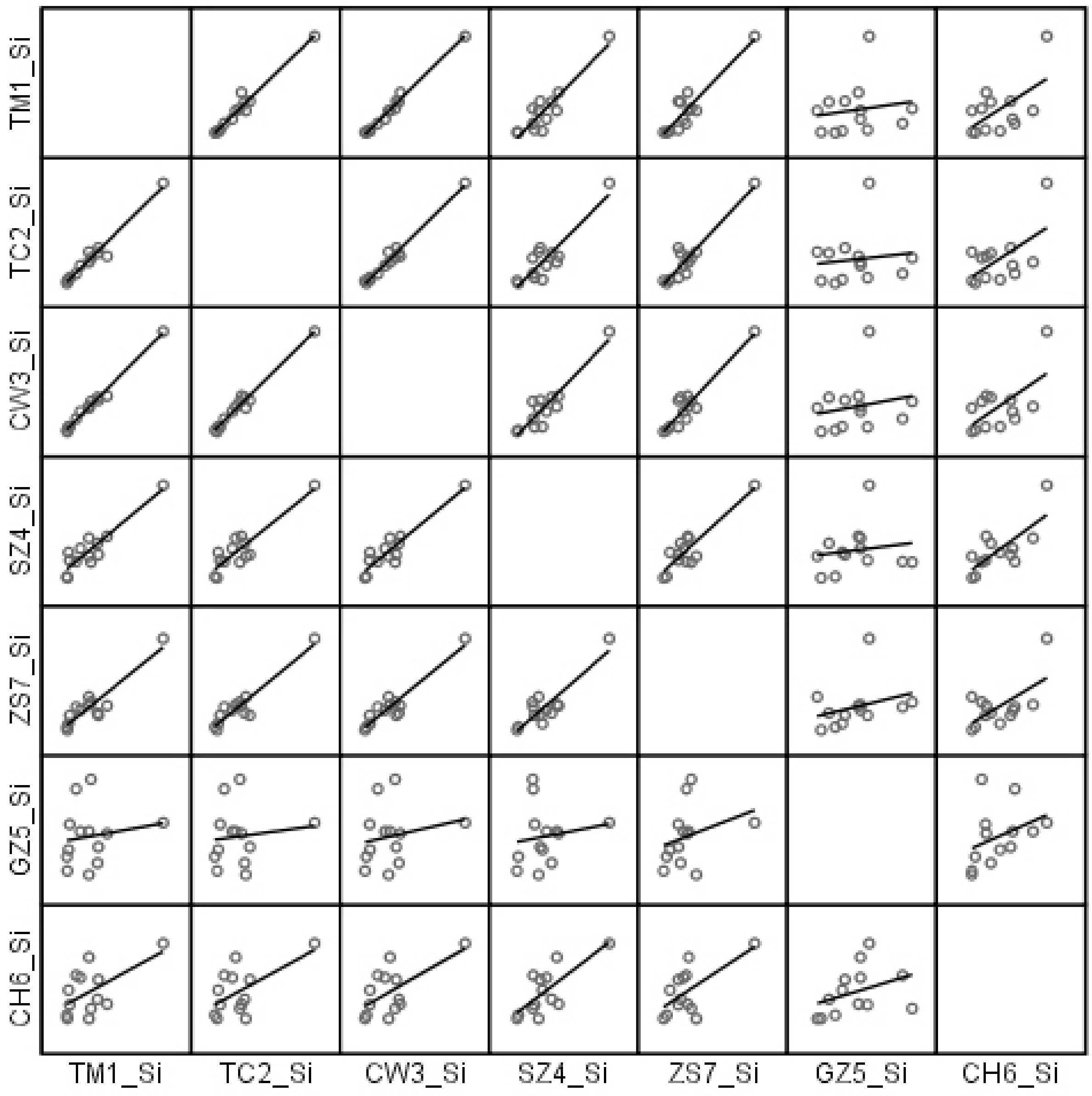


Figure 35. A matrix of least-squares linear fit of silica measurements paired by site. Note that the axes for each pair of sites have been scaled to best show the data points.

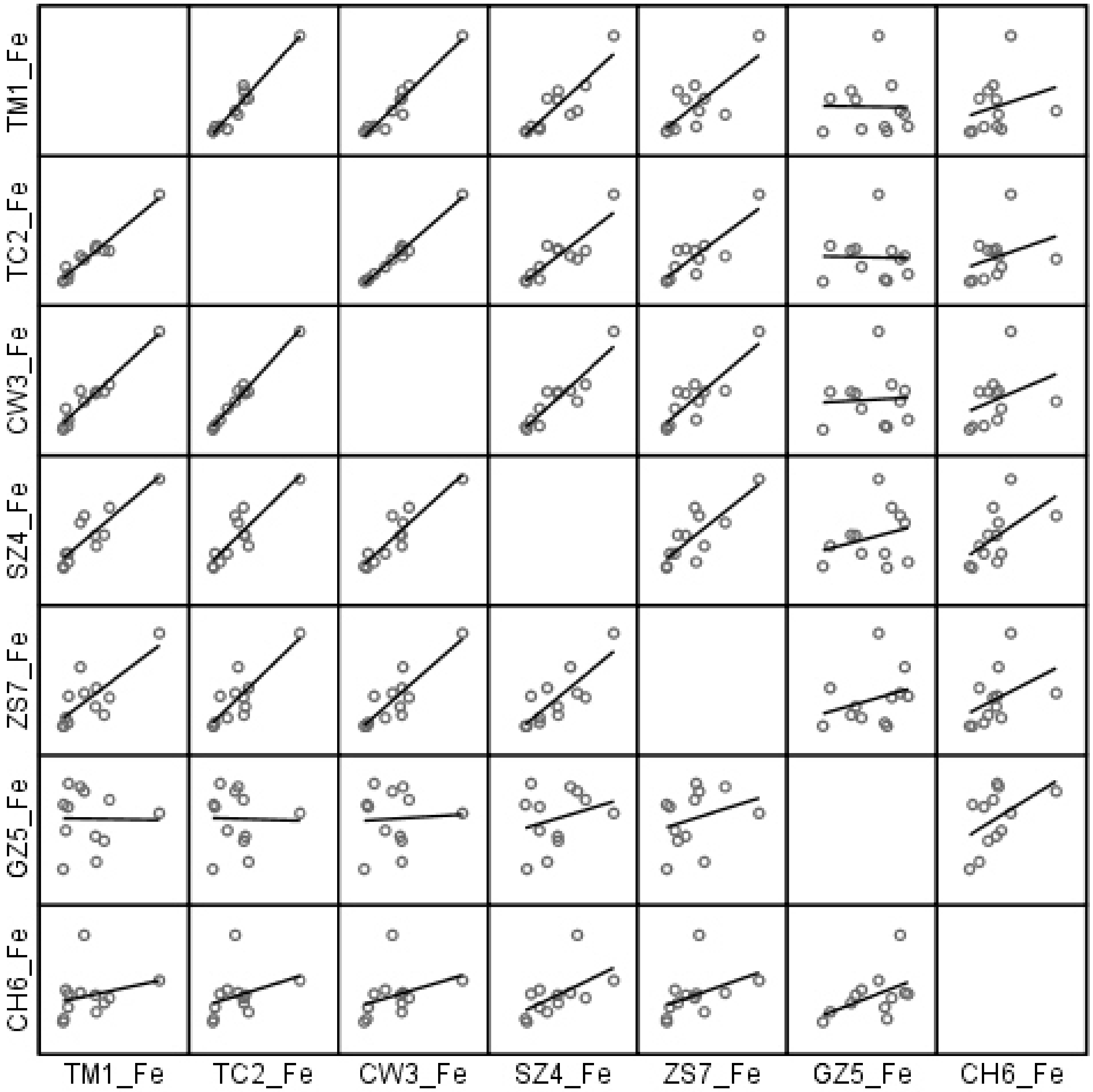


Figure 36. A matrix of least-squares linear fit of iron measurements paired by site. Note that the axes for each pair of sites have been scaled to best show the data points.

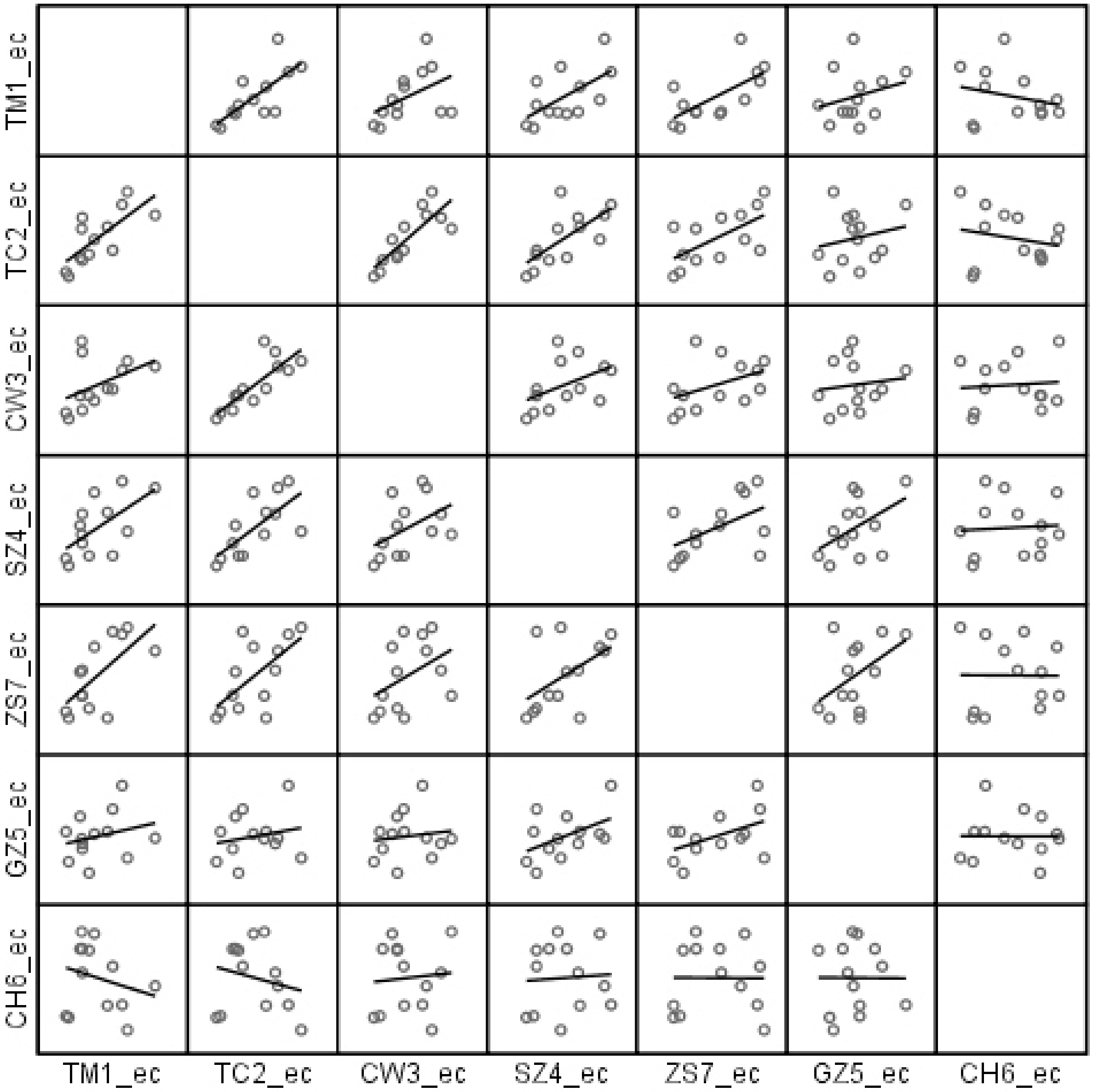


Figure 37 A matrix of least-squares linear fit of elemental carbon measurements paired by site. Note that the axes for each pair of sites have been scaled to best show the data points.

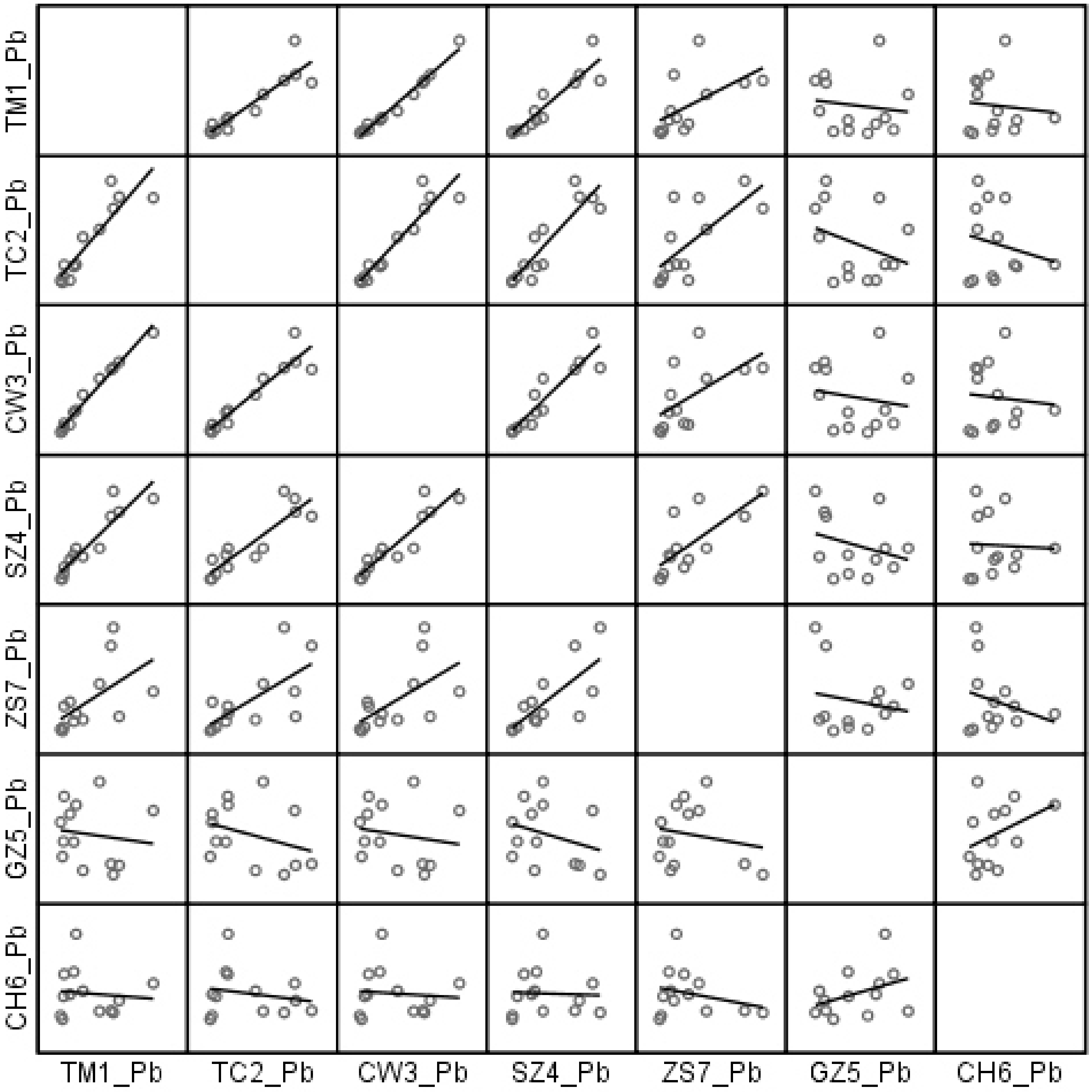


Figure 38 A matrix of least-squares linear fit of lead measurements paired by site. Note that the axes for each pair of sites have been scaled to best show the data points.

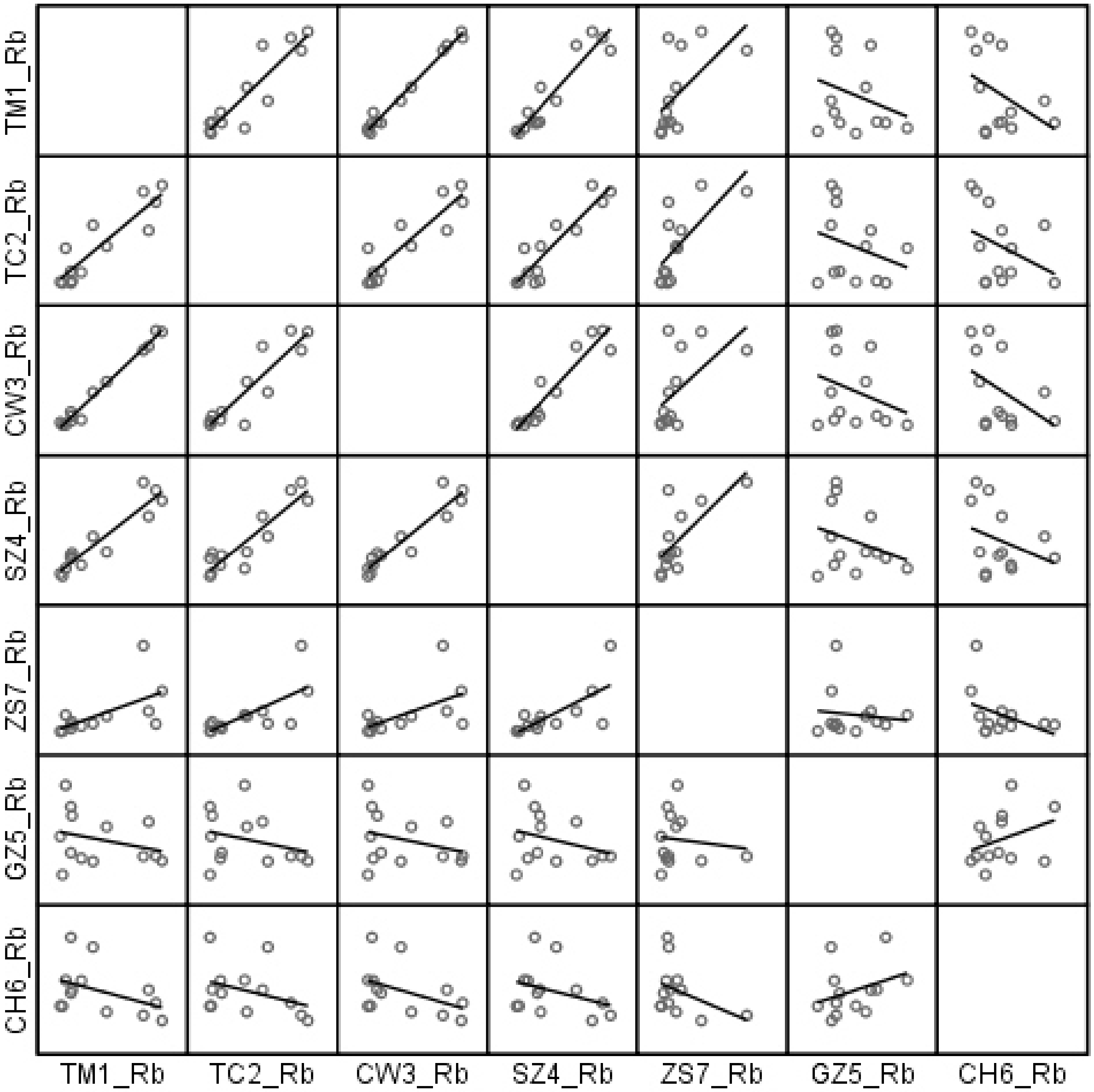


Figure 39 A matrix of least-squares linear fit of rubidium measurements paired by site. Note that the axes for each pair of sites have been scaled to best show the data points.

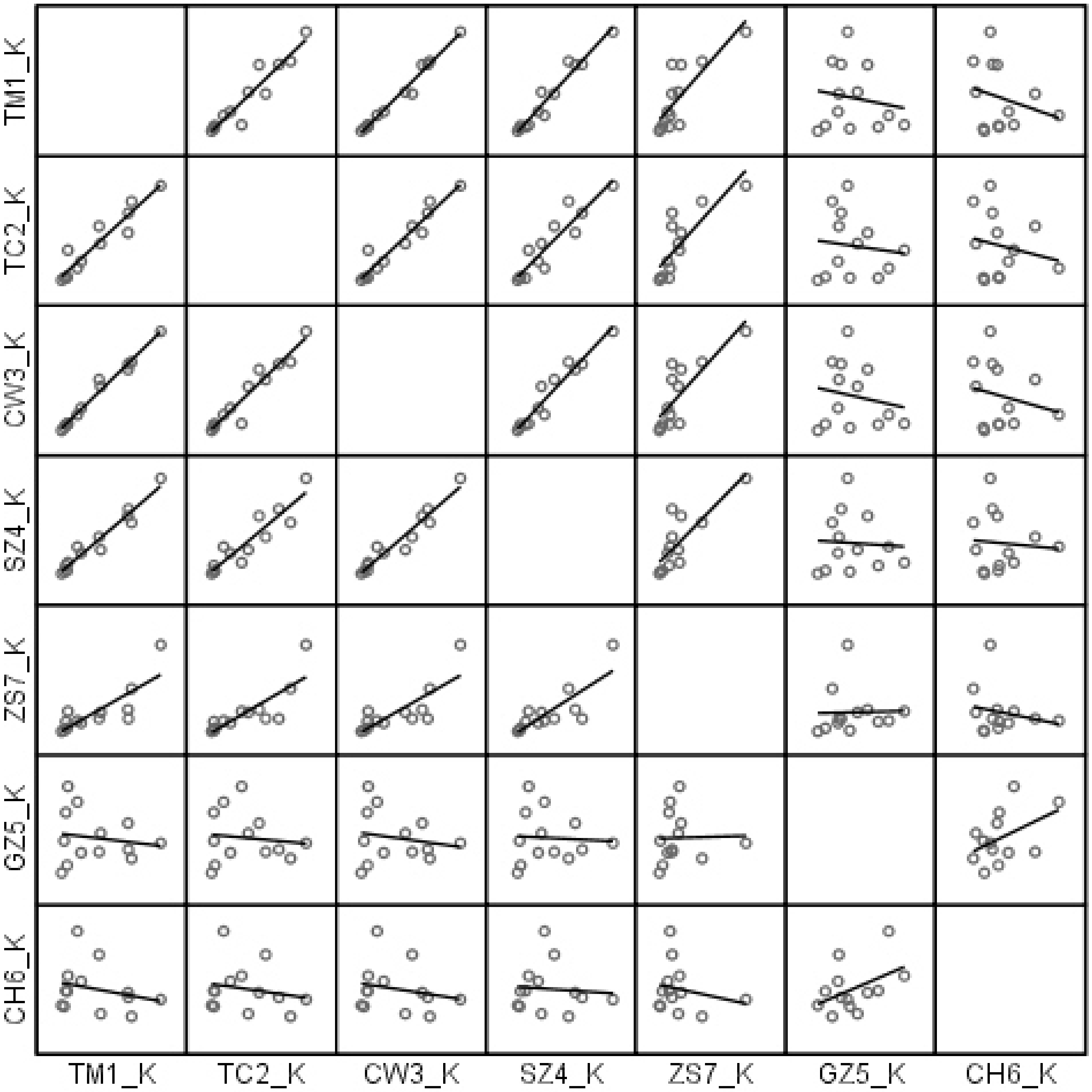


Figure 40 A matrix of least-squares linear fit of potassium measurements paired by site. Note that the axes for each pair of sites have been scaled to best show the data points.

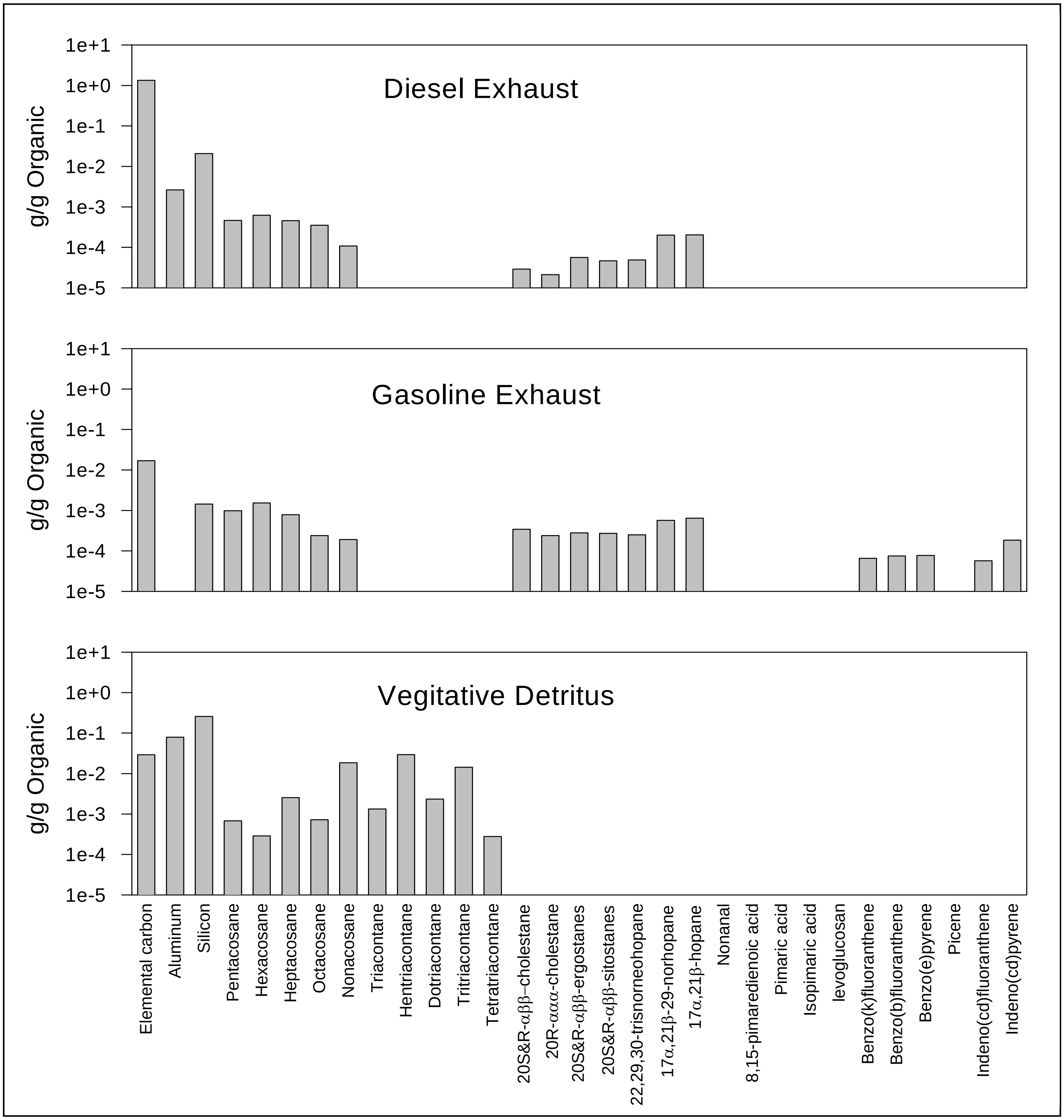


Figure **41a**. Source Profiles for diesel exhaust, gasoline exhaust, and vegetative detritus (Rogge et al., 1993; Schauer et al., 1999; Schauer et al., 2002)

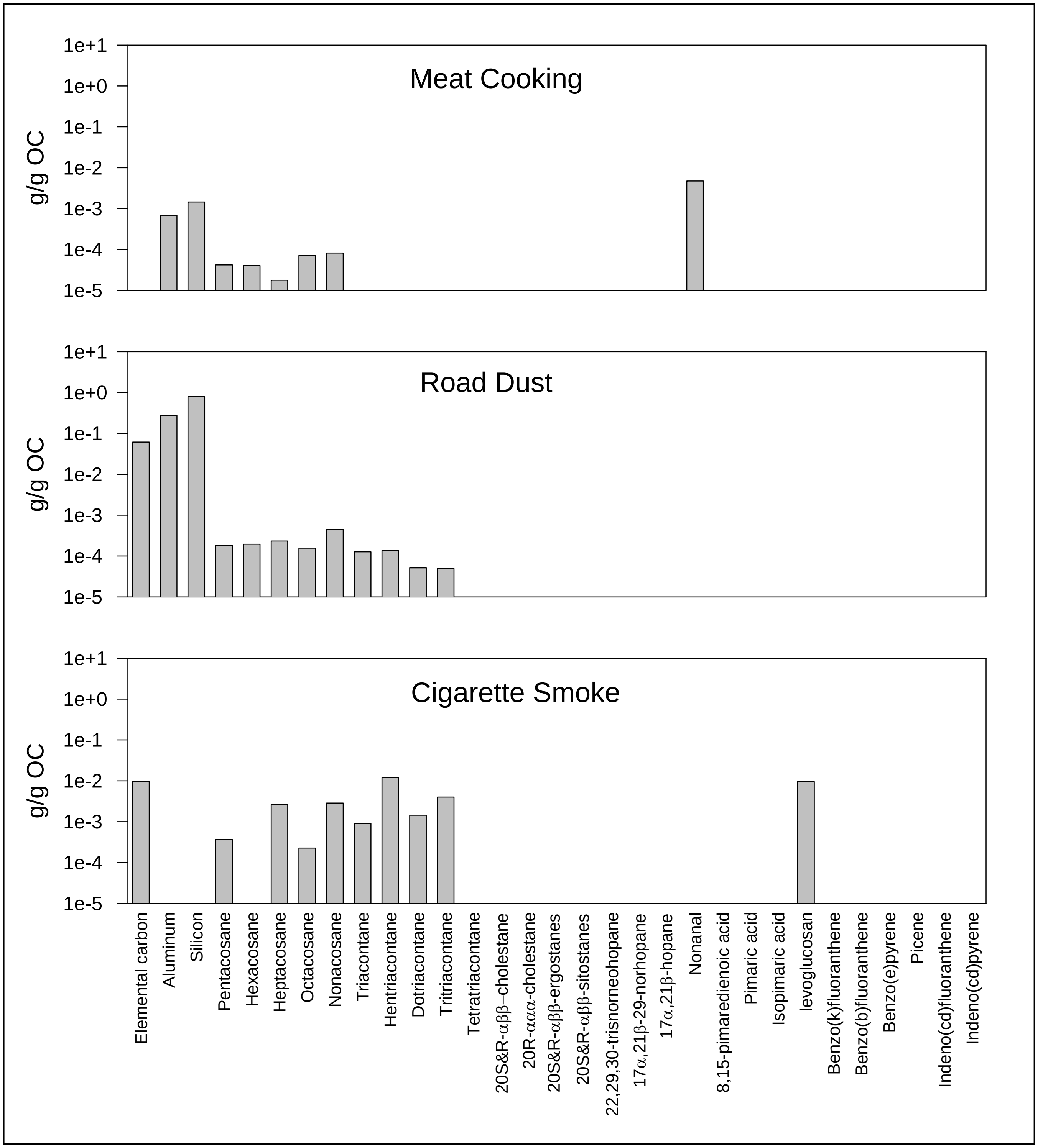


Figure **41b**. Source profiles for meat cooking, road dust, and cigarette smoke (Rogge et al., 1993; Schauer et al., 1998; Schauer et al., 1999)

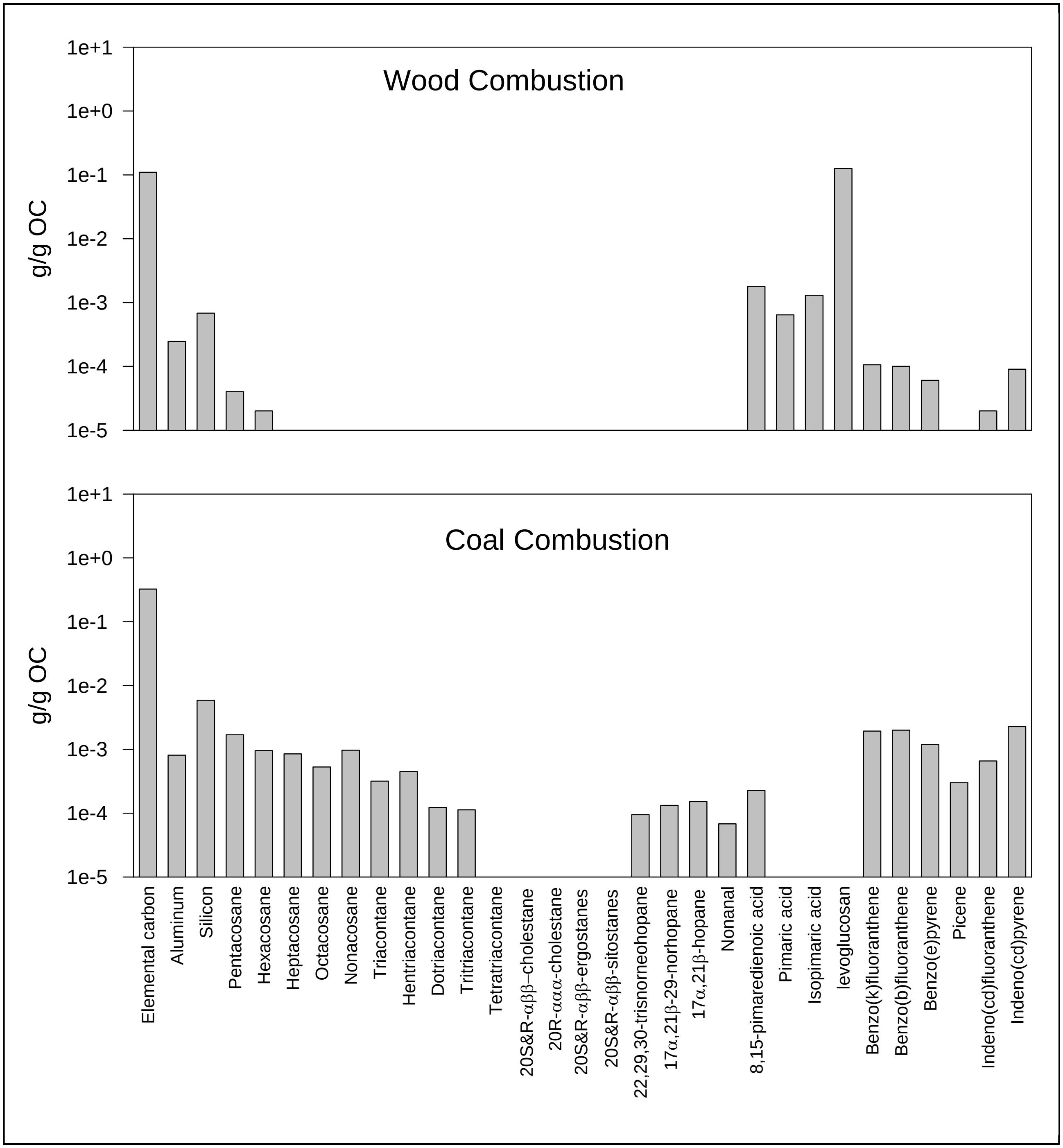


Figure 41c. Source profiles for wood combustion and coal combustion (Zheng et al., 2002; Zheng et al., in preparation)

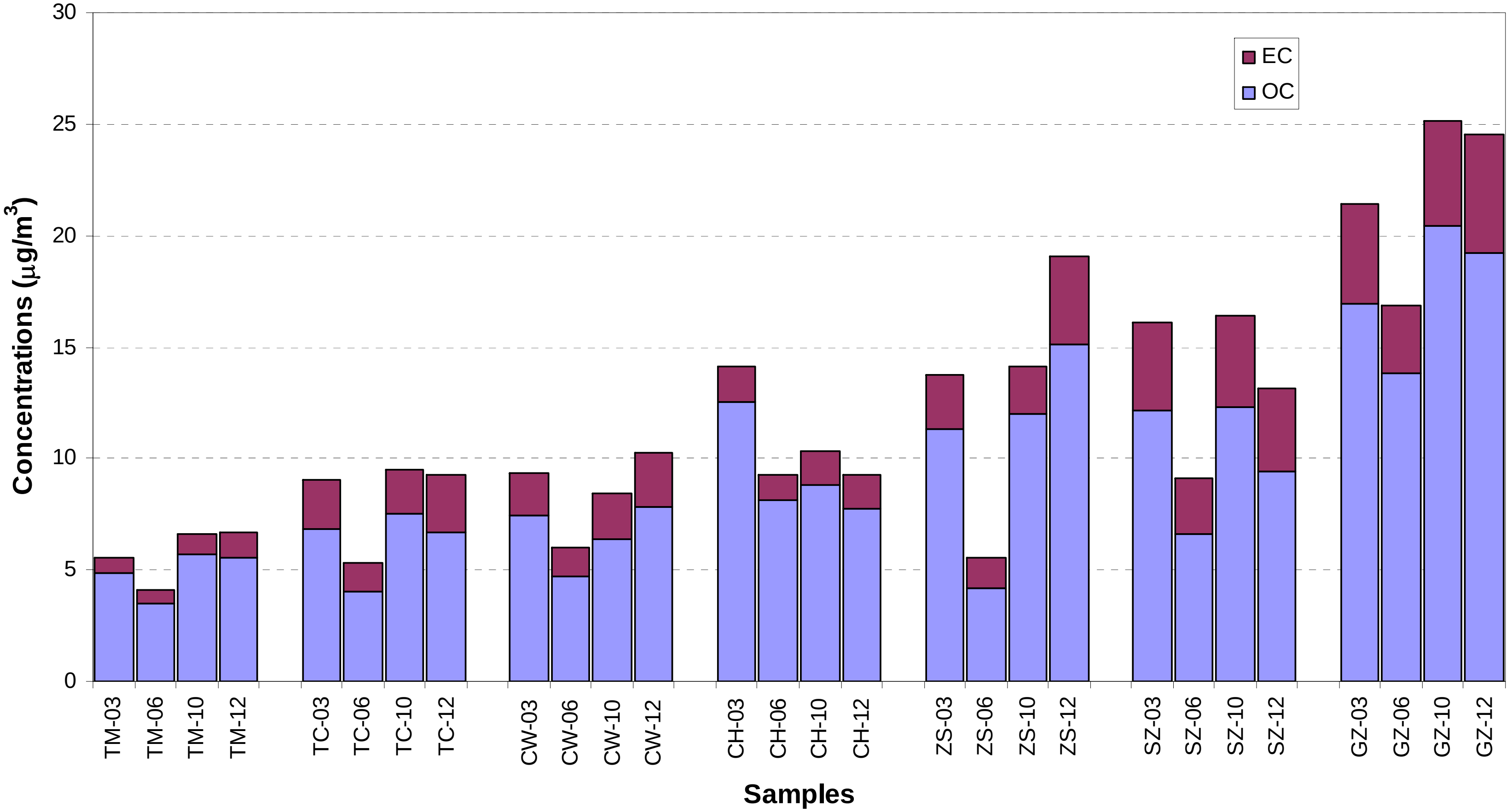


Figure 42. Seasonal and spatial distribution of elemental (EC) and organic carbon (OC) (TM: Tap Mun, TC: Tung Chung, CW: Central and Western, CH: Conghua, ZS: Zhongshan, SZ: Shenzhen, GZ: Guangzhou)

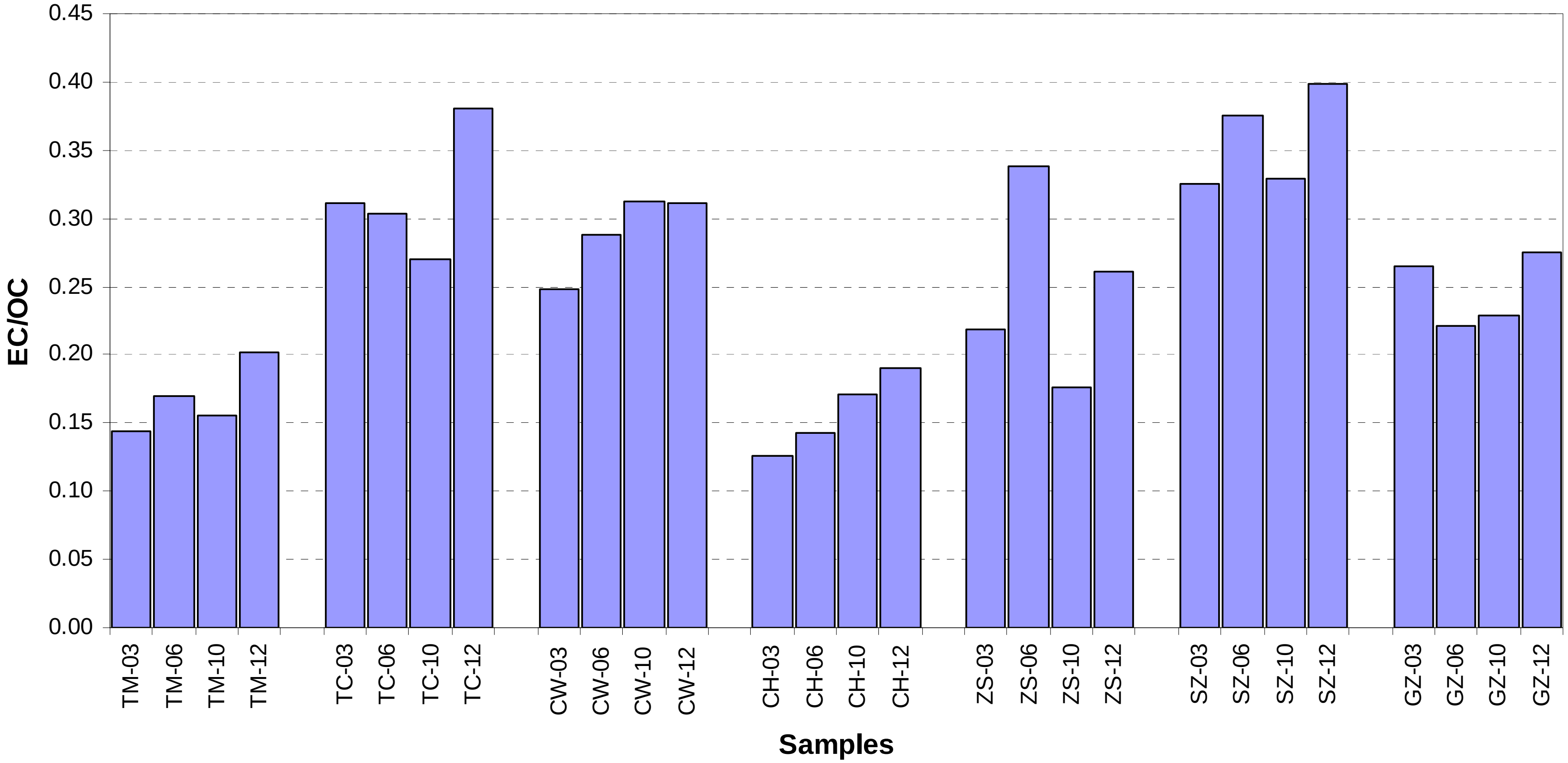


Figure 43. Seasonal and spatial distribution of the EC to OC ratios (TM: Tap Mun, TC: Tung Chung, CW: Central and Western, CH: Conghua, ZS: Zhongshan, SZ: Shenzhen, GZ: Guangzhou)

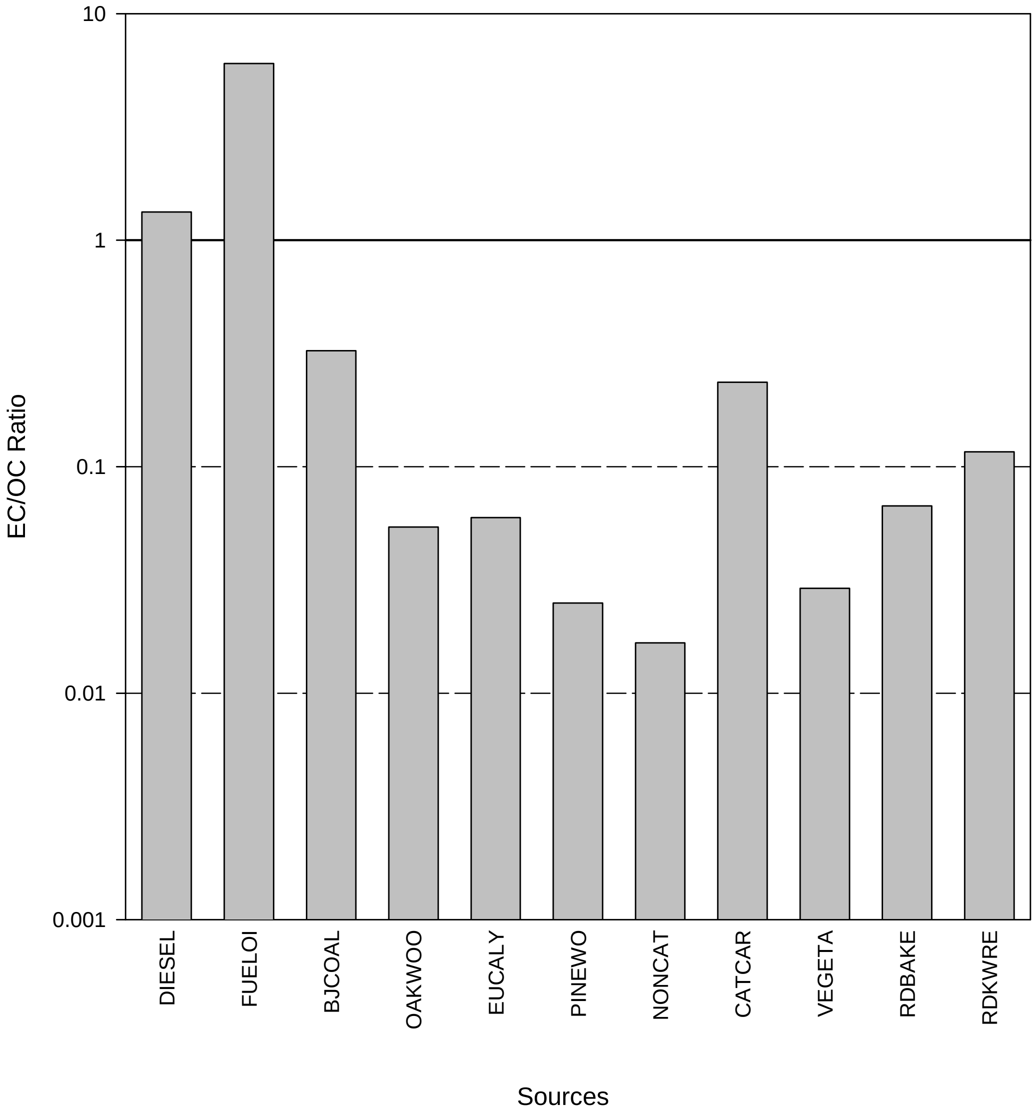


Figure 44. Ratios of elemental carbon (EC) to organic carbon (OC) from different source tests. DIESEL, diesel trucks; FUELOI, fuel oil combustion; BJCOAL, Beijing coal combustion; OAKWOO, oak wood combustion; EUCLAY, eucalyptus wood combustion; PINEWO, pine wood combustion; NONCAT, non-catalyst gasoline vehicles; CATCAR., catalyst gasoline vehicles; VEGETA, vegetative detritus; RDBAKE, Bakersfield road dust; RDKWRE, Kern Wildlife Refuge road dust

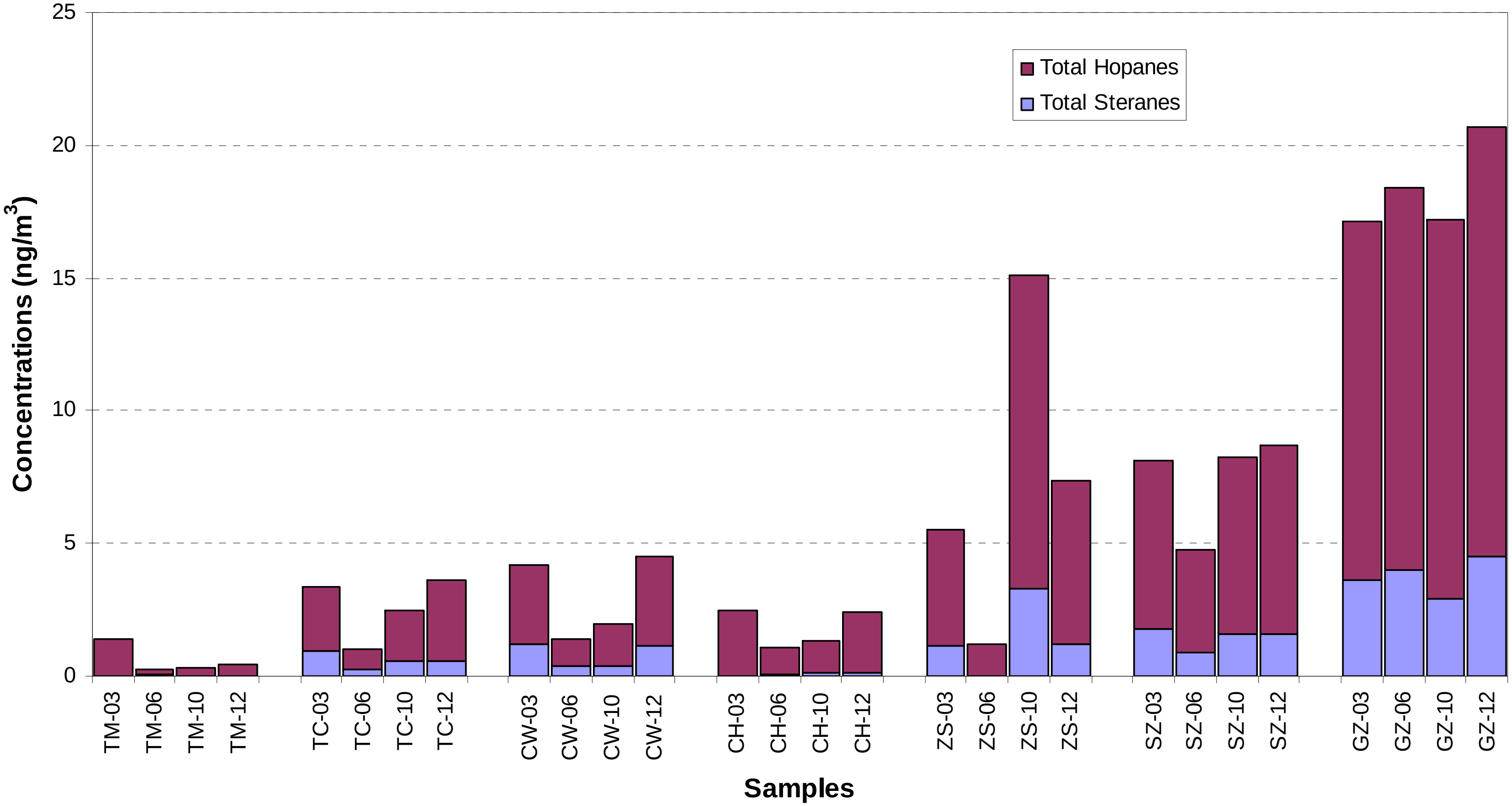


Figure 45. Seasonal and spatial distribution of hopanes and steranes (TM: Tap Mun, TC: Tung Chung, CW: Central and Western, CH: Conghua, ZS: Zhongshan, SZ: Shenzhen, GZ: Guangzhou)

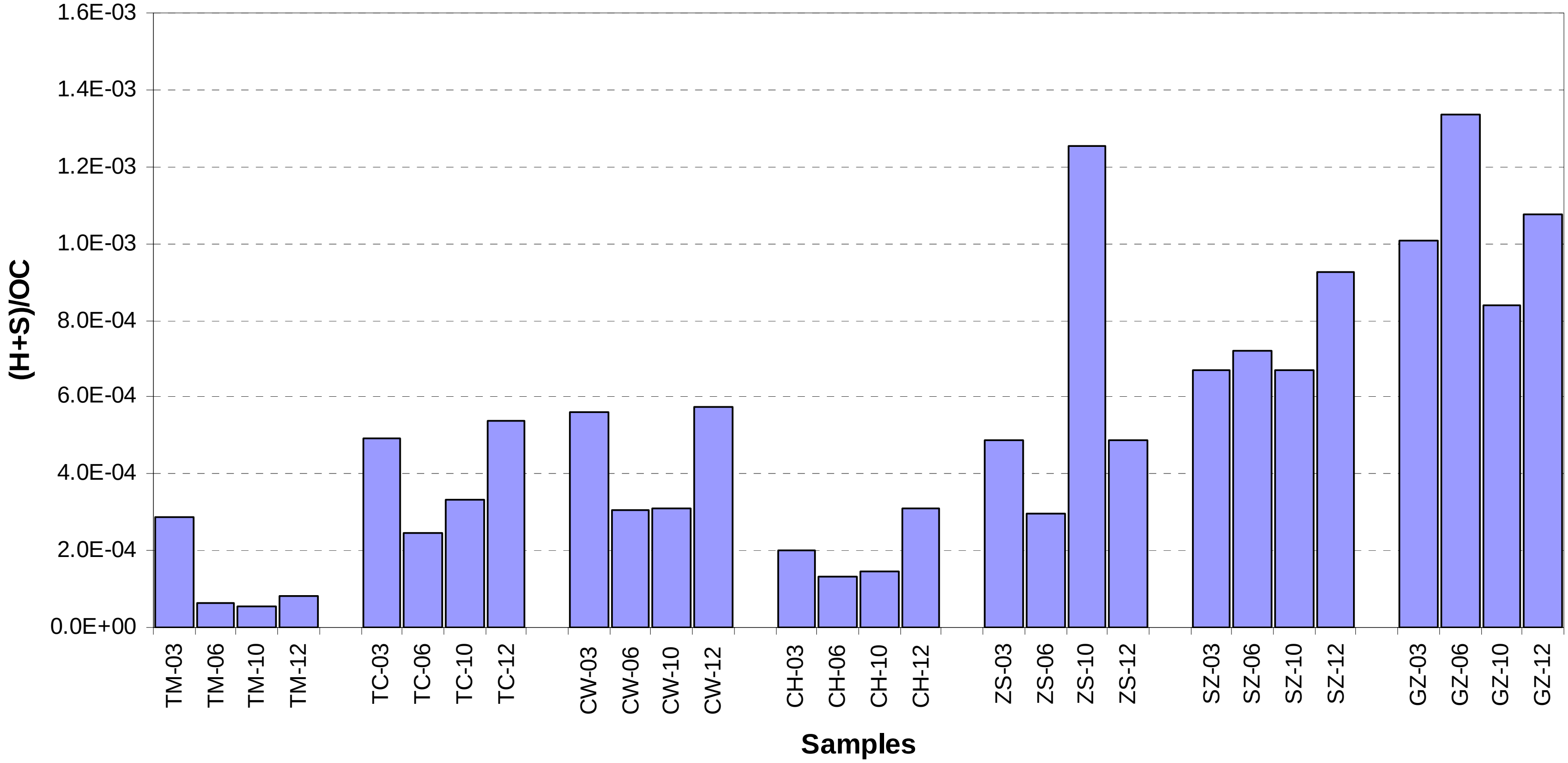


Figure 46a. Seasonal and spatial distribution of the hopanes and steranes (H+S) to OC ratios (TM: Tap Mun, TC: Tung Chung, CW: Central and Western, CH: Conghua, ZS: Zhongshan, SZ: Shenzhen, GZ: Guangzhou)

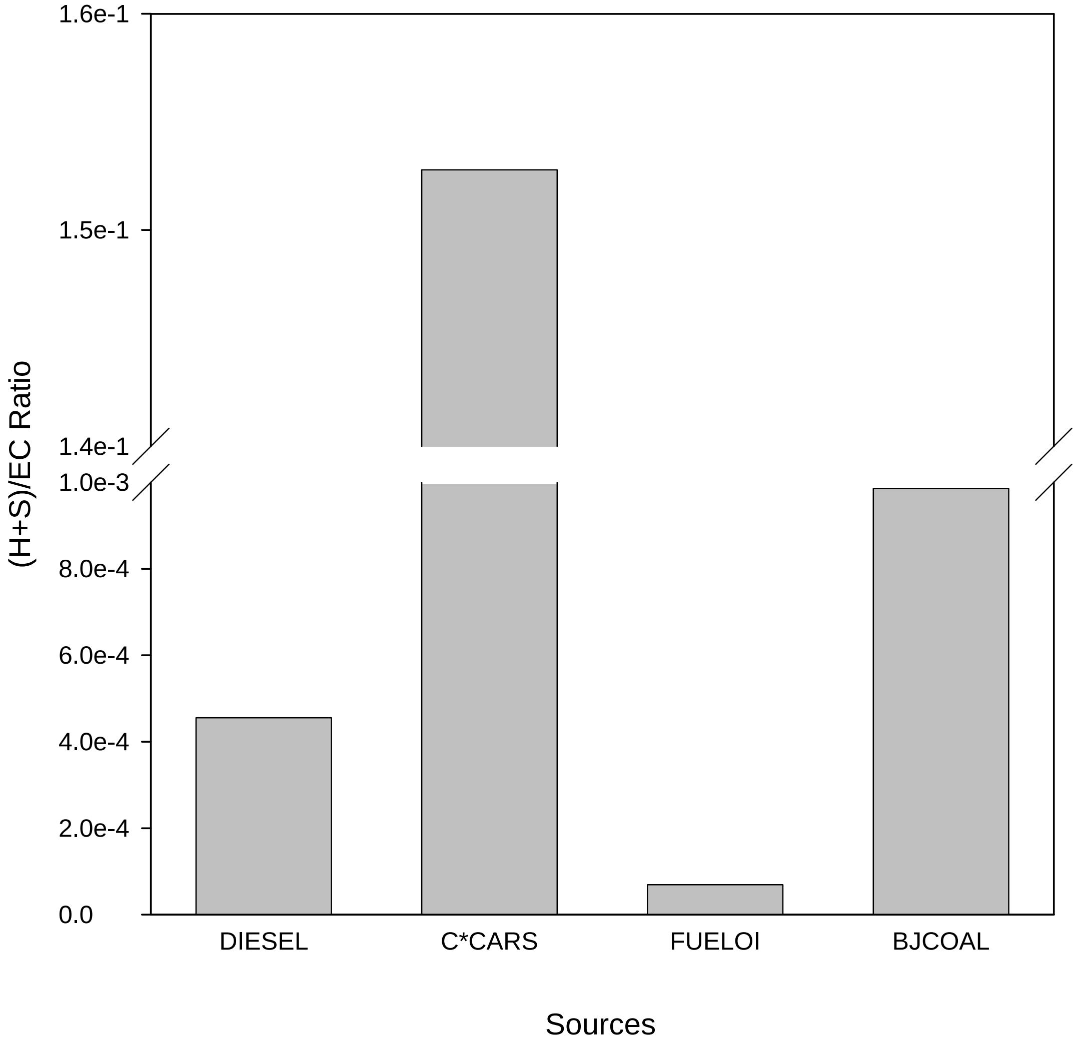


Figure 46b. Ratios of hopanes (H) and steranes (S) to elemental carbon (EC) from different source tests. DIESEL, diesel trucks; C*CARS, gasoline vehicles; FUELOI, fuel oil combustion; BJCOAL, Beijing coal combustion.

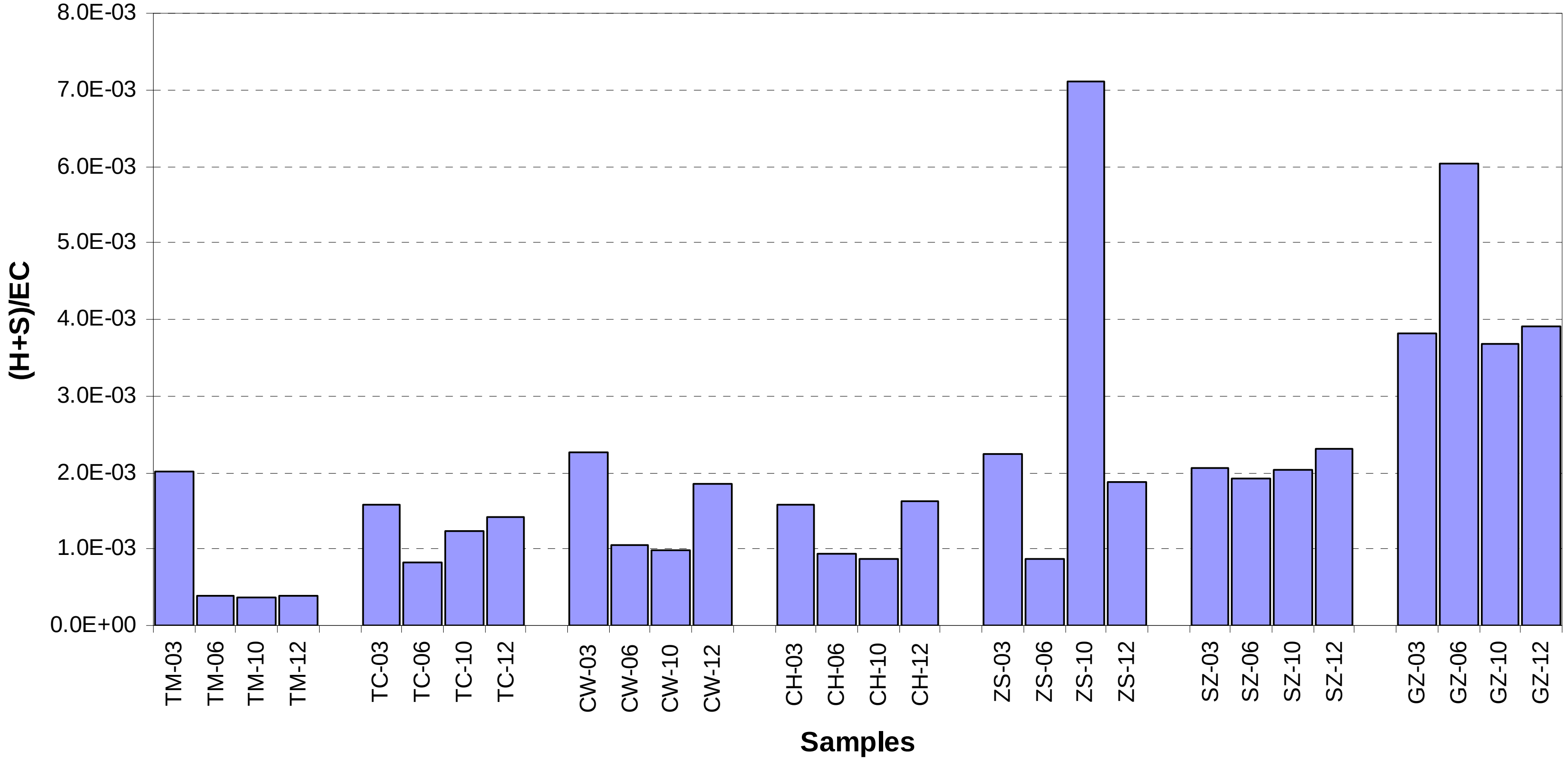


Figure 46c. Seasonal and spatial distribution of the hopanes and steranes (H+S) to EC ratios (TM: Tap Mun, TC: Tung Chung, CW: Central and Western, CH: Conghua, ZS: Zhongshan, SZ: Shenzhen, GZ: Guangzhou)

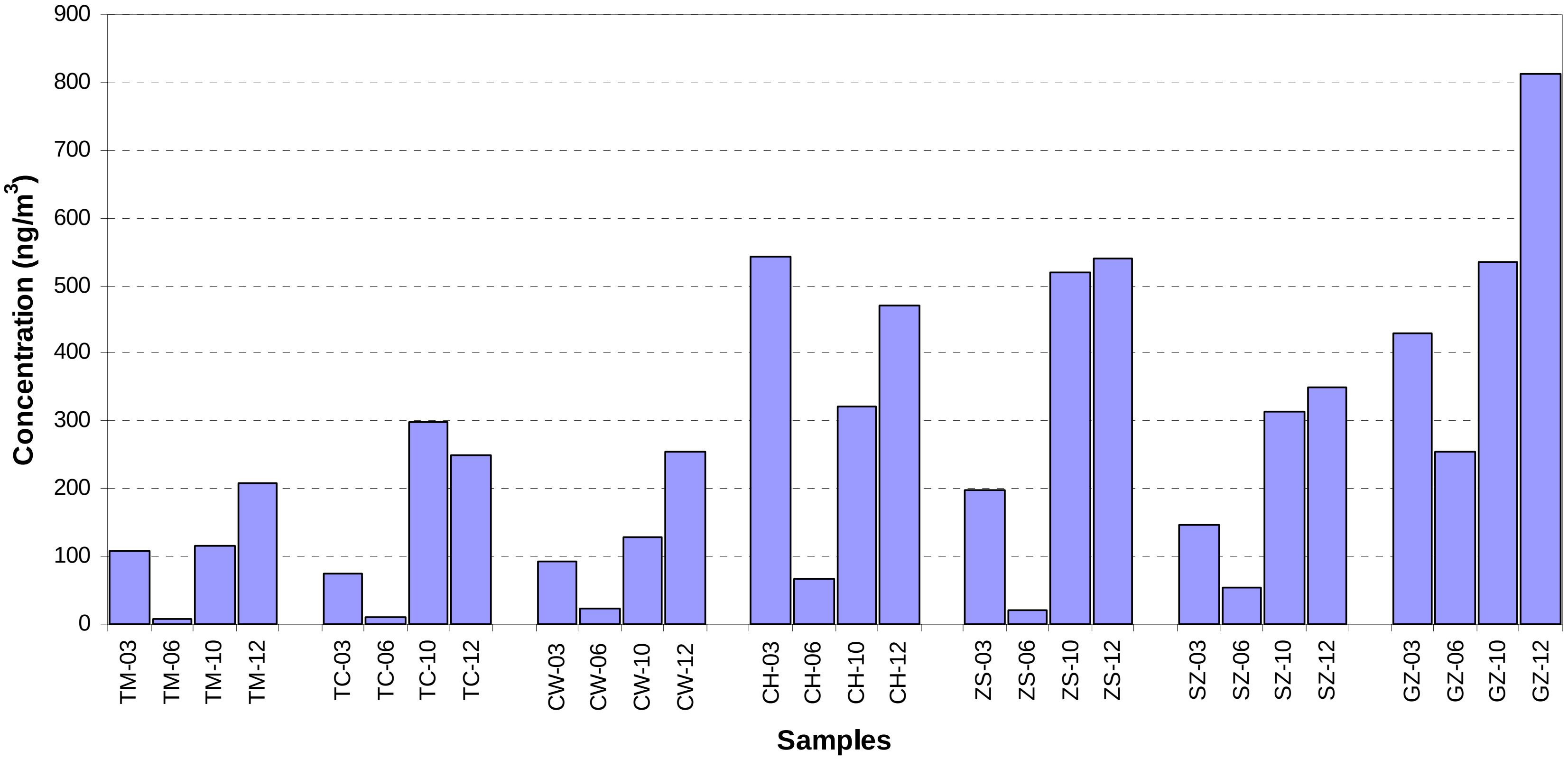


Figure 47. Seasonal and spatial distribution of levoglucosan (TM: Tap Mun, TC: Tung Chung, CW: Central and Western, CH: Conghua, ZS: Zhongshan, SZ: Shenzhen, GZ: Guangzhou)

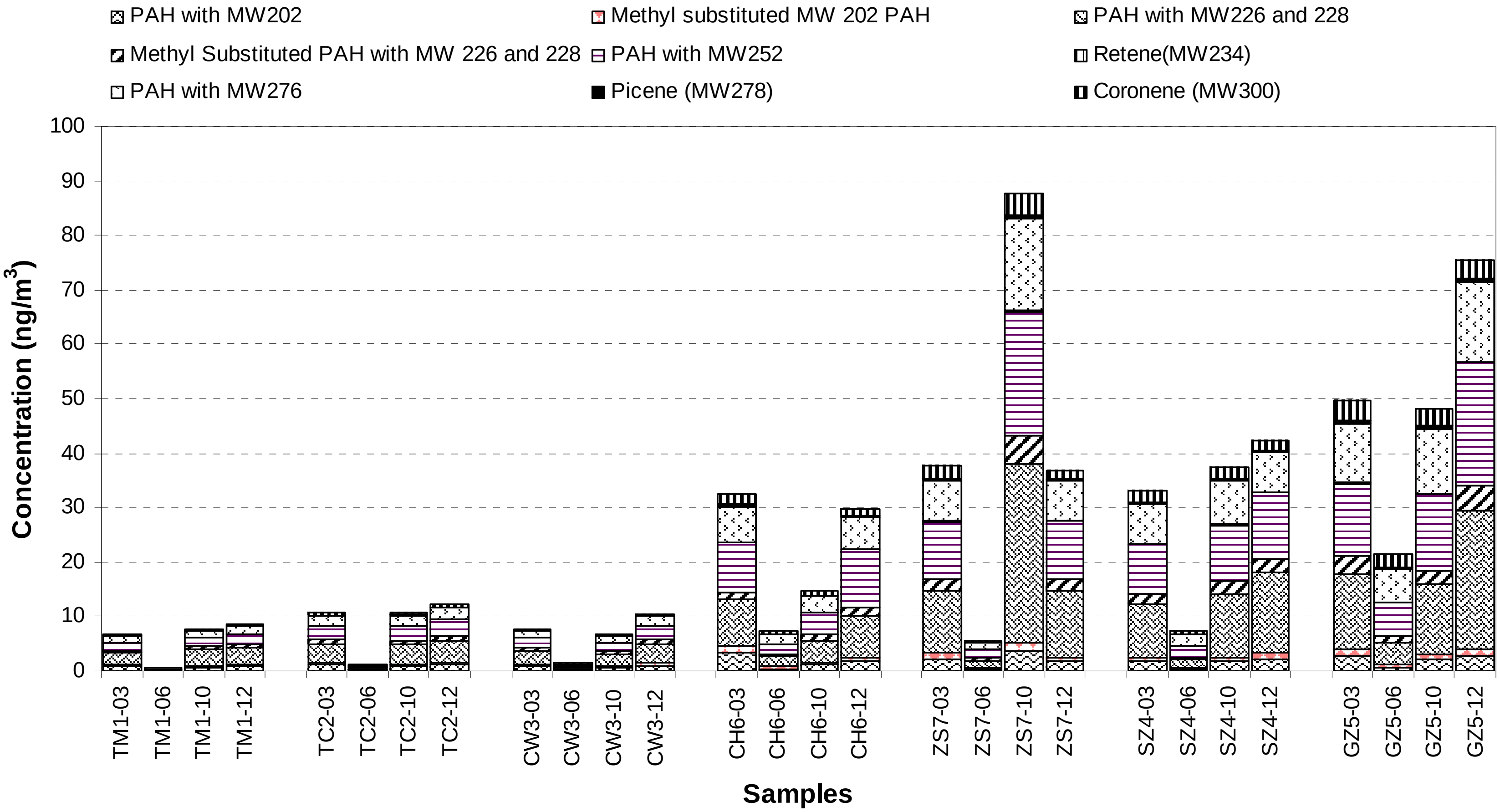


Figure 48. Spatial and seasonal distribution of PAHs (TM: Tap Mun, TC: Tung Chung, CW: Central and Western, CH: Conghua, ZS: Zhongshan, SZ: Shenzhen, GZ: Guangzhou)

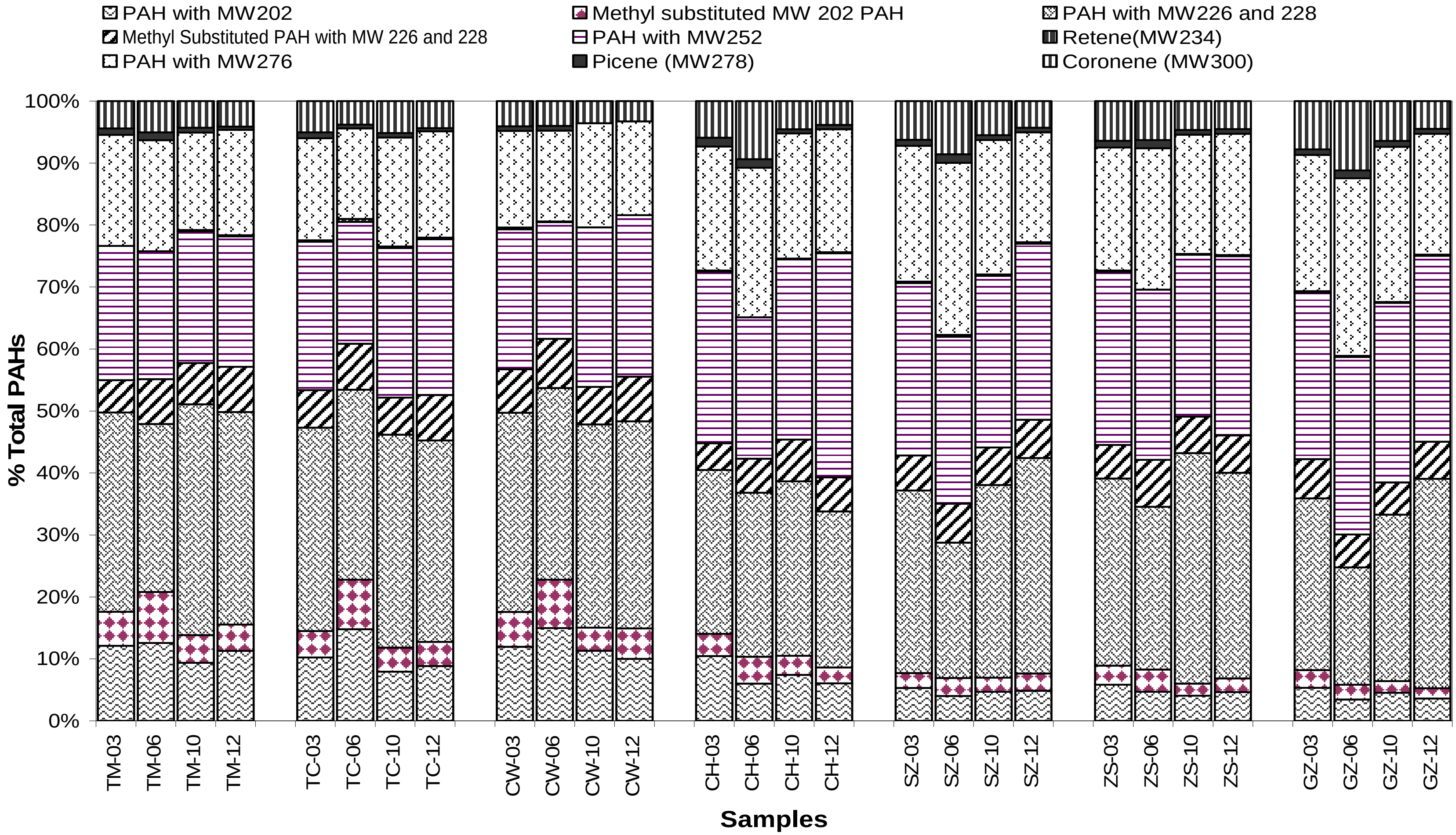


Figure 49. Seasonal and spatial distribution of percentage of PAH to Total PAHs (TM: Tap Mun, TC: Tung Chung, CW: Central and Western, CH: Conghua, ZS: Zhongshan, SZ: Shenzhen, GZ: Guangzhou)

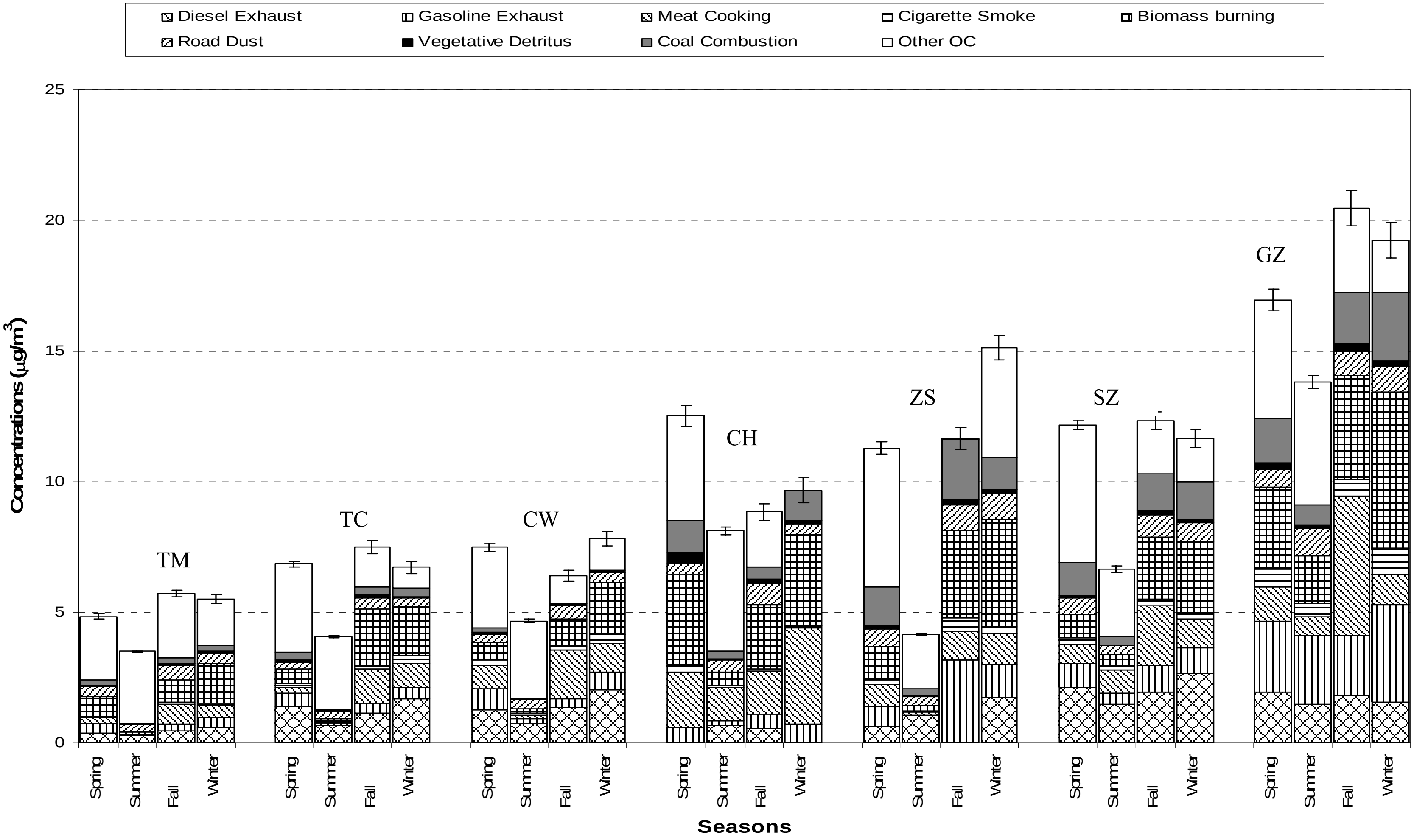


Figure 50. Source contributions to fine particulate organic carbon in PM2.5. The error bars show the error propagated from the error associated with each source identified from the CMB model.

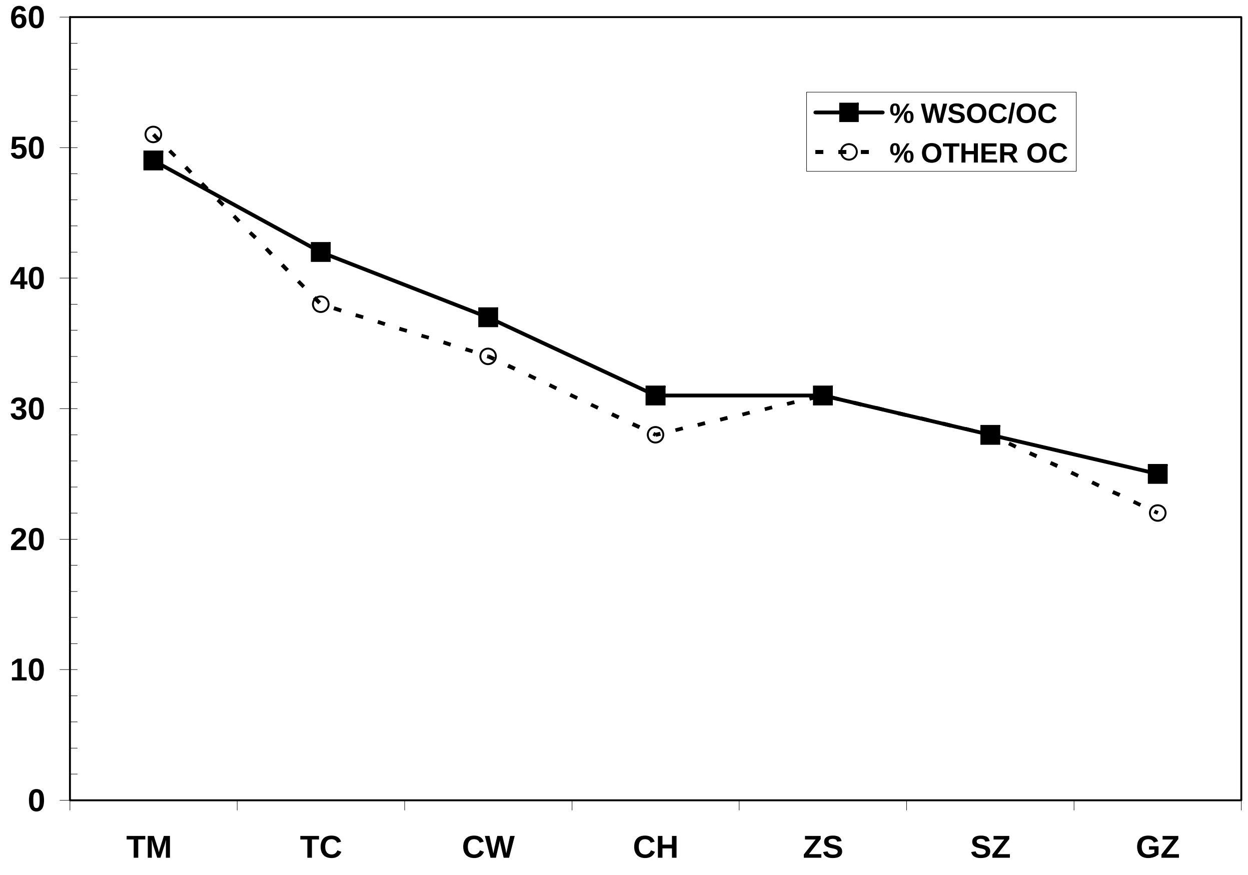


Figure 51. Comparison of measured WSOC/OC and CMB estimated % Other/ OC concentrations

Appendix A

Hong Kong and PRD Air Quality Study: Aerosol Project

I. Fine particulate matter (PM2.5) site selection for the PRD study
II. Sampling Methodology
III. Additional supporting measurements during the PRD study
IV. PM2.5 sampling schedule and timetable

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July 11, 2002

I. Fine particulate matter (PM2.5) site selection for the PRD study

Introduction

The major policy-relevant, scientific objectives of the PRD PM2.5 study are to assess:

1. The relative contributions of various types of sources of pollution to the PM2.5 mass and chemical composition in the Pearl River Delta;
2. The relative contributions of sources from within and outside of the Pearl River Delta to PM2.5 in the Pearl River Delta; and
3. The relative contributions of pollution sources from various subregions of the Delta (i.e., Guangdong, Hong Kong) to PM2.5 in the Pearl River Delta .

In order to achieve these objectives, the Science Team will undertake an observation-based approach involving the detailed analysis of PM2.5 mass concentration and chemical composition (including major ions, organic and elemental carbon, and selected water soluble and solvent extractable organic tracer compounds) measured at 7 sites in the PRD region. Four of the sites are to be located in Guangdong province and three are to be located in Hong Kong. In this section we discuss the criteria adopted by the Science Team for selecting these seven sites and then the locations and characteristics of the seven sites chosen.

Site selection criteria

Five major criteria were used to select the locations of the seven sampling sites:

1. *Overarching Logistical Criteria*: Each site must have the infrastructure including power capability and security, as well as skilled personnel to conduct sampling;
2. *Background Sites:* At least one sampling site in Hong Kong and one sampling site in Guangdong should be located in a relatively remote outlying area so that the mass concentration and chemical composition of the so-called "*background*" PM2.5 in Hong Kong and Guangdong can be measured. Note that we use the term background to denote the portion of PM2.5 found in either Hong Kong or Guangdong that is transported into these regions from outside of the Pearl River Delta region and/or produced locally by natural processes and thus can not be affected by local pollution control measures. In general by combining these background measurements with meteorological information and the data we

gather from other sites, it should be possible to diagnose the fractions of this background that is natural and the fraction that is coming from outside of the Pearl River delta. In principle some fraction of the PM2.5 within the region can arise from pollution emanating from other regions in China and/or East Asia (or beyond) and so could be reduced by pollution control measures adopted outside of the Pearl River Delta region.

3. *Receptor Sites:* At least one site in both Hong Kong and in Guangdong should be located in areas where local pollution sources are negligible, but are downwind of major sources of pollution within the Pearl River Delta, so that the impact of these sources on regional PM2.5 can be assessed.
4. *Urban Source Sites:* The remaining sites need to be located within those areas in the Pearl River Delta where the major sources of PM2.5 pollution are found. The data from these sites will be used to assess: (i) the additional PM2.5 mass and chemical constituents added to the background PM2.5 from the individual source areas; and (ii) the so-called “chemical fingerprint” of the PM2.5 emanating from the individual source areas.

Sampling site Selection

In applying the above criteria to the selection of sampling sites, the Science Team had to be cognizant of the monetary and human resources available for the project which ultimately limited the number of sites to be operated to four in Guangdong and three in Hong Kong. (Resource limitations also placed constraints on the amount of sampling to be carried out at each site). To meet the overall objectives of the project with these constraints, the Science Team carefully prioritized sampling needs identified by the criteria listed above. After much discussion the Science Team elected to choose the sites as follows:

- Two Background Sites called for in Criteria #2;
- Two Receptor Sites called for in Criteria #3; and
- Three Urban Source Sites described in Criteria #4. The Science Team further prioritized the selection of these three Urban Source Sites to be located in the three areas believed to represent the major sources of urban air pollution to the region: namely (in alphabetical order) Guangzhou, urban Hong Kong, and Shenzhen, the three largest cities in the PRD.

With these criteria and corresponding prioritizations identified the Science Team then made the specific site selections. These selections were made on the basis of the analysis of available

PM2.5 data from several years of measurements by the Hong Kong EPD as well as a pilot study conducted in the PRD by CH2M Hill. A summary of the findings of this analysis were presented at the science team meeting (the presentation is available through Civic Exchange).

Locations of Sampling Sites

A map indicating the locations of the seven sampling sites selected for the PRD PM2.5 study is illustrated in Figure 1. Table 1 provides pertinent information on each site; i.e., location, organization responsible for operation of the site, and available PM concentration data at the sites.

Figure 1. Locations of sampling sites selected for the PRD PM2.5 Study.

The 2 Background Sites are Tap Mun, which is located on a small, relatively unpopulated island in north-east Hong Kong, and Conghua which is situated ~ 80 km north east of Guangzhou in rural Guangdong. Tap Mun is a routine monitoring station currently being operated by the Hong Kong EPD while the Conghua site is maintained by the local Conghua EPB. As shown in Table 1, both sites are known to have relatively low particulate matter concentrations.

Table 1. Site Descriptions

Site Location	Organization Responsible For Operation	PM Concentration	Site Type
Conghua	Conghua EPB	[1]RSP = 38 μg m^{-3}	Background
Tap Mun	Hong Kong EPD	[2]PM2.5 = 29 μg m^{-3}	Background
Shenzhen	Peking University	[1]RSP = 114 μg m^{-3}	Urban Source
Guangzhou	Guangzhou Municipal EPD	[1]RSP = 158 μg m^{-3}	Urban Source
Central and Western	Hong Kong EPD	[2] RSP = 50 μg m^{-3}	Urban Source
Tung Chung	Hong Kong EPD	[2]PM2.5 = 33 μg m^{-3}	Receptor/Back.
Zongshan	Zhongshan EPB	[3]RSP ~ 60 μg m^{-3}	Receptor/Back.

RSP is particles having diameters less than 10 μm

[1] CH2M Hill Report, 2002; measurements made during Dec. 1999 – May 2000

[2] Based on measurements made by HKEPD during ~1998 - 2002

[3] Based on observed measurements on 5/29/02

As noted above, the three Urban Source Sites are located in Shenzhen, Guangzhou, and Hong Kong. In Hong Kong we plan to use the EPD Central and Western (CW) monitoring site located in a populated area of Hong Kong Island. The sampling site in Shenzhen will be situated at the Peking University Shenzhen Graduate School. The Guangzhou sampling station is located in the city at the Guangzhou Municipal EPD. As shown in Table 1, the particulate matter concentrations at the two urban sites in Guangdong are relatively high compared to the background sites; the urban site in Hong Kong also has elevated particulate matter concentrations, although not nearly as high as the two urban sites in Guangdong.

The two receptor sites will be located near the city of Zhongshan in Guangdong and at Tung Chung on Lantau Island in Hong Kong. The Zhongshan sampling station is maintained and operated by the Zhongshan EPB and is very likely influenced by urban regions in both Hong Kong as well as Guangdong depending on the time of year and air flow patterns, and thus should work well as a Receptor Site (it is also possible that under some meteorological conditions, the Zhongshan site will provide data more representative of a Background Site). The Tung Chung site, under the control of the Hong Kong EPD, is likely most useful as a Receptor Site during the winter, when PM2.5 pollution is generally the worst, due to advection from both Hong Kong and Guangdong. During the summer the site generally experiences relatively low PM2.5 concentrations and likely acts as Background Site (M.H. Bergin, Science Team Meeting Presentation).

II. Sampling Methodology

At 3 sites in Hong Kong and 2 sites in Guangdong ThermoAndersen RAAS PM2.5 chemical speciation samplers (http://www.andersoninstruments.com/raas-400.htm) will be used to collect aerosol samples. The samplers are designed with 4 separate channels. Two of the channels will be operated at 16.7 lpm with quartz filters that will be analyzed for organic (OC) and elemental carbon (EC), and specific water soluble and solvent extractable organic compounds that will serve as tracers for various aerosol sources. The other two sampling lines will collect aerosol particles on Teflon filters at a flowrate of 7.3 lpm that will be used to determine the PM2.5 mass concentration as well as the concentrations of major ions, and elements. At two additional sites in Guangdong 2 prototype samplers designed and fabricated at Caltech will operate under similar conditions as described above.

The sampling will be conducted during one month of each season. The months of sampling will be October and December of 2002, and March and June of 2003 as shown in the project timeline in the Appendix. Sampling will be conducted every sixth day during each sampling month. The filter sample times will be 24-hr.

III. Additional supporting measurements during the PRD study

Particulate Measurements

To the extent possible additional measurements will used to add to our understanding of the spatial and temporal variability of PM concentrations in the study area. Within Hong Kong we will have access to measurements being conducted by the Hong Kong EPD. Measurements of RSP (particulate matter having diameters less than 10 μm) will be available for ~14 locations, and PM2.5 at five locations. Of the five HKEPD PM2.5 measurements sites, three will be co-located with the ThermoAndersen samplers at Tap Mun, Tung Chung, and Central and Western. Both RSP and PM2.5 are being monitored in real-time at the HKEPD sites using Tapered Element Oscillating Microbalance's (TEOM). At the sampling stations the TEOM data will fill in the gaps for PM2.5 concentrations when filter measurements are not being made. In addition, the TEOM data will be used to gain insights into the processes that influence the temporal and spatial variability of PM2.5 concentrations in Hong Kong. There are currently several stations that continuously measure RSP in the PRD, and it is anticipated that some of these measurements will be available during the study.

Meteorological Measurements

Meteorological measurements will be integrated with the PM2.5 data to better understand the influence of transport and meteorological conditions on aerosol concentrations. It is anticipated that basic meteorological measurements (temperature, pressure, relative humidity, wind speed and wind direction) will be available at all sampling locations. In addition, we will use measurements being made by the Hong Kong observatory at several locations around Hong Kong. It is also very likely that we will have meteorological data from each of the sampling locations in Guangdong as well as additional met data from the region

IV. PM2.5 sampling schedule and timetable

A timeline for tasks relevant to the PRD aerosol project is given in the Appendix. At this time the aerosol samplers, additional field equipment, and filters have been purchased. The ThermoAndersen RAAS PM2.5 chemical speciation samplers are currently being tested and prepared for field deployment at Georgia Tech. We are also in the process of developing protocols for field sampling. During the testing of the samplers, standard operations procedures will be developed for the field sampling. Four of the samplers will be shipped to HKUST for deployment in Hong Kong, and two will be shipped to Peking University for deployment in Guangdong province. It is anticipated that the samplers will arrive at both locations in early August. The field samplers will be deployed in Hong Kong and Guangdong during the last part of August and beginning of September. The sampler deployments will be conducted jointly by members of the Georgia Tech research team, Peking University, HKUST, HKEPD, and sponsoring organizations in Guangdong. At each sampling location operators will be trained on standard field operations procedures by members of the Georgia Tech and Peking University research teams. Roughly 2-weeks prior to the first month of sampling in October a coordinated test run will be conducted for a 24-hr sampling period. This will be done in order to insure the samplers are operating properly and that the field technicians are adequately trained. Samples will be refrigerated and shipped directly to HKUST after each month of sampling. HKUST will remove samples being analyzed at that location, and ship the remaining samples to Georgia Tech. It is anticipated that a science team meeting will be held during December 2003. This date has tentatively been chosen since it occurs at a time when most of the chemical analyses will be completed and can be discussed during the meeting. A midterm progress report will be prepared during May-June of 2003, as well as a final project report from January-April 2004.

APPENDIX

PRD Aerosol Project Timeline, Year 1

	2002								***2003***			
Task	***May***	***June***	***July***	***Aug***	***Sept***	***Oct***	***Nov***	***Dec***	***Jan***	***Feb***	***Mar***	***April***
Select sampling sites	____											
Purchase Equipment	____	____	____									
Test field sampling equipment and prepare protocols			____									
Prepare field samples			____	____	____	____		___	____		___	____
Deploy field samplers and train operators				____	____							
Test run of samplers in field					****							
Aerosol Sampling at field sites						****		****			****	
Laboratory analysis of field samples							___	____	____	___	____	____

PRD Aerosol Project Timeline: Year 2

	2003								***2004***			
Task	***May***	***June***	***July***	***Aug***	***Sept***	***Oct***	***Nov***	***Dec***	***Jan***	***Feb***	***Mar***	***April***
Aerosol Sampling at field sites		****										
Laboratory analysis of field samples	____	____	____	____	____	_____	____	____				
Science team meeting								____				
Midterm progress report preparation	____	____										
Final report preparation									____	____	____	____

Appendix B

Prepared for the Hong Kong Civic Exchange

Standard Operating Procedures for Sample Preparation, Handling, and Analysis during the Pilot Study in Hong Kong and the Pearl River Delta

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1 INTRODUCTION

Air monitoring will be conducted at seven locations in Hong Kong and the Pearl River Delta region of China beginning in October, 2002. The study will be conducted under the direction of Professor Michael Bergin at the Georgia Institute of Technology.

The project's collaboration partners include Peking University, Civic Exchange, Environmental Protection Department (Hong Kong), Georgia Institute of Technology, Guangzhou Research Section of Environmental Sciences, Hong Kong Polytechnic University and Hong Kong University of Science & Technology.

The goal of this study is to make fine particle $PM_{2.5}$ measurements to manage air quality in Hong Kong and the Pearl River Delta, China. The design, installation and preliminary operation of a fine particle monitoring network that spans the Hong Kong and Guangdong area will be undertaken. The network will be able to help define the pollutant concentrations in background air advected into the PRD region from upwind at various times of the year.

Each monitoring station has been designated using a two letter identifying code and a site number that will be placed on all sample labels. See Figure 1.

The station ID codes are:

TM1	Tap Mun
TC2	Tung Chung
CW3	Central and Western
SZ4	Shenzhen
GZ5	Guangzhou
CH6	Conghua
ZS7	Zhongshan

Thermo Andersen PM2.5 speciation samplers will be used at the first five stations, and Caltech Gray Box PM2.5 ambient samplers (prototype models for the Thermo Andersen samplers) will be used at the remaining two sites. The Andersen samplers follow the monitoring requirements of the US PM2.5 national Ambient Air Quality Standards, 40 CFR 58, (EPA, 1997) and the Caltech samplers have had over 17 years of worldwide field experience (Solomon, et al. 1988; Salmon, et al. 1994, 1996). Both types of samplers work using pumps connected to a manifold with critical orifices for flow control. Andersen samplers also have mass flow meters to measure flows. Nominal flow rates in the samplers are:

SAMPLER TYPE	QUARTZ FILTERS	TEFLON FILTERS
Andersen Sampler	16.7	7.3
Caltech Samplers	14	10

During each 24-hour sampling event, fine particle samples will be collected on several filters operated in parallel which will be analyzed chemically to determine ionic

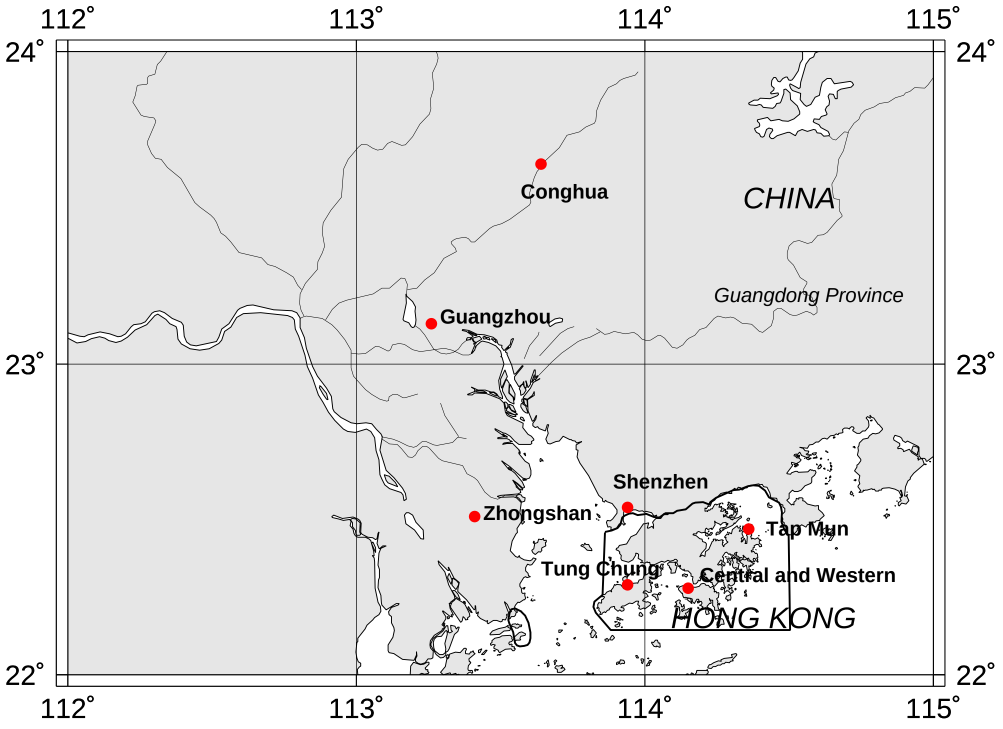


Figure 1: Map Showing Air Quality Monitoring Sites

species (sulfate, nitrate, chloride) concentrations by ion chromatography, ammonium ion by colorimetric analysis, elemental carbon and organic carbon by thermal evolution and combustion analysis, and trace elements by X-ray fluorescence or inductively-coupled plasma mass spectrometry. From these measurements, a material balance on the chemical composition of the particles on each day will be created that generally indicates the overall nature of the local fine particle problem. For example, the relative importance of sulfates from sulfur-bearing fuel use vs. soot from incomplete combustion vs. soil dust from travel over dusty streets may be determined.

Field sampling will be done on a 6 day schedule. This means that a 24-hour sampling event takes place once every 6 days following a predetermined schedule. Loading of filter samples will take place on the day before each sampling event and unloading will take place on the day after. Samplers are equipped with timers that will be set to take samples for the 24-hour period beginning at 12:00AM (midnight) on the day of sampling.

The air monitoring network will be operated by taking samples for 24-hour periods at six-day intervals for one month in each quarter of the sampling year (e.g., October, 2002; December, 2002; March, 2003; and June, 2003). This sampling schedule was chosen to observe conditions that occur throughout the year as well as to permit determination of approximate annual average concentrations.

This Standard Operating Procedures (SOP) for sample preparation, handling, and analysis is to provide guidance for handling and quality control for the 47mm diameter filters that will be used for atmospheric measurements during the Pilot Study in Hong Kong and the Pearl River Delta region. Details for substrate preparation, weighing procedures, loading and unloading filter samples in the field, as well as procedures for organic and elemental carbon analysis, and analysis of Teflon filters will be found in the following sections of this document.

2 PREPARATION OF QUARTZ FIBER FILTERS

2.1 Apparatus and Materials

The following apparatus and materials are used to prepare quartz fiber filters for carbonaceous aerosol collection.

ITEM	SUPPLIER	MODEL or CATALOG NO.
Quartz fiber filters	Pall Gelman	2500QAO-UP
Furnace	Wheelco	292
Tweezers style AA	Ted Pella	5734
Gelman s.s. forceps	VWR	51147
Petri dishes	VWR	25388-606
8oz wide mouth jar	VWR	16195-088
Aluminum foil	Reynolds	
Disposable lab wipe	Kimwipes	
Methanol HPLC Grade	VWR	EM-MX0475-1

2.2 General Information

Quartz fiber filters (type 2500QAO-UP), 47mm diameter, are available from Pall Gelman (formerly Pallflex). Before use the filters must be prepared and stored such that the organic carbon and elemental carbon blank values are low, and care must be used in handling the filters. It is desirable to prepare baked aluminum foil to use as a work surface on the lab bench and for field operations.

2.3 Procedure for Baking Quartz Filters

1. Glass jars should be cleaned and pre-baked in advance. Jars as received, sometimes have cardboard dust in them. They should be cleaned before baking using DI water obtained from the MilliQ dispenser. Rinse the jars 3-4 times using DI water and visually inspect them to make sure they look clean and are not cracked. Set the jars with the open end down on clean kimwipes until they dry. Also briefly rinse the plastic caps in DI water and set them on clean kimwipes to dry. The jar caps contain teflon lid liners. Rinse the teflon liners with methanol and dry on clean kimwipes.

2. For 47mm diameter quartz fiber filters, use 8 oz. annealed glass jars covered with baked aluminum foil to hold filters while baking.

3. Rolls of aluminum foil can be annealed by removing the cardboard core and baking at 550^{o}C overnight.

4. Place approximately 50 quartz filters in each jar. Only clean, solvent-rinsed tweezers are used to touch the filters, and only on filter edges. Individual filters are examined, and filters that have any visible imperfections should be discarded.

5. All of the filters, which come stuck together in their boxes, should be individually separated before baking. Stack the filters loosely in the jar then cover the top of the jar tightly with a double layer of annealed aluminum foil. Several jars of filters can be baked in the oven at one time. It is also possible to bake a jar or two containing quartz filters at the same time that empty glass jars are being baked.

6. Filters are baked at 550°C for approximately 16 hours (or overnight). This includes approximately 2 hours for the oven to heat to 550°C. After baking, the jars with the filters are cooled in the oven. After cooling, jars are capped with a jar lid containing a solvent washed teflon lid liner and stored in a freezer until they have been sealed into prepared petri dishes described below.

7. Each time a set of filters are baked the relevant information is entered onto the filter preparation log sheet. This information includes the lot number from the box of filters, the Caltech assigned batch number (e.g., Q-19), the date, time, and temperature baked. A new batch number is assigned for each batch of filters prepared. See Filter Preparation Log for Baked Quartz Fiber Filters.

8. After baking, allow the jars with filters to cool in the oven with the door ajar until they can be handled. As soon as the jars are cool enough to touch, remove them and replace the foil cover with a jar lid containing a solvent washed teflon lid liner. Cover the jars tightly and note the batch number on a label on the jar lid. Place the jars with baked filters in a freezer until they have been sealed into prepared petri dishes described below.

2.4 Petri Dishes for Baked 47mm Quartz Filters

Prepared petri dishes consist of annealed aluminum foil press-fitted into the top and bottom of petri dishes (VWR, cat. no. 25388-606).

Foil liners are prepared by cutting circular pieces of aluminum foil using a 57mm diameter template, 2 foil circles per petri dish. The aluminum foil circles are annealed in the oven for approximately 16 hours at 550°C. After the aluminum foil circles have cooled, they are handled using only clean, solvent-rinsed tweezers.

On a clean work area on a lab bench covered with pieces of annealed aluminum foil, the circular aluminum foil pieces are press fit, one at a time, into the tops and bottoms of petri dishes. This is done using a solvent-cleaned Lucite cylinder that was machined to be slightly smaller than the inside diameters of the petri dish tops and bottoms.

One baked quartz filter is placed into each foil lined petri dish. The edges of each petri dish are sealed by stretching Teflon tape around the bottom edge of the petri dish sealing the gap. These are stored in a petri dish holder at room temperature in the lab or in a freezer until used for sampling.

FILTER PREPARATION LOG
Baked Quartz Fiber Filters

BAKED QUARTZ

PROJECT ______________________________

CALTECH BATCH NUMBER ______________________

FILTER LOT NUMBER ________________________

BAKED TEMP.__________ BAKED TIME _________HRS

DATE BAKED __________ BY __________________

DATE PACKAGED _______ PACKED BY ____________

BAKED QUARTZ

PROJECT ______________________________

CALTECH BATCH NUMBER ______________________

FILTER LOT NUMBER ________________________

BAKED TEMP.__________ BAKED TIME _________HRS

DATE BAKED __________ BY __________________

DATE PACKAGED _______ PACKED BY ____________

3 PROCEDURE FOR WEIGHING TEFLON FILTERS

3.1 Apparatus and Materials

The following apparatus and materials are used to perform the mass weighing activities.

ITEM	SUPPLIER	MODEL or CATALOG NO.
Microbalance	Mettler Instruments	M5-SA
Calibration Weights	Cahn	10-200 mg
Hygrothermograph	Cole Parmer	8368-60
Digital thermohygrometer	Markson	6612A1281
Sling psychrometer	Ertco	PS100C
210 Polonium strip	VWR	58580-041
Staticmaster positioner	VWR	58582-003
Petri dishes	VWR	25388-606
Disposable lab wipe	Kimwipes	
Tweezers style AA	Ted Pella	5734
Lo Count Mat 18x45	VWR	21924-154
47mm Teflon filter	Pall Gelman	R2PJ047
Teflon tape 1/2” wide	McMaster-Carr	4591K12
Blower bulb	Small Parts	D-HM-915
Aluminum foil	Reynolds	

3.2 Balance Facilities

The balance room located at the California Institute of Technology, Pasadena, CA is completely isolated from the outside. It is located in the sub-basement of Keck Laboratories inside a separate room, 042I, within the specially designed vibration-free microscopy facility, room 042. The balance room is completely isolated from the outside and equipped with 24-hour air conditioning that maintains a constant temperature of 21^{o}C. A Lo Count Mat is installed at the entrance to the balance room to remove loose objects from the bottom of shoes on entering personnel. Only authorized balance users who have been trained are allowed to operate the microbalance.

A filter conditioning and weighing chamber is located next to the microbalance. Temperature and RH inside the chamber is monitored when filters are equilibrating. Pre-sampling filters are equilibrated separately from post-sampling filters.

3.3 Environmental Requirements for Filter Weighing

Before weighing, Teflon filters are equilibrated for at least 24 hours in a constant temperature, constant relative humidity environment. Temperature and relative humidity guidelines from EPA Quality Assurance Document 2.12 (EPA, 1998) are used. Temperature should be in the range 20-23^{o}C and RH should be in the range 30-40%.

3.4 Electrostatic Charge Neutralization

Staticmaster ionizing units (polonium ^{210}Po) are used to reduce electrostatic charges that could interfere with balance operations. A ^{210}Po strip is attached to a staticmaster positioner with a flex spring to allow easy positioning of the unit. For most effective results, the ^{210}Po strip should be approximately 1/2 to 3/4 inch away from the surface to be neutralized.

Strips should be changed every 6 months. Old strips should be disposed of through the safety office.

3.5 General Procedure for Weighing Teflon Filters

Teflon filters (Gelman, 2.0 μm pore size, R2PJ047, Teflon membrane with PMP support rings) are placed individually into clean petri dishes (VWR, cat. no. 25388-606). Each petri dish containing a Teflon filter is assigned a five digit number in addition to the sample label. This code is specific for the individual filter and used to identify it for mass determination.

All filters are visually inspected for defects before the initial weighing. Any filters with defects are discarded. Defects include holes, discoloration, dirt, detached support rings, or severe curl in the filters. Filters are handled using only clean, non-serrated tweezers, and touched only on the support rings around the edge.

The date, filter lot number, pore size, and any comments are recorded in a filter weight log book. There is also a master weight log book kept by the balance for recording calibration filter and calibration weight data along with temperature and relative humidity information.

At the beginning of each weighing session a set of calibration filters is weighed. Calibration filter weights must agree with their historical weighings. See Figure 2, for example. Calibration weights are used as an additional diagnostic tool to verify correct balance operation. Periodically over the course of an experiment enough calibration weighings will be made to completely bracket the expected range of Teflon filter weights.

Teflon filters tend to accumulate static charge. Therefore, each filter is passed under a static discharging strip before weighing. These discharging strips contain a mildly radioactive source ^{210}Po which neutralize electrostatic charges on items brought within one inch.

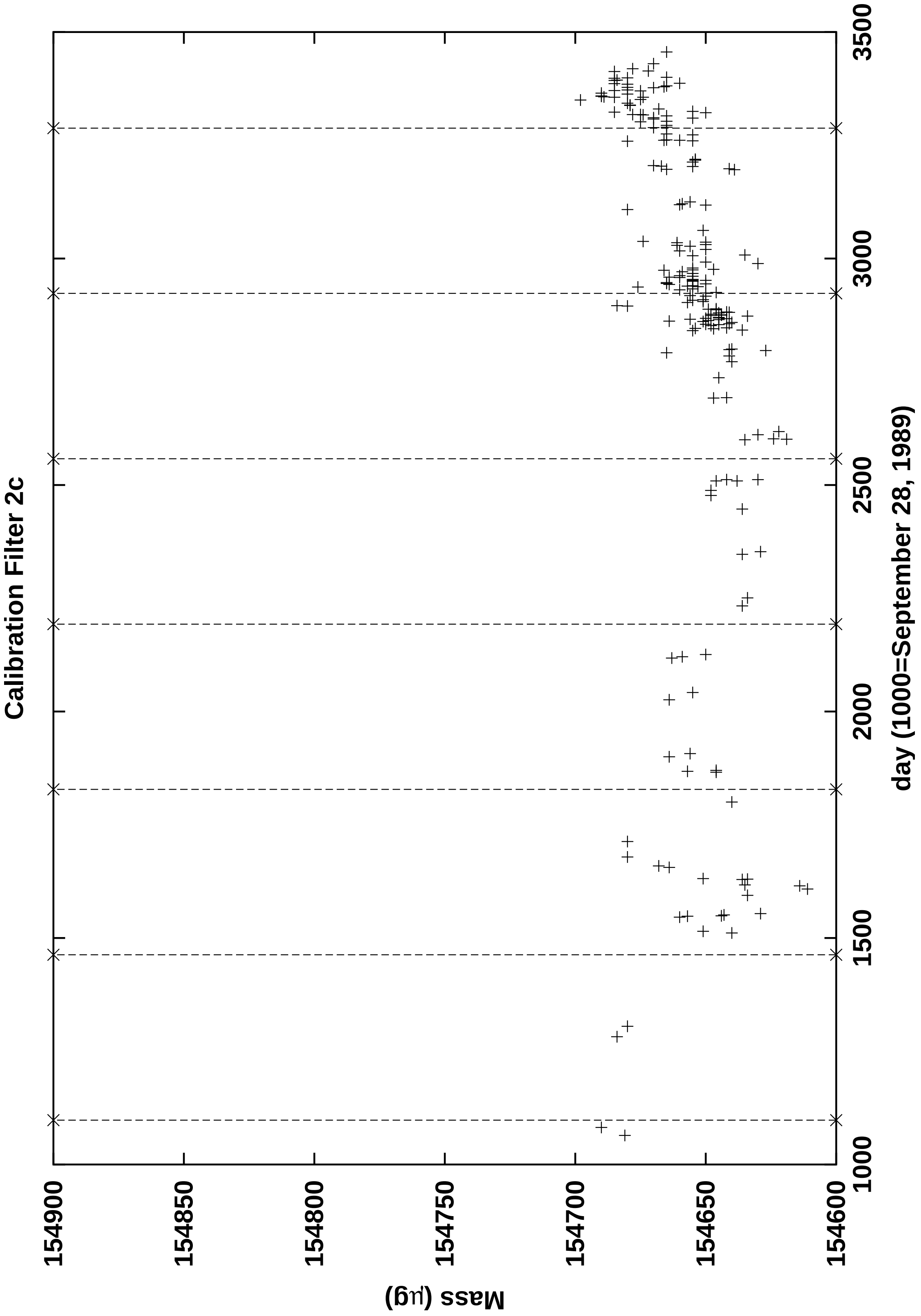


Figure 2: Historical Weighing of Calibration Filter

Each Teflon filter is weighed more than once, how many times depends on how repeatable the operator is finding the masses. Approximately half of each batch of filters are weighed subsequently on a different day to verify repeatability during initial weighings.

After initial weighing, pre-weighed filters are stored in closed petri dishes at room temperature or in a freezer until they are used for sampling. Each petri dish is sealed with teflon tape. Sampled filters containing particles are stored upright in the freezer in petri dishes wrapped around the edges with teflon tape.

3.5.1 Preparation for weighing teflon filters

1. Set out unused filters in slightly open petri dishes for at least 24 hours to equilibrate in a constant temperature, constant relative humidity environment, currently established in room 042I Keck. Extra care should be taken with filters containing samples to avoid losing volatile species while the sample is out of the freezer. Sampled filters should be returned to the freezer as soon as possible after weighing. Equilibrating filters are kept in a chamber to avoid contamination by airborne dust during the equilibration period.

2. If the temperature and humidity of the room are not near the ideal range of 20-23^{o}C and 30-40% RH, contact Physical Plant for HVAC service. Do not equilibrate or weigh filters.

3. The Mettler balance is a mechanical balance and does not need any warm up period. In fact, it is harmful to leave the Mettler balance on with no weights engaged for long periods of time, and this should be avoided. The key to successful use is to be PATIENT. Rotate all knobs and dials SLOWLY and GENTLY when interacting with the balance.

4. Always record the date, filter lot number, and any comments on the Log Sheet for Teflon Filter Weights. There is also a master weight log book kept by the balance for recording calibration filter and calibration weight data along with temperature and humidity information. It also contains pages at the front for assigning filter ID numbers to teflon filters.

5. Check the cleanliness of the balance area. If necessary, put out clean aluminum foil as a work surface near the balance. Use kimwipes to wipe surfaces.

6. At the beginning of each weighing session weigh a set of calibration filters. If calibration filter weights do not agree with their historical weighings, stop and determine if there is a problem with the balance. The balance can be sensitive to vibrations and activities when there is construction work in the building. Other potential problems come from static and air drafts. Calibration weights can be used as an additional diagnostic tool.

7. Periodically over the course of an experiment perform enough calibration weighings to completely bracket the expected range of Teflon filter weights. For 2.0 μm Teflon filters, which usually weigh between 130 and 170 mg, calibration weighings should be made for 130, 140, 150, 160, and 170 mg. The calibration weight data should be recorded BOTH in the master weight log book kept by the balance, and on the project specific Log Sheets for Teflon Filter Weights. See the instructions in the master log book to know which calibration weights to use. **Always** handle calibration weights with plastic tweezers kept in the box with them.
8. The balance zero should be checked approximately once every fifth weighing. Tiny adjustments ($<$ 1mm) to the zero may be required but any significant change is a sign of trouble. Common zero problems include accidentally bumping the balance table. If the zero has drifted, reweigh all filters since the last zero check.
9. Always leave the balance ”off” when weighing is done. This means the front knob should be left in the 12 o’clock position with no weights engaged.
10. Tweezers should be stored in the plastic box labelled “tweezers, for weighing only”. These tweezers should not be used for any purpose other than weighing teflon filters. Inspect tweezers before use, if necessary, clean by rinsing with methanol and wiping with a kimwipe.

3.5.2 Precise weighing procedure

1. Blow off any dust on the weighing pan with a bulb syringe before beginning. Set all balance weights to zero. Then completely release the weighing pan by turning the knob on the front of the balance one-quarter turn to the left. The reading should be exactly zero. To adjust the zero, use the knob toward the top rear on the right side of the balance.
2. If the zero is too far out of alignment to adjust with the zero knob, check the balance is level by looking at the bubble spirit level inside the chamber. If the bubble is not centered, the three balance feet can be adjusted by rotating them.
3. When zero is adjusted, turn off the balance by moving the front knob back to the 12 o’clock position.
4. To access the weighing pan, rotate the knob on the lower right hand side of the balance counterclockwise (slowly). (The knob on the lower left hand side can also be used – it should be rotated clockwise to bring out the pan.) The pan will come out of the window in the front.
5. **Caution**: never move the weighing pan when the pan is fully released (front knob in the 9 o’clock position). This may damage the knife edges in the balance.
6. Place the item to be weighed on the weighing pan. Always handle the filters and calibration weights with tweezers. For a Teflon filter, first discharge it by passing it

several times under a discharging strip. Caution: this is a mildly radioactive source Po^{210}. Handle with care, and have the Safety Office discard old dischargers . Place the discharged filter on the pan so that it will be centered over the weighing pan. Move the pan back into the weighing area by rotating the lower right hand knob slowly clockwise.

7. Pre-weigh the item by turning the knob on the front to the RIGHT (to about 2 o'clock). This partially releases the pan. Adjust the weights to add the most weight possible WITHOUT causing the light meter reading to go ”subzero”.
8. Turn the knob counterclockwise to 9 o'clock to fully release the pan. Then adjust the wheel controlling the μg digits of the weight to get a final reading. (Make sure the edges of the Teflon filter are not touching the pan lifting mechanism.) Record the mass on the Log Sheet for Teflon Filter Weighing.
9. Return the knob to 12 o'clock, then use the knob on the lower right side to take out the pan and remove the item being weighed.
10. Put the empty pan back in, reset the weights to zero, and recheck the zero before continuing. If the zero has drifted off, all items since the last zero check must be reweighed before continuing.

3.5.3 Precautions for weighing teflon filters

1. Teflon filters occasionally are somewhat curled, which can interfere with the position of the pan in the balance. To ensure that this does not result in bad weighings, filters should be weighed repeatedly, rotating the filter 90 degrees each time, until 2 sequential readings are within 15 μg of each other. Occasionally, a filter will not give reproducible results on subsequent weighings and should not be used.
2. Teflon filters tend to accumulate static charge, which is why each filter is passed under a static discharging strip before weighing. In addition to this procedure, it is helpful to place the filter under a discharging strip while it is still in the petri dish bottom for a few minutes before weighing. When weighing one filter, take the next one to be weighed, remove the petri dish lid, and put under a discharging strip.
3. Teflon filters are not cheap, so handle them carefully with tweezers. If you accidentally put a hole in a filter while pre-weighing it, set it aside. It can be used as an analytical blank, but it can't be used to collect an aerosol sample. Also check for tiny existing pinholes in filters directly out of the box. As many as 5-10% of some filter lots may have pre-existing flaws.

3.6 Quality Control

ITEM	MEASUREMENT FREQUENCY	ACCEPTANCE CRITERIA
Temperature	each weighing session	20-23^{o}C (2^{o}C sd)
Relative Humidity	each weighing session	30-40% (5% sd)
Calibration Filters	each weighing session	$\pm$ 15μg
Calibration Weights	Bi-annually	$\pm$ 10μg
Balance calibration	Annually or as needed	not applicable
Temp. & RH verification	Bi-annually	2^{o}C;5%
Duplicate filter weighing	each filter	$\pm$ 15μg
Different day weighing	50% of filters	$\pm$ 15μg
Weighing Lab Blanks	as needed	$\pm$ 15μg
Field Blanks	quarterly	$\pm$ 30μg

3.6.1 Teflon filter weighing lab blanks

Include approximately 5-10% additional teflon filters with each monthly sample set to be used as weighing lab blanks. These filters will be weighed initially with the rest of the samples. However, after their initial weights have been determined, these filters will be kept in petri dishes sealed with teflon tape and will not leave the laboratory facility at Caltech. At the end of each sampling month when sampled filters are returned, the teflon filter weighing lab blanks will be re-weighed when the post-sampling filters final masses are determined.

3.6.2 Teflon filter field blanks

Field blanks are unsampled filters that are used to determine whether contamination is occurring during sample loading/unloading and sample transportation procedures. Weigh enough field blanks during pre-sampling weighing sessions to provide one single-use field blank for each sampler during the upcoming sampling month. Weigh the field blanks with the post-sampling filters. If the weight change in the field blank exceeds 30 μg, contamination during transportation or at the sampling site may be occurring. Take appropriate troubleshooting and corrective action in that event.

3.6.3 Mass error determination

For gravimetric mass determination, the reproducibility of the balance was determined by making a large number ($n > 500$) of replicate weighings over the course of an experiment.

The precision for each weighing was found to be ± 11.2 μg per filter. The initial and final weighing errors are combined to obtain the precision for sample mass determination. Final error bound estimates are obtained by the statistical propagation of the sample, filter blank, and sampling volume precisions.

3.6.4 General precautions

1. Avoid weighing under unusual weather conditions, especially when it is raining or about to rain. Static charging of the balance is especially bad at these times, and interferes with weighing.
2. SIGNS OF STATIC CHARGING: The zero drifts badly from weighing to weighing, up and down without trend. Sometimes, the zero reading won't stabilize – the light meter displays a fuzzy reading. Try using the static discharger gun and shoot it inside the weighing area. Squeezing the trigger releases positive ions; when the trigger is released, negative ions are released such that the static is neutralized. Squeeze and release the trigger slowly, otherwise no ions will be emitted from the crystal inside the gun. If static is not eliminated, turn off the balance and try another day.
3. DRIFTING FILTER WEIGHTS: Sometimes, the filter weights will drift during weighing. Drifting filter weights can be due to inadequate filter equilibration, or to curled filters interfering with the movement of the balance. If the filter has not equilibrated properly, return it to the conditioning chamber and weigh it on a future day.
4. Activities near the room can also interfere with the balance. If workmen are working in the area, vibrations from their activities can disturb the balance readings. Turn off the balance and come back another time.

LOG SHEET for TEFLON FILTER WEIGHTS page 1 of ___

DATE ______________________________ OPERATOR ______________________________________

TIME EQUILIBRATED________________ ROOM TEMP______________ %RH__________________

COMMENTS____

::::::CONTROL FILTERS-SPECIFY ID #:::::::::::

	2c	11c	2a	2b
1ST				
2ND				

CIRCLE: INITIAL or FINAL WEIGHTS LOT NUMBER___________________________

FILTER NO.	SAMPLE ID. NO.	FILTER WEIGHTS			

4 SAMPLE LOADING/UNLOADING IN THE FIELD

The Andersen Instruments RAAS2.5-400 fine particulate chemical speciation sampler is one of two types of instrument that will be used for collecting aerosol samples during the Pilot Study. The fundamental design concept for the RAAS2.5-400 was developed at Caltech by Dr. Glen Cass. The Caltech gray box PM2.5 samplers, prototype for the Andersen instrument, will also be used at two of the PRD monitoring stations.

Each sampler contains 4 filter holders for collecting fine particle samples located inside the cabinet. There are two quartz fiber filters for collecting organic particles. The other two filters are teflon membrane filters used for aerosol mass, ionic species (Cl^-, $SO_4^=$, NO_3^-, NH_4^+), and trace metals determinations. These filter holders are labelled: Quartz 1, Teflon 2, Teflon 3, and Quartz 4. Samplers work using pumps connected to a manifold with critical orifices for flow control. Sample flow rates are calibrated during initial field placement and verified at least once at the start of each sampling month. See Figure 3 for a schematic diagram of the two sampler types.

A notebook and tool box are provided with each sampler. The notebook contains a copy of the field operating procedures and Daily Event Log Sheets (one for each sampling event). Log sheets need to be filled out each time samples are loaded and unloaded. A Reference Flow Sheet is provided with each Log Notebook. The tool box contains the basic needs for filter changing and correcting minor problems with the sampler. Two pairs of tweezers are provided wrapped in annealed aluminum foil. Exercise care to keep the tweezers clean. Spare filter cassettes, o-rings, and a spare filter holder are provided for changing any that become soiled. There is also a cassette loader tool (Andersen only) for opening filter cassettes. In addition, the tool box contains an external flow measuring device and other useful items.

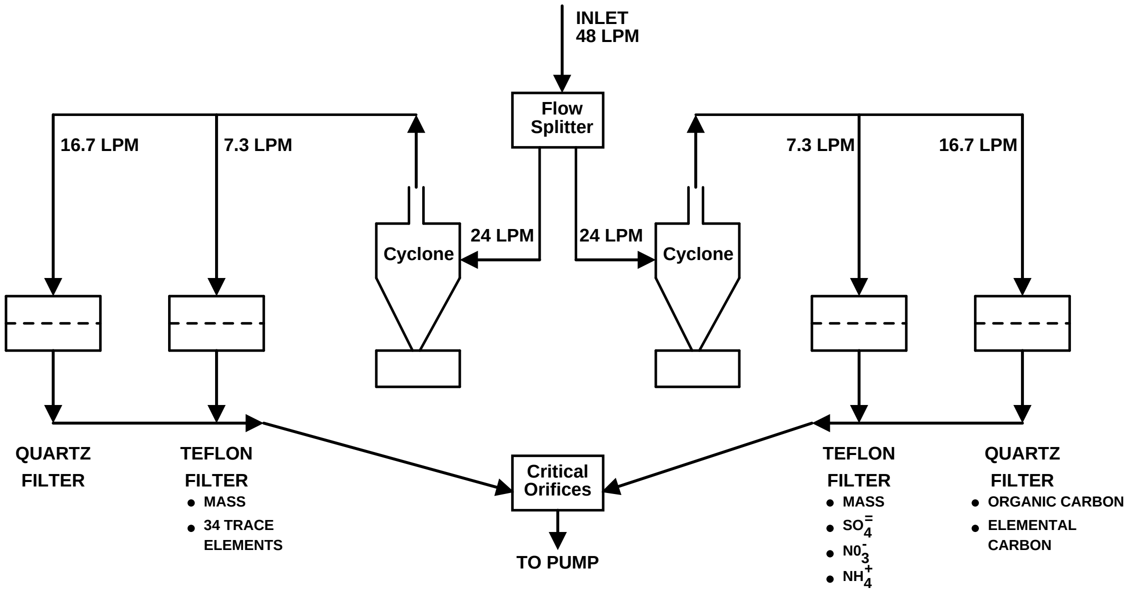
4.1 Filter samples

The filters are pre-packaged in individual petri dishes which are stored in the laboratory before use. Collected samples are transported from the field in a cooler or ice chest with “blue ice” and stored in the freezer immediately upon return to the laboratory to minimize loss of volatile materials.

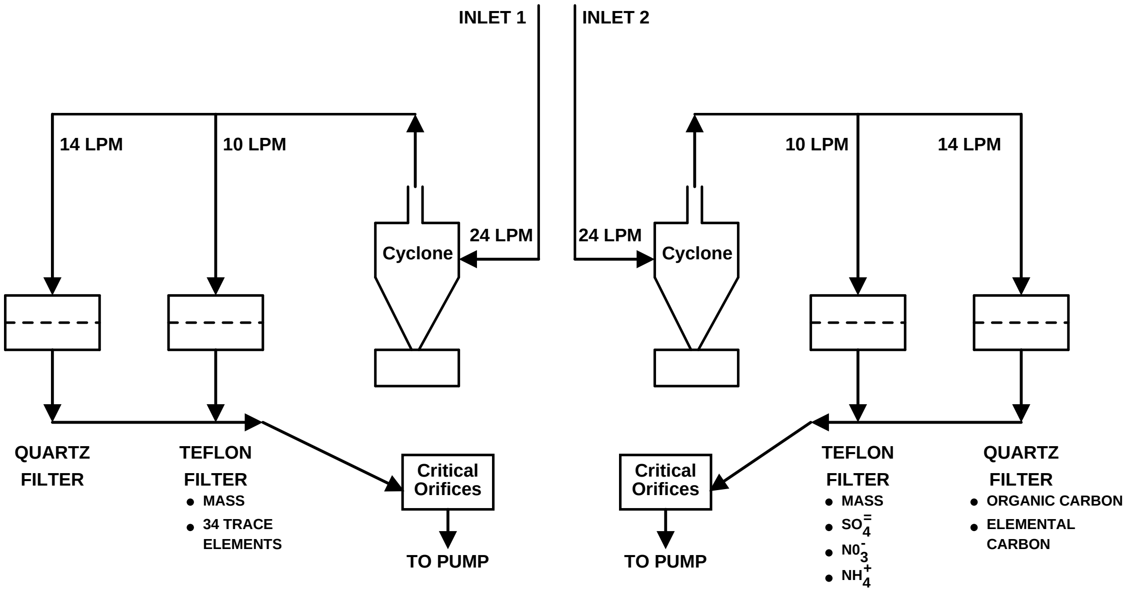
Each sample is given a label in the form:

$$\mathrm{TM1} - \mathrm{Q1} - 021002$$

where TM1 is the site label (TM1, TC2, CW3, SZ4, GZ5, CH6, or ZS7); Q1 is the filter holder label (Q1, T2, T3, or Q4); and 021002 is the sampling period given as year month day (YYMMDD). The corresponding dates for each sampling event are recorded on the log sheets.



(a) Andersen Sampler



(b) Caltech Sampler

Figure 3: Schematic Diagram of (a.) Andersen Sampler and (b.) Caltech Sampler

Site: TM1 **Filter Set ID:** ________________________
Tap Mun

INITIAL Date:___________ **Time:** _________ **Operator:** ________
MIDDLE Date:___________ **Time:** _________ **Operator:** ________
END Date:___________ **Time:** _________ **Operator:** ________

Rotameter ID#: _________

		Initial		Middle		End	
		Initial Flow Rates		Final Flow Rates			
Filter Holder	Filter ID # (FID)	Andersen (L/m)	Rotameter (balls)	Andersen (L/m)	Rotameter (balls)	Avg flow (L/m)	Vol (m3)
Quartz 1		Q1a	black silver		black silver		
Teflon 2		Q2a	black silver		black silver		
Teflon 3		Q3a	black silver		silver black		
Quartz 4		Q4a	black silver		black silver		

Weather Conditions: ____

t end of sampling, record values below:

Sampling Start: Date: ___________ **Time:** ___________
Sampling Stop: Date: ___________ **Time:** ___________
Duration (hours): _____________

	Avg	Min	Max	Comments:
Ambient Temp.				
Barometric Pres.				
Humidity				

Supplies Needed:

Figure 4: Sample Daily Event Log Sheet for Andersen Samplers

Daily Event Log Sheet

Site: ZS7 Filter Set ID: __________________________
Zhongshan

INITIAL Date:____________ Time: __________ Operator: ________

END Date:____________ Time: __________ Operator: ________

Rotameter ID#: __________

Filter Holder	**Filter ID # (FID)**	**Initial Flow Rates Rotameter (balls)**	**Final Flow Rates Rotameter (balls)**
Quartz 1		black ________ silver	black ________ silver
Teflon 2		black ________ silver	black ________ silver
Teflon 3		black ________ silver	black ________ silver
Quartz 4		black ________ silver	black ________ silver

Weather Conditions: _______________________________________

At end of sampling, record values below:

Sampling Start: Date: __________ Time: __________
Sampling Stop: Date: __________ Time: __________
Duration (elapsed time):___________

Supplies Needed: _______________________________________

Comments:

Figure 5: Sample Daily Event Log Sheet for Caltech Samplers

One filter set includes 4 filters in petri dishes:

(Q1)	Quartz fiber filter, in foil lined petri dish
(T2)	Teflon membrane filter
(T3)	Teflon membrane filter
(Q4)	Quartz fiber filter, in foil lined petri dish

When loading filters, the most important thing is to make sure the correct filter is loaded into the correct holder. Each filter has a designation (e.g., Q1) on the petri dish and the filter holders are labelled similarly (e.g., Quartz 1).

Do not use any filter with a hole or other imperfection. If a filter is dropped on the ground while loading, do not use it. In either case, take a spare filter from the set of spares provided and write the sample label on the spare filter petri dish. Cross out the label on the original problem filter and write BAD on it to avoid mistaken use in the future. Bad filters should be kept and returned with the other samples.

Each filter sample also has a unique 5 digit filter ID number (FID) on the petri dish. This number is specific for the individual filter. These ID numbers should be written on the daily event log sheets.

When using a spare filter, make sure it remains with its original petri dish and write the sample label for the site and date of the sample on the spare filter petri dish. Don’t change the FID on the spare filter.

All filters are loaded maintaining the same side up that is currently up in the petri dish. Filters are handled only using tweezers, never touched with hands or gloves. Operators should wear a clean pair of gloves (provided) when loading filter cassettes. A clean piece of aluminum foil should be placed on top of the sampler as a work surface. No smoking is allowed in the sampler area or when loading or unloading samples.

4.2 Loading Filter Samples

The filter holders are located downstream of a cyclone for collecting fine particles. The filter holders are left in the sampler between sampling periods with the empty filter cassettes inside. They should be completely assembled and connected so that the interior remains clean when not in use. The filter holders are connected to critical flow orifices on the manifold at the bottom of the sampler. A reference flow sheet with the calibrated flow rates for each site is provided. Operators will verify flows are in acceptable ranges when loading samples.

Filters should be loaded as close to the sampling start time as possible to minimize contamination. Ideally, samples should be loaded no more than 12 hours in advance of sample start time. Special exceptions will be made for situations when the sampler cannot be accessed within this time frame. Please check with one of the contact help list people for permission to load a sample outside the 12 hour window.

Only authorized operators who have been trained may load/unload samples. The samplers and operators will be audited at least once to verify that proper procedures are being followed. See the Operator Training and Audit Checklists for details.

4.2.1 Field blank

A field blank is a set of samples that are taken to the field and loaded normally and then immediately removed without running the sampler. The field blank should be taken on the last sampling day of each month after the final sample has finished. Field blank designations are: 0210FB - October, 0212FB - December, 0303FB - March, and 0306FB - June.

See the sample Field Blank Log Sheet.

4.3 Andersen Samplers

4.3.1 Filter loading for Andersen samplers

1. Set out a piece of clean annealed aluminum foil on top of the sampler as a work surface. Replace aluminum foil with fresh pieces as needed during the loading process.
2. Get items needed for filter load: tweezers, cassette loader tool, gloves, and 4 petri dishes with filters to be loaded.
3. Open the cabinet door which may be dirty, then put on a pair of clean disposable gloves. Do not touch anything dirty with gloves. If the gloves become dirty, throw them out and put on a new clean pair before continuing.
4. Beginning with the first filter holder, unscrew the black hand ring in the middle of the filter holder and remove the white filter cassette. Place the cassette on the clean foil work surface.
5. Loosely reconnect the filter holder so the interior remains clean while loading the filter into the cassette. Do not set anything down on a dirty surface.
6. Open the cassette using the aluminum cassette loader tool. Handle the cassette only on the edges, and take care not to touch the interior.
7. Using tweezers, take a filter from the correct petri dish and load it into the filter cassette. Only grasp the filter on the edge with tweezers.
8. Using the cassette loader to provide even pressure, carefully push the top of the filter cassette on to close. Inspect the loaded filter and make sure it is centered with no wrinkles. If the filter is wrinkled or uneven, reopen the cassette and press closed again so the filter is smooth and flat. A spare filter may be needed if the filter is unable to lay flat.

Operator Training Checklist

DATE:_______________
TRAINER:__________________
OPERATOR:
____

Operator is aware of:

YES	NO	
		Smoking is not allowed near samplers.
		Sampler interior must be kept neat and clean.
		Fans must be kept unblocked.
		Supplies that are required for operation of the sampler, and how to obtain them if needed.
		That tweezers must be kept clean, wrapped in baked aluminum foil.
		Time frame for loading and unloading filters for a sampling event?
		That the sampled filters must be transported in coolers with blue ice after each event?

Loading/Unloading Filters:

YES	NO	
		Did operator wear clean gloves when touching the filter cassettes?
		Did operator use only tweezers to touch filters?
		Did operator keep aluminum cassette loader clean - placing it on aluminum foil during use and storing in a clean plastic bag?
		Did operator load filters properly into the cassettes?
		Did operator load cassettes properly into the filter holders?
		Did operator avoid placing any portion of the filter holders on a dirty surface during loading/unloading?
		Were filter holders hand-tightened prior to starting a sampling event?
		Did operator place filter into correct petri dish after event was finished?
		Did operator seal samples in petri dishes with Teflon tape?

Running an event and flow checks:

YES	NO	
		Did operator program an event correctly?
		Did operator perform the Rotameter and Andersen flow checks properly?
		Given a problem in operation, does the operator know who to contact for help?

Data acquisition and sample transportation:

YES	NO	
		Did the operator fill out the sample log sheets completely and accurately?
		Can the operator download data using the Datalink device?

Operator Authorization:

YES	NO	
		Did operator pass training program?

Figure 6: Operator Training Checklist

AUDIT CHECKLIST

SITE: _______________
DATE:_______________
AUDITOR:__________________
OPERATOR: _________________

Sampler Appearance

YES	NO	
		Is the outside of the sampler undamaged?
		Is the inside of the sampler neat and clean?
		Are any fans blocked by items left in the sampler?
		Are there any incidents of operators smoking around the sampler?
		Are all necessary supplies in tool box?
		Is the power cord secure and undamaged?

Loading/Unloading Filters:

YES	NO	
		Are operators wearing clean gloves when touching the filter cassettes?
		Are tweezers kept clean, wrapped in clean foil?
		Are operators using only tweezers to touch filters?
		Are operators keeping aluminum cassette loader clean - placing it on aluminum foil during use and storing in a clean plastic bag?
		Are filters being loaded properly into the cassettes?
		Are cassettes being loaded properly into the filter holders?
		Are operators placing any portion of the filter holders on a dirty surface during loading/unloading?
		Are filter holders hand-tightened prior to starting a sampling event?
		Are operators taking care to place filter into correct petri dish after event is finished?
		Are all samples in petri dishes sealed with Teflon tape?

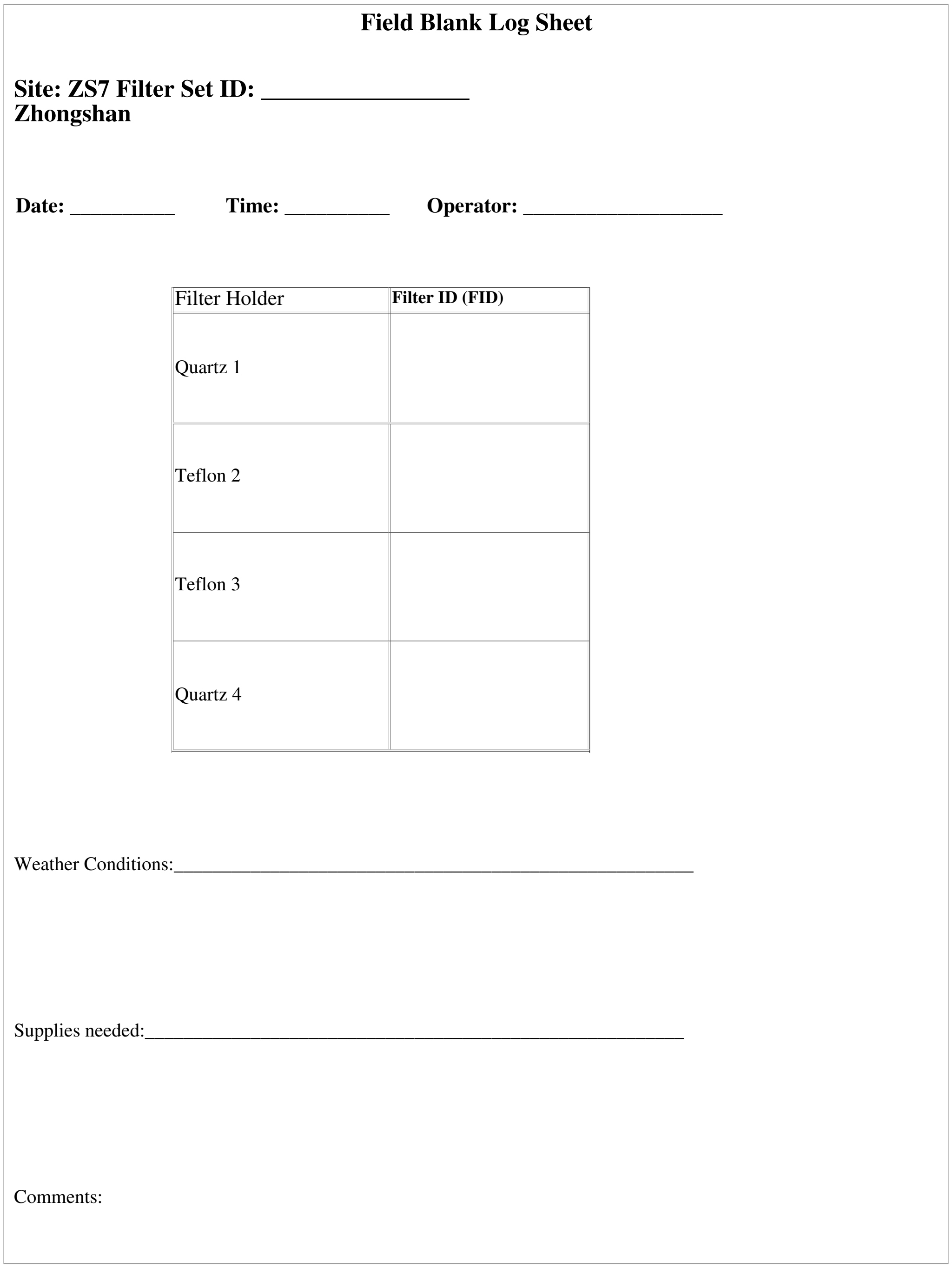
Running an event and flow checks:

YES	NO	
		Are filters loaded and unloaded within the set time-frame?
		Are operators programming an event correctly?
		Are the sampling events being done on the correct dates?
		Are operators doing the initial, middle, and final checks for each sampling event?
		Are operators performing the Rotameter and Andersen flow checks properly?
		Given a problem in operation, do the operators know who to contact for help?

Data acquisition and sample transportation:

YES	NO	
		Are the log sheets being filled out completely and accurately?
		Are operators obtaining data using the Datalink device for each event and bringing it to the appropriate person?
		Are the sampled filters transported in coolers?

Figure 7: Audit Checklist



Field Blank Log Sheet

Site: ZS7 Filter Set ID: ________________
Zhongshan

Date: __________ Time: __________ Operator: ___________________

Filter Holder	**Filter ID (FID)**
Quartz 1	
Teflon 2	
Teflon 3	
Quartz 4	

Weather Conditions:____

Supplies needed:____

Comments:

Figure 8: Field Blank Log Sheet

9. Place the loaded filter cassette back into the correct filter holder and tighten. The filter cassette should be oriented with the stainless steel screen on the bottom and the filter facing up.
10. Repeat steps 3-9 for each of the other 3 filter holders.
11. Leave empty petri dishes in the sampler to collect filters after the run. Throw away used gloves.
12. Program the sampling event and record details such as the FID numbers on the log sheet as described below. Also note if any supplies are running low and in need of replacement.

4.3.2 Leak check procedure

LEAK CHECK PROCEDURE: To be done after filters are loaded into cassettes and filter holders are hand-tightened. After leak check is completed, the operator should do the initial flow rate check.

1. Remove the inlet tube rain shield by sliding it vertically off the inlet.
2. Take the leak check adapter out of the orange tool box (the piece is a small valve attached to a small metal column) and put it on top of the inlet tube, pushing it down into place.
3. Close the valve by rotating the lever so that it is horizontal.
4. On the sampler, select “Maintenance>”, then “QC>”, and then “Leak Check”. Press the “Enter” button for “Leak Check”, the leak check will automatically begin. The counter will display a 45 second zero-flow check and then the pump will automatically start.
5. When the pump is running, the following is on screen:

FLOW 1 = (number)

FLOW 1 =

FLOW 2 =

FLOW 2 =

FLOW 3 =

FLOW 3 =

FLOW 4 =

FLOW 4 =

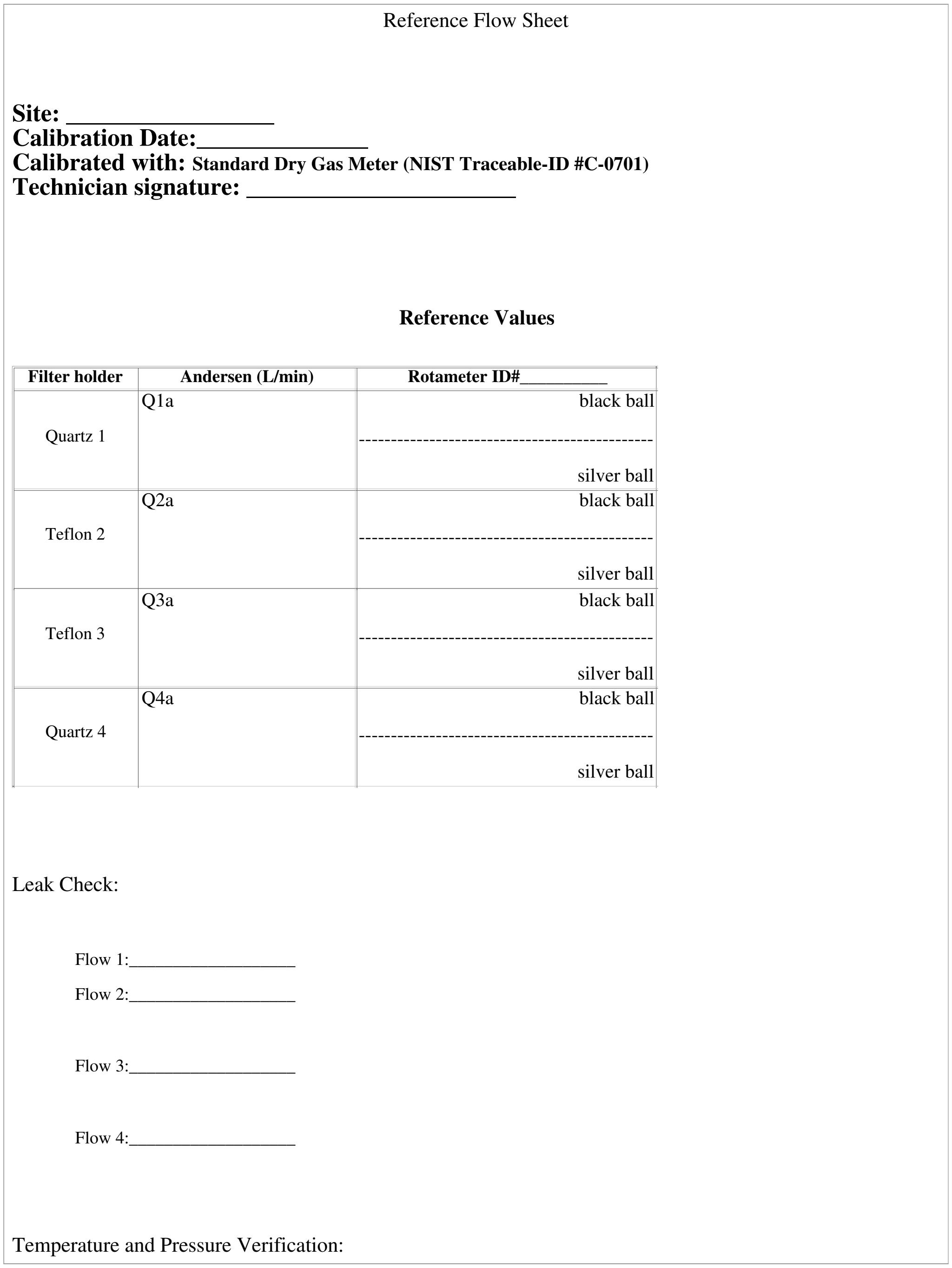
Look at only the top value for each flow (the top value is corrected for system noise while the bottom value is a raw uncorrected number). If the value is at or below 0.15 L/min, the flow channel is working properly. If any of the top values for a single flow channel are above 0.15 L/min, hand-tighten the filter holders. If, after tightening, there is still a problem, stop the pump by pressing “Cancel”, open the filter cassettes and check the filters are loaded correctly. Repeat the leak check. If the problem still exists, get in touch with one of the contact people right away.

6. If the leak check fails, continue the normal sample unless instructed otherwise by the contact people.
7. After completing the leak check, open the leak check valve by slowly rotating the lever. Slide the leak check piece off and put the inlet tube rain shield back on. Continue with the initial flow rate check.

4.3.3 Initial flow rate check

Check the flow rates given by the electronic flow sensors in the Andersen sampler, and also check flow rates using the external rotameter provided. Verify the flows are in the correct ranges from the Reference Flow Sheet.

1. Press the Cancel button to get to the >>>>Main Menu<<<<.
2. Use arrow key to select “Maintenance>” and press enter.
3. Enter maintenance, use arrow key to select “Yes” and press enter.
4. Use arrow key to select “Diagnostics>” and press enter.
5. Use arrow key to select “Flow Valves” and press enter.
6. There are three columns of numbers. The last column has the flow rates. Wait approximately 15 seconds for the flow rates to stabilize. Record the initial values for Quartz 1 = Q1a, Teflon 2 = Q2a, Teflon 3 = Q3a, and Quartz 4 = Q4a on the event log sheet under Initial Flow Rates, Andersen (L/m).
7. An adapter is provided to measure flows using the external flowmeter/rotameter. To measure the flow with the external rotameter, disconnect each filter holder one-at-a-time by unscrewing the black plastic fitting located at the bottom of each filter holder. Attach the rotameter to the adapter and attach the adapter to the black plastic fitting. The flow through the orifice will be measured in this manner. Hold the rotameter vertically while reading the flow. There are two balls inside the glass tube on the rotameter (black and silver). Read the number nearest to the center of each ball and record the readings under Initial Flow Rates, Rotameter (balls). Also note the Rotameter ID# on the log sheet.
8. Stop pump running by pressing cancel.



Reference Flow Sheet

Site: _________________
Calibration Date:______________
Calibrated with: Standard Dry Gas Meter (NIST Traceable-ID #C-0701)
Technician signature: _______________________

Reference Values

Filter holder	Andersen (L/min)	Rotameter ID#__________
Quartz 1	Q1a	black ball -- silver ball
Teflon 2	Q2a	black ball -- silver ball
Teflon 3	Q3a	black ball -- silver ball
Quartz 4	Q4a	black ball -- silver ball

Leak Check:

Flow 1:___________________
Flow 2:___________________

Flow 3:___________________

Flow 4:___________________

Temperature and Pressure Verification:

Figure 9: Reference Flow Sheet for Andersen Samplers

9. Compare the measured flow rates with the reference flow sheet. The Andersen values should be within ± 10% of the reference values. The rotameter values should be within ± 10% of the reference values.
10. If the the instrument is operating within specified ranges, close the cabinet door and leave the instrument to run overnight. If there are problems, refer to the trouble shooting section, or contact one of the people from the contact help list.

4.3.4 Programming an event to run

1. Go to the >>>>Main Menu<<<< on the programming screen. Use the Cancel key to return to the previous menu until >>>>Main Menu<<<< is reached.
2. Use the arrow key “V” to select “Events>” and press enter.
3. Use the arrow key to select “Add Event>” and press enter.
4. Use the arrow key to select “Manual Event” and press enter.
5. Event Start Date: change the date that appears automatically to be the current date that sampler should start on. Date is given in Month - Day - Year (MMDDYY) format. Press enter.
6. Event Start Time: enter the time sampling should begin (for sampling starting at 12:00am enter 0000). Press enter.
7. Event Duration 24:00 24 hours, press enter.
8. Enter Filter Set ID (SID). This will be the site number followed by the date as given on the top of the event log sheet. (e.g., 1-021002).
9. Enter Filter ID (FID1): 5-digit number from petri dish
10. Enter Filter ID (FID2): 5-digit number from petri dish
11. Enter Filter ID (FID3): 5-digit number from petri dish
12. Enter Filter ID (FID4): 5-digit number from petri dish
13. Record date, time of loading, and sign name as initial operator on the log sheet.

4.3.5 Middle flow check

Visit the site at least once during the 24 hours the sample is running to verify the sampler is operating and perform middle flow checks.

1. Press the Cancel button to get to the >>>>Main Menu<<<<.

2. Use arrow key to select “Events>” and press enter.
3. Use arrow key to select “View Event>” and press enter.
4. Select the current event and press enter.
5. You will see a screen with the header “Status: Executing”
6. Use the arrow key to page through the status screens and verify the settings are correct.
7. Record the current values for Flow 1, Flow 2, Flow 3, and Flow 4 on the event log sheet under Initial Flow Rates, Andersen (L/m).
8. Use the adapter provided to measure flows using the external flowmeter/rotameter. To measure the flow with the external rotameter, disconnect each filter holder one-at-a-time by unscrewing the black fitting below the filter holder. Attach the flowmeter adapter to the top of the black fitting and hold the rotameter vertically while reading the flow. There are two balls inside the glass tube on the rotameter (black and silver). Read the number nearest to the center of each ball and record the readings under Middle Flow Rates, Rotameter (balls).
9. If the instrument is operating correctly, close the cabinet door and leave the instrument to complete the run. If there are problems, refer to the trouble shooting section, or contact one of the people from the contact help list for further instructions.
10. Record date, time of middle flow check and sign name as middle operator. Also, note down what weather conditions were like on the day the samplers were run (i.e., windy, rain, etc.)

4.3.6 Unloading filter samples from Andersen samplers

Filter samples should be unloaded as soon as possible after the end of sampling. Samples should remain in the field for no more than 16 hours after the sample end time. Special exceptions will be made for situations when the sites cannot be accessed on the day after operation. Contact one of the people on the contact help list for permission to unload a sample outside the 16 hour window.

After the sample run has ended, record average values on the log sheet as follows:

1. Press the Cancel button to get to the >>>>Main Menu<<<<.
2. Use arrow key to select “Events>” and press enter.
3. Use arrow key to select “View Event>” and press enter.
4. Choose the desired event and press enter.
5. You will see a screen with the header “Status: Completed”

6. Use the arrow key to page through the status screens and record information onto the log sheet. Use the Actual Information for START - Date - Time and STOP - Date - Time.
7. Record the “Duration” of the run (should be 24 hours unless there was a problem).
8. Use the arrow key to page through status screens and record the Ambient Temp: Avg, Min and Max values.
9. Record the Barometric Pressure: Avg, Min and Max values.
10. Record the Humidity: Avg, Min and Max values.
11. For each flow record the Avg. Flow and volume of air sampled (Vol, m3) on the log sheet.
12. Record any problems that occurred while sampling in the comments section. Continue comments on the back of the log sheet or on addition pages if necessary.
13. Record date, time of unloading and sign name as End Operator on the log sheet.

4.3.7 Steps for filter unloading

1. Set out a piece of clean aluminum foil on top of the sampler as a work surface.
2. Get items needed for filter unloading: tweezers, cassette loader tool, and 4 empty petri dishes.
3. Open the cabinet door, then put on a pair of clean disposable gloves. Do not touch anything dirty with gloves. If the gloves become dirty, throw them out and put on a new clean pair before continuing.
4. Beginning with the first filter holder, unscrew the black hand ring in the middle of the filter holder and remove the white filter cassette. Place the cassette on the clean foil work surface.
5. Loosely reconnect the filter holder so the interior remains clean while loading the filter into the cassette. Do not set anything down on a dirty surface.
6. Open the cassette using the aluminum cassette loader tool. Handle the cassette only on the edges, and take care not to touch the interior.
7. Using tweezers, carefully remove the sampled filter from the cassette and place it into the correct petri dish. Touch the filter only with tweezers and only near the edges of the filter.
8. Replace the lid on the petri dish and set sample aside where it will not be disturbed.

9. Close the cassette and place the empty filter cassette back into the filter holder and tighten.
10. Repeat steps 4-9 to unload each of the other 3 filter holders.
11. Wrap Teflon tape around the edge of each petri dish, pulling it tight to seal. Make sure to hold the dish upright while doing this.
12. Put samples in cooler with “blue ice”.
13. Download data using the DataLink attachment (see below).
14. Remove DataLink and turn power to the instrument “OFF” between sampling events.
15. Bring samples, Datalink, and log sheets to the appropriate local office after each sampling event. See sample handling/shipping.

4.3.8 Downloading data with DataLink

1. Plug in the DataLink to the RS-232 port inside the instrument. The green light will illuminate.
2. Press the Cancel button to get to the >>>>Main Menu<<<<.
3. Use arrow key to select “Data Transfer>” and press enter.
4. Use arrow key to select “Transmit All” and press enter. The screen will read “Data Log Transmission in Progress” and the green light on the DataLink will flash.
5. This process will take a few minutes. Wait for the transfer to finish and remove the DataLink from the RS-232 port.

4.4 Caltech Gray Box Samplers

Caltech Gray Box samplers have two pumps connected to manifolds with critical orifices for flow control. The pumps have been wired to run on 220V power, however, the fans and elapsed timers require 110V power, and a 240-110 step-down transformer has been provided inside each sampler.

4.4.1 Filter loading for Caltech samplers

1. Set out a piece of clean aluminum foil on top of the sampler as a work surface. Replace aluminum foil with fresh pieces as needed during the loading process.
2. Get items needed for filter load: tweezers, flow meter, gloves, and 4 petri dishes with filters to be loaded.

3. Open the cabinet door which may be dirty, then put on a pair of clean disposable gloves. Do not touch anything dirty with gloves. If the gloves become dirty, throw them out and put on a new clean pair before continuing.

4. Begin with the first filter holder. Disconnect the swagelock fitting at the top of the filter holder to make it easier to handle. Leave the bottom connected to the accordion style Teflon tubing.

5. Unscrew the center ring on the holder which can be removed, then lift off the top cone-shaped part of the filter holder. Be careful not to tip the bottom of the filter holder over while the top is off because the two metal support screens inside are loose and may fall out. If the screens do fall out, replace them with clean spares and note that the smaller diameter screen needs to be oriented with its more curved side down, otherwise spots will appear on the filter where this screen touches the support screen on top and causes uneven air flow through the filter. Do not set anything down on a dirty surface.

6. Using tweezers, take a filter from the correct petri dish and place it centered on top of the stainless steel screen. Quartz fiber filters have a stainless steel gasket that is placed on top of the filter. Teflon filters do not use these gaskets. The gasket should be handled only using tweezers.

7. Next, the cone shaped part of the filter holder is placed on top of the loaded filter and the center ring is screwed tightly in place.

8. Loosely reconnect the top swagelock fitting. It will be tightened after all of the filters are loaded and flow rates have been measured.

9. Repeat steps 3-8 for each of the other 3 filter holders.

10. Leave empty petri dishes in the sampler to collect filters after the run.

11. Set the elapsed time meter to read 0.

12. Program the sampling event and record details like the FID numbers and flow rates on the log sheet as described below.

13. Record date, time of loading, and sign name as initial operator on the log sheet.

4.4.2 Flow measurement and programming a sampling event:

1. Before sample start time, turn the pump on briefly for flow measurements. The pump can be turned on by switching the Intermatic timer from “AUTO” to “MANUAL” mode (upper right corner). Then press the “ON/OFF” button to turn pump on and off.

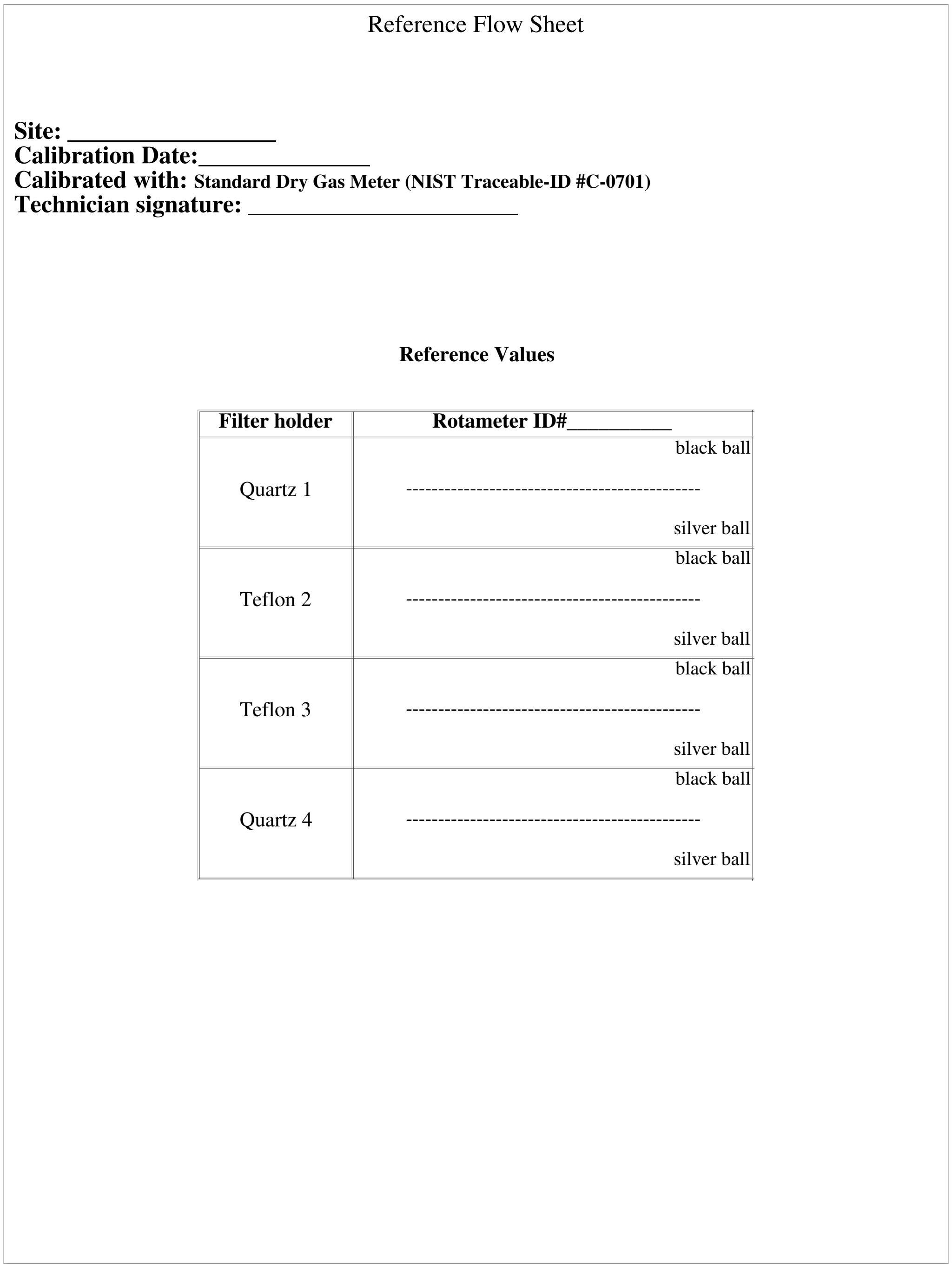
2. The flows are measured at the top of the filter holders by attaching the rotameter to the swagelock fitting. Measure the filter holder flows one at a time and reconnect the swagelock fitting to the cyclone manifold after the flow is measured.

3. Hold the rotameter vertically when taking a flow reading. There are two balls inside the glass tube on the rotameter (black and silver). Read the number nearest to the center of each ball and record the readings under Initial Flow Rates, Rotameter (balls) on the log sheet. Record both readings unless the top, black ball is off scale in which case the silver ball alone should be used. Also note the Rotameter ID# on the log sheet.
4. Compare the measured flow rates with the reference flow sheet. The rotameter values should be within ± 10% of the reference values. If flows are less than they should be, all fittings should be examined for leaks. It is also possible for critical flow orifices to clog with particles, and they may need to be cleaned or replaced.
5. Make sure all filter holder fittings are tightly connected to the cyclone. The swagelock fittings should seal when finger tight.
6. Program the timer to start the sample event at 12:00am. Slide the switch in the upper right corner to "PROGRAM" mode. The switch next to it should be set to "OUTPUT". Press the HOUR, MIN, and DAY buttons to program the first set point time desired (12:00am) and day of week. Day 1 is Monday, day 2 is Tuesday, etc. Press the ON/OFF button to select ON for the current day. Press ENTER and program the second set point to turn the sampler OFF at 12:00am on the following day. Slide the upper right corner switch to "AUTO" mode for program to run. (Additional detailed timer instructions are provided.)
7. If the instrument is operating correctly, close the cabinet door and leave the instrument to run overnight. If there are problems, refer to the trouble shooting section, or contact one of the people from the help list.

4.4.3 Unloading filter samples from Caltech samplers

Filter samples should be unloaded as soon as possible after the end of sampling. Samples should remain in the field for no more than 16 hours after the sample end time. Special exceptions will be made for situations when the sites cannot be accessed on the day after operation. Contact one of the people on the contact help list for permission to unload a sample outside the 16 hour window.

1. After sampling has ended, check the final flow rates before unloading samples.
2. Check flow rates using the external rotameter provided. The details for final flow rate checks are the same as in steps 1-3 above. Record black and silver ball readings on the log sheet under Final Flow Rates (balls).
3. Record any problems that occurred while sampling in the comments section. Continue comments on the back of the log sheet or on additional pages if necessary. Also, note what weather conditions were like on the day the samplers were run (i.e., windy, rain, etc.)
4. Record the elapsed time number on the log sheet under Duration.



Reference Flow Sheet

Site: _________________
Calibration Date:______________
Calibrated with: **Standard Dry Gas Meter (NIST Traceable-ID #C-0701)**
Technician signature: ______________________

Reference Values

Filter holder	Rotameter ID#_________
Quartz 1	black ball -- silver ball
Teflon 2	black ball -- silver ball
Teflon 3	black ball -- silver ball
Quartz 4	black ball -- silver ball

Figure 10: Reference Flow Sheet for Caltech Samplers

4.4.4 Steps for filter unloading

1. Set out a piece of clean aluminum foil on top of the sampler as a work surface.
2. Get items needed for filter unloading: tweezers, gloves, and 4 empty petri dishes.
3. Open the cabinet door, then put on a pair of clean disposable gloves. Do not touch anything dirty with gloves. If the gloves become dirty, throw them out and put on a new clean pair before continuing.
4. Beginning with the first filter holder. Disconnect the swagelock fitting at the top of the filter holder to make it easier to handle. Leave the bottom connected to the accordion style Teflon tubing.
5. Unscrew the center ring on the holder which can be removed, then lift off the top cone-shaped part of the filter holder. Be careful not to tip the bottom of the filter holder over while the top is off because the sample inside may fall out. Do not set anything down on a dirty surface, but use the foil work surface if necessary.
6. Using tweezers, remove a filter from the filter holder and place it in the correct petri dish. Touch the filter only with tweezers and only near the edges of the filter.
7. Reassemble the empty filter holder and reconnect it so that the interior will remain clean between sampling events.
8. Repeat steps 4-7 to unload each of the other 3 filter holders.
9. Wrap Teflon tape around the edge of each petri dish, pulling it tight to seal. Make sure to hold the dish upright while doing this.
10. Transport samples to the local office in a cooler with “blue ice” and store frozen until time for sample shipment at the end of the month.

4.5 Trouble shooting

During the course of the PRD project, operators may encounter a variety of problems. Some possible problems that may occur and recommendations for solving them are below.

4.5.1 Spare parts

If there are problems with either the filter cassettes or the filter holders, there are spares in the orange toolbox. There are five spare filter cassettes (Andersen samplers), a spare filter holder, and spare filter internal screens (Caltech samplers). When loading, visually inspect the filter cassettes to make sure the metal screens are not bent or misshapen - replace with a spare if there is even any minor damage.

4.5.2 Problems that may occur during sample loading/initial check

1. Sampler will not turn on (Andersen)
   (a) Operator should first check to make sure the sampler is plugged in and that there is no damage to the electrical cord. If the sampler is plugged in and the problem remains, the operator should check whether the problem is with the sampler or with the power source - either by using the pump/electronics by-pass cord to plug the pump-box into the outlet or by checking the outlet with another electrical device.
   (b) If the pump/electronics by-pass cord is able to turn on the pump, this means there is a problem with the electronics portion of the sampler and the sampler must be run in manual mode (see MANUAL MODE section) and people on the Contact Help List should be notified.
   (c) If there is simply no power to the site at all, operator should get in touch with whoever is in charge of power to the site. If power is not restored until after normal start time, samples should be loaded for a 24-hour sample as soon as possible after power is regained (a sample begun late does not have to start at midnight but should run for a full 24 hour period).
2. Timer not working (Caltech)
   - For Caltech samplers: If there is a problem with the timer in the sampler, samples can be taken in manual operation mode. For manual operation, disconnect the timer and plug the power strip directly into the wall outlet. In this mode, the sampler can be turned on and off by plugging/unplugging the power to the pump.
3. The electronics are malfunctioning
   (a) If the operator arrives at the site and finds the electronics have failed so that the operator cannot program an event or run initial flow checks, operator should run the sampler in MANUAL MODE or use the ”flow valves” command (used for initial flow checks) to manually turn the pump on for sampling.
   (b) For all sampling done in manual mode, operators may start the 24-hour sample during their normal loading time, instead of the normal midnight starting time. Unloading may be done 24 hours later, during what would have been the ”middle check” period.
4. MANUAL MODE
   (a) Operator should first check to see if it is possible to use the ”flow valves” command to start the pump. If this is possible, use ”flow valves” instead of the pump/electronics by-pass cord and proceed to step (c). Manual mode for Caltech samplers should begin with step (c).

- (b) Find the pump/electronics by-pass cord - either located within the sampler or in the orange toolbox. Unplug the interior power cord and plug the pump/electronics by-pass cord into the interior outlet.
- (c) Load all filters, following normal filter-loading procedures.
- (d) Once filters are loaded into the filter holders, begin sampling by plugging in the pump/electronics by-pass cord (or press ”flow valves” to begin Andersen pump if possible). For Caltech samplers plug in the power strip by-passing the timer. Note the time on the Daily Event Log Sheet.
- (e) Check flow rates using a rotameter, following the normal rotameter flow check process.
- (f) 24-hours later, return to the site.
- (g) Check flow rates using the rotameter.
- (h) Note the time and unplug the pump/electronics by-pass cord (or hit ”cancel” to exit ”flow valves” to stop the pump), ending the 24-hour sampling run.
- (i) Unload the filters as normal.
- (j) Take note of problems on the Daily Event Log Sheet and notify Contact Help List people.

5. Initial flow rates are too high/too low.

   - (a) Case 1: The rotameter is reading flow rates that are in normal range, the Andersen readings are too high or too low: Operator should run sampling as normal and should notify Contact Help List people as soon as possible.
   - (b) Case 2: The rotameter is reading flow rates that are too high/too low, the Andersen readings are in normal range: Operator should inspect rotameter to make sure the exhaust port is not blocked. If the rotameter has a valve, the operator should make sure the valve is open. If there is still a problem, operator should run the sampler as normal and notify Contact Help List people as soon as possible.
   - (c) Case 3: Both the Andersen and rotameter flow checks read flows that are too high/too low: Operator should check to make sure the plastic accordion tubes are not pinched or blocked by an object, that the filters were loaded correctly, and that the filter holders were correctly closed and tightened. If the problem remains, call someone from the Contact Help List immediately for instructions. If operator is unable to get in touch with anyone from the Contact Help List, operator should unload all filters and reseal petri dishes with Teflon tape. Filters may be reused for a make-up sample.

6. The site is inaccessible due to dangerous conditions.

   - Operator should not go to site and should notify Contact Help List people.

7. Filters are damaged during loading.

    - If a filter is damaged by holes or tears which would prevent a proper seal in the filter cassettes, dirty from being dropped, or has become wet, a spare should be used in its place. When using a spare, be sure to put the FID of the spare filter on the log sheet in the place of the original FID. On the spare filter petri dish, change the label to match the label of the filter that is being replaced (for example, change from ”spare quartz filter” to ”TC2-Q1-021002”). On the petri dish of the damaged filter, write ”BAD” and keep the petri dish with the rest of the petri dishes for this event. If the operator has run out of spares, the operator should use a filter from a later event date. The operator should first use the field blanks for that month, followed by the filters for the latest date. If the operator has run out of spares and needs to use filters from later planned events, notify Lynn Salmon immediately so that replacements can be prepared and sent.

4.5.3 Problems that may occur during sample middle check

1. Sampler is not running, electronics appear to be fine.

    (a) Operator should first check for incorrect programming by going to ”View Event” and checking the date that was programmed. If there is an error in programming, operator should program a new event to begin a 24-hour run, starting immediately. Operator should delete the old event that had been incorrectly programmed by going to ”Events”, ”Delete Event”, selecting the event, and pressing ”Enter”. After the replacement event has begun, operator should complete the middle flow checks and return 24 hours later to unload the sample as normal. Operator should take note of problem in log sheet and notify contact people.

    (b) If there is no error in programming, operator should visually inspect the filters. If the filters are clean and blank - operator should switch to run the sampler in manual mode, (see MANUAL MODE). If filters are dirty - operator should unload filters following normal unloading and Datalink procedures, note problem in log sheet, and notify contact people. If possible, include the Datalink file with the notification email.

2. Operator finds electronics reading an error message or screen is blank.

    (a) If screen is blank, operator should rotate ”contrast” knob to make sure screen is at the proper contrast level. (knob is located directly to the right of the screen)

    (b) If error message/blank screen remains, operator should visually inspect the filters. If the filters are clean and blank - operator should switch to run the sampler in manual mode, (see MANUAL MODE). If filters are dirty - operator should unload filters following normal unloading procedures, note problem in log sheet, and notify contact people.

3. Flow rates are too high/too low

    - Operator should continue sampling as normal, note problem on Daily Event Log Sheet.

4. Power is out at the site

    - Operator should make note of the problem on Daily Event Log Sheet and should return the next day to unload the samples. If possible, operator should contact the person in charge of power supply to investigate the problem. Operator should notify contact people of the power problem as soon as possible.

4.5.4 Problems that may occur during sample unloading

1. Sampler has no power.

    (a) Operator should first unload all samples, following normal unloading procedures.

    (b) Operator should next do a brief check of the possible source of power failure, checking to see if the sampler is unplugged, if there is damage to the power cord, if there is information about power failure to the entire building. If possible, operator should use the pump/electronics by-pass cord to plug in the pump directly, checking to see if the problem is solely in the electronics. After doing a brief check, operator should notify contact people for troubleshooting help.

    (c) Operator should plan on returning at a later point to download data with the Datalink once power is resumed.

2. Datalink is malfunctioning

    (a) Unload samples following normal unloading procedures.

    (b) If Datalink is showing ”memory full” signal, the Datalink needs to be taken to a computer with the winDatalink program to have its memory cleared.

    (c) If Datalink is showing fatal/non-fatal errors, or if the data transfer function is not working, notify contact people for help.

3. Filters are damaged during unloading.

    - If damage occurs to filters during unloading, operator should unload as normal and describe damage on the Daily Event Log Sheet. Also, the operator should notify the contact people, describing the damage that occurred.

4.5.5 Reset Calibration (Andersen sampler)

If one of the Andersen samplers loses the stored calibration for any reason, it can be reset as follows.
To reset calibration:

1. Turn on sampler
2. Go to “MAINTENANCE>”, choose “Yes” to enter.
3. Go to “Archive values>”
4. Go to “Restore Cal Values” and hit the “Enter” button.
5. Exit by hitting the “Cancel” button until you get to the main menu.

To check to see if it works:

1. Go to “MAINTENANCE>”, choose “Yes” to enter.
2. Go to “Calibrate>”.
3. Go to “Flow 1>”
4. Press the “Cancel” button to proceed.
5. Select “Dry Gas Meter” and hit the “Enter” button.
6. Hit the “Enter” button to accept the Reference DGM Coefficient
7. You will now be at the calibration screen for Flow 1. Toward the lower-middle of the screen you will see the following:

```
               GAIN           OFFSET
OLD:           XXX (number)     XXX
NEW:           XXX              XXX
```

8. Write down the values for the gain and offset for Flow 1.
9. Repeat 1-8 for Flow 2, 3, 4.

If there are any problems that occur and are not mentioned here, please notify the people on the Contact Help List.

4.5.6 Make-up sampling event

If problems prevented a sample to be obtained during the normal course of sampling, an additional “make-up” sample may be taken. For example, if a power failure or programming error caused an instrument to not sample, a “make-up” sample may be scheduled for the next day at that site only. If more serious problems, like a typhoon, affect multiple sites, a “make-up” sample may be scheduled for all sites later in the month. Contact one of the people on the contact help list to determine if a “make-up” sample is required and when to schedule it.

5 CONTACT HELP LIST

The Pilot Study is being conducted by Georgia Institute of Technology, Hong Kong University of Science & Technology, Peking University, and the California Institute of Technology.

People to contact concerning the project are listed below.

5.1 For Field Operation or Sample Questions Contact:

Lynn Salmon, Research Engineer
Environmental Quality Laboratory
California Institute of Technology
1200 E. California Blvd. (mail code 138-78)
Pasadena, CA 91125
email: lynn@thesalmons.org or salmon@caltech.edu
Tel: 1(626)395-6420 fax: 1(626)395-2940

Gayle Willis, Graduate Student
Georgia Tech student spending fall semester at HKUST
email: gwillis.ce02@gtalumni.org
Tel: (852)2719-1352

HKUST Ph.D. students:
Wan Chun Hong, Eric
email: waneric@ust.hk
Tel: 97846708

Wu Wai Shing
email: waishing@ust.hk
Tel: 91618958

Yang Qiang, Peking Univ. student
email:qiangyang@ccermail.net
Tel: (86) 136 6117-6858

Zeng Limin, Research Engineer
email: lmzeng@ces.pku.edu.cn

5.2 Monitoring Stations

There are seven air monitoring stations in Hong Kong and the Pearl River Delta region of China. See Figure 1.

- TM1 - Tap Mun - located on roof of police station on Tap Mun Island, Hong Kong. Lat: N 22^{o} 28.277’ Lon: E 114^{o} 21.642
- TC2 - Tung Chung - located on roof of shopping mall near Tung Chung MTR station, Hong Kong. Lat: N 22^{o} 17.334’ Lon: E 113^{o} 56.620
- CW3 - Central and Western - located on roof of Crime Wing Hong Kong Island Regional Headquarters, High Street. Lat: N 22^{o} 17.122’ Lon: E 114^{o} 08.713
- SZ4 - Shenzhen - located on roof of Peking University Shenzhen campus. Lat: N 22^{o} 32.183’ Lon: E 113^{o} 56.340
- GZ5 - Guangzhou - located on roof of Guangzhou EPB building. Lat: N 23^{o} 07.969’ Lon: E 113^{o} 15.585
- CH6 - Conghua - located on roof of Conghua Jing Xiu Hotel. Lat: N 23^{o} 38.530’ Lon: E 113^{o} 38.345
- ZS7 - Zhongshan - located on roof of building in amusement park. Lat: N 22^{o} 30.660’ Lon: E 113^{o} 24.429

5.3 Principal Investigators:

Dr. Mike Bergin, Assistant Professor
School of Civil and Environmental Engineering and
School of Earth and Atmospheric Sciences
Georgia Institute of Technology
200 Bobby Dodd Way
Atlanta, GA, 30332-0512
email: mike.bergin@ce.gatech.edu
Tel: 404-894-9723 fax: 404-894-8266

Dr. Jian Yu, Assistant Professor
Department of Chemistry
Hong Kong University of Science & Technology
Clear Water Bay, Kowloon, Hong Kong
email: chjianyu@ust.hk
Tel: 852-2358-7389, fax: 852-2358-1594

Professor Zhang Yuanhang, Director
Center for Environmental Sciences
Peking University
Beijing 100871, China
email: yhzhang@ces.pku.edu.cn
Tel: 86-10-62756592 fax: 86-10-62751927

6 SAMPLE TRANSPORTATION AND SHIPPING

As previously discussed, all samples will be immediately put into coolers with blue ice each time samples are collected in the field. In Hong Kong, the coolers will be delivered to the HKEPD office in Wan Chai on the same day samples were collected. Operators will also bring the DataLink and log sheets to the HKEPD office. The DataLink information will be downloaded into a HKEPD computer and emailed to lynn@thesalmons.org and to gwillis.ce02@gtalumni.org in a timely manner to allow review before the next sampling event.

The HKEPD office will fax (or email scans) daily event log sheets to Lynn Salmon at 1(626)395-2940 after each sampling event. The original log sheet will be stored at HKEPD until the end of the month and forwarded to Jian Yu with the samples. Copies of the log sheets will be kept in the field notebooks.

At HKEPD the samples will be stored under frozen (-4^{o}C or lower) conditions. At the end of each month, Dr. Jian Yu will collect the filters from the HKEPD, remove the filters that will be analyzed at HKUST, and ship the remaining filters to Lynn Salmon at Caltech within 10 days.

In the PRD, the samples will be delivered to the pertinent local office and will be placed in a freezer. Samples will be transported from the field to the local office in a cooler on the same day of sample collection. Operators will also bring the daily log sheets to the local office. Daily log sheets should be faxed to Lynn Salmon at 1(626)395-2940 after each sampling event. The original log sheet will be stored at the office until the end of the month and forwarded to Jian Yu with the samples. Copies of the log sheets will be kept in the field notebooks.

At the end of each month, samples from each PRD site will be delivered (frozen) to the Guangzhou sampling site. The samples will be collected by a student from Prof. Jian Yu's group at HKUST within one week of being received in Guangzhou. Dr. Yu will sort and ship the remaining samples to Caltech with the Hong Kong samples. Shipments will be made in insulated mailing boxes with blue ice packets. Fedex, or other fast delivery will be used.

7 SAMPLING SCHEDULE

7.1 Sample Dates

Samples will be collected during four seasons beginning in October, 2002. Subsequent sampling will occur during December, 2002, March, 2003 and June, 2003. During each month there will be five 24-hour samples and one set of field blanks collected. Sampling dates will be (see calendar):

October, 2002 Sampling Dates: 2, 8, 14, 20, 26

December, 2002 Sampling Dates: 1, 7, 13, 19, 25

March, 2003 Sampling Dates: 1, 7, 13, 19, 25

June, 2003 Sampling Dates: 5, 11, 17, 23, 29

Samples will be loaded on the day before sampling. Timers will be used to start the samplers and turn them off after 24 hours. After samples finish, operators will unload samples and place them immediately in a cooler with blue ice.

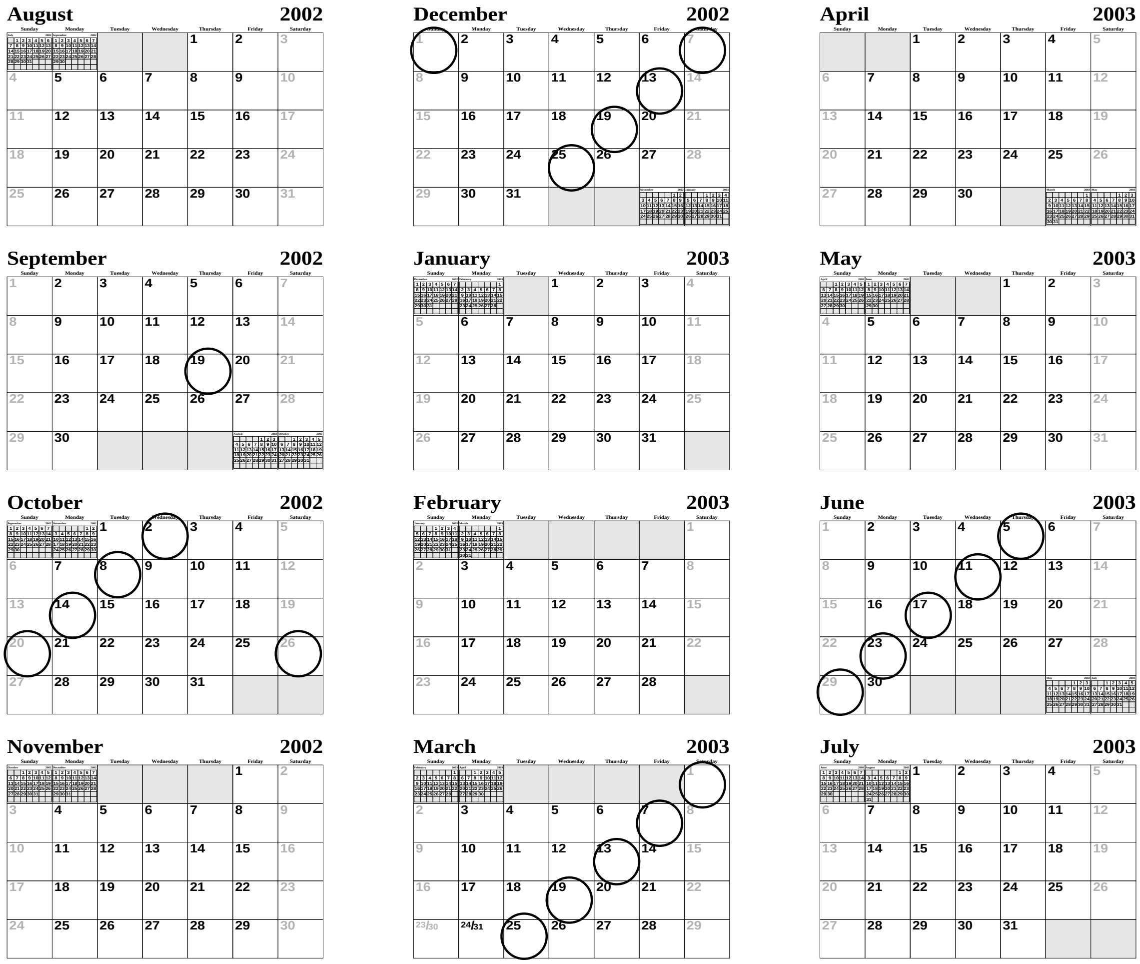
Special arrangements will be made for situations when the sites cannot be accessed on the day before or after operation. Please check with one of the contact help list people for permission to load or unload a sample outside the normal time frame.

7.2 Calibrating Samplers

Sampler flow rates will be calibrated using a dry gas meter prior to the start of sampling each month. Sampler calibrations will be verified by operators during each sampling event. It should only be necessary to recalibrate the instruments if problems arise and the flows deviate from the reference flow sheet. If there are any questions about the calibration, operators should contact one of the people on the contact help list and arrangements for sampler calibration/verification will be made.

The following apparatus and materials are used to perform sampler calibration.

ITEM	SUPPLIER	MODEL or CATALOG NO.
Dry Gas Meter	Schlumberger	Gallus 1000, No. 3600046
Barometer	Oakton	s/n 51062
Thermometer		s/n 9266
Baked Quartz filters	Pall Gelman	2500QAO-UP
47mm Teflon filter	Pall Gelman	R2PJ047
Flow check adapter	Andersen	none



Hong Kong and Pearl River Delta Sampling Schedule

October, 2002 Sampling Dates: 2, 8, 14, 20, 26, 0210FB

December, 2002 Sampling Dates: 1, 7, 13, 19, 25, 0212FB

March, 2003 Sampling Dates: 1, 7, 13, 19, 25, 0303FB

June, 2003 Sampling Dates: 5, 11, 17, 23, 29, 0306FB

**** September 19, 2002: Test Run all sites**

Figure 11: Sampling Schedule

7.2.1 Calibration/verification of Andersen samplers

According to the instrument manual (Thermo Andersen, 2001), the sampler needs to be calibrated every time it is moved to a new location. The frequency of calibration and verification will be user determined. Andersen recommends that the sampler should be verified or calibrated within 90 days of the previous calibration.

Temperature verification:

Sampler thermocouples were calibrated by the manufacturer, refer to the instrument manual for details (Thermo Andersen, 2001). A thermometer, which reads in degrees C, NIST traceable, and accurate to $\pm 2^{C}$ is used to verify that the sampler thermocouples are accurately measuring the ambient and manifold temperatures.

1. Hold reference thermometer close to the ambient thermocouple, located on the outside right side of the sampler under a white solar radiation shield.
2. On the sampler, go to "MAINTENANCE>", press enter.
3. Select "QC>", press enter.
4. Select "Ambient", press enter.
5. The thermocouple temperature output is displayed on the screen. When the reference thermometer has come to rest on a value, press "Enter" and input the reference value when prompted.
6. The screen will display the difference between the reference and the sampler temperatures - this value should nominally be smaller than 2 degrees Celsius.
7. Press "Cancel" to exit the ambient temperature verification, select "Yes" to save the verification.
8. Repeat 1-7 for the manifold temperature, selecting "Manifold" from the "QC>" list and holding the reference thermometer near the manifold thermocouple (located on the upper right inside the sampler).

Pressure verification:

Sampler pressure was calibrated by the manufacturer. A pressure measurement device with a range of at least 500 to 900 mm Hg absolute is used to verify the accuracy of the sampler pressure sensor. The device should have a readability of 1 mm Hg and an accuracy of ±5mmHg.

1. On the sampler, go to "MAINTENANCE>", press enter.
2. Select "QC>", press enter.
3. Select "Barometer", press enter.

4. The sampler pressure reading is displayed on the screen. Press “Enter” to input the reference pressure reading.

5. The sampler will show the difference between the reference and the sampler. This value should nominally be smaller than 10 mm Hg.

6. Press “Cancel” to exit the pressure verification, select “Yes” to save the verification.

Flow calibration:

A NIST traceable reference dry gas meter is used to calibrate the flow sensors in the Andersen sampler. The dry gas meter should read in cubic meters and have a readability of at least 0.0002 cubic meters.

1. Load filters in cassettes into the four filter holders; quartz fiber filters in Q1 and Q4, teflon filters in T2 and T3. These filters should be the same type as the filters used during sampling.

2. Place the dry gas meter in a stable location and do not move it during calibration.

3. Disconnect the Q1 filter holder by unscrewing the white hand ring located above the filter holder. Attach the filter holder to the flow check adapter and attach the flow check adapter to the dry gas meter with accordion style teflon tubing. The teflon tubing has swagelocks on each end which will give a proper seal when finger-tightened. The Q1 filter holder may be laid down within the sampler, being sure not to block any fans or cause tight bending in the teflon tubing.

4. On the sampler computer, go to “MAINTENANCE>”. Select “Calibrate>”. Select “Flow 1”.

5. The screen displays current outputs of the pressure and temperature sensors, verify that the sensors are working properly by comparing them with a reference. Press “Cancel” to proceed.

6. Under “Select Flow Device”, choose “Dry Gas Meter” and press enter. The system will now ask for a Reference DGM Coefficient. This number is located on a label on the dry gas meter. Input this number into the computer and press enter.

7. The calibration screen for Flow 1 is displayed. Write down the old “gain” and “offset” in the field logbook. Next, press “Enter” to add a point.

8. The sampler will alternate measuring two types of points - zero flow points and full flow points. The first point will be a zero flow point which will take approximately one minute.

9. After the zero point finishes, press “Enter” to add another point. The system will now ask for the initial reading on the dry gas meter. Look on the dial of the dry gas meter and key this number into the computer, also write it down in the field logbook as Vo,DGM. After keying in the number, press enter.

10. The pump will come on the system will display a screen showing the flow rate, flow variation (CV%), etc. Once the Volume parameter is equal or greater than 0.1000, a prompt at the bottom of the screen appears - “Hit Cancel to Enter Reference Data”. After this prompt appears, press enter. Write down the time in the field logbook.
11. The screen will prompt for the final volume reading on the dry gas meter. Write down the number on the screen in the field logbook as Vf,sampler. Write down the final dry gas meter value in the field logbook as Vf,DGM. Key in the final dry gas meter value, replacing the value on the screen. Press enter.
12. Repeat steps 8-11, taking two more zero points and two more flow points - totaling 6 calibration points for Flow 1. At the end, write down the new “gain” and offset” in the field notebook.
13. Press “Cancel” to exit calibration for Flow 1. Choose “Yes” to save the calibration.
14. Repeat steps 3-13 for Flow 2 (T2), Flow 3 (T3), and Flow 4 (Q4).
15. At the end of calibration, go to “MAINTENANCE>”, select “Archive Values”, and select “Archive Cal Values”. Press enter, choose “Yes” to overwrite past calibration values. This will save the updated calibrations which may be restored if the sampler loses the stored calibrations.
16. Calculate the flow rate in L/min by

$$\frac{(\mathrm{Vf,DGM} - \mathrm{Vo,DGM}) \times \mathrm{coefficient} \times 1000}{\mathrm{time}}$$

Take an average of the three results for each filter holder to obtain the calibrated orifice flow rate.

7.2.2 Calibrating Caltech samplers

A NIST traceable reference dry gas meter is used to calibrate the critical orifices used for flow control in the Caltech samplers. The dry gas meter should read in cubic meters and have a readability of at least 0.0002 cubic meters.

1. Load unused filters into the four filter holders; quartz fiber filters in Q1 and Q4, teflon filters in T2 and T3. These filters should be the same type as the filters used during sampling.
2. Place the dry gas meter in a stable location and do not move it during calibration.
3. Disconnect the Q1 filter holder by unscrewing the top swagelock fitting. Attach the filter holder to the dry gas meter with accordion style teflon tubing.
4. Write down the initial reading on the dry gas meter in a field notebook. Call this value Vo,DGM.

5. Simultaneously start power to the pump and start timing with a stop watch. Run the sampler pump for several minutes until approximately 0.1000 m^3 of air has been drawn through the filter holder.
6. Simultaneously stop the pump and stop the stop watch.
7. Write down the elapsed time and the final reading on the dry gas meter, Vf,DGM in the field logbook. Also note the reference DGM coefficient value from the dry gas meter label.
8. Calculate the flow rate in L/min by

$$\frac{(\mathrm{Vf,DGM} - \mathrm{Vo,DGM}) \times \mathrm{coefficient} \times 1000}{\mathrm{time}}$$

9. Repeat the flow calibration measurement and take an average of the results to obtain the calibrated orifice flow rate.
10. Follow the same steps for filter holder T2, T3, and Q4.

7.3 Sampler Maintenance

Samplers were thoroughly cleaned with hexane and methanol before being brought to the field. It should not be necessary to disassemble and clean the equipment during the course of the year sampling study which will have 21 sampling days. Andersen recommends cleaning after 30 sampling days. However, care should be taken to keep the filter holders closed and all sampling lines connected between sampling months so that the parts remain as clean as possible.

At the start of each sampling month, the large particle collection cup at the bottom of each cyclone should be emptied. This cup unscrews and any large particles collected can be discarded. There are two cyclones per sampler.

Filter cassettes should be inspected for cleanliness before each sample load. Spares are provided should any be found dirty. Dirty cassettes can be rinsed in methanol, allowed to dry on clean kimwipes, and then returned to the tool box as spares.

The filter cassette loader should be inspect for cleanliness before each trip to the field. It can be wiped with a clean kimwipe, or rinsed in methanol should it become soiled.

8 ORGANIC AND ELEMENTAL CARBON ANALYSIS

8.1 Apparatus and Materials

The following apparatus and materials are used to analyze quartz fiber filters for organic (OC) and elemental (EC) carbon.

ITEM	SUPPLIER	MODEL or CATALOG NO.
Carbon Analyzer	Sunset Laboratory	May, 1997
Tweezers style AA	Ted Pella	5734
Gelman s.s. forceps	VWR	51147
Quartz filters	Pall Gelman	2500QAO-UP
Petri dishes	VWR	25388-606
Sucrose, ACS reagent	Sigma	S5016
Syringe, 25 μl	Hamilton	81265

8.2 Analysis Description

Quartz fiber filters are analyzed for OC and EC content by the thermal evolution and combustion technique of Birch and Cary (1996). In the thermal-optical organic and elemental carbon concentration measurement method, 1.5 cm^2 rectangular filter punches are first placed in a temperature and atmosphere-controlled oven. The analysis process occurs in two stages. In the first stage, the temperature is raised progressively to approximately 850^{o}C in a pure helium atmosphere in order to volatilize organic carbon from the sample. The volatilized carbon is oxidized catalytically to CO_2, which is then reduced to CH_4. The CH_4 is then quantified using a flame ionization detector (FID). During this process, the filter may darken somewhat due to production of artifact EC by pyrolysis. Elemental carbon measurement and correction for any artifact EC formed by pyrolysis during OC analysis are accomplished during stage two. At the beginning of this second stage of analysis, the oven temperature is initially reduced, a 4% oxygen, 96% helium mixture is introduced, and the temperature is then raised progressively to approximately 900^{o}C. As the black elemental carbon is oxidized and CO_2 is evolved, there is an increase in filter transmittance.

In order to correct for any contribution to the elemental carbon present due to OC pyrolysis during stage 1 of the analysis, the amount of EC oxidation necessary to return the filter to its initial transmittance is first measured. The point at which the filter transmittance equals its initial value is taken to be the point at which the actual EC begins to evolve from the sample. Any EC oxidized prior to that point is assumed to be due to OC pyrolysis earlier in the analysis and thus is added to the OC concentration measured in the first step of this analysis. This analysis method is known as the NIOSH (National Institute of Occupational Safety and Health) protocol.

8.3 Daily Run

1. The carbon analyzer is generally kept in standby mode when not in use. A Windows-based personal computer is dedicated to instrument operation. If the

instrument is not in standby mode, click the “ocecin55.exe” icon on the computer. Otherwise, begin operation by clicking on the continue option to leave standby mode. The status line on the computer screen will change from red to green when the instrument has warmed up and is ready for operation.

2. Check the parameter file being used by the program is correct, and change the output raw data file name following the convention of 3-4 letter project code followed by 4 digit current date. A maximum of 8 characters can be used for the saved file name which puts data into filename.txt.
3. Set analyzer and adjust gas flows according to manufacturer’s recommended settings which can be found in the OC/EC Analysis Log Book.
4. Light the flame in the FID and verify that all gas flows are in the correct ranges.
5. Pull down the computer menu under “Run” and choose “CLEAN OVEN”. This will do an 8 minute heating cycle to 800^{o}C in the front sampling oven which will burn off any contamination.
6. When the oven cools down, “SAFE to put in a new sample” will appear on the status line of the computer screen and analysis may proceed.
7. Run at least one quality control standard to ensure that instrument calibration is in control. Quality control standards can be prepared at the beginning of the day, or made up to a week in advance and stored in the freezer.
8. If the quality control standard(s) looks fine and FID1 MAX is within proper range (1550-1950), proceed with running samples. If FID1 MAX is too high/too low, adjust gas flow settings and run additional quality control standards or blank filters until FID1 MAX is within range.

To run a sample

1. Remove the teflon tape sealing a petri dish containing a 47mm quartz fiber filter. Filter samples are kept in the freezer until time for analysis. To avoid frequent opening of the freezer, remove 5-6 samples at one time and set them aside on the lab bench. Keep samples sealed with teflon tape until one is needed.
2. Using the punch tool, take a 1.5 cm^2 punch from the sampled area of the filter. Leave the filter in the foil lined petri dish and do not touch the remainder of the sample that will be used in GC/MS analyses. Close and tape the petri dish with new teflon tape. Return the remainder of analyzed samples to the freezer when the next set of samples is retrieved for analysis.
3. Open the sample insertion port of the carbon analyzer, and using the curved tweezers that are dedicated for this purpose, pull out the quartz sample holder boat. Be very careful handling the sample holder boat which is very fragile. If it comes in contact with anything other than the clean tweezers, it can be returned to the oven and “CLEAN OVEN” run again to remove contaminants.

4. Remove the 1.5 cm^2 rectangular piece of quartz filter from the punch tool using the tweezers that have been dedicated for use with the carbon analyzer. Tweezers are solvent cleaned and wiped with a clean kimwipe. Take care not to disturb deposited material and avoid hand contact with the sample.
5. Place the sample punch on the quartz sample holder boat. There is a ridge on the sample holder boat indicating where the punch should be placed so that it lines up with the laser during analysis.
6. Push the sample holder boat back into position with the curved tweezers and close the sample insertion port.
7. Choose “Start Analysis” on the computer.
8. Each sample will take approximately 20 minutes for a complete run including a calibration injection at the end and a cool down phase. The computer screen will display “Safe to put in a new sample” when the next sample can be inserted.

After the days run is complete

1. Put the carbon analyzer program into standby mode.
2. Turn all gas flows to zero except for helium. A small helium flow (approx. 20) should be kept running through the system while in standby mode. Turning hydrogen flow to zero will put out the flame in the FID.
3. A program to calculate carbon concentrations can be run by clicking on the “Calc60.exe” icon. Organic and elemental carbon are reported in terms of μg per cm^2 of filter area. The total OC and EC on the filter are calculated by multiplying the reported values by the deposit area. A homogeneous sample deposit is assumed.
4. The calculation program will write calculated data into the file filename.csv which should be backed up to another computer storage medium.

8.4 Quality Control

8.4.1 Instrument specifications

See NIOSH (1999) or Birch and Cary (1996) for additional details.

- A calibration peak is achieved by methane injection included at the end of each sample run. Operator will verify the FID MAX for each sample run is in the correct range according to manufacturer’s recommendations. If any problems occurred during a sample run, a new punch will be taken and the sample rerun.
- The estimated detection limit is 0.15 $\mu g/cm^2$ C.

- The ideal range for sample analysis is 1 to 105 μg per filter portion analyzed. For heavily loaded samples, a smaller sample punch tool can be used reduce the carbon load analyzed.
- Instrument precision has been found to be 0.19 at 1 μg C and 0.01 at 10-72 μg C.
- The split between organic-based carbon (OC) and EC may be inaccurate if the sample transmittance is too low. In general, the OC-EC split may be inaccurate when EC loadings are above 20 $\mu g/cm^2$ of filter. The split should be reassigned manually (prior to EC peak) in such cases.

8.4.2 Quality control standards

1. Prepare clean filter punches. Use the sample punch tool to cut several 1.5 cm^2 rectangles. These can be stored until needed in the box labelled "punches for standards, unbaked."
2. Place 2-3 rectangular punches on the quartz sample boat and insert them in the sample oven. Run "CLEAN OVEN" to bake them.
3. Remove clean, baked punches and using tweezers, carefully place them on the pin rack used to hold them for spiking.
4. With a 25 μl syringe, apply aliquots of OC standard solution directly to the clean filter punches. Quality control standards are made containing 5 μl, 10 μl, 15 μl, and 20 μl of sucrose solution.
5. Sucrose ($C_{12}H_{22}O_{11}$) solution is prepared by putting 5.848 g/l of sucrose yielding 2.46 $\mu g/\mu l$ "C".
6. Allow water to evaporate from punches. After drying, either run punches for analysis, or transfer them to petri dishes lined with annealed aluminum foil, seal with teflon tape, and store in the freezer for use later in the week.

8.4.3 Freezer storage on samples

The effect of long freezer storage time on OC/EC results has been investigated by our laboratory. Samples were originally analyzed in 1997 have since been stored frozen at -21^{o}C. New punches were analyzed in 2001 for signs of sample degradation (See Table 8.1). There is no statistical evidence that results for OC/EC analysis have been affected by freezer storage to date.

In order to account for oxygen and hydrogen associated with organic material, the OC concentrations were next multiplied by 1.2 to estimate the organic matter concentrations. Factors used to convert organic carbon into organic mass in material balance studies range from 1.2 to 1.4 (Gray et al., 1986).

Table 8.1 Effect of freezer storage on OC/EC results of archived samples

Sample Name	Date Analyzed	Organic Carbon (ug cm^{-2})	Elemental Carbon (ug cm^{-2})	Total Carbon (ug cm^{-2})
OG-C-970428	8-01-1997	3.47 ± 0.37	0.29 ± 0.21	3.76 ± 0.49
OG-C-970428	4-16-2001	3.17 ± 0.36	0.21 ± 0.21	3.37 ± 0.47
OG-C-970416	8-01-1997	5.89 ± 0.49	1.18 ± 0.29	7.07 ± 0.65
OG-C-970416	4-20-2001	5.53 ± 0.48	1.14 ± 0.26	6.66 ± 0.63
OG-C-970410	8-01-1997	5.52 ± 0.48	1.49 ± 0.27	7.00 ± 0.65
OG-C-970410	4-16-2001	5.04 ± 0.45	1.13 ± 0.26	6.18 ± 0.61
OG-C-970422	8-01-1997	6.02 ± 0.50	1.73 ± 0.29	7.75 ± 0.69
OG-C-970422	4-16-2001	5.32 ± 0.47	1.48 ± 0.27	6.81 ± 0.64
OG-C-970814	9-30-1997	5.51 ± 0.48	1.11 ± 0.25	6.62 ± 0.63
OG-C-970814	4-16-2001	5.19 ± 0.46	0.62 ± 0.23	5.81 ± 0.59
OG-C-971212	12-30-1997	13.00 ± 0.85	1.21 ± 0.26	14.21 ± 1.01
OG-C-971212	4-16-2001	13.04 ± 0.85	1.27 ± 0.26	14.31 ± 1.02
OG-C-971118	12-29-1997	12.19 ± 0.81	3.80 ± 0.39	15.99 ± 1.10
OG-C-971118	4-16-2001	12.49 ± 0.82	3.50 ± 0.38	15.99 ± 1.10
OCy-C-970430	12-30-1997	5.61 ± 0.48	1.81 ± 0.29	7.42 ± 0.67
OCy-C-970430	4-20-2001	5.30 ± 0.47	1.31 ± 0.27	6.61 ± 0.63
OCy-C-970709	12-31-1997	5.78 ± 0.49	0.38 ± 0.22	6.16 ± 0.61
OCy-C-970709	4-20-2001	5.43 ± 0.47	0.20 ± 0.21	5.63 ± 0.58
ICy-C-970727	12-30-1997	4.63 ± 0.43	0.31 ± 0.22	4.93 ± 0.55
ICy-C-970727	4-20-2001	4.15 ± 0.41	0.25 ± 0.21	4.41 ± 0.52

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OCEC ANALYSIS LOG SHEET Date:__________ Initials:________

Sample Description____

Parameter file used: ____________________ Data file: ___________________

Gas tank pressures (psi):

He ____/____ Air ____/____ H2 ____/____ He+Ox ____/____ Cal ____/____

Flow rates*: Cal____ He2____ H2____ He+Ox____ He1____ He3____ Air____

(*black ball except for air) silver

Sample ID	FIDmax	Comments

9 GC/MS ANALYSIS OF QUARTZ FILTERS

This section describes the resources and analytical procedures for the measurement of trace organic compounds in the atmospheric particulate matter.

9.1 Apparatus and Materials

The following equipment and materials are required for analyzing quartz fiber filters for organic compounds.

ITEM	SUPPLIER	MODEL or CATALOG NO.
GC/MS	Agilent	HP 5973 MSD
Sonicator	Fisher	FS60
Solvent Evaporator	Fisher	24/40 R124A
Nitrogen Blow Down	Fisher	PI18870, PI 18780
Muffle Furnace	VWR	F30420C-80
Distillation	Fisher	K547110-3000
Flask	Fisher	09-559B
Test Tube	Fisher	14-958F
Sample Vial	Supelco	2-7083U
Diazomethane Generator	Aldrich	Z10159-1
Benzene	VWR	EMBX0212-6
Isopropyl Alcohol	Fisher	A464-4
Hexane	Fisher	H303-4
Methanol	Fisher	A454-1
Dichloromethane	Fisher	D151-4
Ether	Aldrich	30996-6
Syringe	Fisher	Gas-tight syringe
Sample Jar	Scientific Specialties	270808
GC Column	Agilent	HP5 MS
Internal Standards	Wisconsin State Hygiene Lab	sealed in the ampule
Quantification Standards	Wisconsin State Hygiene Lab	sealed in the ampule

9.2 Analysis Description

The important aspects for organic tracer analysis of aerosol samples include preventing any contamination from reagents and sample processing, and maintaining consistent robust quantification. Blank filters will be routinely analyzed along with the ambient samples. To ensure the quality of quantitative analysis by GC/MS, an amount of 1 milligram of organic carbon or higher in each sample is recommended. Quartz fiber filters are analyzed for organic compound content by the technique developed by Glen Cass and his colleagues using GC/MS (gas chromatography/mass spectrometry) (Schauer et al., 1996). It includes extraction, concentration, derivatization, and GC/MS analysis.

9.2.1 Baking

To avoid any possible contamination, all glassware and quartz fiber filters should be baked in the Muffle furnace prior to use.

9.2.1.1. Glassware Cleaning

1. Rinse glassware twice with distilled/deionized water. (For used glassware, it is first soaked in and cleaned in cleaning solution with detergent, and then rinsed with tap water until the detergent has been removed.)
2. Cover any openings with aluminum foil.
3. Bake glassware in the Muffle furnace at 550^{o}C for 12 hours.
4. Place the baked glassware in the clean storage area.
5. Rinse two times with dichloromethane before use.

9.2.1.2. Gas-tight Syringe

1. Prior to use, take syringe apart.
2. Sonicate it in a beaker filled with dichloromethane for 30 min.
3. Sonicate in a beaker filled with methanol for 30 min.
4. Resemble syringe.
5. Using the same solvents as in sample, rinse syringe 15 times. Then the syringe is ready for use.
6. Rinse the syringe with the same solvents immediately after contact with a sample or standards for 15 times.
7. Repeat cleaning procedure from 1 to 4, and store syringe in the clean storage area.

8. When measuring a volume with a syringe, the appropriate size syringe should be used. Take entire sample into syringe, turn syringe up-side-down, remove air bubbles by striking it gently, and read the volume.

9.2.1.3. Nitrogen Blow Down

1. Check to ensure enough N_2 gas in the tank (above 200 psi).
2. Clean the needles in the blow down apparatus with dichloromethane twice and leave it on a piece of clean aluminum foil to air-dry.
3. Put the clean needles (or tips) in the blow down stand. The rest opening should be capped.
4. Open slowly and ensure that the head pressure of the flow to the blow down apparatus is less than 2 psi.
5. Let it flow for 5 min to equilibrate and clean the system.
6. The needles should be at least 1 inch above the solvent surface.
7. Increase the head pressure slowly until you see a dent in the meniscus. If the solvent is bubbling, then the head pressure is too high.
8. Blow down the samples and watch closely.

9.2.2 Extraction and concentration

Before extraction, each sample containing at least 1 milligram of organic carbon is spiked with 250 μl of the injection concentration of internal standard #1 and 250 μl of the injection concentration of internal standard #2. The deuterated standards included in internal standards #1 and #2 include benzaldehyde-d_6, dodecane-d_{26}, decanoic acid-d_{19}, phthalic acid-3,4,5,6-d_4, acenaphthene-d_{10}, levoglucosan-$^{13}C_6$ (carbon-13 uniform-labeled compound), hexadecane-d_{34}, eicosane-d_{42}, heptadecanoic acid-d_{33}, 4,4'-dimethoxybenzophenone-d_8, chrysene-d_{12}, octacosane-d_{58}, ααα-20*R*-cholestane-d_4, cholesterol-2,2,3,4,4,6-d_6, dibenz (ah)anthracene-d_{14}, and hexatriacontane-d_{74}. The sample is then extracted twice with hexane (Fisher Optima Grade), followed by three successive extractions with distilled benzene/2-propanol (2:1 mixture) (benzene: E & M Scientific Ominosolv benzene; 2-propanol: Fisher Optima Grade) under mild sonication for 15 min for each extraction. The five extractions are combined, filtered, and reduced to 5-10 mL by a rotary evaporator. The extract is transferred to a test tube and the volume is further reduced to 1 mL by high purity nitrogen blow down. Then, the extract is split into two fractions with one fraction stored in the freezer and the other fraction derivatized with diazomethane to convert organic acids to their methyl analogues for GC/MS analysis.

The deuterated internal standards, which are used for quantifying the target compounds after GC/MS analysis, were spiked before extraction. Therefore, the recovery is corrected for the quantification results reported. With this type of procedure, past work indicates that, for the filter analysis, the recovery was 81 ± 6% for the deuterated n-tetradecane internal standard, 65 ± 4% for deuterated n-pentadecane internal standard, and 69 ± 15% for deuterated n-alkanoic acid internal standard. The average detection limit is 0.01 ng m^{-3} and the average uncertainties of quantification of organic compounds were determined to be ±20% (Schauer et al., 2002).

9.2.3 Derivatization

The concentration sample should be derivatized with an equal volume of a diazomethane solution. After derivatization, the sample is further concentrated by high purity nitrogen gas blow down. The final volume is the same as the spike volume of internal standard #1 or #2 to ensure that the concentrations of internal standards in the final volume are the same as the injection standards.

9.2.4 Quantification and GC/MS analysis

Quantification of each target organic compound is made by reference to a deuterated internal standard, which has chemical characteristics and retention time similar to the target compound. Quantification standards include 6 PMSTD standard mixtures (PMSTD#1 - #6). Relative response factor (RRF) for each organic compound is calculated from the GC/MS analysis of the quantification standards, which contain isotopically labeled internal standards. For those target compounds which are not present in the quantification standards PMSTD#1 - #6, secondary standards including Wood Smoke Secondary Standard, Motor Oil Secondary Standard, and Candle Wax Secondary Standard are used to assist the identification. The RRF of these compounds are estimated from the response factors of compounds having similar chemical structure and retention time.

9.2.4.1 Conditions for the Analysis

GC CONDITIONS	
Column	HP5 MS 30 m length 0.25 mm diameter 0.25 μm film thickness
Injector Temperature (^{o}C)	300
GC/MS Interface Temperature(^{o}C)	300
Initial Oven Temperature (^{o}C)	65
Initial Oven Hold Time (min)	2
Oven Temperature Ramp Rate (^{o}C/min)	10
Final Oven Temperature (^{o}C)	300
Final Oven Temperature Hold Time (min)	30
Carrier Gas	Ultrapure Helium
Carrier Gas Flowrate (mL/min)	1.0
Injection	Splitless, Autosampler

MS CONDITIONS	
Solvent Delay (min)	4.5
Data Collection Mode	Scan
Scan Range (amu)	50-650

RINSE (before and after injection)	
Rinse with Hexane	4 times
Rinse with Methanol	4 times
Sample Pump	5 times
Sample Rinse	1 time
Post Rinse with Hexane	4 times
Post Rinse with Methanol	4 times

9.2.4.2. QA/QC for GC/MS Analysis

1. Before running any sample or standards, run standard autotune to check the performance of the instrument and potential problems such as air leaks

2. Before running any sample or standards, run unconcentrated solvent blanks including all of the solvents in the analysis

3. Run PMSTD#1 1:10 and PMSTD#4 1:10. The sensitivity and contamination checks for daily PMSTD#1 1:10 and PMSTD#4 1:10 include the following:

    (a) PMSTD#1 (coronene 300 to pyrene 202 ion ratio): Min 25 percent

    (b) PMSTD#1 (coronene 300 abundance): Minimum area of 10000
    (c) PMSTD#4 (cholestane-D4 221+222 to cholesterol 386 ion ratio): Min 3 times
    (d) PMSTD#4 (cholesterol 386 abundance): Minimum area of 1,000,000

4. At the beginning and the end of each sample set (or minimum of every 3 days), run the following PMSTD standards which contain the deuterated internal standards #1 and #2.

    - PMSTD#1 1:5
    - PMSTD#2 1:5
    - PMSTD#3 1:5 (derivatized with diazomethane before GC/MS analysis)
    - PMSTD#4 1:5
    - PMSTD#5 1:5
    - PMSTD#6 1:5
    - Wood Smoke Secondary Standard
    - Motor Oil Secondary Standard
    - Candle Wax Secondary Standard

5. After each 6 samples, run 1 randomly selected 1:5 dilutions of the above PMSTD standards

6. Relative response factors (RRF) are calculated for target compounds from the PMSTD runs at the beginning and the end of each sample set. These RRF should not vary from historical records more than 50 percent

7. Daily single point RRF checks should not vary more than 10 percent (Target) and should be flagged if vary more than 20 percent (Tolerance)

8. After GC/MS injection, samples will be sealed with solid caps and Teflon tapes and stored in the freezer to minimize the time that samples reside on autosampler tray

9. Other maintenance for GC/MS:

    (a) Change septum every 20 runs (For Merlin injectors, it can last longer. The suggested number is 1000 injections.)
    (b) Check liner every column change or once a month
    (c) Check the ultrapure Helium tank pressure every day (> 500 psi)

9.3 QA/QC

9.3.1 Solvent blanks

Check solvents used in the sample processing by concentrating the same amount of solvent used for a sample and analyzing with GC/MS. All solvents except benzene are optima grade because solvents can be a major source of contamination. Benzene is distilled and tested prior to use.

9.3.2 Filter or procedural blanks

Check the whole procedure by analyzing the pre-baked quartz fiber filters to get an estimate of the background of the procedure before the analysis of the real samples.

9.3.3 Precision

Determine the precision of the analysis by analyzing seven samples prepared by the pre-baked filters with standard mixtures spiked onto each sample. Quantify recovery of these standards.

10 ANALYSIS OF TEFLON FILTERS

The concentrations of all chemical species analyzed by ion chromatography are determined relative to primary or secondary laboratory standards of known concentration. Aqueous daily standards are prepared from more concentrated solutions prepared from ACS grade analytical reagents. Standard log sheets are filled out each time standards or reagents are prepared.

Teflon filters are placed in individual extraction cups and wetted with 0.2 ml of ethanol (100 percent) to reduce the hydrophobic nature of this material (Derrick and Moyers, 1981). A Teflon rod is placed on top of each filter to keep it submerged, the extraction cup is sealed with a tight-fitting lid, and each Teflon filter is extracted by shaking it in a known volume (10-20 ml) of distilled, deionized water for 3 hours or more.

After extraction, the concentrations of the major water soluble particulate species (SO_4^{-2}, NO_3^{-}, and Cl^{-}) are determined using a Dionex ion chromatograph. The same Teflon filter extracts also are analyzed for particulate ammonium ion (NH_4^{+}) by an indophenol colorimetric procedure employing a rapid flow analyzer (RFA-300 TM, Alpkem Corp.) (Bolleter et al., 1961).

10.1 Extracting Teflon Filters for Analysis

10.1.1 Apparatus and Materials for extraction

ITEM	SUPPLIER	MODEL or CATALOG NO.
Balance	Ohaus	E400D
Tweezers style AA	Ted Pella	5734
Gelman s.s. forceps	VWR	51147
Teflon filters	Pall Gelman	R2PJ047
Sample cups	VWR	25384-148
Pippettor	Eppendorf	25 μl
Pipette tips	VWR	53512-350
Teflon round rod	McMaster Carr	8546K12
Copier Labels	Avery	8460
Ethyl Alcohol	Quantum	200 proof
Rocking platform	VWR	100
Refrigerator	Sanyo	small
Repipette Dispenser	LabIndustries	none

10.1.2 Preparing teflon filter extracts

Instructions for preparing teflon filters to be analyzed by IC and Alpkem (Derrick and Moyers, 1981).

1. Prepare a set of sample ID labels on stickers (e.g., Avery Copier Labels).
2. Place a filter in a sample cup with top (dark) side up. Use tweezers at all times to handle filters.
3. Using Eppendorf pipette, add 200 μl of EtOH (100%) to each filter. Carefully place EtOH on filter sample drop by drop, tipping cup so that EtOH runs across filter to cover entire sample surface evenly. The ethanol is used to ”wet” the teflon surface, (i.e., it reduces the hydrophobic nature of this filter material.)
4. Add 10-30 ml of DI water from Repipette dispenser for typical 24-hour ambient samples. Obtain DI water from MilliQ dispenser in room 102. Use the Ohaus Balance to measure how much DI water is added to each sample cup and record on the sample label.
5. Place one long teflon rod on top of the filter in each sample cup to hold down the filter, otherwise they float.
6. Tightly cap the sample cup and make sure it has the appropriate ID label.
7. Keep the samples in order. Put them in a box and place on the rocking platform. Agitate the samples vigorously for approximately three (3) hours. After shaking, store samples in the refrigerator until analyzed.

10.2 Ion Chromatography

Ion chromatography employing the Dionex 2020i allows for chemical analysis of aqueous solutions for various ionic species depending on which IC column is used. The user is referred to the Dionex manual, Dionex application sheets (available from Dionex) and to ”A Handbook for Ion Chromatography,” by J. Weiss published by Dionex for additional information.

The AS4 anion column with an AG4 guard column is used to detect strong acid anions (e.g., Cl^-, $NO_2{}^-$, $NO_3{}^-$, $SO_4{}^=$). See IonPac AS4 spec. sheet for general information about this column.

10.2.1 Apparatus and Materials for IC Analysis

The following apparatus and materials are used to analyze teflon filters by ion chromatography (IC).

ITEM	SUPPLIER	MODEL or CATALOG NO.
Ion Chromatograph	Dionex	2020i
HPIC-AS4 anion separator column	Dionex	P/N 35311
HPIC-AG4A anion guard column	Dionex	P/N 37042
Balance	Ohaus	E400D
Tweezers style AA	Ted Pella	5734
Teflon filter extracts	see previous section	
Acrodisc LC13 syringe filters	VWR	28143-989
B-D syringes	VWR	BD309585
Pipettor 1-5 ml	Labnet	E-24600-25
Electronic pipettor	Rainin	EP-2500
Pipette tips	VWR	53512-350
Pipette tips	Rainin	RC-2500
Glass pipettes, size 5 x 1/10 ml	VWR	53283-738
IC chloride standard	VWR	EM-19897-1
IC nitrate standard	VWR	EM-19811-1
IC sulfate standard	VWR	EM-19813-1
Sodium carbonate	Mallinckrodt	7527
Sodium Bicarbonate	Mallinckrodt	7412
Sulfuric acid	JT Baker	JT9681-2
Spatula	VWR	57901-140
Weighing boats	VWR	12577-027
Volumetric flasks	Kimax	various sizes
diSpo beakers, 5ml	VWR	13915-985
4270 integrator	Spectra Phys	4270

10.2.2 Advance preparations

Daily paper work should be filled out to insure quality control. See attached copies of daily standard preparation and log sheets for examples. Blank forms are located in the plastic file holder next to the Dionex manuals. Make additional copies of any blank forms when supplies run low.

10.2.3 Master standards

Refer to the master standard preparation sheets for the appropriate amount of each reagent. Prepare the master standards from analytical grade reagents which can be obtained from several vendors if new stocks are desired. When opened, reagents should be marked with the date so that their age can later be determined. Prepare new master standards at least every 30 days.

First, prepare a concentrated master standard from which daily standards will later be prepared. The master standard should contain at least Cl^-, NO_3^-, and $SO_4^=$ which are the main species of interest found on Teflon filters used to collect particles. Bromide and phosphate can also be detected with this column but are rarely seen in any of our typical samples.

Concentrated solutions of individual ionic species are available from VWR and are stored in the refrigerator. Verify expiration dates listed on the bottles and replace when needed. The amounts to use for preparing the master standard are listed at the top of the daily standard preparation log sheet. After preparation store this standard in the designated polypropylene bottle in the refrigerator labelled with date prepared and preparer's initials.

A concentrated mixed standard is available from Dionex and can be used as an independent test for quality control. This standard contains (Cl^-, F^-, NO_3^-, and $SO_4^=$) and should be diluted to the concentration range of the daily standards. The dilute standard should be analyzed periodically along with the samples and standards. Analyzed concentrations of QA/QC standard should be within 5 to 10% of known concentrations.

10.2.4 Eluent

Eluent: (HCO_3^- / $CO_3^=$)

Refer to the eluent preparation sheet and have the eluent prepared at least a day in advance of intended use. Make up one liter of concentrated sodium carbonate/sodium bicarbonate eluent (100x) following the directions on the eluent preparation log sheet. Store it in the refrigerator in the designated polypropylene bottle. Label the bottle with the date prepared and preparer's initials. Make a new concentrated eluent approximately every 30 days.

To prepare the eluent for daily use, add 40 ml of the concentrate to 4 liters of DI water. There is a 4 liter plastic bottle designated for this purpose located in the cabinet beneath the IC and a graduated cylinder designated for measuring 40 ml of eluent marked with the label "eluent."

Allow the dilute eluent to equilibrate for 24 hours before using. The dilute eluent will later be transferred into the appropriate cubitainer located on top of the IC. These cubitainers hold slightly more than 4 liters of fluid and will last for approximately 14 hours of IC operation.

10.2.5 Acid

A pressurized 4 liter bottle of dilute acid is located on top of the IC. A full container of acid will last for approximately 9 hours of IC operation.

Make 25 mN H_2SO_4 by adding 2.8 ml conc. H_2SO_4 to 4 liters DI water.

Use designated bottles located beneath the IC to prepare acid and then top off the acid in the containers on top. Always get 4 liters of water first, then add acid to water under the fume hood using a disposable glass pipette.

10.2.6 Preparing to turn on the IC

Check the sample loop size (50 μl, 100 μl, and 200 μl currently exist). Larger loop sizes will give improved detection limits by increasing the amount of sample injected into the column at one time but will also require more sample and additional rinse quantities. The Dionex 2020i with an AS4 column can efficiently use loop sizes up to 1000 μl. Typically, the 50 μl loop is used unless sample concentrations are expected to be very small. Once one size loop is chosen and the integrator calibrated, changing the loop will require a new calibration. This is true of changing the IC range also. Also note, the sample injection valve ports are very sensitive to being over tightened.

Check that the correct column is in place and oriented correctly. Note: the flow will be from right to left as one faces the instrument.

Check that eluent and acid levels are adequate. It is best to have the containers full when planning a long days run, rather than turning off the machine to refill them during the day. **Important**, do not let the fluid levels get too low or air may be pumped through the column and/or suppressor. Passing bubbles through the column may result in a loss of efficiency and resolution and could damage the instrument.

Check pressures. Two regulators located behind the IC control the air input to the acid container and to the valves controlling sample injection. A third regulator is attached where the air comes from the wall supply and should be open full (approx. 80 psi). These are set where marked on the regulator and should not be adjusted unless they are far off the marks.

The IC column pressure is displayed on the front panel. If this pressure exceeds 1400 psi, it may be necessary to change one or more of the inline filters (normal pressure is 1000 - 1200 psi). See the problem section for more information.

Periodically check for leaks, especially around the column joints and valves behind the panel containing the columns. If the anion micro-membrane suppressor located below the columns develops a leak, it will need to be replaced. (model AMMS-1 P/N 038019).

Side note: The sample injection valve has eight ports numbered with 1 and 5 above and below the hole and other ports are numbered sequentially clockwise from these. Tubing should be connected as follows: Sample port ⇒ port 7; Eluent in line ⇒ port 1; line to column ⇒ port 5; line to waste ⇒ port 3; sample loop, port 2 ⇒ port 6; other loop, port 4 ⇒ port 8. Also, yellow air line is at top, green air line is at bottom.

The IC waste lines all empty into the sink located next to the instrument. Periodically check that these have not pulled free or become clogged.

10.2.7 Turning on the instrument

The IC and integrator power stay on full time - DO NOT TURN IT OFF. Turning off the integrator power will erase ALL calibrated files in the integrator. If the integrator ever looses power the date and time will need to be reset and the command ATTEN=1024 issued.

Start the flow of acid by pushing Switch A ON. Switch A is located on the SYS 1 strip in the top left corner of the IC unit. Other switches in this strip should be left set on B OFF and LOCAL. The Load-inject button can be in either position.

The eluent flow is controlled by the switches in the System 1 Analytical Pump module located below the door into the column compartment.

There are two Pressure Limit Select switches:

- x 10 psi (lower limit)
- 00, (for turn on then raise to 80) This is the lower limit, below which the pump automatically turns off and the eluent flow stops.
- x 100 psi (upper limit)
- 14, this will turn the pump off automatically if the column pressure exceeds 1400 psi.

Check settings:

- LOCAL-REMOTE on LOCAL
- FLOW: 2.0
- Choose eluent number: 1 = carbonate
- START - turns eluent flow on

The pressure will be 1000-1400 psi and gradually rise during weekly use. If above 1400 psi the column prefilters should be changed.

The System 1 Conductivity Detector is located in the module on the top left beneath the eluent cubitainers. On start-up the Cell should be turned ON with the Auto offset switch left OFF until the instrument has warmed up. The range will probably be set (usually 3). Lower ranges may give increased sensitivity (lower detection limits) but more signal noise. The temperature compensation should be 1.7.

Allow the IC to warm up with acid and eluent flowing through the columns before injecting the first standard. (Approximately 15-30 minutes.) The conductivity should be 21-24 μs.

Before running the first standard switch the Auto Offset on the conductivity detector to ON. This compensates for the conductivity of the eluent and will change the displayed conductivity to zero. If the conductivity increases above 25 μs, the columns may need to be cleaned or the eluent or DI water supply may be contaminated.

Record pressure and conductivity data onto the Dionex 2020i IC log sign in sheet located next to the IC.

10.2.8 Daily run

Prepare and run a set of daily standards. (Refer to the daily standard prep sheet.) Note that dedicated volumetric flasks labelled IC-A, B, C, etc have been set aside for this purpose for the strong acid standards.

If no calibration curves exist the data will have to be programmed into the integrator. Generally, the integrator will have 2 or more files programmed with calibration curves covering a range of standards.

Choose an appropriate file. Press ’USE FILE’ on the integrator and then press the desired number (e.g., ’2’) followed by ’ENTER’. This sets the integrator file to which data will be entered. Do not use a file that contains data (unless it’s your own) or you might write over someone else’s data.

The LOAD - INJECT button at the top of the IC must be in the LOAD position to load a sample into the sample loop. Install a new prefilter (located in front of the sample port) at the start of the day and change it periodically as it becomes clogged. Additional prefilters can be obtained from VWR, Cat No. 28143-989, Acro LC13 0.2 μm syringe filters.

Use a 3 ml syringe to load samples (available from VWR cat. no. BD309585). Pour a small amount (3-5 ml) of a low standard into a disposable beaker. Rinse the syringe 2-3 times with DI water and then rinse with a small amount (approx. 1.5 ml) of standard. Fill the syringe with standard and load it into the SYS 1 sample port. The volume injected into the IC should be at least 5-10 times the volume of the sample loop. Discard any remaining standard and the beaker.

Press INJECT on the IC and INJ A on the integrator simultaneously. The integrator will print out a graph of the sample and eluent conductivity over time. When the preset end run time is reached, the integrator will give a listing of the concentration of each species for which a calibration curve exists. A sample run takes approximately 8 min.

To calculate the concentrations of a just run standard or sample with a calibration curve in another file, change the file and recalculate the sample values (e.g., press ’USE FILE’ ’1’ on the integrator and then press ’RECALC’).

Run a few standards over the range expected. If standards are reproducible, start running samples. Low standards should be reproduced to within 15%, high standards to within 5% of the calculated concentrations. If the reproducibility of a standard is poor rerun it. If reproducibility is still unacceptable, remake the standard and analyze it again. Also, run other standards and make sure they are reproducible. If standards are not reproducible, it may be necessary to recalibrate the integrator.

To run a sample, rinse a syringe several times with DI water. Pour a small amount of sample into a disposable beaker. Teflon filter samples are extracted in DI water and need to have 1% of concentrated (100x) eluent added to the portion of the sample in the disposable beaker and thoroughly mixed before injecting. This will eliminate the negative water dip which would occur at the beginning of the run.

Load a sample and inject it in the same manner as the standards. Wait for the run to finish and check whether the integrator was in the file with the correct range. If not, enter the other file and recalculate the sample concentrations. Many samples may have one species in the range of one calibrated file, and other species in the range of the other calibrated file. If any species of interest is off scale, the sample will need to be diluted and rerun.

Run a different standard every 10-12 samples during the day, and run a couple standards at the end of the day to insure that the IC is functioning properly and the calibration curve has not changed. A typical 8 hour day run will generally encompass approximately 30-40 samples.

10.2.9 Calibrating the integrator

Detailed instructions are given in the Spectra-Physics (SP4270) Operators Manual under the dialog function in section 3.

Enter DIALOG and answer the questions as printed on the integrator output. When finished with DIALOG you are in calibrate mode. Now run each standard, in order, from the lowest concentration standard to the highest. The integrator will fit a calibration curve and retain this in its memory.

An alternate method of calibrating is to analyze each standard 2-3 times and record the peak areas. Then in calibrate mode, instead of running a standard, enter the average area of each species for the lowest concentration. This is done by typing:

- PSR(1)=2340000

where (1) is the species and 2340000 is the peak area. Continue for species 2-N and then press ’RECALC’. Repeat this procedure for all species at the next concentration, and again until you reach the highest concentration standard in the calibration curve. This can be tricky because the N in PSR(N) does not necessarily follow 1, 2, 3 ... For example, if the last run before calibration had unidentified species appear in the printout, such as the eluent peak in the first position, then you would enter PSR(2) for the first species you wish calibrated, PSR(3) for the second, etc.

To review what is contained in a file press ’PR FILE’ which prints the information stored in the integrator. See example PR FILE. One thing that might need to be changed is the peak threshold, PT. This can be changed outside of DIALOG by typing:

- PT=new #

The higher the PT value, the higher a peak needs to be above the background noise to be detected.

A note about entering items into the integrator memory. A light on the top right corner of the integrator panel has a variety of blinks. A solid light allows the bottom key function to be entered. A steady blink allows the left symbols on keys (i.e., numbers) to be entered. An irregular blink allows the right symbols (i.e., letters) to be entered. The latter two may be switched between by pressing SHIFT once, and switch back to the solid light by pressing SHIFT twice quickly.

10.2.10 Shutdown

Turn off acid flow by pressing “A OFF.” Turn off eluent flow by pressing “STOP.” Making sure the fluid flows have stopped is the most important part of the shutdown procedure.

Also turn the conductivity CELL - OFF and Auto Offset - OFF. Fold up the integrator paper and clean up the area around the IC.

Close the air valve located behind the instrument.

Sign time finished on the Dionex 2020i log sheet and note any problems on the log sheet.

10.2.11 Calculations

Concentrations in ppm of all species are printed on the integrator and should be copied to the daily sample log sheet or a lab notebook for more convenient reference. Also the integrator paper is thermal sensitive paper and degrades over time.

Convert ppm to μg/filter by multiplying by the dilution factor. The dilution factor equals the ml of H_2O added for extraction divided by the fraction of filter used. (e.g., the DF of 1/2 filter extracted in 20 ml of H_2O is 20 divided by 1/2 = 40).

Divide μg/filter values by the volume of air sampled in m^3 to arrive at $\mu g/m^3$ values for all species and samples.

10.2.12 Cleaning the columns

Temporary cleaning procedure:

Prepare a strong solution of the regular eluent being used. It should be from 20 to 200 times as concentrated as the regular eluting ion. Using the regular sample injection procedure, inject this strong eluent and run it through the separation column. The guard column should be removed and flushed separately. Repeat this procedure several times. The suppressor column and conductivity detector should be disconnected during this procedure by disconnecting the end of the column and allowing it to drain into a beaker.

Normal cleaning of a poisoned column:

Note: avoid pumping strong eluent cleaning solutions through the suppressor column and conductivity detector. Also separate the guard and anion columns and flush separately to avoid flushing contaminants from the guard column into the separator column.

Prepare a solution of 0.1 to 1 N Na_2CO_3 and fill the designated eluent cubitainer. Pump the strong eluent through the guard and separator columns for 30-40 minutes each. Replace normal strength eluent cube and pump eluent through the separator and guard columns for approximately 30 minutes each. Reconnect columns and the suppressor column. Note: water is not normally used to rinse the separator columns. It is only used to remove the previous eluent from the separator column when a second eluent is incompatible with the first.

Cleaning Dionex IC Lines:

Prepare a solution of 21 gms $NaHCO_3$ in 1 liter DI water plus 1 liter methanol. Put inlet eluent line into a beaker of cleaning solution. Remove the columns from the IC and connect the lines using unions. Pump the cleaning solution, at a high flow rate, through the lines for approximately 20 minutes. After 20 minutes, rinse the instrument with DI water for 30 minutes.

10.2.13 Common problems

After a long period of non-use the IC usually requires more time to stabilize upon start-up. Column cleaning, and flushing the column for several hours may be required if the IC has been inactive for more than a month.

No calibrated files exist on the integrator. The power has been turned off, perhaps in a routine building shutdown.

Conductivity is too high. There is probably a clog in the suppressor flow. Check the flow rate of regenerant out of the waste line. It should be approximately 3-5 ml/min. The two most common places for a clog to develop are in the prefilter to the suppressor line inside the regenerant container or at the waste line constrictor fitting.

Column pressure is too high. The prefilters to the guard column and/or the separator column may need to be changed or the inline filters may need changing. Each of the columns has a 10 μm filter inside the fitting at the the beginning of the column. Be very careful not to over tighten this fitting when changing the filters. The inline filters do not need changing very frequently, however, if changing the prefilters does not help, these too should be changed. The inline filters are located between the eluent reservoir and the guard column. There are two filters, a 35 μm followed by a 10 μm, both located back-to-back in the gray filter holder. See Dionex instruction sheets for more information on changing filters and refer to column maintenance sheets which are supplied with the columns.

Drifting baseline. Allow more time for the IC to warm-up and stabilize after insuring that the acid and eluent containers have been connected properly.

Sample won't load. Check the LOAD/INJECT button is in the LOAD position, possibly cycle the button in and out to release trapped air in the valve. Change the injection prefilter if it becomes more difficult to make injections during an IC run.

See Dionex manual for more trouble shooting information.

10.2.14 Quality control standards

Refer to the IC Daily Standards Preparation Sheet for details on how to prepare quality control standards for the IC. At least one set of quality control standards is run daily when the instrument is in use.

Table 10.1 shows standard values, means, and percent differences of analyzed daily ion analysis standards.

10.2.15 Instrument specifications

IC detection limits were determined by running progressively more dilute standards until the species could not be reliably detected by the instrument. The estimated detection limits based on extraction of samples in 10μl of distilled, deionized water are:

- sulfate 0.4 μg/filter
- nitrate 0.4 μg/filter
- chloride 0.6 μg/filter

For heavily loaded samples, sample extracts are diluted and rerun to bring the concentration within the instrument's calibrated analysis range.

Sample precision based on replicate analyses is shown in Table 10.2.

Table 10.1 Ion Analysis Standards

Standard Value (ppm)	Mean of Analyzed Standards (ppm)	Difference (ppm)	Percent Difference %	Average Sample (ppm)
Sulfate Standards:				
B-(0.174)	0.195	0.021	12.0	2.34
C-(0.349)	0.364	0.015	4.2	
D-(0.700)	0.707	0.007	1.0	
E-(0.877)	0.888	0.011	1.3	
F-(1.750)	1.768	0.018	1.0	
G-(3.500)	3.471	-0.029	0.8	
Nitrate Standards:				
B-(0.150)	.158	.008	5.3	0.74
C-(0.300)	.311	.011	3.7	
D-(0.600)	.585	-.015	2.5	
E-(0.750)	.745	-.005	0.7	
F-(1.500)	1.465	-.035	2.3	
G-(3.000)	3.021	.021	0.7	
Chloride Standards:				
B-(0.050)	.064	.014	28.0	0.16
C-(0.100)	.111	.011	11.0	
D-(0.200)	.199	-.001	0.5	
E-(0.250)	.256	.006	2.4	
F-(0.500)	.485	-.015	3.0	
G-(1.000)	.972	-.028	2.8	

Table 10.2 PRD Sample Replicate Analysis

Species	No. of Samples	Precision (μg/filter)	Average Sample (μg/filter)	Sample Range (μg/filter)
Sulfate	72	1.10	137	13 - 346
Nitrate	107	0.58	21	1.3 - 147
Chloride	51	0.19	4	0.2 - 35

Eluent Preparation Sheet
Strong Acids

Date Prepared__________

Initials ______________

100X Concentrated Carbonate Eluent

$CO_3^{=} / HCO_3^{-}$

Dionex 2020i

Species	#gm/1000ml	Actual gm
Na_2CO_3	23.32	
$NaHCO_3$	23.52	

DILUTION:

40 ml concentrate to 4000 ml DI water – Dionex 2020i

IC Daily Standards Preparation Sheet

Date:__________ Initials_____

Master Std. Conc. Date Prepared __________ Initials_______
(Stock solutions from VWR are 1000 ppm)

(10 ml) (20 ml) (30 ml) (35 ml) --> 1000 ml DI

Cl^{-} ______ NO_2^{-} ______ NO_3^{-} ______ $\mathrm{SO}_4^{=}$ ______ (ppm)

Pipet Calibrations ____________ Calibration Date __________ Initials_____
(milliliters)

0.20 __________ 0.50 __________ 2.00 __________ 5.00 __________

0.25 __________ 1.00 __________ 2.50 __________ 10.0 __________

Eluent: Date prepared 100x __________ 1x __________

Prepared by 100x __________ 1x __________

Standards	Dilution (master->vol) (milliliters)	Cl	NO2		NO3	SO4
		Calculated Concentrations (ppm)				
A	0.50 -> 200					
B	1.00 -> 200					
C	2.00 -> 200					
D	2.00 -> 100					
E	2.50 -> 100					
F	5.00 -> 100					
G	5.00 -> 50					
Retention Times						

page 1 of ___

IC SAMPLE LOG SHEET
(Strong Acids)

Date: ____________________

Initials: ________________

Sample Description____

Leaching Solution Matrix ____

Date Leached _____________________ Shaker Table Time ___________________________

IC Range __________ Sample loop size ____________

Filter ##	Sample ID	Dil. Fact.	ppm (not blank corrected)				Comments
	//////////////////		Cl	NO2	NO3	SO4	

10.3 Alpkem Rapid Flow Analyzer for Ammonium Analysis

We use the Model RFA-300 Alpkem Rapid Flow Analyzer for Ammonium ion (NH_4^+) analysis. There are a variety of other colorimetric methods, such as formaldehyde and S(IV) aldehyde adducts, which can also be run on the Alpkem. The user is referred to the Alpkem manual and application sheets.

Ammonium ion in aqueous solutions reacts with alkaline phenol and sodium hypochlorite to form a green-blue complex. An aliquot of sample is mixed by the auto-analyzer with the complexing reagent, Na_3PO_4, alkaline phenol, nitroprusside and sodium hypochlorite. The color is allowed to develop, the absorbance is measured, and the NH_4^+ concentration is calculated from a standard curve.

10.3.1 Apparatus and Materials for Ammonium Analysis

The following apparatus and materials are used to analyze teflon filters for ammonium ion by Alpkem.

ITEM	SUPPLIER	MODEL or CATALOG NO.
Alpkem Analyzer	Alpkem	RFA-300
pH tester	Cole Parmer	E-59000-62
Ammonia standard 1000ppm	VWR	34120-309
Pump tube, 74 ul/min	Alpkem	A903-1015P01
Pump tube, 118 ul/min	Alpkem	A903-1020P01
Pump tube, 226 ul/min	Alpkem	A903-1030P01
Digital stopwatch	McMaster Carr	1314T11
Volumetric flasks	Kimax	various sizes
Pipettor 1-5 ml	Cole Parmer	E-24600-25
Pipette tips	VWR	53512-350
Glass pipettes, size 5 x 1/10 ml	VWR	53283-738
Chart recorder	Omniscribe	D5000

10.3.2 Paper work

Daily paper work should be filled out to insure quality control. See attached copies of standard preparation and log sheets for examples.

10.3.3 Set up

1. Prepare reagents as outlined on the reagent preparation sheet. A 1000 ppm ammonia master standard can be purchased from the VWR stockroom (cat. no. 34120-309). Prepare the master standard substock as indicated on the daily standards log sheet. Prepare master standard substock, complexing reagent, and nitroprusside solution fresh each month, and store them in glass bottles in the refrigerator. Alkaline phenol solution should also be prepared fresh each week, but stored in an amber bottle in the refrigerator. Prepare sodium hypochlorite solution fresh daily. Suppressed peak heights may indicate that the reagents or standard are old and should be remade.

2. Replace all reagent tubing before starting each day. Also check that air and sample tubing lines are in good condition. Change the tubing when tubes appear flat.

ALPKEM TUBING FOR NH4 ANALYSIS

A - complex - black -- black - 226 UL/min

S - sample tube - black -- black - 226 UL/min

B - phenolate - orange -- yellow - 118 UL/min

C - NaOCl - orange -- yellow - 118 UL/min

D - nitropruss - green -- orange - 74 UL/min

E - wash tube - yellow -- yellow - 642 UL/min

F - air - yellow -- orange - 118 UL/min

3. Make sure correct lens filters are installed in the photometer. We use 305-1640-0885 (two of them). Install with purple side toward the light beam (toward the right as one faces the instrument.) These are only changed if analyses other than NH_4^+ have been performed with the instrument.

4. Insure that the heat bath (located under panel in front of tubing) is connected. The connections are under the mixing coils.

5. Set up the strip chart recorder to record peak heights. Using the top dial on the right hand side set the recorder to 1 Volt FULL SCALE after checking the zero. It is convenient to position the zero line along the 1" ruling of the paper to allow for negative dips. Using the dial and switches on the left side, set the chart speed to 4 inch/min ÷ 10.

   (a) Note: An integrator can be used instead of the strip chart recorder. Settings include: PH = 1; MN = 0; PT = 5000 to 10000.

   (b) Time functions include:
   (c) TT(1)=0 PM 1
   (d) TT(2)=655.35 ER 0 (Maximum setting)

6. Check the waste beaker is properly positioned under the drain tube behind the detector. Use **caution** in handling waste, WEAR GLOVES. Dispose of waste in an appropriate container located in the hood and have it removed by Safety Office.

10.3.4 Turn on

1. Place all reagent tubes in the appropriate solution and put the sample tube in a beaker of fresh DI water.

2. Turn on 304 power switch, heat bath, light source, and pump (302). All four platens must be latched for pump to start.

3. Run briefly (approx. 20-30 min) to stabilize. It takes 9 minutes for solution to go completely through the system. Verify a smooth and consistent bubble pattern through the manifold. Refer to the Alpkem manual for adjusting bubbles if the pattern is erratic.

4. Set up the photometer. See next section for appropriate settings.

5. Make up the daily standards while waiting. Refer to the daily standards preparation sheet for instructions. Note: the matrix of the standards should match the matrix of the leaching solution (e.g., water, or water + EtOH).

10.3.5 Set up the photometer

1. The two dials on the left should be set with absorbance=1, and damping=2.

2. Set the bottom part of the two dials on the right to 0.1; this adjusts the gain of the photomultiplier. If the light bulbs are weak (old), the settings below will not be obtained, and the gain may need to be set to 1.0.

3. Turn the center dial to check:

   (a) - reference beam (close to 5, slightly greater)
   (b) - sample (5.05 to 5.10)
   (c) - absorbance (0.02)
   (d) - Note: the reference and sample voltages will be off-scale for the strip chart, briefly power off the strip chart while performing the above checks.

4. Adjust reference, sample, and absorbance as necessary to fall within the above guidelines with the absorbance value being the most important. Adjust sample using top of right knob labeled sample, and adjust absorbance using top of right knob labeled reference. To view each setting while adjusting knobs the center dial must be set to the appropriate indicator. Allow 2-3 seconds between adjustments for photometer to up-date the reading.

10.3.6 Typical days run

1. Adjust the photometer settings again. This will be necessary since the instrument has warmed up and the reagents have had time to equilibrate.

2. Pour standards into cups and load them into the cup holders on the autosampler. The cup holders are numbered (1 - - - -); (6 - - - -), etc. The auto-analyzer sometimes skips the first cup, so either put in an empty cup or put an extra DI water at the beginning. Note: Currently the auto sampler is not working. Manual loading of samples is performed by dipping the sample tube needle into the sample for 20 seconds followed by 40 seconds in rinse water, repeat 20 seconds in sample; 40 seconds rinse water.

3. For the first set of standards (A through G) run 3 replicates for each. In later runs use 2 standard replicates each time.

4. Before running samples, make sure the standards are consistent and the peak heights are reasonable. Standard G should be approximately 9-10 on the strip chart.

5. Teflon samples are ready to run after extraction. (See separate section for filter extraction).

6. Each sample should be run in replicate. Place the sample needle into the solution in the sample cup for 20 seconds. Avoid touching the filter with the tip of the needle. Sample for 20 seconds, rinse water 40 seconds, re-sample 20 seconds, rinse for 40 seconds (or until ready for the next sample). **Important**: Keep careful note of each sample (or standard) on the log sheets indicating the order samples are run. If you get samples and the order mixed up you will have to start over.

7. Run approximately 10 samples followed by a standard (in replicate). Repeat this sequence until all samples are analyzed, then end the day with a full set of standards.

10.3.7 End of day

1. After the last standard of the day is run, and the peak comes out on the strip chart power off the Alpkem and the strip chart recorder.

2. Transfer all reagent tube ends into a small waste beaker. Cap the reagent bottles, and store them in the refrigerator.

3. Leave latches over rollers open so tubing is not left in a compressed state.
4. Empty waste solution into the waste bottle under the hood.

10.3.8 Calibration Curves

1. Transfer the peak height information from the strip chart onto the daily log sheets.
2. Examine the peak heights of all standards, and take an average of the entire day for each standard. Sometimes it may be necessary to break a days run up into smaller segments, for example, if there were problems with the machine and the peak heights of the standards changed significantly (due to a baseline shift, for example).
3. Fit a linear curve to the final peak ht. averages and known concentration (ppm) of standards. Using the calibration curve, calculate the concentration (ppm) of each standard. Calculated values should be within 10% for the lowest standards (A-C) and 5% for higher standards (F-G).
4. Use the final calibration curve(s) to calculate the ppm (NH_4^+) of each sample.
5. Convert calculated ppm to μg/filter by multiplying by the dilution factor. The dilution factor equals the ml of H_2O and ethanol added for extraction divided by the fraction of filter used. [i.e., the DF equals 40 if 1/2 of a filter is extracted in 20 ml (20 divided by 1/2 = 40)].
6. Divide μg/filter values by the volume of air sampled in m^3 to arrive at $\mu g\ m^{-3}$ values for all filters.

10.3.9 Reagent Preparation for the Alpkem

Follow the reagent preparation sheet for NH_4^+ analysis. Reagents should be prepared new at least every 30 days.

Use only DI water from the MilliQ dispenser in room 102 for preparing standards and insure that all glassware is thoroughly cleaned to avoid contamination. Refer to lab ware cleaning description.

A. Complexing Reagent

1. Weigh appropriate amounts of sodium tartrate and sodium citrate and add to DI water in an Erlenmeyer flask. (80% of final volume). Shake gently until dissolved.
2. Measure the pH of this solution (usually 8.6) and adjust pH to 5.0 by adding concentrated H_2SO_4 with a disposable glass pipette (approx. 1-1.5 ml).
3. Transfer solution to a volumetric flask and fill almost to the line with DI water.

4. Add 1% Brij-35 (30%) at the end because it is a surfactant, then fill to final volume with DI water.
5. Transfer to a glass bottle and store in the refrigerator. Label all reagent bottles with preparer's initials and the date prepared.

B. Other reagents

1. Alkaline Phenol - Weigh out NaOH pellets and dissolve in 2/3 of the water in a volumetric flask. Add liquid phenol and dilute to volume with DI water. Store in an amber bottle in the refrigerator. **Safety Note:** Phenol is a high risk material. Wear plastic gloves when handling. Discard waste into a waste bottle designated for phenol or organics. DO NOT POUR DOWN THE SINK - HAVE SAFETY OFFICE REMOVE WASTE.
2. Sodium Nitroprusside - Weigh out $Na_2Fe(CN)_5$ in 2/3 of the water in a volumetric flask. Shake gently to dissolve, then add DI water to dilution line. Transfer to a glass bottle and refrigerate.
3. Sodium Hypochlorite - Mix new **every** day. Only use Clorox and replace stock bottle every 30 days.

C. Wash Solution

1. Use DI water in the wash beaker when analyzing samples. Get fresh water daily and fill the beaker.

10.3.10 Quality control standards

Refer to the NH4 Analysis Daily Standards Preparation Sheet for details on how to prepare quality control standards for ammonium ion analysis. At least three sets of quality control standards are run daily when the instrument is in use.

Table 10.3 shows standard values, means, and percent differences of analyzed daily ammonium analysis standards.

Table 10.3 Ammonium Analysis Standards

Standard Value (ppm)	Mean of Analyzed Standards (ppm)	Difference (ppm)	Percent Difference %	Average Sample (ppm)
B-(0.102)	.103	.001	1.0	1.49
C-(0.204)	.211	.007	3.4	
D-(0.408)	.413	.005	1.2	
E-(0.997)	.981	-.016	1.6	
F-(1.49)	1.498	.008	0.5	
G-(2.00)	1.992	-.008	0.4	

10.3.11 Instrument specifications

Ammonium detection limits were determined by running progressively more dilute standards until the species could not be reliably detected by the instrument. The estimated detection limit based on extraction of samples in 10μl of distilled, deionized water is 0.2 μg/filter.

For heavily loaded samples, sample extracts are diluted and rerun to bring the concentration within the instrument's calibrated analysis range.

Reagent Preparation Sheet -- NH4 Analysis

Date____________________

Initials________________

	Amount Added Per Final Volume		
	250 ml	500 ml	1000 ml
A. Complexing Reagent			
1. Sodium Tartrate *2H2O	6.83 gm ______	13.66 gm ______	27.3 gm ______
2. Sodium Citrate	6.00 gm ______	12.00 gm ______	24.0 gm ______
3. Conc. H2SO4 *	* ______	* ______	* ______
4. Brij-35 (30%)	0.25 ml ______	0.5 ml ______	1.0 ml ______
	Dissolve 1. & 2. in DI water, * adjust pH to 5.0 with conc. H2SO4, dilute to volume. Add 4.		
B. Alkaline Phenol			
1. Liquid Phenol (88%)	23.5 ml ______	47.0 ml ______	94.0 ml ______
2. NaOH pellets	9.0 gm ______	18.0 gm ______	36.0 gm ______
	Dissolve NaOH in 2/3 water, add phenol, dilute to volume. Safety note: use caution when handling phenol.		
C. Sodium Hypochlorite			
1. NaOCl (Chlorox)	50.0 ml ______	Mix new daily.	
D. Sodium Nitroprusside			
1. $Na_2Fe(CN)_5$	0.125 gm ______	0.25 gm ______	0.50 gm ______
E. Wash Solution			
1. DI water			

NH4 Analysis
Daily Standards Preparation Sheet

Date:__________ Initials______

Master Std. Conc. __ 1000 __ (ppm) NH4

From VWR Stockroom: Date Opened ________

Master Substock Conc. __________ (ppm) NH4
(20 ml of conc. std into 100 ml DI water)

Date Prepared _________ Initials_______ Calib. Value 20 ml_________

Pipet Calibrations _______________ Calibration Date _______________
(milliliters)

0.05	__________	0.20	__________	0.50	__________	1.00	__________
0.10	__________	0.25	__________	0.75	__________	2.00	__________

Reagents prepared:	Date	Prepared By
NaOCl	___________	___________
Alkaline Phenol	___________	___________
Complexing Reagent	___________	___________
Nitroprusside	___________	___________

Standards	Dilution (substock->vol) (milliliters)	Dil. Fact.	Calculated Concentrations
___	____ -> ____	_____	_________
___	____ -> ____	_____	_________
A	0.05 -> 200	4000	_________
B	0.05 -> 100	2000	_________
C	0.05 -> 50	1000	_________
D	0.10 -> 50	500	_________
E	0.25 -> 50	200	_________
F	0.75 -> 100	133	_________
G	0.50 -> 50	100	_________
H	0.75 -> 50	67	_________
___	____ -> ____	_____	_________

page 1 of ____

NH4 SAMPLE LOG SHEET

Date: ____________________

Initials: ________________

Sample Description____

Leaching Solution Matrix ____

Leaching Solution Volume __________________ Calibrated on_________________

Leaching Time ______________________________ Date Leached_________________

Sample ID	Alpkem position	Dil. Fact.	Peak Height	ppm	Comments

11 LAB WARE CLEANING

Lab ware (glass and plastic) is used in the chemical analysis of trace elements and compounds. Some elements are measured in the part per billion range (ng/ml). This level of analysis requires immaculately clean lab ware, therefore, special care must be taken to prevent contamination from previous analysis, dirt, and air dust.

1. A plastic soaking tub is kept next to the sink in the lab. It is filled with tap water and 2-5% Contrad brand cleaning solution is added, (80-200 ml of Contrad per 4000 ml of water). Keep the soaking tub covered with a piece of plastic at all times to minimize dust contamination.
2. Lab ware to be cleaned should first be rinsed in tap water to remove chemicals. Caution: Hazardous chemicals should not be discarded down the drain. They should be placed in labeled waste containers and be discarded by Caltech's Safety Office.
3. Remove all tape, labels, and ink before soaking. Ink can be removed with acetone or ethanol.
4. Submerge lab ware in the soaking tub. Make sure each piece is filled with solution (i.e., no air bubbles) so all surfaces are in contact with soap solution. DO NOT soak anodized aluminum. The soap solution removes the anodized coating.
5. Soak lab ware for at least one hour, but not more than a few days.
6. Rinse each piece with tap water to remove all soap (i.e., until no bubbles remain). This usually takes about four rinses.
7. Rinse each piece with distilled/deionized water three or four times to remove all traces of tap water.
8. Place on clean kimwipe toweling to dry. Invert or cover pieces with clean kimwipes to prevent dust from settling on the lab ware.
9. When dry, store pieces in appropriate cabinets. Volumetrics should be stoppered. Beakers and other containers should be turned upside down or covered with pieces of aluminum foil to prevent contamination by dust.

12 ERROR DETERMINATION FOR ATMOSPHERIC CONCENTRATIONS

Error analysis is based on the statistical propagation of individual errors (or precisions) (Skoog and West, 1988). In this section we denote the absolute error in a quantity, y as σ'_y and the relative error as, σ^*_y. In general, these are related by

$$\sigma^*_y = \frac{\sigma'_y}{y}$$

12.1 Obtaining Precision Data

Each measured quantity in an experimental protocol has an associated precision. Precision is typically obtained by making a number, N, of repeated (replicate) measurements of the same underlying quantity. (Typically $N > 30$ for good statistics.)

1. The estimate of the value of a quantity, x, is the mean of the replicated measurements, x_i, i.e.,

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i$$

2. The absolute precision in the estimate of x is given by the standard deviation of the individual measurements:

$$\sigma'_x = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N-1}}$$

When $N = 2$, i.e., when the same quantity has been measured exactly twice, the above formulas simplify to:

$$\bar{x} = \frac{x_1 + x_2}{2}$$

$$\sigma_x{}' = \frac{|x_1 - x_2|}{\sqrt{2}}$$

12.2 Propagation of errors in formulas

1. For a sum or difference (e.g., y = a + b - c ...), the absolute error is the square root of the sum of the squares of the individual absolute errors:

$$\sigma'_y = \sqrt{\sigma'^{\,2}_a + \sigma'^{\,2}_b + \sigma'^{\,2}_c \ldots}$$

$$\sigma^*_y = \frac{\sqrt{\sigma'^{\,2}_a + \sigma'^{\,2}_b + \sigma'^{\,2}_c \ldots}}{y}$$

2. For a product or quotient (e.g., $y = \frac{ab}{c}$) the relative error is the square root of the sum of the squares of the individual relative errors:

$$\sigma'_y = y \times \sqrt{\left(\frac{\sigma'_a}{a}\right)^2 + \left(\frac{\sigma'_b}{b}\right)^2 + \left(\frac{\sigma'_c}{c}\right)^2}$$

$$\sigma^*_y = \sqrt{\sigma^{*2}_a + \sigma^{*2}_b + \sigma^{*2}_c \ldots}$$

3. A general example

   For the case of blank correcting a measured concentration (A - B), multiplying by the dilution factor (C), and dividing by the volume (D), each of which has an associated absolute precision.

$$y = \frac{(A - B)C}{D}$$

   (a) Calculate the relative error of the difference in the numerator:

$$M = A - B$$

$$\sigma_M^* = \frac{\sigma'_M}{M} = \frac{\sqrt{{\sigma'_A}^2 + {\sigma'_B}^2}}{M}$$

   (b) Then the result, y, is a product, whose absolute error is:

$$y = \frac{MC}{D}$$

$$\sigma'_y = y \times \sigma_y^* = y\sqrt{\left(\frac{\sigma'_M}{M}\right)^2 + \left(\frac{\sigma'_C}{C}\right)^2 + \left(\frac{\sigma'_D}{D}\right)^2}$$

   Report $y \pm \sigma'_y$.

12.3 Example: Error Analysis for Atmospheric Concentrations

Atmospheric concentration measurements typically use ’field blanks’, i.e., samples which are handled and stored according to the same protocols as ’normal’ samples, but which are not exposed to the actual measurement process. These blanks allow one to account for background processes that would otherwise lead to systematic errors.

If the measurement of a filter blank is less than the instrument detection limit (IDL), no blank correction is necessary.

If the filter blank is detectable (i.e., greater than the IDL), then blank correction is necessary and the filter detection limit is 2 times the error in the average blank (σ_b).

The fundamental measurements for the sample in this example consist of initial and final weights, wt_i and wt_f, a blank correction, B, the sampling duration t, and the flow rate Q. Each of these quantities has an absolute precision, σ'_x, obtained from a number of independent replicated measurements.

The volume of air sampled is given by:

$$v = t \times Q$$

with

$$\sigma_v^* = \sqrt{\left(\frac{\sigma'_t}{t}\right)^2 + \left(\frac{\sigma'_Q}{Q}\right)^2}$$

Then the atmospheric concentration is given by:

$$C_{atmos} = \frac{\Delta M}{v}$$

where

$$\Delta M = (wt_f - wt_i) - B$$

$$\sigma'_{atmos} = C_{atmos} \times \sigma^*_{atmos} = C_{atmos}\sqrt{\frac{(\sigma'_{wt_i})^2 + (\sigma'_{wt_f})^2 + (\sigma'_B)^2}{(\Delta M)^2} + (\sigma^*_v)^2}$$

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Appendix C – Mass and Carbon Data in μg m^{-3}

Site	Date	Mass	Organics (OC *1.4)	Elemental Carbon
CH6	20021002	25.57 ± 0.66	10.18 ± 0.73	1.16 ± 0.20
CH6	20021008	35.19 ± 0.88	11.56 ± 0.85	1.40 ± 0.25
CH6	20021014	50.19 ± 0.94	18.10 ± 1.18	1.93 ± 0.23
CH6	20021020	37.00 ± 0.78	12.94 ± 0.88	1.93 ± 0.23
CH6	20021026	28.76 ± 0.69	9.18 ± 0.67	1.12 ± 0.19
CH6	20021201	18.10 ± 0.88	8.61 ± 0.63	1.68 ± 0.21
CH6	20021207	32.27 ± 0.97	9.84 ± 0.70	1.59 ± 0.21
CH6	20021213	26.60 ± 0.93	10.68 ± 0.74	1.35 ± 0.20
CH6	20021219	46.27 ± 1.10	19.43 ± 1.25	2.02 ± 0.23
CH6	20021225	18.16 ± 0.88	6.09 ± 0.49	0.77 ± 0.17
CH6	20030301	68.47 ± 1.26	23.27 ± 1.47	2.18 ± 0.25
CH6	20030307	26.05 ± 1.03	8.90 ± 0.73	0.58 ± 0.24
CH6	20030313	71.44 ± 1.30	23.97 ± 1.51	2.15 ± 0.25
CH6	20030319	no data	no data	no data
CH6	20030325	36.59 ± 0.88	11.51 ± 0.81	1.13 ± 0.20
CH6	20030605	80.19 ± 1.61	26.18 ± 1.62	1.91 ± 0.23
CH6	20030611	29.37 ± 1.12	8.27 ± 0.62	1.26 ± 0.20
CH6	20030617	27.11 ± 1.10	9.60 ± 0.69	0.72 ± 0.17
CH6	20030623	23.60 ± 1.08	7.25 ± 0.56	0.97 ± 0.19
CH6	20030629	18.61 ± 1.06	5.47 ± 0.46	0.95 ± 0.18
CW3	20021002	34.52 ± 0.88	10.12 ± 0.71	4.34 ± 0.35
CW3	20021008	46.81 ± 1.01	16.35 ± 1.06	2.21 ± 0.23
CW3	20021014	19.03 ± 0.76	4.97 ± 0.42	1.23 ± 0.19
CW3	20021020	13.07 ± 0.73	2.18 ± 0.27	0.75 ± 0.16
CW3	20021026	37.27 ± 0.91	11.44 ± 0.78	1.47 ± 0.20
CW3	20021201	36.76 ± 1.27	8.40 ± 0.62	1.45 ± 0.20
CW3	20021207	32.44 ± 1.24	11.31 ± 0.78	2.70 ± 0.26
CW3	20021213	34.22 ± 1.25	10.63 ± 0.74	2.39 ± 0.25
CW3	20021219	51.46 ± 1.39	13.55 ± 0.91	3.23 ± 0.29
CW3	20021225	33.72 ± 1.25	11.17 ± 0.77	2.39 ± 0.25
CW3	20030301	40.09 ± 1.05	11.38 ± 0.78	3.05 ± 0.28
CW3	20030307	30.93 ± 0.97	11.12 ± 0.77	2.16 ± 0.24
CW3	20030313	35.50 ± 1.01	8.90 ± 0.64	1.07 ± 0.18
CW3	20030319	34.65 ± 1.00	8.55 ± 0.63	0.90 ± 0.18
CW3	20030325	55.77 ± 1.21	12.38 ± 0.84	2.08 ± 0.23
CW3	20030605	52.86 ± 1.56	9.62 ± 0.69	1.24 ± 0.19
CW3	20030611	20.15 ± 1.37	3.86 ± 0.36	2.35 ± 0.24
CW3	20030617	55.24 ± 1.58	15.78 ± 1.02	2.02 ± 0.23
CW3	20030623	13.58 ± 1.35	2.04 ± 0.27	0.66 ± 0.16
CW3	20030629	8.22 ± 1.34	1.50 ± 0.24	0.46 ± 0.15
GZ5	20021002	84.76 ± 1.50	41.71 ± 2.49	4.49 ± 0.35
GZ5	20021008	54.49 ± 1.10	21.53 ± 1.34	4.35 ± 0.34
GZ5	20021014	102.46 ± 1.74	44.94 ± 2.67	5.99 ± 0.43
GZ5	20021020	43.06 ± 0.97	14.25 ± 0.94	3.53 ± 0.30
GZ5	20021026	46.43 ± 1.01	18.90 ± 1.20	4.84 ± 0.37

Site	Date	Mass	Organics (OC *1.4)	Elemental Carbon
GZ5	20021201	100.69 ± 1.94	45.58 ± 2.70	6.55 ± 0.46
GZ5	20021207	84.63 ± 1.74	27.54 ± 1.68	3.92 ± 0.32
GZ5	20021213	49.80 ± 1.38	19.39 ± 1.22	5.91 ± 0.43
GZ5	20021219	96.17 ± 1.88	31.33 ± 1.90	7.28 ± 0.50
GZ5	20021225	30.76 ± 1.24	11.13 ± 0.76	2.83 ± 0.26
GZ5	20030301	84.49 ± 1.57	24.25 ± 1.50	4.29 ± 0.34
GZ5	20030307	41.75 ± 1.08	13.55 ± 0.90	2.45 ± 0.24
GZ5	20030313	116.25 ± 2.01	34.71 ± 2.10	4.66 ± 0.36
GZ5	20030319	32.63 ± 1.00	9.02 ± 0.64	2.71 ± 0.26
GZ5	20030325	122.06 ± 2.08	37.42 ± 2.25	8.35 ± 0.57
GZ5	20030605	74.95 ± 1.76	21.01 ± 1.32	1.69 ± 0.20
GZ5	20030611	77.76 ± 1.79	22.57 ± 1.40	3.02 ± 0.27
GZ5	20030617	98.59 ± 2.02	29.85 ± 1.82	3.16 ± 0.28
GZ5	20030623	44.11 ± 1.48	14.07 ± 0.92	4.83 ± 0.37
GZ5	20030629	25.97 ± 1.38	9.51 ± 0.67	2.54 ± 0.25
SZ4	20021002	55.95 ± 1.11	26.95 ± 1.67	5.34 ± 0.41
SZ4	20021008	69.83 ± 1.29	28.31 ± 1.75	5.42 ± 0.41
SZ4	20021014	26.17 ± 0.80	10.19 ± 0.73	3.27 ± 0.30
SZ4	20021020	17.98 ± 0.75	4.09 ± 0.38	2.25 ± 0.24
SZ4	20021026	43.88 ± 0.97	17.00 ± 1.11	4.02 ± 0.34
SZ4	20021201	34.05 ± 1.25	8.30 ± 0.62	1.52 ± 0.21
SZ4	20021207	30.14 ± 1.22	10.25 ± 0.73	3.92 ± 0.33
SZ4	20021213	59.74 ± 3.44	22.11 ± 1.68	5.46 ± 0.66
SZ4	20021221	70.29 ± 3.64	26.05 ± 1.92	10.73 ± 0.95
SZ4	20021225	39.68 ± 1.29	13.89 ± 0.92	2.93 ± 0.28
SZ4	20030102	94.19 ± 1.85	27.93 ± 1.72	4.78 ± 0.38
SZ4	20030301	53.13 ± 1.19	14.90 ± 0.99	2.75 ± 0.28
SZ4	20030307	40.17 ± 1.06	13.16 ± 0.90	2.19 ± 0.25
SZ4	20030313	56.78 ± 1.23	18.33 ± 1.19	5.16 ± 0.41
SZ4	20030319	50.42 ± 1.16	16.84 ± 1.11	3.89 ± 0.34
SZ4	20030325	72.57 ± 1.42	21.83 ± 1.39	5.80 ± 0.44
SZ4	20030605	59.41 ± 1.61	13.03 ± 0.88	1.51 ± 0.21
SZ4	20030611	33.90 ± 1.42	11.00 ± 0.77	6.26 ± 0.46
SZ4	20030617	57.16 ± 1.59	16.56 ± 1.08	2.27 ± 0.24
SZ4	20030623	12.89 ± 1.33	3.56 ± 0.35	1.35 ± 0.20
SZ4	20030629	11.38 ± 1.33	2.34 ± 0.29	0.94 ± 0.18
TC2	20021002	35.48 ± 0.87	13.94 ± 0.92	3.59 ± 0.31
TC2	20021008	43.96 ± 0.96	15.48 ± 1.01	2.58 ± 0.25
TC2	20021014	20.81 ± 0.75	8.33 ± 0.60	0.96 ± 0.17
TC2	20021020	9.26 ± 0.69	1.72 ± 0.25	0.86 ± 0.17
TC2	20021026	36.15 ± 0.88	13.29 ± 0.88	2.13 ± 0.23
TC2	20021201	29.33 ± 1.20	6.29 ± 0.49	1.24 ± 0.18
TC2	20021207	15.52 ± 1.13	3.61 ± 0.34	2.48 ± 0.24
TC2	20021213	37.26 ± 1.25	13.52 ± 0.90	2.93 ± 0.27
TC2	20021219	37.76 ± 1.25	10.88 ± 0.74	2.70 ± 0.25
TC2	20021225	36.09 ± 1.24	12.95 ± 0.87	3.47 ± 0.30
TC2	20030301	34.84 ± 1.01	7.06 ± 0.53	2.06 ± 0.23
TC2	20030307	40.60 ± 1.07	11.90 ± 0.81	1.90 ± 0.22
TC2	20030313	33.46 ± 1.00	7.48 ± 0.56	1.65 ± 0.21

Site	Date	Mass	Organics (OC *1.4)	Elemental Carbon
TC2	20030319	45.87 ± 1.12	10.63 ± 0.74	2.09 ± 0.23
TC2	20030325	44.84 ± 1.11	11.09 ± 0.76	2.98 ± 0.27
TC2	20030605	58.34 ± 1.61	9.39 ± 0.66	1.08 ± 0.18
TC2	20030611	13.63 ± 1.35	2.67 ± 0.29	2.21 ± 0.23
TC2	20030617	55.75 ± 1.59	13.75 ± 0.91	2.24 ± 0.23
TC2	20030623	11.89 ± 1.34	1.40 ± 0.22	0.40 ± 0.15
TC2	20030629	8.92 ± 1.34	1.19 ± 0.21	0.24 ± 0.14
TM1	20021002	24.78 ± 0.81	8.55 ± 0.63	0.97 ± 0.18
TM1	20021008	48.63 ± 1.03	15.72 ± 1.04	1.80 ± 0.22
TM1	20021014	15.78 ± 0.75	2.87 ± 0.32	0.37 ± 0.16
TM1	20021020	10.85 ± 0.73	3.37 ± 0.34	0.41 ± 0.16
TM1	20021026	29.06 ± 0.84	9.70 ± 0.69	0.89 ± 0.18
TM1	20021201	31.65 ± 1.23	6.45 ± 0.50	0.99 ± 0.18
TM1	20021207	23.12 ± 1.19	4.00 ± 0.38	0.41 ± 0.16
TM1	20021213	31.49 ± 1.23	8.95 ± 0.64	1.60 ± 0.21
TM1	20021219	44.65 ± 1.33	10.00 ± 0.70	1.29 ± 0.19
TM1	20021225	30.62 ± 1.23	9.34 ± 0.67	1.27 ± 0.19
TM1	20030301	29.94 ± 0.99	3.95 ± 0.38	0.40 ± 0.16
TM1	20030307	20.40 ± 0.93	5.85 ± 0.48	0.50 ± 0.16
TM1	20030313	32.88 ± 1.01	5.63 ± 0.46	0.64 ± 0.17
TM1	20030319	27.30 ± 0.97	6.71 ± 0.53	0.74 ± 0.17
TM1	20030325	53.94 ± 1.21	11.41 ± 0.78	1.17 ± 0.19
TM1	20030605	44.13 ± 1.49	7.31 ± 0.56	0.54 ± 0.16
TM1	20030611	11.67 ± 1.34	2.28 ± 0.28	0.98 ± 0.18
TM1	20030617	47.00 ± 1.52	12.39 ± 0.84	1.21 ± 0.19
TM1	20030623	10.75 ± 1.34	1.30 ± 0.24	0.10 ± 0.14
TM1	20030629	6.18 ± 1.33	1.36 ± 0.24	0.15 ± 0.15
ZS7	20021002	no data	no data	no data
ZS7	20021008	79.55 ± 1.35	30.41 ± 1.85	3.21 ± 0.28
ZS7	20021014	43.92 ± 0.87	21.74 ± 1.36	2.51 ± 0.25
ZS7	20021020	13.95 ± 0.58	4.96 ± 0.42	1.72 ± 0.21
ZS7	20021026	32.29 ± 0.74	8.15 ± 0.59	0.97 ± 0.17
ZS7	20021201	62.12 ± 1.29	22.22 ± 1.39	3.85 ± 0.32
ZS7	20021207	30.87 ± 0.98	9.66 ± 0.67	2.56 ± 0.25
ZS7	20021213	69.89 ± 1.38	32.51 ± 1.97	4.46 ± 0.35
ZS7	20021219	78.64 ± 1.49	23.56 ± 1.46	4.87 ± 0.37
ZS7	20021225	50.82 ± 1.16	18.09 ± 1.15	3.99 ± 0.32
ZS7	20030301	44.98 ± 0.97	12.57 ± 0.85	1.71 ± 0.22
ZS7	20030307	41.96 ± 0.94	14.15 ± 0.95	1.65 ± 0.22
ZS7	20030313	51.42 ± 1.05	17.56 ± 1.13	3.34 ± 0.31
ZS7	20030319	57.35 ± 1.12	11.56 ± 0.80	1.92 ± 0.23
ZS7	20030325	81.40 ± 1.44	23.25 ± 1.46	3.76 ± 0.33
ZS7	20030605	52.65 ± 1.34	8.46 ± 0.62	1.29 ± 0.19
ZS7	20030611	15.93 ± 1.09	4.00 ± 0.36	2.12 ± 0.23
ZS7	20030617	55.22 ± 1.37	12.29 ± 0.83	1.43 ± 0.20
ZS7	20030623	10.74 ± 1.09	2.66 ± 0.29	1.18 ± 0.19
ZS7	20030629	9.49 ± 1.07	1.60 ± 0.24	0.97 ± 0.17

Appendix D – Ions Data in μg m^{-3}

Site	Date	Chloride	Nitrate	Sulfate	Ammonium
CH6	20021002	0.02 ± 0.04	0.19 ± 0.04	6.95 ± 0.22	1.75 ± 0.05
CH6	20021008	0.20 ± 0.05	0.47 ± 0.05	7.92 ± 0.35	2.36 ± 0.08
CH6	20021014	0.05 ± 0.10	0.23 ± 0.05	13.31 ± 1.01	2.61 ± 0.09
CH6	20021020	0.01 ± 0.04	0.20 ± 0.04	12.11 ± 1.02	2.46 ± 0.16
CH6	20021026	0.06 ± 0.04	0.36 ± 0.04	8.66 ± 0.30	1.93 ± 0.06
CH6	20021201	0.05 ± 0.04	0.22 ± 0.04	2.34 ± 0.18	0.62 ± 0.04
CH6	20021207	0.05 ± 0.04	0.22 ± 0.04	10.84 ± 0.92	2.32 ± 0.14
CH6	20021213	0.02 ± 0.04	0.33 ± 0.04	6.86 ± 0.22	1.49 ± 0.11
CH6	20021219	0.01 ± 0.04	0.32 ± 0.04	11.28 ± 0.36	2.51 ± 0.17
CH6	20021225	0.00 ± 0.03	0.05 ± 0.04	7.27 ± 0.70	1.77 ± 0.11
CH6	20030301	0.12 ± 0.05	0.65 ± 0.05	22.11 ± 1.57	4.98 ± 0.18
CH6	20030307	0.01 ± 0.05	0.11 ± 0.06	9.01 ± 0.27	2.22 ± 0.07
CH6	20030313	0.04 ± 0.05	0.67 ± 0.05	18.21 ± 1.47	3.29 ± 0.22
CH6	20030319	no data	no data	no data	no data
CH6	20030325	0.02 ± 0.04	0.88 ± 0.05	8.99 ± 0.32	2.00 ± 0.07
CH6	20030605	0.02 ± 0.05	0.44 ± 0.05	23.02 ± 1.64	5.63 ± 0.26
CH6	20030611	0.00 ± 0.03	0.13 ± 0.04	8.04 ± 0.29	1.82 ± 0.06
CH6	20030617	0.01 ± 0.04	0.06 ± 0.04	6.97 ± 0.28	1.81 ± 0.06
CH6	20030623	0.02 ± 0.04	0.32 ± 0.04	8.14 ± 0.69	1.67 ± 0.08
CH6	20030629	0.05 ± 0.04	0.37 ± 0.04	6.14 ± 0.21	1.52 ± 0.05
CW3	20021002	0.02 ± 0.05	0.42 ± 0.05	8.36 ± 0.28	1.58 ± 0.06
CW3	20021008	0.09 ± 0.05	0.75 ± 0.06	10.02 ± 0.37	2.47 ± 0.08
CW3	20021014	0.49 ± 0.09	1.50 ± 0.10	5.46 ± 0.24	1.16 ± 0.05
CW3	20021020	0.00 ± 0.04	0.18 ± 0.05	5.99 ± 0.25	1.98 ± 0.06
CW3	20021026	0.05 ± 0.05	0.65 ± 0.06	11.20 ± 0.39	3.87 ± 0.11
CW3	20021201	0.71 ± 0.05	1.80 ± 0.07	11.22 ± 0.94	3.19 ± 0.15
CW3	20021207	0.11 ± 0.05	1.42 ± 0.07	9.85 ± 0.92	2.45 ± 0.14
CW3	20021213	0.10 ± 0.05	1.09 ± 0.07	8.19 ± 0.28	1.96 ± 0.14
CW3	20021219	0.25 ± 0.05	2.44 ± 0.09	15.98 ± 1.36	4.04 ± 0.21
CW3	20021225	0.06 ± 0.05	1.00 ± 0.07	9.02 ± 0.29	2.24 ± 0.14
CW3	20030301	0.13 ± 0.05	1.23 ± 0.06	12.29 ± 0.41	2.97 ± 0.14
CW3	20030307	0.04 ± 0.05	1.19 ± 0.07	6.87 ± 0.27	2.41 ± 0.07
CW3	20030313	0.25 ± 0.05	1.82 ± 0.08	8.06 ± 0.28	2.75 ± 0.09
CW3	20030319	0.07 ± 0.05	1.54 ± 0.08	9.12 ± 0.37	2.64 ± 0.09
CW3	20030325	0.09 ± 0.05	2.02 ± 0.08	13.39 ± 0.42	3.69 ± 0.15
CW3	20030605	0.03 ± 0.05	0.22 ± 0.05	16.94 ± 1.32	3.85 ± 0.15
CW3	20030611	0.32 ± 0.05	0.33 ± 0.05	2.34 ± 0.23	0.56 ± 0.05
CW3	20030617	0.01 ± 0.05	0.25 ± 0.05	17.06 ± 1.32	4.33 ± 0.16
CW3	20030623	0.23 ± 0.05	0.30 ± 0.05	2.65 ± 0.23	0.64 ± 0.05
CW3	20030629	0.31 ± 0.05	0.32 ± 0.05	1.67 ± 0.08	0.39 ± 0.04
GZ5	20021002	0.29 ± 0.06	4.83 ± 0.17	15.39 ± 0.52	4.36 ± 0.13
GZ5	20021008	0.09 ± 0.05	0.97 ± 0.06	11.08 ± 0.39	2.91 ± 0.09
GZ5	20021014	0.17 ± 0.06	2.55 ± 0.11	22.57 ± 1.75	4.21 ± 0.27
GZ5	20021020	0.39 ± 0.05	0.76 ± 0.06	10.42 ± 0.38	2.96 ± 0.09
GZ5	20021026	0.05 ± 0.05	0.49 ± 0.06	11.38 ± 0.39	3.75 ± 0.10
GZ5	20021201	3.02 ± 0.19	4.10 ± 0.13	13.06 ± 0.52	4.73 ± 0.29

Site	Date	Chloride	Nitrate	Sulfate	Ammonium
GZ5	20021207	1.57 ± 0.07	7.43 ± 0.22	19.00 ± 0.60	5.94 ± 0.30
GZ5	20021213	0.31 ± 0.05	2.36 ± 0.09	9.22 ± 0.37	2.31 ± 0.20
GZ5	20021219	2.77 ± 0.19	9.00 ± 0.31	20.24 ± 1.89	7.62 ± 0.32
GZ5	20021225	0.08 ± 0.05	1.02 ± 0.07	8.50 ± 0.29	2.09 ± 0.19
GZ5	20030301	0.91 ± 0.06	5.80 ± 0.20	23.24 ± 0.81	6.51 ± 0.23
GZ5	20030307	0.18 ± 0.05	1.54 ± 0.09	10.98 ± 0.52	3.76 ± 0.11
GZ5	20030313	1.06 ± 0.07	13.43 ± 0.40	21.30 ± 0.61	7.46 ± 0.39
GZ5	20030319	0.50 ± 0.05	4.17 ± 0.15	5.48 ± 0.25	2.73 ± 0.08
GZ5	20030325	0.51 ± 0.07	10.70 ± 0.29	20.47 ± 0.64	8.76 ± 0.57
GZ5	20030605	0.03 ± 0.06	0.81 ± 0.06	20.91 ± 1.79	6.97 ± 0.23
GZ5	20030611	1.08 ± 0.06	3.86 ± 0.12	14.13 ± 0.43	3.70 ± 0.19
GZ5	20030617	1.06 ± 0.06	5.01 ± 0.16	22.58 ± 1.31	6.03 ± 0.22
GZ5	20030623	0.39 ± 0.05	0.87 ± 0.06	9.04 ± 0.36	2.02 ± 0.08
GZ5	20030629	0.12 ± 0.05	0.41 ± 0.05	5.20 ± 0.24	1.33 ± 0.05
SZ4	20021002	0.68 ± 0.18	2.44 ± 0.18	9.68 ± 0.49	2.35 ± 0.08
SZ4	20021008	0.23 ± 0.06	1.34 ± 0.07	13.17 ± 0.49	4.21 ± 0.12
SZ4	20021014	0.03 ± 0.05	0.48 ± 0.05	5.58 ± 0.45	0.88 ± 0.05
SZ4	20021020	0.03 ± 0.05	0.36 ± 0.05	5.29 ± 0.24	1.71 ± 0.06
SZ4	20021026	0.08 ± 0.05	0.54 ± 0.05	10.16 ± 0.37	3.25 ± 0.10
SZ4	20021201	0.58 ± 0.05	2.07 ± 0.10	11.05 ± 0.94	3.25 ± 0.12
SZ4	20021207	0.30 ± 0.05	1.19 ± 0.07	7.92 ± 0.28	2.71 ± 0.08
SZ4	20021213	0.35 ± 0.14	4.25 ± 0.22	9.84 ± 0.71	3.98 ± 0.16
SZ4	20021221	1.05 ± 0.14	4.71 ± 0.24	8.18 ± 0.74	4.07 ± 0.17
SZ4	20021225	0.22 ± 0.05	1.97 ± 0.08	9.30 ± 0.32	2.60 ± 0.16
SZ4	20030102	1.08 ± 0.06	6.78 ± 0.24	24.53 ± 0.84	7.17 ± 0.39
SZ4	20030301	0.28 ± 0.05	3.42 ± 0.16	15.47 ± 0.58	4.22 ± 0.16
SZ4	20030307	0.26 ± 0.05	2.87 ± 0.10	8.43 ± 0.36	3.39 ± 0.10
SZ4	20030313	0.55 ± 0.06	3.43 ± 0.14	9.30 ± 0.38	3.66 ± 0.10
SZ4	20030319	0.95 ± 0.06	3.87 ± 0.12	7.37 ± 0.27	3.63 ± 0.10
SZ4	20030325	0.40 ± 0.06	4.49 ± 0.14	12.23 ± 0.38	4.65 ± 0.13
SZ4	20030605	0.21 ± 0.05	1.39 ± 0.08	16.76 ± 0.97	4.46 ± 0.16
SZ4	20030611	0.21 ± 0.05	1.23 ± 0.06	3.82 ± 0.24	1.02 ± 0.07
SZ4	20030617	0.01 ± 0.05	0.85 ± 0.06	16.67 ± 0.96	4.34 ± 0.16
SZ4	20030623	0.21 ± 0.05	0.45 ± 0.05	2.46 ± 0.23	0.68 ± 0.05
SZ4	20030629	0.30 ± 0.04	0.44 ± 0.05	1.74 ± 0.07	0.43 ± 0.04
TC2	20021002	0.00 ± 0.03	0.23 ± 0.05	8.92 ± 0.35	2.45 ± 0.08
TC2	20021008	0.09 ± 0.05	0.74 ± 0.05	9.82 ± 0.36	3.04 ± 0.09
TC2	20021014	0.13 ± 0.05	1.10 ± 0.07	5.33 ± 0.24	1.12 ± 0.05
TC2	20021020	0.00 ± 0.03	0.18 ± 0.05	4.00 ± 0.23	1.29 ± 0.05
TC2	20021026	0.02 ± 0.05	0.26 ± 0.05	11.24 ± 0.39	3.55 ± 0.10
TC2	20021201	0.12 ± 0.05	0.75 ± 0.05	11.39 ± 0.92	3.47 ± 0.12
TC2	20021207	0.09 ± 0.05	0.54 ± 0.05	3.61 ± 0.16	1.12 ± 0.05
TC2	20021213	0.11 ± 0.05	1.51 ± 0.08	7.93 ± 0.33	2.45 ± 0.19
TC2	20021219	0.02 ± 0.05	0.65 ± 0.05	13.60 ± 1.19	3.20 ± 0.19
TC2	20021225	0.08 ± 0.05	1.72 ± 0.07	8.91 ± 0.29	2.42 ± 0.14
TC2	20030301	0.00 ± 0.04	0.37 ± 0.05	13.23 ± 0.43	3.28 ± 0.10
TC2	20030307	0.12 ± 0.05	2.74 ± 0.11	10.16 ± 0.38	3.58 ± 0.10
TC2	20030313	0.05 ± 0.05	1.09 ± 0.07	7.99 ± 0.24	2.00 ± 0.06
TC2	20030319	0.19 ± 0.05	2.64 ± 0.10	9.66 ± 0.38	3.66 ± 0.10

Site	Date	Chloride	Nitrate	Sulfate	Ammonium
TC2	20030325	0.02 ± 0.05	0.35 ± 0.06	11.84 ± 0.34	3.15 ± 0.10
TC2	20030605	0.00 ± 0.04	0.15 ± 0.05	19.15 ± 0.53	4.05 ± 0.15
TC2	20030611	0.16 ± 0.05	0.23 ± 0.05	1.05 ± 0.07	0.39 ± 0.04
TC2	20030617	0.00 ± 0.05	0.10 ± 0.05	19.07 ± 1.65	4.26 ± 0.16
TC2	20030623	0.26 ± 0.05	0.29 ± 0.05	2.27 ± 0.23	0.63 ± 0.05
TC2	20030629	0.34 ± 0.05	0.35 ± 0.05	1.58 ± 0.08	0.35 ± 0.04
TM1	20021002	0.00 ± 0.04	0.18 ± 0.05	7.96 ± 0.28	1.74 ± 0.06
TM1	20021008	0.03 ± 0.05	0.54 ± 0.06	12.01 ± 0.41	3.76 ± 0.10
TM1	20021014	0.55 ± 0.09	0.90 ± 0.05	5.40 ± 0.25	1.27 ± 0.05
TM1	20021020	0.01 ± 0.05	0.21 ± 0.05	4.47 ± 0.24	1.40 ± 0.05
TM1	20021026	0.02 ± 0.05	0.27 ± 0.05	11.22 ± 0.93	2.44 ± 0.14
TM1	20021201	0.19 ± 0.05	0.69 ± 0.05	11.51 ± 0.94	2.61 ± 0.15
TM1	20021207	0.02 ± 0.05	0.15 ± 0.05	9.52 ± 0.30	2.21 ± 0.14
TM1	20021213	0.09 ± 0.05	0.63 ± 0.05	8.47 ± 0.29	1.95 ± 0.14
TM1	20021219	0.03 ± 0.05	0.38 ± 0.05	17.15 ± 1.23	3.80 ± 0.19
TM1	20021225	0.02 ± 0.05	0.44 ± 0.05	9.37 ± 0.30	2.11 ± 0.18
TM1	20030301	0.02 ± 0.05	0.20 ± 0.05	13.19 ± 1.00	3.01 ± 0.12
TM1	20030307	0.02 ± 0.05	0.30 ± 0.05	6.77 ± 0.28	2.15 ± 0.07
TM1	20030313	0.15 ± 0.05	1.00 ± 0.07	7.64 ± 0.28	2.23 ± 0.07
TM1	20030319	0.05 ± 0.05	0.89 ± 0.07	6.90 ± 0.27	1.92 ± 0.06
TM1	20030325	0.01 ± 0.05	0.83 ± 0.06	16.03 ± 1.38	5.21 ± 0.29
TM1	20030605	0.01 ± 0.05	0.17 ± 0.05	15.13 ± 0.56	3.36 ± 0.10
TM1	20030611	0.19 ± 0.05	0.26 ± 0.05	1.41 ± 0.08	0.32 ± 0.04
TM1	20030617	0.02 ± 0.05	0.22 ± 0.05	15.08 ± 1.32	3.58 ± 0.15
TM1	20030623	0.16 ± 0.04	0.27 ± 0.05	2.60 ± 0.17	0.75 ± 0.05
TM1	20030629	0.28 ± 0.05	0.39 ± 0.05	1.73 ± 0.08	0.43 ± 0.04
ZS7	20021002	no data	no data	no data	no data
ZS7	20021008	0.25 ± 0.04	1.46 ± 0.08	17.91 ± 1.34	3.15 ± 0.20
ZS7	20021014	0.06 ± 0.04	0.51 ± 0.04	10.41 ± 0.99	2.22 ± 0.11
ZS7	20021020	0.00 ± 0.03	0.17 ± 0.04	5.07 ± 0.20	1.76 ± 0.05
ZS7	20021026	0.07 ± 0.04	0.59 ± 0.04	13.52 ± 1.02	3.04 ± 0.16
ZS7	20021201	0.92 ± 0.05	2.28 ± 0.09	15.20 ± 1.38	4.38 ± 0.22
ZS7	20021207	0.19 ± 0.04	0.70 ± 0.04	9.00 ± 0.28	2.31 ± 0.14
ZS7	20021213	0.44 ± 0.05	4.44 ± 0.15	13.69 ± 0.44	3.63 ± 0.22
ZS7	20021219	0.88 ± 0.05	4.50 ± 0.15	19.86 ± 1.40	5.51 ± 0.23
ZS7	20021225	0.72 ± 0.04	2.45 ± 0.10	10.85 ± 1.03	4.09 ± 0.22
ZS7	20030301	0.06 ± 0.04	0.67 ± 0.05	15.58 ± 0.50	3.58 ± 0.13
ZS7	20030307	0.25 ± 0.04	2.22 ± 0.08	10.69 ± 0.35	2.97 ± 0.16
ZS7	20030313	0.21 ± 0.04	1.81 ± 0.07	12.23 ± 1.06	3.23 ± 0.09
ZS7	20030319	1.62 ± 0.06	4.78 ± 0.16	11.46 ± 0.42	4.16 ± 0.23
ZS7	20030325	0.25 ± 0.05	5.67 ± 0.15	15.70 ± 1.04	5.10 ± 0.24
ZS7	20030605	0.01 ± 0.04	0.12 ± 0.04	17.87 ± 1.56	5.88 ± 0.16
ZS7	20030611	0.08 ± 0.04	0.35 ± 0.04	1.92 ± 0.18	0.60 ± 0.04
ZS7	20030617	0.04 ± 0.04	0.15 ± 0.04	20.18 ± 1.17	4.71 ± 0.14
ZS7	20030623	0.04 ± 0.04	0.44 ± 0.04	3.24 ± 0.12	0.98 ± 0.04
ZS7	20030629	0.19 ± 0.04	0.58 ± 0.04	2.15 ± 0.18	0.39 ± 0.04

Appendix E.1 – Metals Data from X-Ray Fluorescence in μg m^{-3}

Site	Date	Aluminum	Silicon	Sulfur	Potassium	Calcium
CH6	021002	.1486 ± .0125	.4731 ± .0094	2.7330 ± .0145	1.3265 ± .0097	.1462 ± .0075
CH6	021008	.4184 ± .0210	1.2628 ± .0164	3.1397 ± .0150	1.2336 ± .0108	.4391 ± .0085
CH6	021014	.1932 ± .0164	.8062 ± .0125	5.2043 ± .0213	2.1338 ± .0123	.2957 ± .0117
CH6	021020	.2140 ± .0147	.5947 ± .0109	4.7960 ± .0175	1.5445 ± .0104	.1633 ± .0086
CH6	021026	.1499 ± .0160	.4633 ± .0098	3.5746 ± .0153	1.3152 ± .0098	.1987 ± .0077
CH6	021201	.0489 ± .0154	.3321 ± .0079	.9795 ± .0087	.6886 ± .0069	.0688 ± .0043
CH6	021207	.1715 ± .0131	.3859 ± .0090	4.2145 ± .0168	1.5733 ± .0106	.1217 ± .0086
CH6	021213	.1158 ± .0122	.4731 ± .0093	2.6126 ± .0132	1.0616 ± .0086	.1248 ± .0063
CH6	021219	.1419 ± .0166	.6394 ± .0108	4.7442 ± .0195	1.6452 ± .0108	.2131 ± .0092
CH6	021225	.0400 ± .0132	.1867 ± .0066	2.9521 ± .0129	.5877 ± .0066	.0569 ± .0039
CH6	030301	.2261 ± .0169	.7740 ± .0129	7.5054 ± .0248	1.9270 ± .0120	.2740 ± .0107
CH6	030307	.0760 ± .0139	.1999 ± .0085	3.0822 ± .0161	.5079 ± .0077	.1163 ± .0046
CH6	030313	.2265 ± .0364	1.0654 ± .0168	7.5020 ± .0332	3.8482 ± .0190	.3482 ± .0204
CH6	030319	.0437 ± .0113	.0622 ± .0046	.7716 ± .0091	.5564 ± .0072	.0350 ± .0039
CH6	030325	.0659 ± .0127	.3967 ± .0091	3.0393 ± .0175	1.4956 ± .0109	.1457 ± .0085
CH6	030605	.2464 ± .0163	.7454 ± .0124	8.3378 ± .0230	2.9424 ± .0146	.3041 ± .0157
CH6	030611	.1514 ± .0130	.5332 ± .0100	3.1424 ± .0142	1.5912 ± .0106	.1509 ± .0088
CH6	030617	.0962 ± .0114	.3294 ± .0083	2.4016 ± .0122	.7732 ± .0077	.0985 ± .0050
CH6	030623	.1083 ± .0111	.2376 ± .0074	2.9166 ± .0129	.9713 ± .0085	.1947 ± .0062
CH6	030629	.0851 ± .0104	.1897 ± .0068	2.1439 ± .0112	1.0106 ± .0086	.1244 ± .0061
CW3	021002	.1438 ± .0143	.3746 ± .0102	2.7897 ± .0149	1.2643 ± .0112	.0998 ± .0074
CW3	021008	.3728 ± .0221	1.2282 ± .0170	3.3273 ± .0164	1.3536 ± .0117	.3962 ± .0090
CW3	021014	.0776 ± .0116	.1811 ± .0074	1.7948 ± .0116	.1241 ± .0041	.0629 ± .0029
CW3	021020	.0254 ± .0322	.0880 ± .0062	2.0284 ± .0118	.1151 ± .0037	.0274 ± .0025
CW3	021026	.1034 ± .0146	.4358 ± .0108	3.8564 ± .0172	.9189 ± .0096	.1359 ± .0061
CW3	021201	.1260 ± .0147	.3878 ± .0102	3.8166 ± .0173	.6196 ± .0078	.1114 ± .0048
CW3	021207	.0133 ± .0368	.0843 ± .0067	3.0187 ± .0145	.1119 ± .0037	.0855 ± .0032
CW3	021213	.0947 ± .0152	.6158 ± .0124	2.7180 ± .0152	.9630 ± .0098	.1694 ± .0065
CW3	021219	.0478 ± .0158	.3519 ± .0108	5.2222 ± .0192	.5501 ± .0075	.1545 ± .0048
CW3	021225	.1307 ± .0134	.3101 ± .0092	3.0154 ± .0152	.9454 ± .0095	.0865 ± .0059
CW3	030301	.0578 ± .0153	.2675 ± .0107	4.4951 ± .0205	.3310 ± .0068	.1286 ± .0045
CW3	030307	.0791 ± .0137	.2558 ± .0096	2.4327 ± .0159	.5918 ± .0089	.0960 ± .0051
CW3	030313	.1392 ± .0143	.3275 ± .0106	2.8241 ± .0167	.2424 ± .0057	.1351 ± .0045
CW3	030319	.0274 ± .0378	.1945 ± .0090	3.2811 ± .0174	.2837 ± .0061	.0774 ± .0040
CW3	030325	.0885 ± .0165	.4535 ± .0127	4.8150 ± .0220	.8445 ± .0102	.1124 ± .0061
CW3	030605	.1348 ± .0177	.4019 ± .0125	6.5196 ± .0237	.7111 ± .0093	.1307 ± .0057
CW3	030611	.1527 ± .0138	.3804 ± .0106	.9250 ± .0096	.1481 ± .0049	.1006 ± .0038
CW3	030617	.1711 ± .0175	.5748 ± .0136	6.1889 ± .0233	.9222 ± .0106	.1549 ± .0066
CW3	030623	.0484 ± .0102	.0459 ± .0055	.9198 ± .0096	.0693 ± .0034	.0340 ± .0030
CW3	030629	.0677 ± .0087	.0295 ± .0046	.6023 ± .0080	.0328 ± .0027	.0236 ± .0028
GZ5	021002	.1246 ± .0203	.7483 ± .0144	4.9076 ± .0219	1.5931 ± .0128	.2551 ± .0096
GZ5	021008	.3110 ± .0213	1.1017 ± .0164	3.6290 ± .0176	1.4964 ± .0124	.4762 ± .0099
GZ5	021014	.4392 ± .0271	1.5859 ± .0204	7.2203 ± .0318	3.6537 ± .0190	.6511 ± .0199
GZ5	021020	.1798 ± .0184	.7159 ± .0136	3.2560 ± .0206	.6502 ± .0081	.1795 ± .0054
GZ5	021026	.1294 ± .0171	.5262 ± .0123	3.7721 ± .0184	1.2472 ± .0112	.1967 ± .0078
GZ5	021201	.2375 ± .0237	1.7231 ± .0199	4.4609 ± .0311	1.8709 ± .0134	.3828 ± .0112

Site	Date	Aluminum	Silicon	Sulfur	Potassium	Calcium
GZ5	021207	.3155 ± .0228	1.0784 ± .0168	5.6245 ± .0276	2.6627 ± .0160	.6379 ± .0153
GZ5	021213	.0472 ± .0485	.6163 ± .0127	3.0175 ± .0174	1.5383 ± .0121	.3739 ± .0096
GZ5	021219	.1543 ± .0212	1.0012 ± .0161	6.1834 ± .0279	1.7502 ± .0130	.3052 ± .0104
GZ5	021225	.1553 ± .0139	.3592 ± .0089	2.6693 ± .0164	.9117 ± .0094	.1302 ± .0060
GZ5	030301	.3221 ± .0248	.9767 ± .0183	7.8793 ± .0308	1.1305 ± .0119	.3058 ± .0084
GZ5	030307	.0851 ± .0158	.4352 ± .0123	3.8104 ± .0216	1.0529 ± .0114	.1773 ± .0074
GZ5	030313	.1606 ± .0257	.9773 ± .0189	7.1005 ± .0339	3.0627 ± .0196	.3335 ± .0171
GZ5	030319	.0672 ± .0182	.2063 ± .0095	1.7195 ± .0146	.6463 ± .0090	.0747 ± .0051
GZ5	030325	.2302 ± .0222	.9482 ± .0180	7.0612 ± .0326	2.2558 ± .0166	.3461 ± .0132
GZ5	030605	.1952 ± .0218	.7553 ± .0161	7.9344 ± .0270	1.1596 ± .0117	.2563 ± .0081
GZ5	030611	.5392 ± .0257	1.2273 ± .0194	5.0244 ± .0270	1.7005 ± .0141	.3146 ± .0106
GZ5	030617	.5602 ± .0287	1.5177 ± .0221	7.3795 ± .0351	3.0925 ± .0192	.5728 ± .0177
GZ5	030623	.1990 ± .0200	.6159 ± .0145	3.2001 ± .0246	1.5802 ± .0138	.2500 ± .0098
GZ5	030629	.1669 ± .0156	.4147 ± .0119	1.9394 ± .0172	.3589 ± .0067	.1648 ± .0049
SZ4	021002	.2134 ± .0178	.8022 ± .0140	3.1175 ± .0171	1.1761 ± .0108	.2157 ± .0076
SZ4	021008	.4123 ± .0250	1.6406 ± .0195	4.2942 ± .0199	1.7432 ± .0130	.8209 ± .0118
SZ4	021014	.1001 ± .0139	.3636 ± .0096	1.8536 ± .0116	.3294 ± .0058	.1195 ± .0039
SZ4	021020	.2087 ± .0169	.5172 ± .0112	1.8109 ± .0112	.1964 ± .0046	.1772 ± .0040
SZ4	021026	.1975 ± .0181	.6698 ± .0132	3.3776 ± .0171	1.2287 ± .0110	.2039 ± .0078
SZ4	021201	.0813 ± .0142	.3547 ± .0100	3.4527 ± .0162	.5476 ± .0073	.1196 ± .0045
SZ4	021207	.1752 ± .0152	.3868 ± .0101	2.4230 ± .0133	.2809 ± .0056	.1510 ± .0041
SZ4	021213	.2225 ± .0410	1.0646 ± .0307	3.6887 ± .0346	1.6176 ± .0245	.5394 ± .0161
SZ4	021221	.3118 ± .0422	1.0322 ± .0322	3.2912 ± .0367	1.7452 ± .0254	.2954 ± .0151
SZ4	021225	.0940 ± .0152	.4533 ± .0112	3.0868 ± .0163	1.0040 ± .0098	.1328 ± .0064
SZ4	030102	.2006 ± .0225	.8220 ± .0151	7.3367 ± .0249	1.8153 ± .0132	.2936 ± .0106
SZ4	030301	.2281 ± .0196	.5850 ± .0142	5.6226 ± .0231	.4934 ± .0081	.1985 ± .0055
SZ4	030307	.0970 ± .0155	.4297 ± .0123	2.9686 ± .0191	.9836 ± .0111	.1665 ± .0070
SZ4	030313	.2830 ± .0198	.7564 ± .0148	3.3267 ± .0185	.5995 ± .0087	.2413 ± .0061
SZ4	030319	.0638 ± .0165	.4441 ± .0122	2.6345 ± .0179	.8165 ± .0102	.2137 ± .0067
SZ4	030325	.2188 ± .0194	.7870 ± .0155	4.4336 ± .0224	1.1145 ± .0117	.2478 ± .0080
SZ4	030605	.1188 ± .0190	.4806 ± .0137	6.5368 ± .0237	.7648 ± .0096	.1900 ± .0062
SZ4	030611	.0504 ± .0142	.3738 ± .0105	1.5938 ± .0124	.3766 ± .0068	.1259 ± .0046
SZ4	030617	.1616 ± .0187	.5921 ± .0142	6.4291 ± .0236	.9437 ± .0106	.1939 ± .0069
SZ4	030623	.0253 ± .0357	.1139 ± .0067	.9322 ± .0095	.1780 ± .0049	.0549 ± .0034
SZ4	030629	.0165 ± .0321	.0928 ± .0063	.6167 ± .0081	.1467 ± .0045	.0698 ± .0035
TC2	021002	.0674 ± .0137	.3914 ± .0103	2.9214 ± .0148	.8559 ± .0090	.0998 ± .0056
TC2	021008	.3667 ± .0193	1.1652 ± .0158	3.1667 ± .0155	1.2956 ± .0111	.4082 ± .0087
TC2	021014	.0560 ± .0112	.1260 ± .0066	1.6738 ± .0109	.4364 ± .0065	.0456 ± .0036
TC2	021020	.0326 ± .0085	.0568 ± .0048	1.2901 ± .0092	.0800 ± .0034	.0153 ± .0022
TC2	021026	.0811 ± .0136	.3593 ± .0099	3.6639 ± .0163	.9328 ± .0094	.1022 ± .0059
TC2	021201	.0281 ± .0414	.3049 ± .0094	3.8304 ± .0163	.5245 ± .0071	.0888 ± .0042
TC2	021207	.0313 ± .0085	.0785 ± .0051	1.1554 ± .0091	.0650 ± .0032	.0598 ± .0027
TC2	021213	.0922 ± .0139	.4775 ± .0108	2.4743 ± .0144	1.1160 ± .0102	.1211 ± .0068
TC2	021219	.0489 ± .0147	.2795 ± .0096	4.2934 ± .0166	.4215 ± .0064	.1393 ± .0043
TC2	021225	.0720 ± .0134	.3730 ± .0103	3.2197 ± .0162	1.0877 ± .0102	.0901 ± .0065
TC2	030301	.1233 ± .0145	.2178 ± .0096	4.8587 ± .0207	.2861 ± .0062	.1069 ± .0043
TC2	030307	.1294 ± .0152	.3752 ± .0116	3.3074 ± .0196	.9069 ± .0107	.1253 ± .0065
TC2	030313	.0803 ± .0151	.2571 ± .0103	2.9152 ± .0164	.1958 ± .0056	.1248 ± .0043
TC2	030319	.0212 ± .0407	.2163 ± .0093	3.3586 ± .0182	.3352 ± .0067	.0719 ± .0041

Site	Date	Aluminum	Silicon	Sulfur	Potassium	Calcium
TC2	030325	.0844 ± .0150	.3238 ± .0113	4.7483 ± .0212	.6686 ± .0094	.0758 ± .0052
TC2	030605	.1096 ± .0182	.4193 ± .0134	7.3606 ± .0253	.7566 ± .0096	.1806 ± .0062
TC2	030611	.0673 ± .0136	.2782 ± .0093	.3859 ± .0067	.1101 ± .0041	.0955 ± .0038
TC2	030617	.1629 ± .0183	.4987 ± .0135	6.4754 ± .0237	.9247 ± .0106	.1404 ± .0065
TC2	030623	.0427 ± .0094	.0151 ± .0154	.7951 ± .0093	.0678 ± .0034	.0235 ± .0028
TC2	030629	.0346 ± .0099	.0438 ± .0050	.6530 ± .0082	.0367 ± .0028	.0316 ± .0029
TM1	021002	.0786 ± .0136	.4031 ± .0104	2.4690 ± .0142	1.0158 ± .0100	.0970 ± .0063
TM1	021008	.3087 ± .0222	1.3257 ± .0175	3.9066 ± .0174	1.4514 ± .0120	.3764 ± .0093
TM1	021014	.0636 ± .0109	.1563 ± .0068	1.5535 ± .0109	.1217 ± .0039	.0495 ± .0029
TM1	021020	.0259 ± .0304	.0556 ± .0054	1.4829 ± .0101	.1104 ± .0036	.0277 ± .0025
TM1	021026	.0960 ± .0162	.4435 ± .0116	3.8527 ± .0171	.9861 ± .0098	.1199 ± .0063
TM1	021201	.1659 ± .0135	.3547 ± .0100	3.6810 ± .0166	.5902 ± .0077	.0984 ± .0045
TM1	021207	.0513 ± .0099	.0706 ± .0055	3.3172 ± .0146	.0931 ± .0033	.0220 ± .0023
TM1	021213	.0649 ± .0152	.5601 ± .0118	2.8150 ± .0154	1.0314 ± .0099	.1284 ± .0065
TM1	021219	.0769 ± .0162	.4035 ± .0110	6.0108 ± .0201	.7048 ± .0084	.1492 ± .0053
TM1	021225	.0980 ± .0134	.3266 ± .0095	3.3100 ± .0157	1.0305 ± .0099	.0730 ± .0062
TM1	030301	.0289 ± .0446	.2144 ± .0101	5.0713 ± .0212	.3108 ± .0065	.0739 ± .0040
TM1	030307	.0283 ± .0406	.2543 ± .0097	2.5212 ± .0161	.5872 ± .0087	.0483 ± .0047
TM1	030313	.1021 ± .0149	.3277 ± .0109	2.7073 ± .0162	.2569 ± .0060	.1281 ± .0045
TM1	030319	.0433 ± .0136	.2186 ± .0094	2.5163 ± .0159	.4375 ± .0078	.0458 ± .0041
TM1	030325	.1169 ± .0179	.5709 ± .0140	6.3593 ± .0256	.9806 ± .0112	.0780 ± .0064
TM1	030605	.1452 ± .0165	.4530 ± .0122	5.6245 ± .0221	.5659 ± .0083	.1003 ± .0049
TM1	030611	.1045 ± .0138	.3294 ± .0096	.5298 ± .0076	.1110 ± .0044	.0706 ± .0035
TM1	030617	.1046 ± .0181	.4903 ± .0134	5.6094 ± .0222	.8949 ± .0105	.1329 ± .0065
TM1	030623	.0502 ± .0098	.0340 ± .0050	.9366 ± .0097	.0677 ± .0035	.0213 ± .0028
TM1	030629	.0279 ± .0282	.0394 ± .0047	.6780 ± .0083	.0330 ± .0027	.0225 ± .0028
ZS7	021008	.6394 ± .0261	2.2478 ± .0207	6.3557 ± .0280	4.1689 ± .0178	.8429 ± .0222
ZS7	021014	.1813 ± .0155	.6156 ± .0112	3.9676 ± .0155	1.0078 ± .0089	.1410 ± .0062
ZS7	021020	.0807 ± .0105	.2185 ± .0071	2.0774 ± .0105	.2004 ± .0040	.0572 ± .0025
ZS7	021026	.1277 ± .0139	.4727 ± .0100	5.1936 ± .0166	.6477 ± .0071	.1421 ± .0047
ZS7	021201	.1181 ± .0166	.7346 ± .0124	6.1011 ± .0208	.9498 ± .0084	.1345 ± .0058
ZS7	021207	.1513 ± .0137	.4176 ± .0097	3.5935 ± .0151	.5086 ± .0063	.1084 ± .0039
ZS7	021213	.2852 ± .0183	1.2607 ± .0151	4.7351 ± .0228	2.6532 ± .0139	.2839 ± .0142
ZS7	021219	.3770 ± .0204	1.2545 ± .0154	7.6061 ± .0239	1.4068 ± .0102	.2994 ± .0086
ZS7	021225	.1859 ± .0189	.8584 ± .0130	4.3201 ± .0231	2.0836 ± .0123	.2410 ± .0114
ZS7	030301	.1990 ± .0149	.5454 ± .0108	5.2831 ± .0177	.4484 ± .0087	.1843 ± .0044
ZS7	030307	.1751 ± .0157	.6346 ± .0114	3.6721 ± .0183	.8667 ± .0082	.1635 ± .0057
ZS7	030313	.2081 ± .0159	.6710 ± .0117	4.1224 ± .0161	.5583 ± .0068	.2017 ± .0048
ZS7	030319	.1057 ± .0162	.6486 ± .0116	3.8660 ± .0207	1.2461 ± .0100	.1845 ± .0074
ZS7	030325	.1845 ± .0150	.6473 ± .0113	5.2221 ± .0193	1.0810 ± .0092	.1270 ± .0065
ZS7	030605	.1757 ± .0145	.4207 ± .0100	5.5927 ± .0175	.6544 ± .0072	.1207 ± .0047
ZS7	030611	.1081 ± .0114	.4115 ± .0085	.7293 ± .0068	.1664 ± .0037	.0891 ± .0029
ZS7	030617	.2025 ± .0157	.5871 ± .0113	6.7480 ± .0198	.7773 ± .0079	.1271 ± .0052
ZS7	030623	.0596 ± .0086	.1407 ± .0056	1.1469 ± .0081	.0913 ± .0029	.0538 ± .0023
ZS7	030629	.0369 ± .0077	.0679 ± .0046	.6807 ± .0066	.0483 ± .0024	.0375 ± .0022

Appendix E.2 – Metals Data from X-Ray Fluorescence in μg m^{-3}

Site	Date	Titanium	Vanadium	Chromium	Manganese	Iron
CH6	021002	.0000 ± .0232	.0000 ± .0136	.0023 ± .0037	.0121 ± .0007	.1569 ± .0015
CH6	021008	.0361 ± .0090	.0037 ± .0115	.0094 ± .0008	.0207 ± .0008	.4427 ± .0029
CH6	021014	.0147 ± .0214	.0022 ± .0092	.0045 ± .0006	.0287 ± .0008	.3271 ± .0022
CH6	021020	.0224 ± .0068	.0234 ± .0030	.0060 ± .0007	.0123 ± .0006	.2132 ± .0018
CH6	021026	.0024 ± .0203	.0000 ± .0087	.0054 ± .0006	.0143 ± .0006	.2492 ± .0019
CH6	021201	.0057 ± .0188	.0005 ± .0081	.0100 ± .0006	.0187 ± .0007	.1888 ± .0016
CH6	021207	.0192 ± .0203	.0205 ± .0030	.0282 ± .0010	.0140 ± .0007	.3616 ± .0022
CH6	021213	.0000 ± .0203	.0000 ± .0087	.0071 ± .0006	.0192 ± .0007	.2154 ± .0018
CH6	021219	.0750 ± .0068	.0160 ± .0031	.0183 ± .0008	.0251 ± .0008	.4849 ± .0026
CH6	021225	.0035 ± .0200	.0020 ± .0086	.0127 ± .0007	.0088 ± .0005	.1723 ± .0016
CH6	030301	.0327 ± .0070	.0311 ± .0030	.0146 ± .0009	.0216 ± .0007	.3370 ± .0023
CH6	030307	.0062 ± .0283	.0020 ± .0115	.0232 ± .0010	.0095 ± .0007	.1670 ± .0019
CH6	030313	.0055 ± .0301	.0000 ± .0170	.0143 ± .0017	.0569 ± .0014	.8308 ± .0040
CH6	030319	.0000 ± .0280	.0000 ± .0161	.0016 ± .0046	.0023 ± .0007	.0674 ± .0012
CH6	030325	.0080 ± .0225	.0014 ± .0091	.0237 ± .0009	.0149 ± .0007	.2929 ± .0021
CH6	030605	.0076 ± .0254	.0218 ± .0050	.0087 ± .0015	.0161 ± .0008	.3180 ± .0022
CH6	030611	.0072 ± .0224	.0158 ± .0043	.0065 ± .0013	.0073 ± .0006	.1786 ± .0016
CH6	030617	.0062 ± .0224	.0004 ± .0090	.0137 ± .0007	.0139 ± .0006	.2179 ± .0018
CH6	030623	.0124 ± .0206	.0224 ± .0029	.0079 ± .0007	.0055 ± .0005	.1134 ± .0013
CH6	030629	.0119 ± .0222	.0232 ± .0031	.0069 ± .0007	.0043 ± .0004	.0875 ± .0012
CW3	021002	.0008 ± .0310	.0073 ± .0189	.0005 ± .0051	.0151 ± .0009	.1959 ± .0020
CW3	021008	.0252 ± .0317	.0000 ± .0193	.0000 ± .0053	.0231 ± .0011	.4844 ± .0031
CW3	021014	.0094 ± .0274	.0062 ± .0118	.0010 ± .0020	.0042 ± .0005	.0623 ± .0012
CW3	021020	.0000 ± .0293	.0037 ± .0126	.0000 ± .0020	.0022 ± .0005	.0332 ± .0010
CW3	021026	.0026 ± .0303	.0068 ± .0131	.0010 ± .0023	.0179 ± .0008	.1948 ± .0020
CW3	021201	.0000 ± .0281	.0025 ± .0121	.0023 ± .0007	.0168 ± .0008	.1487 ± .0018
CW3	021207	.0059 ± .0295	.0381 ± .0044	.0002 ± .0026	.0066 ± .0006	.1149 ± .0016
CW3	021213	.0000 ± .0287	.0002 ± .0124	.0021 ± .0022	.0188 ± .0008	.2059 ± .0021
CW3	021219	.0012 ± .0276	.0102 ± .0120	.0015 ± .0021	.0163 ± .0007	.1901 ± .0020
CW3	021225	.0076 ± .0270	.0066 ± .0116	.0019 ± .0021	.0137 ± .0007	.1951 ± .0020
CW3	030301	.0000 ± .0374	.0080 ± .0218	.0008 ± .0062	.0127 ± .0010	.2003 ± .0023
CW3	030307	.0000 ± .0364	.0000 ± .0148	.0016 ± .0026	.0159 ± .0009	.2242 ± .0024
CW3	030313	.0127 ± .0349	.0084 ± .0142	.0021 ± .0025	.0100 ± .0007	.1491 ± .0020
CW3	030319	.0000 ± .0358	.0078 ± .0146	.0015 ± .0025	.0142 ± .0008	.1453 ± .0020
CW3	030325	.0136 ± .0348	.0099 ± .0142	.0047 ± .0009	.0214 ± .0010	.2298 ± .0025
CW3	030605	.0000 ± .0381	.0000 ± .0225	.0000 ± .0064	.0110 ± .0010	.1872 ± .0022
CW3	030611	.0194 ± .0318	.0068 ± .0129	.0017 ± .0022	.0068 ± .0006	.1622 ± .0020
CW3	030617	.0091 ± .0361	.0066 ± .0207	.0012 ± .0058	.0193 ± .0011	.2353 ± .0025
CW3	030623	.0000 ± .0374	.0000 ± .0216	.0000 ± .0060	.0003 ± .0024	.0280 ± .0010
CW3	030629	.0000 ± .0358	.0068 ± .0146	.0018 ± .0024	.0003 ± .0014	.0150 ± .0009
GZ5	021002	.0305 ± .0306	.0335 ± .0045	.0016 ± .0027	.0249 ± .0009	.3518 ± .0027
GZ5	021008	.0389 ± .0101	.0197 ± .0044	.0017 ± .0024	.0291 ± .0010	.4940 ± .0031
GZ5	021014	.0458 ± .0104	.0582 ± .0047	.0051 ± .0011	.0428 ± .0012	.6634 ± .0037
GZ5	021020	.0336 ± .0093	.0387 ± .0042	.0054 ± .0010	.0334 ± .0010	.5308 ± .0033
GZ5	021026	.0202 ± .0295	.0138 ± .0043	.0026 ± .0008	.0301 ± .0010	.3364 ± .0026
GZ5	021201	.0770 ± .0092	.0399 ± .0042	.0075 ± .0012	.2547 ± .0026	2.0712 ± .0065

Site	Date	Titanium	Vanadium	Chromium	Manganese	Iron
GZ5	021207	.0563 ± .0102	.0499 ± .0063	.0064 ± .0018	.0261 ± .0011	.3956 ± .0028
GZ5	021213	.0183 ± .0305	.0134 ± .0184	.0000 ± .0050	.0245 ± .0010	.3193 ± .0025
GZ5	021219	.0303 ± .0311	.0308 ± .0064	.0021 ± .0054	.0374 ± .0012	.4669 ± .0030
GZ5	021225	.0000 ± .0274	.0024 ± .0118	.0005 ± .0020	.0174 ± .0008	.2169 ± .0021
GZ5	030301	.0160 ± .0400	.0472 ± .0077	.0024 ± .0067	.0368 ± .0014	.6447 ± .0040
GZ5	030307	.0029 ± .0397	.0000 ± .0228	.0000 ± .0064	.0264 ± .0013	.3486 ± .0030
GZ5	030313	.0243 ± .0423	.0280 ± .0083	.0076 ± .0024	.0633 ± .0017	.6188 ± .0040
GZ5	030319	.0010 ± .0383	.0031 ± .0219	.0003 ± .0061	.0175 ± .0011	.1756 ± .0022
GZ5	030325	.0433 ± .0120	.0432 ± .0051	.0057 ± .0011	.0493 ± .0014	.5710 ± .0038
GZ5	030605	.0411 ± .0113	.0379 ± .0048	.0044 ± .0010	.0265 ± .0010	.3628 ± .0030
GZ5	030611	.0529 ± .0112	.0975 ± .0050	.0070 ± .0015	.0385 ± .0012	.5164 ± .0035
GZ5	030617	.0089 ± .0437	.0623 ± .0085	.0042 ± .0076	.0460 ± .0016	.8291 ± .0045
GZ5	030623	.0425 ± .0121	.0585 ± .0052	.0046 ± .0012	.0438 ± .0013	.5435 ± .0036
GZ5	030629	.0224 ± .0329	.0383 ± .0046	.0008 ± .0027	.0197 ± .0009	.1756 ± .0021
SZ4	021002	.0267 ± .0285	.0304 ± .0042	.0025 ± .0026	.0233 ± .0009	.3326 ± .0026
SZ4	021008	.0381 ± .0104	.0554 ± .0066	.0008 ± .0057	.0340 ± .0012	.5919 ± .0034
SZ4	021014	.0127 ± .0293	.0133 ± .0042	.0003 ± .0021	.0079 ± .0006	.1176 ± .0016
SZ4	021020	.0126 ± .0275	.0107 ± .0119	.0010 ± .0020	.0070 ± .0006	.1663 ± .0018
SZ4	021026	.0307 ± .0102	.0242 ± .0045	.0020 ± .0026	.0216 ± .0009	.2719 ± .0024
SZ4	021201	.0127 ± .0264	.0093 ± .0114	.0016 ± .0020	.0167 ± .0007	.1540 ± .0018
SZ4	021207	.0166 ± .0275	.0216 ± .0040	.0013 ± .0023	.0100 ± .0006	.1658 ± .0018
SZ4	021213	.0299 ± .1078	.0097 ± .0617	.0009 ± .0172	.0471 ± .0031	.5019 ± .0062
SZ4	021221	.0613 ± .1008	.0485 ± .0138	.0107 ± .0026	.0475 ± .0025	.5114 ± .0063
SZ4	021225	.0218 ± .0280	.0274 ± .0041	.0033 ± .0008	.0206 ± .0008	.2099 ± .0021
SZ4	030102	.0373 ± .0093	.0223 ± .0041	.0042 ± .0008	.0391 ± .0010	.4174 ± .0028
SZ4	030301	.0106 ± .0350	.0319 ± .0049	.0027 ± .0029	.0263 ± .0010	.3422 ± .0029
SZ4	030307	.0113 ± .0370	.0096 ± .0215	.0036 ± .0062	.0262 ± .0012	.2620 ± .0026
SZ4	030313	.0232 ± .0387	.0147 ± .0224	.0017 ± .0063	.0340 ± .0013	.3817 ± .0031
SZ4	030319	.0379 ± .0120	.0289 ± .0050	.0037 ± .0010	.0273 ± .0011	.2613 ± .0026
SZ4	030325	.0060 ± .0379	.0264 ± .0053	.0036 ± .0010	.0377 ± .0012	.4292 ± .0033
SZ4	030605	.0215 ± .0349	.0177 ± .0048	.0027 ± .0009	.0174 ± .0009	.2693 ± .0026
SZ4	030611	.0132 ± .0371	.0065 ± .0218	.0000 ± .0062	.0233 ± .0012	.2691 ± .0026
SZ4	030617	.0000 ± .0393	.0274 ± .0075	.0023 ± .0063	.0350 ± .0013	.3460 ± .0029
SZ4	030623	.0000 ± .0380	.0000 ± .0218	.0000 ± .0060	.0075 ± .0010	.0851 ± .0016
SZ4	030629	.0060 ± .0336	.0028 ± .0136	.0003 ± .0021	.0108 ± .0007	.0938 ± .0016
TC2	021002	.0153 ± .0266	.0123 ± .0039	.0023 ± .0007	.0144 ± .0007	.2015 ± .0020
TC2	021008	.0378 ± .0093	.0051 ± .0120	.0009 ± .0021	.0235 ± .0009	.5068 ± .0031
TC2	021014	.0000 ± .0284	.0055 ± .0122	.0000 ± .0019	.0027 ± .0005	.0509 ± .0011
TC2	021020	.0024 ± .0262	.0031 ± .0112	.0002 ± .0018	.0020 ± .0004	.0207 ± .0008
TC2	021026	.0107 ± .0271	.0121 ± .0039	.0013 ± .0021	.0178 ± .0008	.1864 ± .0019
TC2	021201	.0137 ± .0252	.0109 ± .0109	.0022 ± .0007	.0135 ± .0007	.1288 ± .0016
TC2	021207	.0035 ± .0264	.0083 ± .0114	.0006 ± .0019	.0060 ± .0005	.0923 ± .0014
TC2	021213	.0160 ± .0284	.0094 ± .0123	.0018 ± .0022	.0175 ± .0008	.1999 ± .0020
TC2	021219	.0103 ± .0298	.0120 ± .0129	.0019 ± .0023	.0133 ± .0007	.1626 ± .0018
TC2	021225	.0170 ± .0270	.0095 ± .0116	.0011 ± .0021	.0171 ± .0007	.2129 ± .0020
TC2	030301	.0000 ± .0415	.0000 ± .0231	.0000 ± .0062	.0043 ± .0009	.1537 ± .0021
TC2	030307	.0000 ± .0371	.0095 ± .0153	.0028 ± .0009	.0213 ± .0010	.2685 ± .0027
TC2	030313	.0095 ± .0375	.0134 ± .0153	.0000 ± .0025	.0073 ± .0007	.1369 ± .0020
TC2	030319	.0000 ± .0413	.0000 ± .0229	.0000 ± .0062	.0102 ± .0010	.1751 ± .0022

Site	Date	Titanium	Vanadium	Chromium	Manganese	Iron
TC2	030325	.0124 ± .0364	.0221 ± .0050	.0018 ± .0027	.0159 ± .0009	.1843 ± .0022
TC2	030605	.0000 ± .0359	.0059 ± .0146	.0011 ± .0025	.0126 ± .0008	.1939 ± .0023
TC2	030611	.0132 ± .0357	.0022 ± .0145	.0012 ± .0023	.0038 ± .0006	.1262 ± .0019
TC2	030617	.0000 ± .0377	.0000 ± .0217	.0000 ± .0061	.0183 ± .0011	.2167 ± .0024
TC2	030623	.0002 ± .0332	.0022 ± .0134	.0010 ± .0021	.0010 ± .0014	.0132 ± .0008
TC2	030629	.0000 ± .0364	.0000 ± .0208	.0000 ± .0058	.0003 ± .0023	.0082 ± .0008
TM1	021002	.0107 ± .0294	.0139 ± .0043	.0004 ± .0022	.0123 ± .0007	.1662 ± .0019
TM1	021008	.0400 ± .0093	.0249 ± .0041	.0020 ± .0024	.0234 ± .0009	.4653 ± .0030
TM1	021014	.0036 ± .0290	.0054 ± .0125	.0000 ± .0020	.0021 ± .0005	.0322 ± .0010
TM1	021020	.0000 ± .0287	.0004 ± .0124	.0005 ± .0020	.0024 ± .0005	.0300 ± .0009
TM1	021026	.0157 ± .0306	.0270 ± .0045	.0006 ± .0025	.0160 ± .0008	.2012 ± .0021
TM1	021201	.0109 ± .0265	.0050 ± .0114	.0017 ± .0020	.0157 ± .0007	.1242 ± .0016
TM1	021207	.0030 ± .0271	.0206 ± .0039	.0008 ± .0021	.0014 ± .0004	.0189 ± .0008
TM1	021213	.0000 ± .0279	.0123 ± .0040	.0011 ± .0021	.0160 ± .0007	.1736 ± .0019
TM1	021219	.0127 ± .0267	.0141 ± .0039	.0025 ± .0007	.0155 ± .0007	.1405 ± .0017
TM1	021225	.0098 ± .0260	.0178 ± .0038	.0005 ± .0021	.0124 ± .0007	.1644 ± .0018
TM1	030301	.0000 ± .0378	.0124 ± .0216	.0001 ± .0060	.0065 ± .0009	.0882 ± .0016
TM1	030307	.0013 ± .0360	.0051 ± .0146	.0017 ± .0025	.0130 ± .0008	.1965 ± .0023
TM1	030313	.0000 ± .0416	.0000 ± .0236	.0000 ± .0065	.0031 ± .0010	.1062 ± .0018
TM1	030319	.0113 ± .0348	.0350 ± .0049	.0010 ± .0028	.0099 ± .0007	.1592 ± .0021
TM1	030325	.0000 ± .0370	.0000 ± .0216	.0000 ± .0061	.0180 ± .0011	.2272 ± .0025
TM1	030605	.0000 ± .0332	.0095 ± .0136	.0015 ± .0024	.0098 ± .0007	.1599 ± .0020
TM1	030611	.0125 ± .0344	.0049 ± .0140	.0010 ± .0023	.0038 ± .0006	.1143 ± .0018
TM1	030617	.0078 ± .0392	.0071 ± .0226	.0000 ± .0063	.0176 ± .0011	.1886 ± .0022
TM1	030623	.0010 ± .0346	.0040 ± .0140	.0005 ± .0022	.0009 ± .0014	.0087 ± .0008
TM1	030629	.0013 ± .0328	.0057 ± .0133	.0014 ± .0023	.0007 ± .0015	.0061 ± .0008
ZS7	021008	.0912 ± .0079	.0677 ± .0038	.0223 ± .0012	.0444 ± .0011	.8487 ± .0036
ZS7	021014	.0343 ± .0078	.0447 ± .0035	.0283 ± .0011	.0181 ± .0008	.3111 ± .0022
ZS7	021020	.0133 ± .0214	.0137 ± .0031	.0036 ± .0006	.0056 ± .0004	.0823 ± .0012
ZS7	021026	.0158 ± .0215	.0115 ± .0031	.0012 ± .0017	.0143 ± .0006	.1501 ± .0016
ZS7	021201	.0121 ± .0238	.0745 ± .0049	.0088 ± .0016	.0291 ± .0009	.3045 ± .0021
ZS7	021207	.0098 ± .0224	.0436 ± .0047	.0036 ± .0042	.0075 ± .0006	.1260 ± .0014
ZS7	021213	.0615 ± .0077	.0619 ± .0036	.0082 ± .0010	.0315 ± .0009	.3907 ± .0024
ZS7	021219	.0219 ± .0254	.0440 ± .0053	.0035 ± .0047	.0399 ± .0011	.4927 ± .0027
ZS7	021225	.0339 ± .0076	.0308 ± .0034	.0104 ± .0009	.0251 ± .0008	.3810 ± .0024
ZS7	030301	.0000 ± .0277	.0355 ± .0052	.0858 ± .0020	.0212 ± .0013	.5601 ± .0030
ZS7	030307	.0326 ± .0079	.0212 ± .0046	.0056 ± .0013	.0193 ± .0008	.2924 ± .0022
ZS7	030313	.0204 ± .0254	.0436 ± .0050	.0152 ± .0016	.0216 ± .0009	.3358 ± .0023
ZS7	030319	.0241 ± .0074	.0301 ± .0031	.0251 ± .0010	.0195 ± .0008	.3394 ± .0023
ZS7	030325	.0191 ± .0252	.0479 ± .0036	.0080 ± .0009	.0238 ± .0008	.2994 ± .0022
ZS7	030605	.0222 ± .0234	.0259 ± .0033	.0098 ± .0008	.0111 ± .0006	.2211 ± .0019
ZS7	030611	.0156 ± .0227	.0114 ± .0031	.0022 ± .0006	.0060 ± .0005	.1638 ± .0016
ZS7	030617	.0000 ± .0248	.0266 ± .0047	.0054 ± .0014	.0141 ± .0008	.2433 ± .0020
ZS7	030623	.0011 ± .0226	.0029 ± .0131	.0012 ± .0037	.0027 ± .0005	.0540 ± .0010
ZS7	030629	.0000 ± .0247	.0007 ± .0142	.0079 ± .0014	.0016 ± .0017	.0555 ± .0010

Appendix E.3 – Metals Data from X-Ray Fluorescence in μg m^{-3}

Site	Date	Cobalt	Nickle	Copper	Zinc	Gallium
CH6	021002	.0002 ± .0026	.0093 ± .0004	.0697 ± .0008	.2381 ± .0013	.0000 ± .0032
CH6	021008	.0030 ± .0068	.0146 ± .0005	.0146 ± .0005	.1251 ± .0011	.0000 ± .0034
CH6	021014	.0014 ± .0051	.0062 ± .0003	.0464 ± .0007	.6062 ± .0021	.0000 ± .0043
CH6	021020	.0013 ± .0034	.0154 ± .0004	.0148 ± .0004	.3600 ± .0016	.0001 ± .0032
CH6	021026	.0004 ± .0039	.0077 ± .0003	.0442 ± .0006	.3214 ± .0015	.0000 ± .0030
CH6	021201	.0012 ± .0030	.0110 ± .0004	.0592 ± .0007	.2269 ± .0012	.0000 ± .0026
CH6	021207	.0023 ± .0056	.0299 ± .0006	.0164 ± .0005	.1725 ± .0011	.0000 ± .0032
CH6	021213	.0013 ± .0034	.0090 ± .0003	.0374 ± .0006	.2741 ± .0014	.0000 ± .0029
CH6	021219	.0028 ± .0074	.0344 ± .0006	.0697 ± .0008	.3479 ± .0015	.0000 ± .0039
CH6	021225	.0011 ± .0028	.0150 ± .0004	.0847 ± .0008	.2018 ± .0012	.0000 ± .0027
CH6	030301	.0017 ± .0053	.0289 ± .0006	.0224 ± .0005	.3696 ± .0016	.0045 ± .0014
CH6	030307	.0016 ± .0029	.0331 ± .0007	.0463 ± .0008	.1204 ± .0012	.0000 ± .0036
CH6	030313	.0053 ± .0127	.0185 ± .0006	.2358 ± .0017	.9591 ± .0030	.0019 ± .0066
CH6	030319	.0011 ± .0015	.0099 ± .0004	.0713 ± .0009	.1814 ± .0013	.0000 ± .0033
CH6	030325	.0021 ± .0047	.0322 ± .0006	.0884 ± .0009	.5147 ± .0019	.0000 ± .0040
CH6	030605	.0017 ± .0050	.0328 ± .0006	.0222 ± .0005	.2930 ± .0014	.0029 ± .0037
CH6	030611	.0009 ± .0029	.0183 ± .0005	.0161 ± .0004	.2234 ± .0013	.0000 ± .0029
CH6	030617	.0021 ± .0035	.0250 ± .0005	.0264 ± .0006	.2768 ± .0014	.0000 ± .0029
CH6	030623	.0012 ± .0020	.0260 ± .0005	.0085 ± .0004	.0933 ± .0008	.0000 ± .0026
CH6	030629	.0002 ± .0017	.0174 ± .0005	.0065 ± .0004	.0830 ± .0008	.0000 ± .0026
CW3	021002	.0015 ± .0033	.0054 ± .0004	.0262 ± .0006	.3124 ± .0018	.0000 ± .0036
CW3	021008	.0013 ± .0075	.0009 ± .0010	.0081 ± .0005	.2714 ± .0016	.0000 ± .0037
CW3	021014	.0015 ± .0005	.0021 ± .0003	.0055 ± .0004	.0419 ± .0007	.0006 ± .0032
CW3	021020	.0008 ± .0012	.0026 ± .0003	.0044 ± .0004	.0297 ± .0007	.0000 ± .0033
CW3	021026	.0007 ± .0033	.0023 ± .0004	.0087 ± .0005	.3570 ± .0019	.0000 ± .0039
CW3	021201	.0011 ± .0026	.0025 ± .0003	.0155 ± .0005	.2560 ± .0016	.0000 ± .0035
CW3	021207	.0013 ± .0022	.0095 ± .0005	.0134 ± .0005	.0780 ± .0009	.0000 ± .0036
CW3	021213	.0013 ± .0034	.0031 ± .0003	.0131 ± .0005	.2897 ± .0017	.0000 ± .0035
CW3	021219	.0003 ± .0032	.0046 ± .0004	.0149 ± .0005	.1849 ± .0014	.0000 ± .0034
CW3	021225	.0011 ± .0032	.0014 ± .0003	.0083 ± .0005	.3323 ± .0018	.0000 ± .0034
CW3	030301	.0025 ± .0035	.0092 ± .0005	.0157 ± .0006	.1046 ± .0012	.0000 ± .0040
CW3	030307	.0013 ± .0039	.0029 ± .0004	.0111 ± .0006	.3324 ± .0020	.0000 ± .0043
CW3	030313	.0027 ± .0028	.0041 ± .0004	.0054 ± .0005	.1396 ± .0014	.0000 ± .0042
CW3	030319	.0020 ± .0028	.0039 ± .0004	.0080 ± .0005	.1521 ± .0014	.0010 ± .0043
CW3	030325	.0023 ± .0039	.0043 ± .0004	.0164 ± .0006	.3182 ± .0020	.0000 ± .0046
CW3	030605	.0010 ± .0033	.0043 ± .0004	.0136 ± .0006	.1614 ± .0014	.0000 ± .0041
CW3	030611	.0008 ± .0029	.0035 ± .0004	.0084 ± .0005	.0769 ± .0010	.0000 ± .0036
CW3	030617	.0030 ± .0040	.0060 ± .0005	.0171 ± .0006	.3098 ± .0019	.0000 ± .0040
CW3	030623	.0006 ± .0013	.0013 ± .0003	.0061 ± .0005	.0259 ± .0007	.0000 ± .0039
CW3	030629	.0004 ± .0012	.0026 ± .0004	.0053 ± .0005	.0113 ± .0006	.0000 ± .0040
GZ5	021002	.0016 ± .0056	.0068 ± .0004	.0273 ± .0007	.4161 ± .0020	.0000 ± .0046
GZ5	021008	.0026 ± .0076	.0028 ± .0004	.0220 ± .0006	.2029 ± .0014	.0000 ± .0040
GZ5	021014	.0023 ± .0101	.0212 ± .0006	.0426 ± .0008	.7493 ± .0027	.0012 ± .0065
GZ5	021020	.0007 ± .0082	.0117 ± .0005	.0233 ± .0007	1.1798 ± .0034	.0018 ± .0049
GZ5	021026	.0037 ± .0053	.0046 ± .0004	.0607 ± .0009	.2926 ± .0017	.0000 ± .0041
GZ5	021201	.0097 ± .0308	.0109 ± .0006	.0919 ± .0011	.7365 ± .0026	.0045 ± .0069

Site	Date	Cobalt	Nickle	Copper	Zinc	Gallium
GZ5	021207	.0026 ± .0062	.0176 ± .0006	.0320 ± .0007	.5322 ± .0022	.0009 ± .0057
GZ5	021213	.0011 ± .0050	.0051 ± .0004	.0242 ± .0006	.2766 ± .0016	.0000 ± .0039
GZ5	021219	.0052 ± .0072	.0127 ± .0005	.0447 ± .0008	.6318 ± .0024	.0000 ± .0057
GZ5	021225	.0011 ± .0036	.0033 ± .0003	.0624 ± .0009	.2486 ± .0015	.0000 ± .0039
GZ5	030301	.0054 ± .0101	.0207 ± .0007	.0416 ± .0009	.8373 ± .0032	.0039 ± .0055
GZ5	030307	.0012 ± .0056	.0015 ± .0004	.0399 ± .0009	.3183 ± .0020	.0000 ± .0049
GZ5	030313	.0037 ± .0097	.0179 ± .0007	.0930 ± .0013	.8010 ± .0031	.0003 ± .0069
GZ5	030319	.0011 ± .0031	.0026 ± .0004	.0776 ± .0011	.2678 ± .0018	.0025 ± .0045
GZ5	030325	.0058 ± .0090	.0185 ± .0007	.0446 ± .0009	.6055 ± .0027	.0032 ± .0064
GZ5	030605	.0027 ± .0059	.0144 ± .0006	.0179 ± .0007	.4979 ± .0024	.0000 ± .0046
GZ5	030611	.0024 ± .0081	.0281 ± .0008	.0308 ± .0008	1.2073 ± .0037	.0152 ± .0019
GZ5	030617	.0039 ± .0128	.0202 ± .0007	.0560 ± .0010	1.1344 ± .0036	.0000 ± .0073
GZ5	030623	.0039 ± .0085	.0131 ± .0006	.0199 ± .0007	.8393 ± .0031	.0000 ± .0060
GZ5	030629	.0012 ± .0031	.0087 ± .0005	.0133 ± .0006	.3296 ± .0020	.0000 ± .0047
SZ4	021002	.0018 ± .0052	.0078 ± .0004	.0293 ± .0007	.4364 ± .0020	.0000 ± .0040
SZ4	021008	.0039 ± .0090	.0155 ± .0005	.0184 ± .0006	.4933 ± .0022	.0000 ± .0041
SZ4	021014	.0011 ± .0022	.0036 ± .0004	.0065 ± .0005	.1068 ± .0011	.0000 ± .0034
SZ4	021020	.0011 ± .0028	.0032 ± .0003	.0028 ± .0004	.0780 ± .0009	.0000 ± .0032
SZ4	021026	.0010 ± .0044	.0062 ± .0004	.0126 ± .0006	.4652 ± .0021	.0000 ± .0041
SZ4	021201	.0004 ± .0026	.0030 ± .0003	.0116 ± .0005	.2041 ± .0014	.0029 ± .0033
SZ4	021207	.0011 ± .0028	.0074 ± .0004	.0103 ± .0005	.1689 ± .0013	.0000 ± .0033
SZ4	021213	.0045 ± .0090	.0089 ± .0012	.0241 ± .0016	.6778 ± .0049	.0022 ± .0115
SZ4	021221	.0056 ± .0092	.0145 ± .0013	.0275 ± .0016	.7306 ± .0052	.0101 ± .0125
SZ4	021225	.0000 ± .0035	.0077 ± .0004	.0067 ± .0005	.3621 ± .0018	.0000 ± .0038
SZ4	030102	.0018 ± .0065	.0072 ± .0004	.0267 ± .0006	.3728 ± .0019	.0000 ± .0042
SZ4	030301	.0009 ± .0055	.0128 ± .0005	.0196 ± .0007	.1847 ± .0015	.0000 ± .0041
SZ4	030307	.0013 ± .0044	.0064 ± .0005	.0085 ± .0006	.3960 ± .0022	.0054 ± .0015
SZ4	030313	.0021 ± .0061	.0090 ± .0005	.0122 ± .0006	.3210 ± .0020	.0005 ± .0042
SZ4	030319	.0035 ± .0044	.0098 ± .0005	.0165 ± .0007	.3481 ± .0021	.0000 ± .0044
SZ4	030325	.0012 ± .0068	.0110 ± .0006	.0196 ± .0007	.5532 ± .0026	.0031 ± .0050
SZ4	030605	.0001 ± .0044	.0064 ± .0005	.0076 ± .0005	.1718 ± .0015	.0009 ± .0041
SZ4	030611	.0012 ± .0044	.0151 ± .0006	.0085 ± .0005	.1048 ± .0012	.0028 ± .0039
SZ4	030617	.0030 ± .0056	.0153 ± .0006	.0127 ± .0006	.2890 ± .0019	.0000 ± .0043
SZ4	030623	.0017 ± .0019	.0018 ± .0004	.0023 ± .0004	.0253 ± .0007	.0020 ± .0040
SZ4	030629	.0007 ± .0020	.0004 ± .0010	.0013 ± .0004	.0112 ± .0005	.0007 ± .0038
TC2	021002	.0022 ± .0034	.0035 ± .0004	.0235 ± .0006	.3115 ± .0017	.0000 ± .0035
TC2	021008	.0026 ± .0078	.0007 ± .0009	.0120 ± .0005	.2838 ± .0016	.0000 ± .0036
TC2	021014	.0010 ± .0013	.0023 ± .0003	.0097 ± .0005	.0303 ± .0006	.0000 ± .0033
TC2	021020	.0002 ± .0010	.0014 ± .0003	.0131 ± .0005	.0135 ± .0005	.0000 ± .0030
TC2	021026	.0027 ± .0032	.0031 ± .0003	.0238 ± .0006	.4084 ± .0019	.0000 ± .0036
TC2	021201	.0021 ± .0023	.0036 ± .0003	.0138 ± .0005	.2101 ± .0014	.0030 ± .0032
TC2	021207	.0014 ± .0018	.0018 ± .0003	.0153 ± .0005	.0255 ± .0006	.0000 ± .0031
TC2	021213	.0009 ± .0033	.0023 ± .0003	.0151 ± .0005	.2735 ± .0016	.0000 ± .0037
TC2	021219	.0008 ± .0028	.0050 ± .0004	.0159 ± .0006	.1016 ± .0010	.0000 ± .0036
TC2	021225	.0012 ± .0035	.0032 ± .0003	.0135 ± .0005	.3921 ± .0019	.0000 ± .0036
TC2	030301	.0016 ± .0029	.0044 ± .0005	.0197 ± .0007	.0572 ± .0009	.0000 ± .0041
TC2	030307	.0035 ± .0045	.0072 ± .0005	.0148 ± .0007	.4213 ± .0023	.0000 ± .0046
TC2	030313	.0012 ± .0027	.0040 ± .0005	.0115 ± .0006	.0955 ± .0012	.0000 ± .0044
TC2	030319	.0025 ± .0032	.0029 ± .0004	.0167 ± .0006	.2080 ± .0016	.0000 ± .0044

Site	Date	Cobalt	Nickle	Copper	Zinc	Gallium
TC2	030325	.0019 ± .0033	.0070 ± .0005	.0193 ± .0007	.2210 ± .0017	.0037 ± .0046
TC2	030605	.0014 ± .0034	.0038 ± .0004	.0174 ± .0006	.1626 ± .0014	.0000 ± .0044
TC2	030611	.0004 ± .0024	.0008 ± .0011	.0116 ± .0006	.0104 ± .0006	.0023 ± .0043
TC2	030617	.0024 ± .0037	.0124 ± .0006	.0199 ± .0007	.2587 ± .0018	.0000 ± .0041
TC2	030623	.0004 ± .0011	.0013 ± .0003	.0084 ± .0005	.0021 ± .0004	.0007 ± .0038
TC2	030629	.0002 ± .0011	.0010 ± .0010	.0082 ± .0005	.0054 ± .0005	.0000 ± .0037
TM1	021002	.0009 ± .0029	.0042 ± .0004	.0128 ± .0005	.2958 ± .0017	.0000 ± .0038
TM1	021008	.0019 ± .0072	.0057 ± .0004	.0047 ± .0004	.2778 ± .0016	.0000 ± .0036
TM1	021014	.0005 ± .0012	.0012 ± .0003	.0000 ± .0011	.0194 ± .0006	.0000 ± .0033
TM1	021020	.0008 ± .0011	.0025 ± .0003	.0016 ± .0004	.0168 ± .0005	.0000 ± .0033
TM1	021026	.0013 ± .0034	.0073 ± .0004	.0042 ± .0005	.4250 ± .0020	.0000 ± .0040
TM1	021201	.0016 ± .0023	.0021 ± .0003	.0097 ± .0005	.2282 ± .0015	.0000 ± .0033
TM1	021207	.0006 ± .0010	.0057 ± .0004	.0017 ± .0003	.0193 ± .0005	.0016 ± .0030
TM1	021213	.0006 ± .0029	.0050 ± .0004	.0090 ± .0005	.2623 ± .0016	.0000 ± .0037
TM1	021219	.0014 ± .0025	.0058 ± .0004	.0077 ± .0004	.1265 ± .0011	.0000 ± .0033
TM1	021225	.0010 ± .0028	.0047 ± .0004	.0039 ± .0004	.2990 ± .0017	.0027 ± .0034
TM1	030301	.0005 ± .0019	.0107 ± .0005	.0069 ± .0005	.0571 ± .0009	.0000 ± .0040
TM1	030307	.0013 ± .0035	.0016 ± .0004	.0035 ± .0005	.3862 ± .0022	.0014 ± .0045
TM1	030313	.0007 ± .0022	.0064 ± .0005	.0033 ± .0005	.1236 ± .0013	.0000 ± .0041
TM1	030319	.0004 ± .0029	.0112 ± .0005	.0066 ± .0005	.2752 ± .0019	.0030 ± .0041
TM1	030325	.0006 ± .0039	.0078 ± .0005	.0160 ± .0006	.3810 ± .0022	.0000 ± .0047
TM1	030605	.0019 ± .0029	.0045 ± .0004	.0062 ± .0005	.1205 ± .0012	.0000 ± .0039
TM1	030611	.0010 ± .0023	.0016 ± .0004	.0014 ± .0004	.0162 ± .0006	.0000 ± .0039
TM1	030617	.0008 ± .0034	.0060 ± .0005	.0064 ± .0006	.2617 ± .0018	.0000 ± .0043
TM1	030623	.0004 ± .0011	.0025 ± .0004	.0009 ± .0012	.0022 ± .0004	.0004 ± .0040
TM1	030629	.0003 ± .0011	.0015 ± .0004	.0017 ± .0004	.0014 ± .0005	.0023 ± .0037
ZS7	021008	.0053 ± .0128	.0322 ± .0006	.0279 ± .0006	.5330 ± .0020	.0000 ± .0057
ZS7	021014	.0027 ± .0049	.0342 ± .0006	.0110 ± .0004	.2071 ± .0013	.0000 ± .0031
ZS7	021020	.0007 ± .0016	.0054 ± .0003	.0043 ± .0003	.0478 ± .0006	.0000 ± .0025
ZS7	021026	.0011 ± .0025	.0047 ± .0003	.0061 ± .0004	.1443 ± .0011	.0000 ± .0027
ZS7	021201	.0012 ± .0048	.0319 ± .0006	.0390 ± .0007	.8571 ± .0025	.0000 ± .0036
ZS7	021207	.0012 ± .0022	.0191 ± .0005	.0128 ± .0004	.2224 ± .0013	.0000 ± .0029
ZS7	021213	.0033 ± .0060	.0172 ± .0005	.0241 ± .0006	.4981 ± .0019	.0000 ± .0048
ZS7	021219	.0025 ± .0075	.0211 ± .0005	.0394 ± .0007	1.0221 ± .0027	.0000 ± .0043
ZS7	021225	.0025 ± .0059	.0192 ± .0005	.0281 ± .0006	.5911 ± .0020	.0000 ± .0049
ZS7	030301	.0073 ± .0086	.1125 ± .0011	.0192 ± .0006	.1488 ± .0011	.0004 ± .0028
ZS7	030307	.0015 ± .0046	.0166 ± .0005	.0491 ± .0007	.3023 ± .0015	.0032 ± .0036
ZS7	030313	.0026 ± .0053	.0292 ± .0006	.0180 ± .0005	.2771 ± .0015	.0000 ± .0029
ZS7	030319	.0045 ± .0054	.0375 ± .0007	.0452 ± .0007	.4472 ± .0018	.0028 ± .0042
ZS7	030325	.0018 ± .0048	.0236 ± .0006	.0194 ± .0005	.3744 ± .0017	.0000 ± .0035
ZS7	030605	.0019 ± .0036	.0231 ± .0005	.0096 ± .0004	.1486 ± .0011	.0000 ± .0029
ZS7	030611	.0009 ± .0027	.0044 ± .0003	.0031 ± .0003	.0417 ± .0006	.0000 ± .0027
ZS7	030617	.0023 ± .0039	.0166 ± .0005	.0169 ± .0005	.4574 ± .0018	.0000 ± .0030
ZS7	030623	.0004 ± .0012	.0039 ± .0003	.0030 ± .0003	.0312 ± .0005	.0000 ± .0024
ZS7	030629	.0009 ± .0013	.0107 ± .0004	.0024 ± .0003	.0072 ± .0004	.0000 ± .0025

Appendix E.4 – Metals Data from X-Ray Fluorescence in μg m^{-3}

Site	Date	Arsenic	Selenium	Bromine	Rubidium	Strontium
CH6	021002	.0065 ± .0267	.0011 ± .0003	.0021 ± .0023	.0110 ± .0004	.0050 ± .0004
CH6	021008	.0050 ± .0145	.0022 ± .0004	.0170 ± .0007	.0063 ± .0005	.0018 ± .0005
CH6	021014	.0305 ± .0436	.0037 ± .0004	.0196 ± .0014	.0197 ± .0006	.0003 ± .0012
CH6	021020	.0091 ± .0268	.0056 ± .0004	.0039 ± .0008	.0148 ± .0004	.0022 ± .0004
CH6	021026	.0123 ± .0235	.0029 ± .0003	.0617 ± .0010	.0110 ± .0009	.0006 ± .0011
CH6	021201	.0106 ± .0155	.0027 ± .0003	.0953 ± .0010	.0076 ± .0012	.0005 ± .0010
CH6	021207	.0130 ± .0283	.0035 ± .0004	.0213 ± .0009	.0161 ± .0005	.0010 ± .0011
CH6	021213	.0114 ± .0210	.0032 ± .0003	.0288 ± .0008	.0104 ± .0005	.0009 ± .0011
CH6	021219	.0171 ± .0390	.0055 ± .0004	.0699 ± .0014	.0163 ± .0010	.0004 ± .0011
CH6	021225	.0053 ± .0158	.0014 ± .0003	.0644 ± .0009	.0043 ± .0009	.0003 ± .0011
CH6	030301	.0119 ± .0481	.0060 ± .0004	.0155 ± .0013	.0195 ± .0006	.0046 ± .0004
CH6	030307	.0045 ± .0167	.0020 ± .0004	.0478 ± .0010	.0044 ± .0008	.0006 ± .0014
CH6	030313	.0360 ± .0791	.0061 ± .0006	.2502 ± .0027	.0361 ± .0032	.0022 ± .0005
CH6	030319	.0051 ± .0165	.0010 ± .0011	.0654 ± .0010	.0035 ± .0009	.0003 ± .0013
CH6	030325	.0082 ± .0386	.0023 ± .0004	.0396 ± .0012	.0160 ± .0007	.0000 ± .0012
CH6	030605	.0125 ± .0327	.0082 ± .0005	.0123 ± .0010	.0323 ± .0006	.0039 ± .0004
CH6	030611	.0139 ± .0205	.0069 ± .0004	.0000 ± .0019	.0165 ± .0005	.0012 ± .0004
CH6	030617	.0090 ± .0157	.0019 ± .0004	.0115 ± .0006	.0072 ± .0005	.0005 ± .0013
CH6	030623	.0010 ± .0126	.0016 ± .0003	.0072 ± .0005	.0099 ± .0004	.0014 ± .0004
CH6	030629	.0025 ± .0098	.0014 ± .0003	.0043 ± .0005	.0098 ± .0004	.0013 ± .0004
CW3	021002	.0043 ± .0164	.0020 ± .0004	.0057 ± .0006	.0072 ± .0005	.0131 ± .0006
CW3	021008	.0042 ± .0146	.0016 ± .0004	.0046 ± .0006	.0063 ± .0005	.0021 ± .0005
CW3	021014	.0002 ± .0033	.0009 ± .0011	.0091 ± .0004	.0006 ± .0013	.0008 ± .0014
CW3	021020	.0032 ± .0010	.0003 ± .0011	.0010 ± .0010	.0016 ± .0004	.0000 ± .0016
CW3	021026	.0067 ± .0159	.0015 ± .0004	.0040 ± .0006	.0078 ± .0005	.0000 ± .0017
CW3	021201	.0066 ± .0125	.0047 ± .0004	.0151 ± .0006	.0039 ± .0005	.0013 ± .0015
CW3	021207	.0002 ± .0034	.0005 ± .0012	.0058 ± .0004	.0013 ± .0013	.0008 ± .0017
CW3	021213	.0105 ± .0184	.0029 ± .0004	.0036 ± .0007	.0090 ± .0005	.0010 ± .0015
CW3	021219	.0011 ± .0108	.0033 ± .0004	.0118 ± .0006	.0040 ± .0005	.0017 ± .0005
CW3	021225	.0073 ± .0143	.0027 ± .0004	.0032 ± .0005	.0077 ± .0005	.0000 ± .0014
CW3	030301	.0000 ± .0060	.0017 ± .0005	.0106 ± .0006	.0010 ± .0016	.0025 ± .0006
CW3	030307	.0053 ± .0140	.0002 ± .0015	.0032 ± .0006	.0055 ± .0006	.0002 ± .0019
CW3	030313	.0000 ± .0064	.0013 ± .0014	.0163 ± .0006	.0009 ± .0017	.0018 ± .0018
CW3	030319	.0033 ± .0076	.0021 ± .0005	.0087 ± .0006	.0016 ± .0017	.0004 ± .0019
CW3	030325	.0078 ± .0235	.0043 ± .0005	.0073 ± .0008	.0066 ± .0006	.0020 ± .0006
CW3	030605	.0001 ± .0097	.0030 ± .0005	.0113 ± .0006	.0031 ± .0006	.0011 ± .0018
CW3	030611	.0002 ± .0031	.0007 ± .0012	.0041 ± .0004	.0001 ± .0014	.0019 ± .0005
CW3	030617	.0059 ± .0130	.0031 ± .0005	.0065 ± .0007	.0045 ± .0005	.0022 ± .0006
CW3	030623	.0004 ± .0031	.0007 ± .0014	.0034 ± .0004	.0008 ± .0016	.0000 ± .0018
CW3	030629	.0000 ± .0033	.0008 ± .0014	.0013 ± .0004	.0006 ± .0016	.0008 ± .0019
GZ5	021002	.0438 ± .0111	.0106 ± .0006	.0172 ± .0013	.0148 ± .0006	.0005 ± .0017
GZ5	021008	.0335 ± .0071	.0093 ± .0005	.0211 ± .0010	.0099 ± .0006	.0017 ± .0017
GZ5	021014	.0268 ± .0691	.0151 ± .0007	.0206 ± .0020	.0370 ± .0008	.0052 ± .0006
GZ5	021020	.0316 ± .0412	.0074 ± .0005	.0060 ± .0013	.0113 ± .0005	.0025 ± .0005
GZ5	021026	.0366 ± .0089	.0068 ± .0005	.0296 ± .0012	.0100 ± .0007	.0000 ± .0016
GZ5	021201	.0617 ± .0779	.0096 ± .0006	.0573 ± .0025	.0212 ± .0010	.0024 ± .0005

Site	Date	Arsenic	Selenium	Bromine	Rubidium	Strontium
GZ5	021207	.0372 ± .0580	.0070 ± .0006	.0189 ± .0018	.0254 ± .0007	.0053 ± .0006
GZ5	021213	.0183 ± .0289	.0054 ± .0005	.0154 ± .0010	.0150 ± .0006	.0021 ± .0005
GZ5	021219	.0422 ± .0557	.0115 ± .0006	.0348 ± .0018	.0162 ± .0008	.0017 ± .0017
GZ5	021225	.0158 ± .0274	.0034 ± .0004	.0498 ± .0011	.0082 ± .0008	.0000 ± .0015
GZ5	030301	.0172 ± .0434	.0086 ± .0007	.0195 ± .0014	.0092 ± .0007	.0044 ± .0007
GZ5	030307	.0333 ± .0109	.0055 ± .0006	.0069 ± .0012	.0118 ± .0007	.0000 ± .0019
GZ5	030313	.0553 ± .0675	.0102 ± .0008	.0881 ± .0023	.0288 ± .0015	.0028 ± .0007
GZ5	030319	.0193 ± .0197	.0037 ± .0005	.1071 ± .0015	.0045 ± .0015	.0000 ± .0018
GZ5	030325	.0345 ± .0638	.0138 ± .0008	.0146 ± .0019	.0231 ± .0008	.0023 ± .0007
GZ5	030605	.0110 ± .0250	.0084 ± .0006	.0115 ± .0009	.0080 ± .0006	.0038 ± .0006
GZ5	030611	.0427 ± .0521	.0285 ± .0008	.0176 ± .0017	.0162 ± .0007	.0064 ± .0006
GZ5	030617	.0618 ± .0767	.0494 ± .0011	.0100 ± .0023	.0343 ± .0010	.0043 ± .0008
GZ5	030623	.0344 ± .0561	.0083 ± .0007	.0196 ± .0018	.0175 ± .0008	.0025 ± .0007
GZ5	030629	.0244 ± .0338	.0053 ± .0005	.0013 ± .0033	.0029 ± .0005	.0015 ± .0017
SZ4	021002	.0128 ± .0251	.0041 ± .0005	.0227 ± .0009	.0104 ± .0006	.0012 ± .0016
SZ4	021008	.0140 ± .0287	.0054 ± .0005	.0393 ± .0011	.0115 ± .0007	.0023 ± .0005
SZ4	021014	.0036 ± .0055	.0012 ± .0004	.0095 ± .0005	.0016 ± .0004	.0009 ± .0016
SZ4	021020	.0000 ± .0037	.0015 ± .0004	.0019 ± .0003	.0031 ± .0004	.0015 ± .0005
SZ4	021026	.0119 ± .0223	.0030 ± .0005	.0084 ± .0008	.0106 ± .0006	.0007 ± .0018
SZ4	021201	.0040 ± .0112	.0039 ± .0004	.0120 ± .0006	.0035 ± .0004	.0009 ± .0014
SZ4	021207	.0024 ± .0076	.0008 ± .0011	.0066 ± .0005	.0034 ± .0004	.0011 ± .0015
SZ4	021213	.0146 ± .0376	.0063 ± .0014	.0104 ± .0016	.0137 ± .0016	.0003 ± .0049
SZ4	021221	.0183 ± .0546	.0078 ± .0014	.0644 ± .0025	.0191 ± .0019	.0008 ± .0051
SZ4	021225	.0113 ± .0208	.0017 ± .0004	.0090 ± .0008	.0094 ± .0005	.0002 ± .0016
SZ4	030102	.0197 ± .0307	.0070 ± .0005	.0652 ± .0013	.0129 ± .0010	.0026 ± .0005
SZ4	030301	.0007 ± .0099	.0028 ± .0005	.0192 ± .0007	.0020 ± .0006	.0016 ± .0018
SZ4	030307	.0134 ± .0269	.0034 ± .0005	.0059 ± .0009	.0106 ± .0006	.0000 ± .0017
SZ4	030313	.0040 ± .0120	.0018 ± .0005	.0210 ± .0008	.0028 ± .0006	.0029 ± .0006
SZ4	030319	.0073 ± .0200	.0022 ± .0005	.0248 ± .0009	.0069 ± .0007	.0005 ± .0018
SZ4	030325	.0112 ± .0280	.0053 ± .0006	.0168 ± .0010	.0076 ± .0007	.0003 ± .0020
SZ4	030605	.0052 ± .0094	.0028 ± .0005	.0116 ± .0007	.0053 ± .0006	.0026 ± .0006
SZ4	030611	.0024 ± .0063	.0005 ± .0013	.0090 ± .0005	.0022 ± .0005	.0012 ± .0018
SZ4	030617	.0070 ± .0147	.0036 ± .0005	.0087 ± .0007	.0067 ± .0006	.0014 ± .0019
SZ4	030623	.0015 ± .0034	.0000 ± .0013	.0025 ± .0004	.0010 ± .0015	.0004 ± .0018
SZ4	030629	.0000 ± .0032	.0001 ± .0013	.0017 ± .0004	.0007 ± .0015	.0011 ± .0018
TC2	021002	.0054 ± .0174	.0031 ± .0004	.0103 ± .0007	.0071 ± .0005	.0007 ± .0015
TC2	021008	.0077 ± .0150	.0029 ± .0004	.0050 ± .0006	.0087 ± .0005	.0022 ± .0005
TC2	021014	.0016 ± .0046	.0006 ± .0011	.0085 ± .0005	.0033 ± .0005	.0005 ± .0016
TC2	021020	.0000 ± .0027	.0007 ± .0010	.0009 ± .0003	.0011 ± .0011	.0002 ± .0014
TC2	021026	.0067 ± .0171	.0022 ± .0004	.0043 ± .0007	.0077 ± .0005	.0003 ± .0015
TC2	021201	.0034 ± .0110	.0033 ± .0004	.0133 ± .0006	.0035 ± .0004	.0011 ± .0013
TC2	021207	.0018 ± .0025	.0000 ± .0010	.0034 ± .0003	.0002 ± .0012	.0000 ± .0014
TC2	021213	.0112 ± .0184	.0024 ± .0004	.0034 ± .0007	.0090 ± .0005	.0000 ± .0016
TC2	021219	.0019 ± .0072	.0016 ± .0004	.0091 ± .0005	.0028 ± .0005	.0002 ± .0016
TC2	021225	.0067 ± .0201	.0024 ± .0004	.0035 ± .0007	.0093 ± .0005	.0004 ± .0014
TC2	030301	.0007 ± .0050	.0006 ± .0014	.0077 ± .0005	.0010 ± .0017	.0015 ± .0019
TC2	030307	.0080 ± .0257	.0030 ± .0005	.0037 ± .0009	.0072 ± .0006	.0003 ± .0019
TC2	030313	.0000 ± .0055	.0001 ± .0015	.0128 ± .0006	.0000 ± .0018	.0015 ± .0021
TC2	030319	.0005 ± .0105	.0014 ± .0014	.0071 ± .0006	.0017 ± .0017	.0000 ± .0018

Site	Date	Arsenic	Selenium	Bromine	Rubidium	Strontium
TC2	030325	.0067 ± .0181	.0022 ± .0005	.0067 ± .0007	.0050 ± .0006	.0003 ± .0019
TC2	030605	.0060 ± .0105	.0024 ± .0005	.0089 ± .0006	.0055 ± .0006	.0010 ± .0020
TC2	030611	.0009 ± .0034	.0004 ± .0014	.0024 ± .0004	.0015 ± .0017	.0000 ± .0019
TC2	030617	.0055 ± .0133	.0046 ± .0005	.0055 ± .0007	.0060 ± .0006	.0016 ± .0018
TC2	030623	.0000 ± .0030	.0001 ± .0012	.0017 ± .0004	.0001 ± .0014	.0004 ± .0017
TC2	030629	.0013 ± .0030	.0004 ± .0013	.0013 ± .0004	.0000 ± .0015	.0009 ± .0017
TM1	021002	.0084 ± .0185	.0024 ± .0004	.0038 ± .0007	.0090 ± .0005	.0000 ± .0016
TM1	021008	.0041 ± .0169	.0030 ± .0004	.0052 ± .0006	.0079 ± .0005	.0027 ± .0005
TM1	021014	.0017 ± .0030	.0005 ± .0011	.0072 ± .0004	.0005 ± .0013	.0009 ± .0016
TM1	021020	.0027 ± .0029	.0004 ± .0011	.0008 ± .0010	.0010 ± .0012	.0000 ± .0015
TM1	021026	.0065 ± .0187	.0019 ± .0005	.0043 ± .0007	.0091 ± .0005	.0000 ± .0018
TM1	021201	.0026 ± .0127	.0036 ± .0004	.0132 ± .0006	.0044 ± .0004	.0019 ± .0005
TM1	021207	.0000 ± .0039	.0012 ± .0003	.0028 ± .0003	.0011 ± .0004	.0004 ± .0013
TM1	021213	.0088 ± .0198	.0031 ± .0004	.0040 ± .0007	.0096 ± .0005	.0020 ± .0005
TM1	021219	.0068 ± .0121	.0034 ± .0004	.0105 ± .0006	.0037 ± .0004	.0014 ± .0015
TM1	021225	.0056 ± .0161	.0021 ± .0004	.0026 ± .0006	.0097 ± .0005	.0001 ± .0013
TM1	030301	.0007 ± .0057	.0014 ± .0005	.0077 ± .0005	.0020 ± .0006	.0011 ± .0018
TM1	030307	.0076 ± .0146	.0021 ± .0005	.0024 ± .0007	.0053 ± .0006	.0000 ± .0019
TM1	030313	.0023 ± .0065	.0018 ± .0005	.0147 ± .0006	.0010 ± .0018	.0009 ± .0019
TM1	030319	.0033 ± .0120	.0029 ± .0005	.0154 ± .0007	.0042 ± .0006	.0010 ± .0018
TM1	030325	.0123 ± .0309	.0055 ± .0005	.0068 ± .0010	.0084 ± .0006	.0013 ± .0017
TM1	030605	.0044 ± .0084	.0016 ± .0005	.0118 ± .0006	.0031 ± .0005	.0014 ± .0017
TM1	030611	.0007 ± .0032	.0000 ± .0013	.0029 ± .0005	.0014 ± .0016	.0000 ± .0018
TM1	030617	.0038 ± .0132	.0033 ± .0005	.0069 ± .0006	.0069 ± .0006	.0025 ± .0007
TM1	030623	.0000 ± .0031	.0001 ± .0013	.0023 ± .0004	.0000 ± .0016	.0000 ± .0018
TM1	030629	.0000 ± .0030	.0000 ± .0012	.0008 ± .0011	.0002 ± .0014	.0006 ± .0017
ZS7	021008	.0182 ± .0645	.0112 ± .0006	.0224 ± .0018	.0413 ± .0007	.0064 ± .0005
ZS7	021014	.0069 ± .0161	.0041 ± .0004	.0150 ± .0006	.0083 ± .0005	.0019 ± .0005
ZS7	021020	.0008 ± .0035	.0013 ± .0003	.0022 ± .0003	.0018 ± .0003	.0012 ± .0004
ZS7	021026	.0040 ± .0099	.0047 ± .0004	.0111 ± .0005	.0040 ± .0004	.0019 ± .0004
ZS7	021201	.0200 ± .0302	.0139 ± .0005	.0385 ± .0011	.0077 ± .0006	.0008 ± .0011
ZS7	021207	.0091 ± .0188	.0080 ± .0004	.0108 ± .0007	.0050 ± .0004	.0004 ± .0011
ZS7	021213	.0261 ± .0507	.0116 ± .0005	.0217 ± .0015	.0280 ± .0007	.0027 ± .0005
ZS7	021219	.0225 ± .0387	.0128 ± .0005	.0338 ± .0013	.0132 ± .0006	.0028 ± .0004
ZS7	021225	.0214 ± .0532	.0072 ± .0005	.0586 ± .0017	.0197 ± .0009	.0019 ± .0004
ZS7	030301	.0074 ± .0025	.0020 ± .0003	.0142 ± .0005	.0030 ± .0004	.0021 ± .0004
ZS7	030307	.0146 ± .0340	.0063 ± .0004	.0555 ± .0012	.0079 ± .0008	.0022 ± .0004
ZS7	030313	.0046 ± .0121	.0031 ± .0004	.0246 ± .0007	.0036 ± .0005	.0019 ± .0004
ZS7	030319	.0148 ± .0438	.0064 ± .0005	.0589 ± .0014	.0135 ± .0009	.0019 ± .0004
ZS7	030325	.0089 ± .0265	.0043 ± .0004	.0221 ± .0009	.0101 ± .0006	.0011 ± .0014
ZS7	030605	.0003 ± .0084	.0026 ± .0004	.0081 ± .0005	.0042 ± .0004	.0020 ± .0004
ZS7	030611	.0004 ± .0037	.0010 ± .0003	.0029 ± .0004	.0012 ± .0003	.0010 ± .0012
ZS7	030617	.0083 ± .0199	.0231 ± .0006	.0062 ± .0007	.0068 ± .0004	.0015 ± .0004
ZS7	030623	.0000 ± .0025	.0007 ± .0008	.0020 ± .0003	.0005 ± .0009	.0003 ± .0010
ZS7	030629	.0004 ± .0022	.0000 ± .0009	.0021 ± .0003	.0006 ± .0011	.0000 ± .0012

Appendix E.5 – Metals Data from X-Ray Fluorescence in μg m^{-3}

Site	Date	Yttrium	Zirconium	Molybdenum	Palladium	Silver
CH6	021002	.0000 ± .0020	.0000 ± .0015	.0000 ± .0026	.0000 ± .0026	.0440 ± .0019
CH6	021008	.0000 ± .0019	.0034 ± .0007	.0000 ± .0035	.0022 ± .0033	.0827 ± .0029
CH6	021014	.0000 ± .0029	.0010 ± .0017	.0000 ± .0030	.0011 ± .0029	.0390 ± .0019
CH6	021020	.0000 ± .0020	.0017 ± .0005	.0017 ± .0026	.0004 ± .0026	.0409 ± .0019
CH6	021026	.0000 ± .0019	.0003 ± .0015	.0015 ± .0026	.0010 ± .0028	.0930 ± .0026
CH6	021201	.0003 ± .0016	.0000 ± .0013	.0011 ± .0024	.0000 ± .0025	.0561 ± .0021
CH6	021207	.0000 ± .0021	.0005 ± .0015	.0000 ± .0027	.0012 ± .0028	.1457 ± .0031
CH6	021213	.0000 ± .0018	.0007 ± .0015	.0007 ± .0026	.0019 ± .0026	.0425 ± .0019
CH6	021219	.0000 ± .0026	.0023 ± .0005	.0010 ± .0027	.0000 ± .0026	.0962 ± .0026
CH6	021225	.0004 ± .0016	.0004 ± .0015	.0007 ± .0027	.0000 ± .0027	.0803 ± .0024
CH6	030301	.0000 ± .0028	.0076 ± .0005	.0042 ± .0009	.0000 ± .0026	.1008 ± .0028
CH6	030307	.0003 ± .0019	.0001 ± .0020	.0045 ± .0012	.0000 ± .0035	.1247 ± .0036
CH6	030313	.0000 ± .0047	.0023 ± .0007	.0025 ± .0035	.0024 ± .0034	.0853 ± .0030
CH6	030319	.0000 ± .0018	.0003 ± .0018	.0017 ± .0032	.0020 ± .0034	.0446 ± .0023
CH6	030325	.0000 ± .0025	.0000 ± .0017	.0035 ± .0010	.0000 ± .0028	.1844 ± .0036
CH6	030605	.0000 ± .0026	.0024 ± .0006	.0033 ± .0010	.0000 ± .0031	.1387 ± .0031
CH6	030611	.0000 ± .0018	.0022 ± .0005	.0016 ± .0025	.0011 ± .0025	.0466 ± .0020
CH6	030617	.0001 ± .0017	.0000 ± .0018	.0033 ± .0010	.0016 ± .0027	.1006 ± .0027
CH6	030623	.0015 ± .0016	.0001 ± .0016	.0017 ± .0027	.0000 ± .0025	.0993 ± .0027
CH6	030629	.0003 ± .0016	.0003 ± .0017	.0000 ± .0029	.0000 ± .0028	.0455 ± .0020
CW3	021002	.0010 ± .0020	.0007 ± .0021	.0011 ± .0036	.0000 ± .0036	.0009 ± .0047
CW3	021008	.0001 ± .0021	.0017 ± .0023	.0000 ± .0039	.0004 ± .0034	.0000 ± .0049
CW3	021014	.0002 ± .0017	.0005 ± .0020	.0013 ± .0035	.0000 ± .0033	.0023 ± .0047
CW3	021020	.0000 ± .0019	.0001 ± .0022	.0000 ± .0039	.0018 ± .0037	.0000 ± .0046
CW3	021026	.0000 ± .0023	.0003 ± .0024	.0000 ± .0042	.0000 ± .0041	.0000 ± .0050
CW3	021201	.0000 ± .0019	.0000 ± .0021	.0000 ± .0037	.0000 ± .0035	.0000 ± .0047
CW3	021207	.0000 ± .0019	.0006 ± .0023	.0000 ± .0040	.0000 ± .0043	.0000 ± .0051
CW3	021213	.0003 ± .0020	.0001 ± .0020	.0001 ± .0035	.0001 ± .0035	.0000 ± .0047
CW3	021219	.0000 ± .0019	.0013 ± .0021	.0000 ± .0036	.0000 ± .0036	.0000 ± .0046
CW3	021225	.0006 ± .0019	.0011 ± .0020	.0000 ± .0035	.0015 ± .0035	.0012 ± .0043
CW3	030301	.0005 ± .0021	.0006 ± .0024	.0008 ± .0042	.0001 ± .0044	.0008 ± .0052
CW3	030307	.0000 ± .0024	.0006 ± .0028	.0000 ± .0047	.0000 ± .0041	.0022 ± .0058
CW3	030313	.0003 ± .0022	.0014 ± .0026	.0000 ± .0044	.0000 ± .0046	.0016 ± .0055
CW3	030319	.0000 ± .0023	.0014 ± .0027	.0000 ± .0047	.0000 ± .0046	.0000 ± .0058
CW3	030325	.0000 ± .0025	.0006 ± .0026	.0008 ± .0044	.0016 ± .0044	.0000 ± .0056
CW3	030605	.0010 ± .0022	.0014 ± .0026	.0031 ± .0044	.0037 ± .0046	.0038 ± .0056
CW3	030611	.0002 ± .0018	.0012 ± .0022	.0033 ± .0038	.0000 ± .0039	.0027 ± .0057
CW3	030617	.0002 ± .0021	.0019 ± .0023	.0018 ± .0040	.0000 ± .0039	.0000 ± .0050
CW3	030623	.0000 ± .0022	.0000 ± .0026	.0029 ± .0045	.0000 ± .0045	.0000 ± .0055
CW3	030629	.0007 ± .0022	.0000 ± .0027	.0000 ± .0046	.0009 ± .0044	.0054 ± .0056
GZ5	021002	.0000 ± .0028	.0012 ± .0024	.0000 ± .0042	.0018 ± .0036	.0001 ± .0049
GZ5	021008	.0000 ± .0023	.0013 ± .0023	.0000 ± .0040	.0007 ± .0038	.0008 ± .0047
GZ5	021014	.0000 ± .0044	.0045 ± .0008	.0000 ± .0039	.0000 ± .0035	.0030 ± .0047
GZ5	021020	.0000 ± .0028	.0011 ± .0020	.0011 ± .0035	.0008 ± .0033	.0007 ± .0045
GZ5	021026	.0002 ± .0025	.0000 ± .0022	.0000 ± .0039	.0004 ± .0040	.0000 ± .0049
GZ5	021201	.0000 ± .0046	.0019 ± .0021	.0023 ± .0036	.0000 ± .0035	.0020 ± .0048

Site	Date	Yttrium	Zirconium	Molybdenum	Palladium	Silver
GZ5	021207	.0002 ± .0037	.0031 ± .0007	.0004 ± .0037	.0006 ± .0037	.0008 ± .0049
GZ5	021213	.0000 ± .0024	.0004 ± .0020	.0000 ± .0035	.0000 ± .0034	.0000 ± .0047
GZ5	021219	.0000 ± .0036	.0027 ± .0008	.0000 ± .0039	.0015 ± .0036	.0020 ± .0045
GZ5	021225	.0002 ± .0023	.0011 ± .0021	.0000 ± .0036	.0001 ± .0034	.0000 ± .0047
GZ5	030301	.0000 ± .0032	.0043 ± .0009	.0004 ± .0046	.0000 ± .0048	.0002 ± .0059
GZ5	030307	.0000 ± .0029	.0006 ± .0028	.0000 ± .0047	.0000 ± .0045	.0020 ± .0060
GZ5	030313	.0011 ± .0045	.0011 ± .0030	.0000 ± .0052	.0000 ± .0046	.0009 ± .0062
GZ5	030319	.0001 ± .0025	.0000 ± .0026	.0000 ± .0045	.0000 ± .0043	.0020 ± .0055
GZ5	030325	.0000 ± .0040	.0029 ± .0009	.0000 ± .0046	.0000 ± .0045	.0088 ± .0021
GZ5	030605	.0000 ± .0025	.0022 ± .0025	.0020 ± .0043	.0000 ± .0046	.0000 ± .0056
GZ5	030611	.0012 ± .0034	.0070 ± .0008	.0051 ± .0014	.0025 ± .0042	.0023 ± .0049
GZ5	030617	.0000 ± .0048	.0068 ± .0011	.0000 ± .0053	.0000 ± .0046	.0035 ± .0061
GZ5	030623	.0012 ± .0038	.0069 ± .0010	.0000 ± .0048	.0000 ± .0045	.0014 ± .0062
GZ5	030629	.0008 ± .0026	.0028 ± .0008	.0037 ± .0041	.0000 ± .0040	.0012 ± .0052
SZ4	021002	.0000 ± .0023	.0008 ± .0022	.0000 ± .0038	.0012 ± .0036	.0000 ± .0044
SZ4	021008	.0000 ± .0025	.0015 ± .0021	.0000 ± .0037	.0000 ± .0036	.0028 ± .0047
SZ4	021014	.0000 ± .0019	.0000 ± .0022	.0000 ± .0038	.0009 ± .0034	.0005 ± .0046
SZ4	021020	.0002 ± .0017	.0008 ± .0020	.0000 ± .0036	.0002 ± .0036	.0024 ± .0047
SZ4	021026	.0000 ± .0025	.0005 ± .0025	.0000 ± .0043	.0014 ± .0038	.0000 ± .0047
SZ4	021201	.0000 ± .0017	.0000 ± .0019	.0000 ± .0033	.0031 ± .0033	.0000 ± .0042
SZ4	021207	.0000 ± .0018	.0012 ± .0021	.0000 ± .0036	.0006 ± .0036	.0022 ± .0048
SZ4	021213	.0020 ± .0063	.0028 ± .0070	.0076 ± .0122	.0000 ± .0117	.0135 ± .0158
SZ4	021221	.0000 ± .0069	.0070 ± .0074	.0059 ± .0127	.0000 ± .0125	.0124 ± .0158
SZ4	021225	.0000 ± .0022	.0003 ± .0022	.0000 ± .0038	.0000 ± .0037	.0002 ± .0045
SZ4	030102	.0014 ± .0026	.0000 ± .0021	.0000 ± .0037	.0008 ± .0037	.0013 ± .0049
SZ4	030301	.0011 ± .0022	.0006 ± .0025	.0028 ± .0043	.0000 ± .0045	.0000 ± .0057
SZ4	030307	.0013 ± .0026	.0005 ± .0024	.0024 ± .0042	.0000 ± .0040	.0023 ± .0058
SZ4	030313	.0000 ± .0023	.0000 ± .0026	.0009 ± .0045	.0010 ± .0045	.0038 ± .0056
SZ4	030319	.0002 ± .0024	.0018 ± .0025	.0028 ± .0044	.0000 ± .0048	.0000 ± .0061
SZ4	030325	.0000 ± .0028	.0023 ± .0028	.0005 ± .0048	.0000 ± .0045	.0005 ± .0064
SZ4	030605	.0006 ± .0023	.0006 ± .0026	.0026 ± .0045	.0000 ± .0042	.0029 ± .0054
SZ4	030611	.0012 ± .0021	.0011 ± .0025	.0023 ± .0043	.0026 ± .0041	.0039 ± .0051
SZ4	030617	.0000 ± .0024	.0000 ± .0027	.0000 ± .0046	.0000 ± .0043	.0099 ± .0019
SZ4	030623	.0004 ± .0021	.0010 ± .0025	.0007 ± .0044	.0037 ± .0043	.0033 ± .0053
SZ4	030629	.0000 ± .0021	.0009 ± .0025	.0031 ± .0043	.0000 ± .0044	.0013 ± .0056
TC2	021002	.0000 ± .0020	.0013 ± .0020	.0002 ± .0036	.0000 ± .0035	.0031 ± .0046
TC2	021008	.0000 ± .0020	.0012 ± .0021	.0000 ± .0037	.0000 ± .0035	.0000 ± .0045
TC2	021014	.0000 ± .0019	.0000 ± .0022	.0000 ± .0038	.0000 ± .0036	.0007 ± .0047
TC2	021020	.0003 ± .0017	.0008 ± .0020	.0000 ± .0034	.0001 ± .0031	.0024 ± .0044
TC2	021026	.0000 ± .0020	.0000 ± .0020	.0000 ± .0036	.0000 ± .0034	.0015 ± .0046
TC2	021201	.0000 ± .0017	.0000 ± .0018	.0002 ± .0032	.0000 ± .0034	.0000 ± .0044
TC2	021207	.0000 ± .0017	.0000 ± .0020	.0000 ± .0036	.0000 ± .0032	.0001 ± .0042
TC2	021213	.0000 ± .0022	.0012 ± .0022	.0000 ± .0038	.0018 ± .0038	.0000 ± .0048
TC2	021219	.0000 ± .0020	.0000 ± .0023	.0000 ± .0040	.0000 ± .0039	.0000 ± .0049
TC2	021225	.0004 ± .0021	.0008 ± .0020	.0014 ± .0035	.0000 ± .0033	.0053 ± .0014
TC2	030301	.0001 ± .0023	.0012 ± .0027	.0000 ± .0046	.0004 ± .0042	.0045 ± .0055
TC2	030307	.0002 ± .0026	.0023 ± .0027	.0018 ± .0046	.0011 ± .0043	.0010 ± .0060
TC2	030313	.0000 ± .0024	.0000 ± .0029	.0000 ± .0050	.0000 ± .0045	.0022 ± .0057
TC2	030319	.0016 ± .0023	.0020 ± .0026	.0027 ± .0045	.0034 ± .0048	.0012 ± .0056

Site	Date	Yttrium	Zirconium	Molybdenum	Palladium	Silver
TC2	030325	.0000 ± .0025	.0011 ± .0027	.0000 ± .0047	.0000 ± .0045	.0000 ± .0057
TC2	030605	.0001 ± .0024	.0010 ± .0028	.0000 ± .0048	.0014 ± .0046	.0021 ± .0055
TC2	030611	.0009 ± .0023	.0014 ± .0028	.0000 ± .0048	.0023 ± .0043	.0037 ± .0052
TC2	030617	.0000 ± .0022	.0006 ± .0024	.0025 ± .0042	.0013 ± .0038	.0000 ± .0054
TC2	030623	.0006 ± .0020	.0009 ± .0024	.0001 ± .0042	.0018 ± .0041	.0050 ± .0053
TC2	030629	.0010 ± .0020	.0007 ± .0024	.0000 ± .0042	.0000 ± .0043	.0000 ± .0056
TM1	021002	.0000 ± .0022	.0005 ± .0022	.0005 ± .0040	.0000 ± .0037	.0000 ± .0046
TM1	021008	.0000 ± .0021	.0012 ± .0021	.0000 ± .0037	.0000 ± .0034	.0027 ± .0046
TM1	021014	.0000 ± .0019	.0000 ± .0022	.0000 ± .0039	.0000 ± .0036	.0008 ± .0046
TM1	021020	.0006 ± .0019	.0022 ± .0022	.0000 ± .0038	.0000 ± .0035	.0000 ± .0049
TM1	021026	.0000 ± .0024	.0000 ± .0025	.0000 ± .0043	.0000 ± .0041	.0000 ± .0051
TM1	021201	.0001 ± .0018	.0000 ± .0019	.0000 ± .0034	.0000 ± .0031	.0000 ± .0042
TM1	021207	.0002 ± .0016	.0012 ± .0019	.0000 ± .0032	.0000 ± .0036	.0000 ± .0043
TM1	021213	.0000 ± .0021	.0011 ± .0021	.0000 ± .0036	.0000 ± .0036	.0006 ± .0046
TM1	021219	.0000 ± .0019	.0006 ± .0020	.0000 ± .0035	.0000 ± .0033	.0014 ± .0044
TM1	021225	.0000 ± .0019	.0000 ± .0018	.0000 ± .0032	.0019 ± .0033	.0010 ± .0041
TM1	030301	.0011 ± .0021	.0003 ± .0025	.0000 ± .0042	.0000 ± .0043	.0049 ± .0057
TM1	030307	.0000 ± .0024	.0013 ± .0027	.0025 ± .0047	.0000 ± .0047	.0014 ± .0060
TM1	030313	.0015 ± .0023	.0000 ± .0026	.0005 ± .0046	.0004 ± .0048	.0026 ± .0060
TM1	030319	.0000 ± .0022	.0010 ± .0025	.0026 ± .0044	.0000 ± .0048	.0023 ± .0058
TM1	030325	.0000 ± .0025	.0007 ± .0023	.0021 ± .0040	.0000 ± .0041	.0023 ± .0055
TM1	030605	.0017 ± .0020	.0000 ± .0023	.0016 ± .0040	.0000 ± .0038	.0022 ± .0050
TM1	030611	.0007 ± .0022	.0011 ± .0026	.0000 ± .0045	.0004 ± .0043	.0032 ± .0057
TM1	030617	.0002 ± .0024	.0008 ± .0027	.0000 ± .0047	.0000 ± .0045	.0000 ± .0053
TM1	030623	.0000 ± .0021	.0007 ± .0026	.0000 ± .0045	.0000 ± .0043	.0059 ± .0019
TM1	030629	.0000 ± .0020	.0000 ± .0024	.0024 ± .0041	.0000 ± .0045	.0000 ± .0054
ZS7	021008	.0000 ± .0041	.0033 ± .0006	.0022 ± .0032	.0008 ± .0032	.0808 ± .0026
ZS7	021014	.0000 ± .0018	.0002 ± .0018	.0000 ± .0032	.0000 ± .0028	.0574 ± .0022
ZS7	021020	.0001 ± .0013	.0002 ± .0016	.0000 ± .0027	.0000 ± .0025	.0109 ± .0014
ZS7	021026	.0000 ± .0015	.0011 ± .0016	.0004 ± .0028	.0000 ± .0027	.0000 ± .0038
ZS7	021201	.0003 ± .0021	.0021 ± .0005	.0013 ± .0027	.0030 ± .0009	.0133 ± .0014
ZS7	021207	.0000 ± .0016	.0023 ± .0005	.0000 ± .0026	.0001 ± .0025	.0037 ± .0012
ZS7	021213	.0000 ± .0033	.0035 ± .0006	.0000 ± .0031	.0000 ± .0028	.0067 ± .0014
ZS7	021219	.0000 ± .0026	.0047 ± .0006	.0000 ± .0031	.0000 ± .0030	.0054 ± .0014
ZS7	021225	.0000 ± .0033	.0016 ± .0018	.0000 ± .0031	.0000 ± .0029	.0254 ± .0018
ZS7	030301	.0004 ± .0015	.0010 ± .0017	.0128 ± .0010	.0000 ± .0034	.4433 ± .0055
ZS7	030307	.0016 ± .0022	.0020 ± .0005	.0016 ± .0027	.0000 ± .0026	.0218 ± .0016
ZS7	030313	.0001 ± .0016	.0015 ± .0018	.0016 ± .0031	.0000 ± .0027	.0491 ± .0021
ZS7	030319	.0000 ± .0027	.0019 ± .0006	.0060 ± .0010	.0000 ± .0030	.1219 ± .0030
ZS7	030325	.0006 ± .0022	.0007 ± .0019	.0000 ± .0033	.0000 ± .0029	.0229 ± .0017
ZS7	030605	.0005 ± .0017	.0000 ± .0019	.0000 ± .0032	.0018 ± .0030	.0427 ± .0020
ZS7	030611	.0005 ± .0014	.0014 ± .0017	.0022 ± .0029	.0001 ± .0028	.0007 ± .0034
ZS7	030617	.0000 ± .0017	.0025 ± .0005	.0017 ± .0027	.0000 ± .0028	.0236 ± .0017
ZS7	030623	.0005 ± .0012	.0006 ± .0014	.0002 ± .0025	.0014 ± .0026	.0021 ± .0033
ZS7	030629	.0000 ± .0015	.0006 ± .0017	.0000 ± .0030	.0000 ± .0028	.0279 ± .0018

Appendix E.6 – Metals Data from X-Ray Fluorescence in μg m^{-3}

Site	Date	Cadmium	Indium	Tin	Antimony	Barium
CH6	021002	.0043 ± .0012	.0000 ± .0040	.0138 ± .0024	.0067 ± .0074	.0393 ± .0109
CH6	021008	.0000 ± .0045	.0000 ± .0059	.0073 ± .0096	.0051 ± .0095	.0000 ± .0432
CH6	021014	.0115 ± .0015	.0015 ± .0047	.0255 ± .0027	.0144 ± .0028	.0000 ± .0344
CH6	021020	.0027 ± .0035	.0000 ± .0040	.0100 ± .0023	.0045 ± .0073	.0000 ± .0328
CH6	021026	.0033 ± .0037	.0000 ± .0040	.0297 ± .0028	.0157 ± .0025	.0177 ± .0325
CH6	021201	.0011 ± .0034	.0000 ± .0041	.0228 ± .0024	.0110 ± .0022	.0000 ± .0306
CH6	021207	.0031 ± .0036	.0000 ± .0043	.0171 ± .0031	.0095 ± .0024	.0000 ± .0322
CH6	021213	.0000 ± .0034	.0010 ± .0040	.0183 ± .0024	.0130 ± .0025	.0155 ± .0327
CH6	021219	.0031 ± .0034	.0021 ± .0044	.0492 ± .0031	.0095 ± .0025	.0000 ± .0320
CH6	021225	.0016 ± .0034	.0000 ± .0042	.0226 ± .0028	.0051 ± .0075	.0000 ± .0325
CH6	030301	.0022 ± .0038	.0000 ± .0044	.0550 ± .0034	.0074 ± .0077	.0179 ± .0343
CH6	030307	.0031 ± .0050	.0000 ± .0057	.0181 ± .0039	.0027 ± .0102	.0000 ± .0473
CH6	030313	.0049 ± .0050	.0033 ± .0060	.0786 ± .0042	.0246 ± .0036	.0309 ± .0448
CH6	030319	.0000 ± .0043	.0000 ± .0050	.0196 ± .0031	.0050 ± .0094	.0272 ± .0420
CH6	030325	.0015 ± .0040	.0000 ± .0046	.0269 ± .0038	.0130 ± .0028	.0000 ± .0370
CH6	030605	.0037 ± .0041	.0000 ± .0047	.0145 ± .0034	.0045 ± .0085	.0372 ± .0122
CH6	030611	.0002 ± .0035	.0000 ± .0041	.0109 ± .0026	.0021 ± .0076	.0123 ± .0338
CH6	030617	.0035 ± .0040	.0000 ± .0046	.0110 ± .0029	.0001 ± .0081	.0092 ± .0372
CH6	030623	.0000 ± .0036	.0002 ± .0044	.0055 ± .0083	.0000 ± .0075	.0077 ± .0343
CH6	030629	.0000 ± .0034	.0000 ± .0045	.0041 ± .0076	.0000 ± .0078	.0000 ± .0368
CW3	021002	.0019 ± .0048	.0000 ± .0058	.0154 ± .0029	.0105 ± .0032	.0240 ± .0454
CW3	021008	.0002 ± .0049	.0036 ± .0062	.0095 ± .0030	.0050 ± .0100	.0042 ± .0465
CW3	021014	.0008 ± .0046	.0025 ± .0057	.0260 ± .0031	.0001 ± .0094	.0000 ± .0445
CW3	021020	.0000 ± .0047	.0000 ± .0062	.0116 ± .0031	.0037 ± .0099	.0216 ± .0472
CW3	021026	.0003 ± .0049	.0016 ± .0065	.0223 ± .0034	.0012 ± .0108	.0200 ± .0489
CW3	021201	.0005 ± .0049	.0000 ± .0060	.0271 ± .0034	.0047 ± .0099	.0215 ± .0452
CW3	021207	.0000 ± .0050	.0000 ± .0060	.0129 ± .0031	.0000 ± .0103	.0000 ± .0473
CW3	021213	.0061 ± .0016	.0048 ± .0059	.0283 ± .0032	.0134 ± .0032	.0427 ± .0449
CW3	021219	.0015 ± .0044	.0023 ± .0056	.0184 ± .0030	.0010 ± .0095	.0207 ± .0444
CW3	021225	.0046 ± .0049	.0000 ± .0056	.0155 ± .0030	.0035 ± .0094	.0000 ± .0431
CW3	030301	.0071 ± .0020	.0026 ± .0071	.0111 ± .0115	.0000 ± .0120	.0217 ± .0564
CW3	030307	.0030 ± .0060	.0037 ± .0073	.0105 ± .0117	.0009 ± .0133	.0326 ± .0600
CW3	030313	.0000 ± .0055	.0000 ± .0071	.0045 ± .0112	.0084 ± .0125	.0118 ± .0581
CW3	030319	.0000 ± .0063	.0000 ± .0073	.0459 ± .0044	.0000 ± .0128	.0261 ± .0593
CW3	030325	.0038 ± .0058	.0012 ± .0071	.0320 ± .0043	.0000 ± .0128	.0000 ± .0579
CW3	030605	.0000 ± .0058	.0000 ± .0075	.0032 ± .0117	.0000 ± .0124	.0287 ± .0569
CW3	030611	.0000 ± .0052	.0047 ± .0067	.0000 ± .0100	.0000 ± .0114	.0000 ± .0530
CW3	030617	.0063 ± .0019	.0003 ± .0067	.0244 ± .0039	.0000 ± .0120	.0047 ± .0548
CW3	030623	.0001 ± .0058	.0000 ± .0070	.0000 ± .0109	.0008 ± .0123	.0142 ± .0568
CW3	030629	.0002 ± .0055	.0000 ± .0069	.0000 ± .0106	.0002 ± .0125	.0000 ± .0594
GZ5	021002	.0036 ± .0054	.0041 ± .0061	.0292 ± .0033	.0153 ± .0037	.0031 ± .0495
GZ5	021008	.0068 ± .0017	.0035 ± .0060	.0115 ± .0031	.0139 ± .0037	.0000 ± .0481
GZ5	021014	.0120 ± .0017	.0016 ± .0061	.0531 ± .0037	.0203 ± .0035	.0509 ± .0158
GZ5	021020	.0011 ± .0046	.0000 ± .0054	.0225 ± .0030	.0128 ± .0033	.0000 ± .0446
GZ5	021026	.0041 ± .0050	.0000 ± .0058	.0279 ± .0034	.0130 ± .0036	.0066 ± .0478
GZ5	021201	.0000 ± .0049	.0000 ± .0056	.0799 ± .0039	.0275 ± .0036	.0000 ± .0439

Site	Date	Cadmium	Indium	Tin	Antimony	Barium
GZ5	021207	.0037 ± .0051	.0033 ± .0057	.0287 ± .0030	.0321 ± .0036	.0000 ± .0448
GZ5	021213	.0000 ± .0050	.0000 ± .0058	.0183 ± .0030	.0143 ± .0032	.0000 ± .0441
GZ5	021219	.0000 ± .0050	.0039 ± .0055	.0302 ± .0032	.0269 ± .0036	.0057 ± .0457
GZ5	021225	.0016 ± .0048	.0014 ± .0058	.0487 ± .0034	.0100 ± .0032	.0200 ± .0442
GZ5	030301	.0034 ± .0063	.0007 ± .0073	.0229 ± .0040	.0160 ± .0045	.0409 ± .0594
GZ5	030307	.0068 ± .0022	.0000 ± .0078	.0070 ± .0122	.0131 ± .0139	.0198 ± .0602
GZ5	030313	.0000 ± .0070	.0018 ± .0077	.0470 ± .0048	.0200 ± .0051	.0205 ± .0636
GZ5	030319	.0003 ± .0058	.0000 ± .0068	.0231 ± .0040	.0070 ± .0127	.0000 ± .0584
GZ5	030325	.0128 ± .0021	.0000 ± .0070	.0406 ± .0044	.0068 ± .0132	.0000 ± .0592
GZ5	030605	.0018 ± .0054	.0000 ± .0068	.0140 ± .0039	.0000 ± .0123	.0100 ± .0563
GZ5	030611	.0000 ± .0058	.0018 ± .0065	.0121 ± .0038	.0203 ± .0044	.0330 ± .0542
GZ5	030617	.0122 ± .0022	.0008 ± .0078	.0362 ± .0044	.0156 ± .0047	.0671 ± .0210
GZ5	030623	.0018 ± .0061	.0041 ± .0074	.0116 ± .0120	.0000 ± .0133	.0000 ± .0596
GZ5	030629	.0000 ± .0055	.0000 ± .0068	.0000 ± .0109	.0000 ± .0126	.0000 ± .0547
SZ4	021002	.0091 ± .0017	.0000 ± .0058	.0216 ± .0032	.0126 ± .0035	.0134 ± .0459
SZ4	021008	.0043 ± .0050	.0000 ± .0054	.0210 ± .0030	.0120 ± .0034	.0210 ± .0452
SZ4	021014	.0000 ± .0048	.0000 ± .0061	.0100 ± .0030	.0068 ± .0100	.0000 ± .0468
SZ4	021020	.0000 ± .0043	.0016 ± .0057	.0131 ± .0029	.0060 ± .0095	.0000 ± .0448
SZ4	021026	.0028 ± .0053	.0000 ± .0064	.0274 ± .0033	.0100 ± .0109	.0095 ± .0494
SZ4	021201	.0017 ± .0044	.0000 ± .0054	.0140 ± .0030	.0019 ± .0094	.0000 ± .0428
SZ4	021207	.0049 ± .0016	.0034 ± .0054	.0181 ± .0029	.0043 ± .0096	.0056 ± .0446
SZ4	021213	.0000 ± .0160	.0121 ± .0200	.0017 ± .0305	.0000 ± .0355	.0000 ± .1617
SZ4	021221	.0064 ± .0159	.0000 ± .0214	.0287 ± .0350	.0324 ± .0369	.0000 ± .1670
SZ4	021225	.0050 ± .0016	.0009 ± .0057	.0150 ± .0030	.0000 ± .0099	.0141 ± .0452
SZ4	030102	.0018 ± .0049	.0022 ± .0059	.0340 ± .0033	.0114 ± .0033	.0000 ± .0448
SZ4	030301	.0024 ± .0057	.0000 ± .0070	.0112 ± .0037	.0000 ± .0123	.0261 ± .0578
SZ4	030307	.0095 ± .0022	.0031 ± .0065	.0051 ± .0107	.0055 ± .0124	.0000 ± .0555
SZ4	030313	.0015 ± .0059	.0014 ± .0074	.0119 ± .0122	.0002 ± .0128	.0000 ± .0586
SZ4	030319	.0027 ± .0061	.0000 ± .0073	.0107 ± .0124	.0000 ± .0135	.0181 ± .0595
SZ4	030325	.0073 ± .0022	.0022 ± .0074	.0414 ± .0044	.0081 ± .0134	.0543 ± .0609
SZ4	030605	.0004 ± .0058	.0006 ± .0074	.0093 ± .0117	.0000 ± .0126	.0094 ± .0581
SZ4	030611	.0047 ± .0055	.0020 ± .0067	.0047 ± .0111	.0000 ± .0118	.0020 ± .0558
SZ4	030617	.0006 ± .0054	.0000 ± .0078	.0123 ± .0125	.0000 ± .0131	.0570 ± .0577
SZ4	030623	.0005 ± .0054	.0000 ± .0070	.0000 ± .0109	.0000 ± .0118	.0454 ± .0564
SZ4	030629	.0000 ± .0057	.0000 ± .0069	.0000 ± .0111	.0007 ± .0126	.0186 ± .0559
TC2	021002	.0000 ± .0046	.0000 ± .0057	.0129 ± .0029	.0081 ± .0095	.0000 ± .0430
TC2	021008	.0027 ± .0049	.0000 ± .0057	.0028 ± .0084	.0000 ± .0097	.0000 ± .0448
TC2	021014	.0000 ± .0046	.0000 ± .0057	.0089 ± .0029	.0055 ± .0097	.0156 ± .0460
TC2	021020	.0024 ± .0045	.0021 ± .0052	.0075 ± .0079	.0034 ± .0090	.0000 ± .0428
TC2	021026	.0062 ± .0016	.0000 ± .0053	.0172 ± .0029	.0013 ± .0094	.0000 ± .0441
TC2	021201	.0000 ± .0043	.0000 ± .0049	.0152 ± .0027	.0071 ± .0088	.0000 ± .0408
TC2	021207	.0038 ± .0044	.0035 ± .0054	.0000 ± .0080	.0016 ± .0095	.0011 ± .0430
TC2	021213	.0000 ± .0048	.0000 ± .0061	.0118 ± .0031	.0039 ± .0100	.0000 ± .0455
TC2	021219	.0000 ± .0050	.0007 ± .0064	.0165 ± .0030	.0043 ± .0101	.0000 ± .0476
TC2	021225	.0000 ± .0046	.0039 ± .0060	.0215 ± .0030	.0040 ± .0094	.0000 ± .0428
TC2	030301	.0000 ± .0057	.0010 ± .0072	.0025 ± .0114	.0060 ± .0129	.0809 ± .0199
TC2	030307	.0084 ± .0022	.0000 ± .0075	.0011 ± .0116	.0124 ± .0133	.0527 ± .0598
TC2	030313	.0067 ± .0020	.0042 ± .0068	.0112 ± .0113	.0000 ± .0130	.0000 ± .0626
TC2	030319	.0042 ± .0060	.0000 ± .0073	.0094 ± .0124	.0000 ± .0128	.0827 ± .0196

Site	Date	Cadmium	Indium	Tin	Antimony	Barium
TC2	030325	.0017 ± .0059	.0041 ± .0077	.0231 ± .0042	.0000 ± .0134	.0000 ± .0600
TC2	030605	.0040 ± .0062	.0000 ± .0077	.0047 ± .0117	.0000 ± .0128	.0267 ± .0594
TC2	030611	.0018 ± .0060	.0000 ± .0073	.0000 ± .0116	.0000 ± .0130	.0143 ± .0595
TC2	030617	.0019 ± .0061	.0011 ± .0073	.0247 ± .0039	.0041 ± .0125	.0417 ± .0561
TC2	030623	.0012 ± .0054	.0000 ± .0064	.0000 ± .0102	.0047 ± .0115	.0042 ± .0556
TC2	030629	.0000 ± .0056	.0000 ± .0069	.0000 ± .0103	.0026 ± .0119	.0145 ± .0554
TM1	021002	.0025 ± .0048	.0000 ± .0061	.0146 ± .0032	.0000 ± .0101	.0000 ± .0468
TM1	021008	.0000 ± .0049	.0000 ± .0054	.0026 ± .0083	.0054 ± .0094	.0065 ± .0451
TM1	021014	.0000 ± .0048	.0000 ± .0065	.0012 ± .0090	.0038 ± .0102	.0000 ± .0469
TM1	021020	.0000 ± .0049	.0000 ± .0059	.0049 ± .0089	.0000 ± .0099	.0296 ± .0460
TM1	021026	.0014 ± .0053	.0000 ± .0066	.0236 ± .0034	.0024 ± .0105	.0125 ± .0496
TM1	021201	.0000 ± .0046	.0028 ± .0058	.0143 ± .0029	.0069 ± .0090	.0099 ± .0430
TM1	021207	.0027 ± .0043	.0000 ± .0052	.0108 ± .0028	.0000 ± .0091	.0000 ± .0424
TM1	021213	.0038 ± .0045	.0016 ± .0059	.0193 ± .0030	.0075 ± .0096	.0222 ± .0449
TM1	021219	.0005 ± .0044	.0044 ± .0055	.0257 ± .0030	.0000 ± .0097	.0034 ± .0435
TM1	021225	.0070 ± .0015	.0011 ± .0054	.0171 ± .0029	.0026 ± .0091	.0042 ± .0422
TM1	030301	.0023 ± .0055	.0013 ± .0070	.0093 ± .0114	.0000 ± .0122	.0240 ± .0575
TM1	030307	.0000 ± .0062	.0000 ± .0077	.0043 ± .0121	.0007 ± .0132	.0037 ± .0602
TM1	030313	.0021 ± .0062	.0000 ± .0075	.0010 ± .0115	.0000 ± .0129	.0000 ± .0603
TM1	030319	.0058 ± .0059	.0059 ± .0072	.0150 ± .0040	.0026 ± .0127	.0000 ± .0580
TM1	030325	.0081 ± .0017	.0033 ± .0063	.0670 ± .0045	.0012 ± .0118	.0157 ± .0557
TM1	030605	.0000 ± .0053	.0005 ± .0066	.0000 ± .0100	.0000 ± .0113	.0263 ± .0549
TM1	030611	.0043 ± .0058	.0025 ± .0067	.0014 ± .0107	.0000 ± .0122	.0130 ± .0573
TM1	030617	.0000 ± .0059	.0000 ± .0074	.0149 ± .0042	.0000 ± .0130	.0155 ± .0594
TM1	030623	.0033 ± .0055	.0000 ± .0071	.0000 ± .0109	.0000 ± .0121	.0000 ± .0576
TM1	030629	.0000 ± .0053	.0000 ± .0065	.0000 ± .0104	.0000 ± .0117	.0000 ± .0548
ZS7	021008	.0061 ± .0014	.0000 ± .0047	.0255 ± .0030	.0115 ± .0028	.0000 ± .0372
ZS7	021014	.0024 ± .0040	.0000 ± .0047	.0280 ± .0029	.0029 ± .0082	.0055 ± .0377
ZS7	021020	.0016 ± .0034	.0000 ± .0044	.0000 ± .0066	.0020 ± .0074	.0096 ± .0346
ZS7	021026	.0104 ± .0015	.0001 ± .0043	.0062 ± .0068	.0017 ± .0077	.0075 ± .0348
ZS7	021201	.0059 ± .0013	.0028 ± .0041	.0262 ± .0026	.0080 ± .0081	.0359 ± .0112
ZS7	021207	.0000 ± .0036	.0000 ± .0042	.0098 ± .0022	.0049 ± .0071	.0014 ± .0329
ZS7	021213	.0000 ± .0041	.0019 ± .0048	.0296 ± .0028	.0170 ± .0029	.0000 ± .0371
ZS7	021219	.0041 ± .0042	.0000 ± .0045	.0383 ± .0027	.0282 ± .0029	.0312 ± .0360
ZS7	021225	.0033 ± .0042	.0009 ± .0048	.0244 ± .0026	.0075 ± .0081	.0238 ± .0357
ZS7	030301	.0000 ± .0041	.0000 ± .0051	.0000 ± .0187	.0016 ± .0086	.0653 ± .0126
ZS7	030307	.0073 ± .0013	.0000 ± .0043	.0185 ± .0027	.0057 ± .0078	.0000 ± .0359
ZS7	030313	.0023 ± .0039	.0000 ± .0049	.0168 ± .0028	.0072 ± .0084	.0090 ± .0384
ZS7	030319	.0000 ± .0037	.0000 ± .0045	.0264 ± .0033	.0076 ± .0082	.0083 ± .0366
ZS7	030325	.0047 ± .0014	.0000 ± .0048	.0406 ± .0031	.0064 ± .0087	.0412 ± .0132
ZS7	030605	.0015 ± .0039	.0000 ± .0046	.0118 ± .0027	.0000 ± .0085	.0046 ± .0388
ZS7	030611	.0000 ± .0038	.0003 ± .0047	.0000 ± .0070	.0000 ± .0081	.0140 ± .0374
ZS7	030617	.0167 ± .0016	.0040 ± .0044	.0221 ± .0026	.0094 ± .0027	.0376 ± .0120
ZS7	030623	.0008 ± .0033	.0012 ± .0043	.0002 ± .0063	.0000 ± .0073	.0048 ± .0343
ZS7	030629	.0014 ± .0034	.0015 ± .0046	.0034 ± .0076	.0000 ± .0081	.0000 ± .0374

Appendix E.7 – Metals Data from X-Ray Fluorescence in μg m^{-3}

Site	Date	Gold	Mercury	Thallium	Lead	Uranium
CH6	021002	.0000 ± .0079	.0000 ± .0015	.0030 ± .0042	.1639 ± .0021	.0000 ± .0029
CH6	021008	.0000 ± .0054	.0000 ± .0019	.0018 ± .0028	.0858 ± .0020	.0000 ± .0031
CH6	021014	.0000 ± .0199	.0000 ± .0018	.0026 ± .0066	.2686 ± .0027	.0000 ± .0041
CH6	021020	.0000 ± .0116	.0004 ± .0015	.0015 ± .0042	.1632 ± .0021	.0000 ± .0032
CH6	021026	.0000 ± .0106	.0000 ± .0014	.0017 ± .0038	.1430 ± .0020	.0000 ± .0031
CH6	021201	.0001 ± .0083	.0011 ± .0014	.0026 ± .0027	.0923 ± .0016	.0000 ± .0031
CH6	021207	.0000 ± .0062	.0008 ± .0016	.0025 ± .0044	.1730 ± .0021	.0000 ± .0035
CH6	021213	.0000 ± .0095	.0009 ± .0015	.0014 ± .0034	.1274 ± .0019	.0000 ± .0029
CH6	021219	.0000 ± .0116	.0011 ± .0017	.0021 ± .0059	.2393 ± .0025	.0000 ± .0038
CH6	021225	.0000 ± .0070	.0000 ± .0015	.0010 ± .0027	.0951 ± .0017	.0012 ± .0028
CH6	030301	.0003 ± .0123	.0011 ± .0017	.0089 ± .0024	.2802 ± .0028	.0000 ± .0038
CH6	030307	.0011 ± .0053	.0008 ± .0020	.0000 ± .0032	.0939 ± .0021	.0000 ± .0032
CH6	030313	.0000 ± .0309	.0012 ± .0024	.0040 ± .0114	.4614 ± .0040	.0000 ± .0080
CH6	030319	.0012 ± .0067	.0013 ± .0018	.0000 ± .0030	.0933 ± .0020	.0000 ± .0031
CH6	030325	.0000 ± .0173	.0000 ± .0018	.0026 ± .0058	.2249 ± .0025	.0000 ± .0037
CH6	030605	.0000 ± .0100	.0012 ± .0018	.0065 ± .0017	.1885 ± .0024	.0000 ± .0055
CH6	030611	.0000 ± .0078	.0000 ± .0014	.0012 ± .0033	.1163 ± .0019	.0000 ± .0034
CH6	030617	.0000 ± .0091	.0005 ± .0017	.0021 ± .0028	.0890 ± .0018	.0008 ± .0029
CH6	030623	.0000 ± .0042	.0000 ± .0015	.0024 ± .0008	.0713 ± .0016	.0015 ± .0028
CH6	030629	.0000 ± .0039	.0002 ± .0016	.0021 ± .0007	.0540 ± .0015	.0000 ± .0029
CW3	021002	.0000 ± .0110	.0000 ± .0019	.0032 ± .0032	.0975 ± .0021	.0000 ± .0032
CW3	021008	.0000 ± .0094	.0001 ± .0021	.0003 ± .0029	.0862 ± .0021	.0000 ± .0034
CW3	021014	.0020 ± .0037	.0000 ± .0019	.0003 ± .0017	.0119 ± .0013	.0024 ± .0029
CW3	021020	.0000 ± .0037	.0003 ± .0021	.0000 ± .0018	.0064 ± .0014	.0017 ± .0032
CW3	021026	.0000 ± .0121	.0000 ± .0023	.0012 ± .0032	.0940 ± .0022	.0000 ± .0037
CW3	021201	.0000 ± .0090	.0000 ± .0020	.0017 ± .0027	.0719 ± .0019	.0028 ± .0032
CW3	021207	.0000 ± .0046	.0000 ± .0021	.0000 ± .0019	.0103 ± .0015	.0000 ± .0033
CW3	021213	.0000 ± .0102	.0005 ± .0019	.0002 ± .0033	.1102 ± .0022	.0001 ± .0033
CW3	021219	.0000 ± .0069	.0000 ± .0019	.0016 ± .0024	.0620 ± .0018	.0000 ± .0030
CW3	021225	.0000 ± .0111	.0000 ± .0019	.0015 ± .0029	.0840 ± .0020	.0000 ± .0031
CW3	030301	.0054 ± .0055	.0002 ± .0024	.0010 ± .0024	.0267 ± .0017	.0000 ± .0034
CW3	030307	.0000 ± .0120	.0000 ± .0026	.0023 ± .0032	.0764 ± .0024	.0000 ± .0041
CW3	030313	.0008 ± .0064	.0000 ± .0023	.0000 ± .0024	.0296 ± .0018	.0000 ± .0036
CW3	030319	.0000 ± .0067	.0000 ± .0025	.0003 ± .0026	.0362 ± .0020	.0000 ± .0038
CW3	030325	.0000 ± .0114	.0000 ± .0025	.0028 ± .0043	.1331 ± .0028	.0000 ± .0038
CW3	030605	.0000 ± .0069	.0000 ± .0023	.0011 ± .0028	.0503 ± .0020	.0000 ± .0037
CW3	030611	.0000 ± .0047	.0000 ± .0021	.0000 ± .0020	.0064 ± .0014	.0002 ± .0031
CW3	030617	.0031 ± .0107	.0005 ± .0022	.0000 ± .0030	.0707 ± .0021	.0008 ± .0035
CW3	030623	.0000 ± .0042	.0004 ± .0024	.0007 ± .0021	.0000 ± .0045	.0004 ± .0037
CW3	030629	.0000 ± .0042	.0005 ± .0025	.0001 ± .0021	.0024 ± .0047	.0000 ± .0038
GZ5	021002	.0000 ± .0145	.0000 ± .0024	.0045 ± .0056	.2001 ± .0029	.0007 ± .0043
GZ5	021008	.0000 ± .0075	.0000 ± .0022	.0027 ± .0039	.1252 ± .0024	.0000 ± .0038
GZ5	021014	.0000 ± .0242	.0009 ± .0025	.0080 ± .0104	.4237 ± .0039	.0000 ± .0068
GZ5	021020	.0000 ± .0365	.0004 ± .0021	.0021 ± .0065	.2517 ± .0030	.0000 ± .0035
GZ5	021026	.0000 ± .0101	.0000 ± .0022	.0017 ± .0046	.1606 ± .0026	.0000 ± .0037
GZ5	021201	.0000 ± .0235	.0017 ± .0025	.0040 ± .0117	.4795 ± .0040	.0000 ± .0048

Site	Date	Gold	Mercury	Thallium	Lead	Uranium
GZ5	021207	.0000 ± .0174	.0019 ± .0024	.0049 ± .0088	.3563 ± .0035	.0000 ± .0052
GZ5	021213	.0020 ± .0094	.0006 ± .0020	.0038 ± .0048	.1750 ± .0026	.0000 ± .0039
GZ5	021219	.0000 ± .0204	.0007 ± .0024	.0046 ± .0085	.3410 ± .0035	.0000 ± .0043
GZ5	021225	.0000 ± .0086	.0000 ± .0020	.0035 ± .0046	.1659 ± .0025	.0013 ± .0035
GZ5	030301	.0000 ± .0263	.0015 ± .0028	.0036 ± .0069	.2499 ± .0036	.0022 ± .0043
GZ5	030307	.0000 ± .0116	.0000 ± .0027	.0033 ± .0055	.1866 ± .0032	.0000 ± .0044
GZ5	030313	.0000 ± .0261	.0000 ± .0030	.0080 ± .0102	.3912 ± .0044	.0000 ± .0065
GZ5	030319	.0000 ± .0097	.0000 ± .0025	.0020 ± .0039	.1090 ± .0026	.0000 ± .0045
GZ5	030325	.0000 ± .0196	.0000 ± .0028	.0059 ± .0096	.3695 ± .0042	.0000 ± .0053
GZ5	030605	.0026 ± .0165	.0012 ± .0025	.0000 ± .0044	.1409 ± .0028	.0000 ± .0039
GZ5	030611	.0000 ± .0382	.0020 ± .0026	.0034 ± .0081	.2959 ± .0038	.0000 ± .0043
GZ5	030617	.0000 ± .0351	.0000 ± .0032	.0093 ± .0113	.4363 ± .0048	.0000 ± .0069
GZ5	030623	.0000 ± .0276	.0000 ± .0028	.0072 ± .0086	.3254 ± .0039	.0000 ± .0049
GZ5	030629	.0000 ± .0118	.0000 ± .0023	.0042 ± .0056	.1940 ± .0031	.0000 ± .0034
SZ4	021002	.0000 ± .0144	.0000 ± .0021	.0025 ± .0042	.1513 ± .0025	.0032 ± .0038
SZ4	021008	.0000 ± .0164	.0000 ± .0020	.0014 ± .0047	.1735 ± .0026	.0000 ± .0038
SZ4	021014	.0000 ± .0051	.0000 ± .0020	.0000 ± .0020	.0275 ± .0016	.0005 ± .0031
SZ4	021020	.0000 ± .0044	.0000 ± .0019	.0003 ± .0018	.0148 ± .0014	.0000 ± .0029
SZ4	021026	.0000 ± .0154	.0000 ± .0023	.0000 ± .0039	.1340 ± .0025	.0012 ± .0040
SZ4	021201	.0016 ± .0074	.0005 ± .0018	.0001 ± .0025	.0643 ± .0018	.0005 ± .0028
SZ4	021207	.0000 ± .0064	.0000 ± .0019	.0030 ± .0007	.0421 ± .0017	.0006 ± .0031
SZ4	021213	.0029 ± .0255	.0000 ± .0066	.0012 ± .0085	.2042 ± .0063	.0000 ± .0103
SZ4	021221	.0053 ± .0280	.0000 ± .0069	.0047 ± .0107	.3050 ± .0073	.0000 ± .0109
SZ4	021225	.0000 ± .0125	.0008 ± .0021	.0011 ± .0037	.1256 ± .0023	.0017 ± .0036
SZ4	030102	.0000 ± .0122	.0000 ± .0020	.0031 ± .0050	.1856 ± .0027	.0000 ± .0040
SZ4	030301	.0031 ± .0077	.0000 ± .0024	.0002 ± .0028	.0515 ± .0020	.0000 ± .0036
SZ4	030307	.0000 ± .0134	.0009 ± .0024	.0000 ± .0046	.1532 ± .0029	.0000 ± .0039
SZ4	030313	.0000 ± .0116	.0014 ± .0026	.0011 ± .0030	.0642 ± .0022	.0000 ± .0038
SZ4	030319	.0009 ± .0119	.0000 ± .0024	.0023 ± .0039	.1120 ± .0026	.0000 ± .0039
SZ4	030325	.0000 ± .0184	.0000 ± .0026	.0015 ± .0049	.1593 ± .0030	.0000 ± .0042
SZ4	030605	.0000 ± .0073	.0018 ± .0025	.0019 ± .0028	.0476 ± .0020	.0000 ± .0039
SZ4	030611	.0000 ± .0055	.0004 ± .0023	.0000 ± .0023	.0290 ± .0018	.0010 ± .0036
SZ4	030617	.0000 ± .0103	.0000 ± .0025	.0000 ± .0032	.0801 ± .0024	.0006 ± .0041
SZ4	030623	.0000 ± .0041	.0000 ± .0023	.0005 ± .0022	.0053 ± .0015	.0006 ± .0036
SZ4	030629	.0041 ± .0041	.0000 ± .0024	.0004 ± .0020	.0051 ± .0015	.0000 ± .0035
TC2	021002	.0000 ± .0107	.0000 ± .0019	.0008 ± .0031	.1040 ± .0021	.0012 ± .0032
TC2	021008	.0000 ± .0101	.0000 ± .0020	.0010 ± .0029	.0884 ± .0020	.0015 ± .0035
TC2	021014	.0000 ± .0036	.0000 ± .0020	.0014 ± .0020	.0211 ± .0015	.0010 ± .0032
TC2	021020	.0000 ± .0032	.0000 ± .0018	.0010 ± .0017	.0073 ± .0012	.0000 ± .0027
TC2	021026	.0000 ± .0140	.0002 ± .0020	.0021 ± .0032	.1021 ± .0021	.0000 ± .0033
TC2	021201	.0021 ± .0075	.0003 ± .0018	.0015 ± .0024	.0634 ± .0017	.0005 ± .0027
TC2	021207	.0000 ± .0034	.0002 ± .0019	.0011 ± .0017	.0027 ± .0037	.0025 ± .0029
TC2	021213	.0000 ± .0099	.0000 ± .0020	.0010 ± .0034	.1098 ± .0022	.0000 ± .0035
TC2	021219	.0000 ± .0050	.0001 ± .0022	.0014 ± .0022	.0389 ± .0017	.0000 ± .0033
TC2	021225	.0000 ± .0132	.0000 ± .0019	.0023 ± .0036	.1212 ± .0022	.0002 ± .0033
TC2	030301	.0009 ± .0048	.0000 ± .0025	.0013 ± .0023	.0190 ± .0018	.0000 ± .0038
TC2	030307	.0000 ± .0145	.0010 ± .0026	.0029 ± .0045	.1466 ± .0029	.0000 ± .0040
TC2	030313	.0000 ± .0056	.0004 ± .0027	.0023 ± .0026	.0215 ± .0019	.0000 ± .0041
TC2	030319	.0010 ± .0080	.0000 ± .0024	.0000 ± .0029	.0555 ± .0021	.0026 ± .0038

Site	Date	Gold	Mercury	Thallium	Lead	Uranium
TC2	030325	.0000 ± .0087	.0000 ± .0025	.0000 ± .0036	.1010 ± .0026	.0000 ± .0039
TC2	030605	.0000 ± .0072	.0000 ± .0025	.0019 ± .0028	.0542 ± .0022	.0000 ± .0041
TC2	030611	.0007 ± .0044	.0000 ± .0025	.0004 ± .0024	.0012 ± .0048	.0009 ± .0040
TC2	030617	.0013 ± .0092	.0013 ± .0024	.0011 ± .0031	.0719 ± .0022	.0000 ± .0036
TC2	030623	.0000 ± .0038	.0001 ± .0023	.0007 ± .0020	.0024 ± .0043	.0008 ± .0035
TC2	030629	.0007 ± .0039	.0002 ± .0023	.0000 ± .0019	.0002 ± .0042	.0015 ± .0035
TM1	021002	.0000 ± .0097	.0000 ± .0022	.0033 ± .0035	.1108 ± .0023	.0013 ± .0036
TM1	021008	.0000 ± .0099	.0000 ± .0020	.0016 ± .0031	.1004 ± .0021	.0011 ± .0034
TM1	021014	.0000 ± .0036	.0000 ± .0020	.0004 ± .0019	.0066 ± .0014	.0027 ± .0032
TM1	021020	.0000 ± .0035	.0002 ± .0021	.0002 ± .0018	.0054 ± .0013	.0000 ± .0030
TM1	021026	.0000 ± .0151	.0000 ± .0024	.0004 ± .0035	.1115 ± .0024	.0008 ± .0039
TM1	021201	.0000 ± .0081	.0008 ± .0019	.0006 ± .0026	.0741 ± .0019	.0000 ± .0029
TM1	021207	.0000 ± .0032	.0000 ± .0017	.0007 ± .0018	.0176 ± .0013	.0004 ± .0026
TM1	021213	.0000 ± .0092	.0000 ± .0020	.0024 ± .0035	.1190 ± .0022	.0017 ± .0035
TM1	021219	.0000 ± .0054	.0000 ± .0019	.0014 ± .0026	.0703 ± .0019	.0000 ± .0030
TM1	021225	.0000 ± .0103	.0000 ± .0017	.0004 ± .0030	.0962 ± .0020	.0000 ± .0031
TM1	030301	.0019 ± .0046	.0000 ± .0023	.0010 ± .0024	.0249 ± .0017	.0023 ± .0036
TM1	030307	.0009 ± .0132	.0013 ± .0026	.0001 ± .0033	.0795 ± .0024	.0000 ± .0040
TM1	030313	.0007 ± .0062	.0000 ± .0025	.0001 ± .0024	.0294 ± .0019	.0004 ± .0038
TM1	030319	.0000 ± .0096	.0000 ± .0023	.0000 ± .0028	.0638 ± .0022	.0000 ± .0037
TM1	030325	.0009 ± .0136	.0009 ± .0023	.0001 ± .0052	.1767 ± .0030	.0000 ± .0037
TM1	030605	.0055 ± .0059	.0000 ± .0022	.0000 ± .0025	.0424 ± .0019	.0000 ± .0034
TM1	030611	.0000 ± .0042	.0009 ± .0025	.0008 ± .0021	.0020 ± .0046	.0003 ± .0037
TM1	030617	.0000 ± .0100	.0000 ± .0025	.0044 ± .0011	.0713 ± .0023	.0000 ± .0041
TM1	030623	.0000 ± .0040	.0000 ± .0023	.0013 ± .0021	.0000 ± .0045	.0027 ± .0037
TM1	030629	.0037 ± .0039	.0000 ± .0022	.0010 ± .0021	.0034 ± .0042	.0002 ± .0034
ZS7	021008	.0000 ± .0175	.0031 ± .0007	.0092 ± .0096	.3968 ± .0033	.0000 ± .0071
ZS7	021014	.0000 ± .0074	.0000 ± .0018	.0020 ± .0029	.0961 ± .0019	.0013 ± .0031
ZS7	021020	.0000 ± .0035	.0000 ± .0015	.0000 ± .0014	.0164 ± .0011	.0005 ± .0023
ZS7	021026	.0000 ± .0055	.0000 ± .0014	.0019 ± .0021	.0571 ± .0015	.0006 ± .0024
ZS7	021201	.0000 ± .0270	.0007 ± .0017	.0036 ± .0048	.1815 ± .0023	.0000 ± .0028
ZS7	021207	.0000 ± .0077	.0015 ± .0016	.0021 ± .0032	.1126 ± .0019	.0000 ± .0023
ZS7	021213	.0000 ± .0168	.0002 ± .0019	.0046 ± .0076	.3105 ± .0029	.0000 ± .0052
ZS7	021219	.0000 ± .0332	.0000 ± .0019	.0050 ± .0060	.2354 ± .0026	.0000 ± .0035
ZS7	021225	.0000 ± .0192	.0006 ± .0020	.0054 ± .0079	.3269 ± .0029	.0000 ± .0043
ZS7	030301	.0000 ± .0056	.0002 ± .0016	.0004 ± .0019	.0384 ± .0014	.0000 ± .0026
ZS7	030307	.0000 ± .0104	.0005 ± .0016	.0022 ± .0052	.1966 ± .0024	.0000 ± .0029
ZS7	030313	.0000 ± .0095	.0004 ± .0017	.0019 ± .0024	.0669 ± .0017	.0000 ± .0027
ZS7	030319	.0000 ± .0150	.0005 ± .0018	.0040 ± .0065	.2545 ± .0027	.0000 ± .0034
ZS7	030325	.0000 ± .0129	.0000 ± .0018	.0036 ± .0042	.1523 ± .0023	.0000 ± .0032
ZS7	030605	.0000 ± .0057	.0010 ± .0018	.0011 ± .0020	.0450 ± .0015	.0000 ± .0028
ZS7	030611	.0017 ± .0031	.0008 ± .0016	.0002 ± .0016	.0157 ± .0012	.0000 ± .0024
ZS7	030617	.0020 ± .0155	.0002 ± .0015	.0009 ± .0033	.1087 ± .0020	.0003 ± .0026
ZS7	030623	.0024 ± .0027	.0005 ± .0014	.0005 ± .0014	.0083 ± .0009	.0000 ± .0020
ZS7	030629	.0000 ± .0027	.0000 ± .0015	.0009 ± .0014	.0023 ± .0031	.0000 ± .0025

Appendix F

Characterization of Organic Compounds in $PM_{2.5}$ Collected by High Volume Samplers at the Hong Kong sites Tung Chung and Yuen Long

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Introduction

24-hour integrated $PM_{2.5}$ samples were collected by high volume samplers from Tung Chung (TC) and Yuen Long (YL), located in the Hong Kong Special Administrative Region on October 20, 2002, December 13 and 19, 2002, and March 25, 2003 for the analysis of solvent extractable organic compounds. The TC sampling site is located in north Lantau Island, within a residential area adjacent to the highway and railway lines. The YL sampling site is located in an urban district of New Territory in Hong Kong (HK). The sampling days have been discussed in the main body of this report and can be summarized as follows: the samples collected on December 19, 2002 had the highest aerosol concentrations among the HK samples taken in December 2002. Surface winds were relatively light with both north and south components indicating relatively stagnant air with sources throughout the PRD influencing regional concentrations. Light precipitation also occurred in Hong Kong on December, 19. The samples obtained on December 13, 2002 can be characterized by northerly flow with highest observed PM2.5 concentrations observed at Zhongshan suggesting that sources from Guangdong influence fine particle concentrations in Hong Kong. The samples of March 25, 2003 were selected since during this day concentrations are high throughout the PRD, with the highest concentration of PM2.5 measured during the study occurring at Guangzhou (~130 $\mu g/m^3$). This day was characterized by relatively stagnant airflow in the PRD. On October 20, 2002 concentrations of PM2.5 were extremely low throughout the PRD with southerly winds and precipitation throughout the PRD. Overall, the samples represent both periods of high and low PM2.5 concentrations in Hong Kong and the PRD. The overall objective of the high volume sampling is to evaluate the extent to which these samples represent monthly composite samples, and to determine the spatial variability of specific organic tracer compounds across Hong Kong for specific events. In this report we compare specific compounds and classes of compounds between the sites and with monthly composites. One important point that should be noted is that samples were found to be highly contaminated with an unidentified organic compound, which was not present in appreciable amounts in the monthly composite samples. It is hypothesized that the compound is an oil associated with the impactors used in the high volume samplers. The compound not only overlapped with existing tracer compounds, but apparently had a significant impact on the overall organic carbon content of the high volume filters. It should be pointed out that it is possible that the contaminant also influenced the concentrations of other organic compounds such as n-alkanes and PAH's. Nonetheless, we present concentrations of tracer compounds with the caveat that more work must be done to determine the source of the contaminant and possible influence on tracer compound concentrations.

Experimental

The organic carbon (OC) mass collected on the high volume filter samples is relatively high ranging from 6.1 to 26.4 milligrams per filter. Therefore, a fraction of each of the high-volume filters, with OC masses ranging from 1.4 to 2.4 milligrams, was used for the extraction and the gas chromatography/mass spectrometry (GC/MS) analysis. Deuterated internal standard mixtures (IS) including 16 deuterated organic compounds (Table 1) were spiked into samples prior to extraction. The amounts of IS spikes were proportional to OC in the samples, with 250 μL of IS per one milligram of OC. The samples were extracted under mild sonication twice with hexane (Fisher Optima grade) and three times with distilled benzene/2-propanol (2:1 mixture, v/v, benzene: VWR Chromatographic grade; 2-propanol, Fisher Optima grade). The extracts were filtered, combined, and reduced in volume to about 5 mL by a rotary evaporator, then further concentrated to about 250 μL by nitrogen gas blowing down. The final extract was split into two fractions. One fraction was stored in the freezer, and the other fraction was derivatized with diazomethane, followed by GC/MS analysis. More detailed information on sample handling, extraction and analysis is provided in Appendix B of this report.

Results and Discussion

Comparison of Elemental (EC) and Organic Carbon (OC) Concentrations in High Volume and Low Volume Samples at Tung Chung

In order to first determine the quality of the high volume samples their EC and OC concentrations are compared with the co-located ThermoAndersen sampler at Tung Chung used during the present study. Table 2 presents concentrations of solvent extractable organic tracer compounds in the high volume samples as well as monthly composite samples for comparison. The last four rows of Table 2 contain data for OC and EC concentrations measured for all of the high volume samples, as well as the ThermoAndersen sampler low volume concentrations measured at Tung Chung. The low volume (LV) samples at Tung Chung have OC concentrations over the four sampling events that are on average 6,634 ngm^{-3}, as compared to 10,540 ngm^{-3} for the high volume (HV) samples. This discrepancy clearly indicates that the high volume samples contain significantly more organic carbon than the low volume samples. The average EC concentrations for the LV samples are 2375 ngm^{-3} as compared to 2482 ngm^{-3} for the high volume samples, indicating that EC concentrations are somewhat similar for the two samplers. The results generally indicate that the high volume filter samples are contaminated with an organic compound not present in appreciable amounts on the low volume samples. The following section discusses the contamination observed in the high volume filter samples.

Specific Organic Contaminants in High Volume Samples

Figures 4a and 4b show the spectra of the Tung Chung high volume sample collected on 10/20/02. An extremely large peak is observed with an extended retention time spanning 0.4 minutes from 25.4 to 25.8 minutes. The characteristic ion fragments are m/z 469, 313, and 197. The peak is observed in all high volume samples. The compound has never been found in such high abundance in our ambient samples. This compound is believed to be impactor grease (likely R&P WINS impactor oil). This oil was analyzed during the previous pilot study to insure that it did not contribute to contamination in low volume samples. Figure 5 shows the spectra of impactor oil previously analyzed in our lab. As shown in Figure 5, the spectrum is nearly identical to that observed in the current high volume samples. Although, it should be noted that the concentration in the high volume samples is nearly an order of magnitude greater than the concentration used in our analyses of the impactor oil. The organic compounds that clearly overlap the contaminant peak are shown in Table 3. Figure 6 is an example showing that the m/z 252 ion is so abundant in the high volume samples that it is impossible to correctly identify and quantify the compounds of benzo(e)pyrene, benzo(a)pyrene and perylene which using the same quantification ion of m/z 252. It is important to point out that it is also possible that the contaminant interferes with other compounds, in particular alkanes and PAHs, that are related to the combustion of fossil fuels. Below we present concentrations of solvent extractable organic compounds and it must be understood that some of the concentrations may be influenced by the contaminant. In addition, ratios of specific compounds to OC concentrations must also be used with caution since the contaminant had a significant influence on OC levels in the high volume samples. Before the actual impact of the contaminant on other organic concentrations can be determined more detailed labwork is needed to definitively identify the compound, and to analyze the mass spectra of the compound at the concentration levels similar to that observed in samples. Nonetheless, we present results below with the knowledge that a contaminant, most likely impactor oil, may be influencing the concentrations of some of the organic tracer compounds.

In the following section concentrations of specific organic compounds are compared between the sites, as well as with the monthly composite concentrations measured based on low volume filter samples collected as part of this project. Again, it should be noted that the concentrations of the specific organic compounds for the high volume samples may be influenced by the contaminant present in the samples. Given that the contaminant is believed to be an oil, likely derived from petroleum products, the *n*-alkanes and PAHs may be particularly susceptible to contamination. Much of the discussion below is based on concentrations presented in Table 2.

<u>Chemical characterization of the high volume samples at the TC site</u>

March samples

We first begin by discussing the March 25th sampling day, which is characterized by extremely high fine particulate concentrations throughout the PRD. The concentrations of the total *n*-alkanes in the high volume and low volume TC samples are 20.51 and 32.73 ng/m^3, respectively. The results suggest that the *n*-alkanes are present in roughly similar concentrations for the samples. The concentrations of the total fatty acids and hopanes + steranes, H+S, (Figure 2) also are very similar between the high volume and low volume samples, with values of 2.66 and 3.38 ng/m^3 for H+S. Fatty acids are also in general agreement with concentrations of 55.11 and 46.04 ng/m^3, respectively. For the PAHs (Figure 3) and levoglucosan (Figure 1), however, lower concentrations are found in the high volume sample (4.58 and 39 ng/m^3 for the total PAHs and levoglucosan, respectively) as compared with the low volume sample (10.69 and 75 ng/m^3 for the total PAHs and levoglucosan, respectively). The values decrease for both PAHs and levoglucosan by a factor of around 2. Overall a general conclusion that can be drawn from the comparison is that many of the organic tracer compounds are within a factor of 2 between the high volume and low volume samples.

October samples

On October 20th low fine particulate concentrations are observed throughout the PRD with rain occurring throughout the region. The concentrations of the organic compounds in the high volume sample taken on October 20, 2002 (TC10202002) are much lower than that in the corresponding low volume monthly composite sample (TC-10). Some species such as C26-C30 *n*-alkanes, benzo(*ghi*)perylene, and coronene were even undetectable in the high volume sample. The concentrations of the total *n*-alkanes are 3.58 and 26.99 ng/m^3 in the high volume and low volume samples, respectively. The fatty acids, PAHs, and H+S decrease also in concentration from 36.22 (fatty acids), 10.87 (PAHs), and 2.49 (H+S) ng/m^3 in the low volume sample to 18.09 (fatty acids), 0.60 (PAHs) and 0.8 (H+S) ng/m^3 in the high volume sample by factors of 2 – 18. The degree of decrease is even larger for levoglucosan (by a factor of ~40), from 299 ng/m^3 in the low volume sample to 8 ng/m^3 in the high volume sample. The lower concentrations in the high volume samples is not surprising given the abundance of rain throughout the region and generally low concentrations of fine particulate mass observed for the sampling day.

December samples

The high volume samples collected on December 13 and 19, 2002 (TC12132002 and TC12192002) represent meteorological cases of northerly flow and mixed north/south flow as discussed in the main report. The concentrations of the total *n*-alkanes and fatty acids are higher in the high volume samples than that in the low volume sample, with the highest values recorded in the TC12132002 sample (70.58 and 75.87 ng/m^3 for *n*-alkanes and fatty acids, respectively). While for both of the total PAHs and levoglucosan, the highest concentrations are recorded in the low volume monthly composite sample (TC-12), with 12.27 and 250 ng/m^3 for the total PAHs and levoglucosan, respectively. Somewhat lower concentrations of H+S are found in the high volume samples, as compared to the low volume samples. Although the sample taken on December 19, 2002 (TC12192002) is associated with relatively high particulate concentrations in Hong Kong, it does not correspond to the highest yields of organic compounds. The concentrations of *n*-alkanes and PAHs in that sample are the lowest among the three samples (TC12132002, TC12192002, and TC-12). The findings that the two high volume samples taken during December 2002 are characterized with similar levels of H+S, and lower levels of PAH's and levoglucosan suggest that the events are perhaps not as influenced by biomass burning to the extent of the monthly composite sample.

Characterization of organic compounds at YL and comparison with TC

The concentrations of organic compounds including *n*-alkanes, branched alkanes, fatty acids, hopanes, steranes, resin acids, PAHs, alkanedioic acids, and other tracers such as levoglucosan are presented in Table 2. The comparison between the two sites will focus on the compounds of *n*-alkanes, fatty acids, H+S, levoglucosan, and PAHs. H+S are used as molecular tracers for motor vehicles emission (Schauer et al., 1996), and they can be found in diesel fuel, and lubricating oil used by both diesel-powered and gasoline-powered motor vehicles (Cass, 1998). The ratio of H+S to EC is a useful indicator to determine some emission sources such as diesel-powered vehicles and gasoline-powered vehicles. From a previous studies (Schauer et al., 1999; Schauer et al., 2002; Zheng et al., in preparation), the (H+S)/EC ratio for diesel-powered vehicle exhaust ($4.6e^{-4}$) is much lower than that for gasoline-powered vehicle exhausts (0.15). Levoglucosan is a major molecular tracer for biomass burning (Simoneit et al., 1999). PAHs come primarily from the incomplete combustion of organic material and the possible sources for PAHs include motor vehicles, biomass burning, power generation, and fossil fuels burning for heating purpose (Brun et al, 2004).

Different distribution patterns of organic compounds are found between the two sites. For the March samples, The YL sample (YL03252003) shows higher concentration of *n*-alkanes (53.40 ng/m^3) and fatty acids (151.75 ng/m^3) than the TC sample (TC03252003) (20.51 and 55.11 ng/m^3 for *n*-alkanes and fatty acids, respectively), while the concentrations of levoglucosan, and H+S in the two samples are roughly the same. Concentrations of PAH's at Yuen Long are more than two-fold greater than at TC. For the October high volume samples, the YL sample (YL10202002) has higher concentrations of PAHs than the TC sample (TC10202002), while the levels of levoglucosan and H+S are comparable between the two sites. For the December the YL samples generally have higher concentrations for most organic compounds than the corresponding TC samples (i.e., YL12132002 vs. TC12132002 and YL12192002 vs. TC12192002). For example, the concentrations of the total *n*-alkanes for YL12132002, YL12192002, TC12132002, and TC12192002 are 176.67, 163.96, 70.58, and 21.45 ng/m^3, respectively. Such patterns are also found for levoglucosan, PAHs, and fatty acids. The distribution pattern of H+S is an exception. The concentrations of H+S between the YL and TC samples collected on December 19, 2003 are comparable, while on December 13, 2002 the YL sample contains much more H+S than the TC sample (Figure 2). The relative similarities in the H+S concentrations between the two sites across all samples suggests similar mobile source contributions at the sites.

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Table 1. Concentrations of deuterated internal standards.

Deuterated Isotope	Concentration (ng/μL)
dodecane-D_{26}	437±21
hexadecane-D_{34}	94.4±9.4
eicosane-D_{42}	75.2±7.5
octacosane-D_{58}	196±15
hexatriacontane-D_{74}	406±20
decanoic acid-D_{19}	180±13
heptadecanoic acid-D_{33}	176±13
phthalic 3,4,5,6-D_4 acid	184±13
benzaldehyde-D_6	408±20
4,4'-dimethoxybenzophenone-D_8	385±19
acenaphthene-D_{10}	97.6±9.8
chrysene-D_{12}	70.5±7.1
dibenz[ah]anthracene-D_{14}	192±14
levoglucosan-U-13C_6	1250±60
ααα-20R-cholestane-D_4	15.0±0.8
cholesterol-2,2,3,4,4,6-D_6	394±20

Table 2. Concentrations of organic compounds, EC, and OC in PM2.5 in Hong Kong (ng/m^3).

Compound	TC 0325 2003	YL 0325 2003	TC-03	TC 1020 2002	YL 1020 2002	TC-10	TC 1213 2002	TC 1219 2002	YL 1213 2002	YL 1219 2002	TC-12
	D	D	M	D	D	M	D	D	D	D	M
heptadecane						0.22				0.15	0.25
octadecane					0.02	0.07			0.53	1.51	0.25
nonadecane		0.30			0.26	0.32			2.65	2.39	0.33
eicosane	0.70	1.23	0.33	0.71	0.66	0.41	0.77	0.72	3.58	3.85	0.43
heneicosane	0.51	0.72	0.88	0.51	0.60	0.53	0.28	0.44	2.55	2.97	0.45
docosane	0.81	1.22	1.31		0.66	0.62	0.60	0.58	3.10	3.09	0.74
tricosane	0.93	2.50	2.96	0.46	0.74	1.08	1.28	0.82	6.75	4.99	1.86
tetracosane	1.08	3.41	3.96	0.98		0.96	3.37	0.92	10.35	7.51	3.45
pentacosane	1.97	7.15	4.77	0.35	1.11	1.53	8.86	1.69	25.36	15.12	5.04
hexacosane	2.52	8.41	3.68		1.21	1.74	11.81	2.26	26.85	19.57	4.68
heptacosane	1.63	3.92	2.70		0.77	2.75	8.71	1.80	12.85	13.71	4.55
octacosane	1.33	2.72	1.60		1.53	1.84	7.03	1.78	8.53	10.08	3.43
nonacosane	1.89	5.44	2.23			2.89			18.35	18.60	4.37
triacontane	0.91	2.14	0.95		0.72	1.21	4.98	1.02	7.08	8.71	1.84
hentriacontane	3.09	5.91	3.01	0.32	1.85	4.63	7.77	3.42	19.93	22.38	4.61
dotriacontane	0.83	1.66	0.88		0.67	1.31	4.32	1.12	6.71	7.07	1.77
tritriacontane	1.09	2.66	1.06	0.25	1.06	2.29	3.99	1.85	9.37	9.34	1.82
tetratriacontane	0.52	1.23	0.76		0.66	0.61	2.06	0.70	4.19	4.86	0.93
pentatriacontane		0.53	0.46		0.18	0.42	2.05	0.92	1.44	1.59	0.75
hexatriacontane		0.36	0.21		0.09		1.14		0.78	0.89	0.39
iso-nonacosane						0.85					1.07
anteiso-triacontane	0.32	0.83	0.42		0.30	0.19	0.94	0.82	2.18	2.32	0.55
iso-hentriacontane	0.39	1.04	0.55		0.30	0.50	0.63	0.59	3.55	3.26	1.26
tetradecanoic acid	1.35	3.54	1.92	0.66	3.27	0.57	0.37	0.28	10.31	8.13	0.64
pentadecanoic acid	0.85	3.31	1.14	0.27	2.98	0.25	0.13	0.08	6.30	6.43	0.23
hexadecanoic acid	20.49	66.72	18.44	8.76	43.11	6.34	28.33	12.63	298.31	170.29	12.38
heptadecanoic acid	0.68	1.91	0.52	0.34	1.17	0.30	0.72	0.47	8.55	5.66	0.39
octadecanoic acid	7.38	23.78	6.81	3.77	10.17	2.71	15.01	6.19	133.76	71.02	4.10
nonadecanoic acid	0.28	0.78	0.25	0.11	0.28	0.20	0.50	0.28	3.51	2.49	0.21
eicosanoic acid	1.14	3.13	1.06	0.28	0.93	0.98	2.04	1.07	16.40	11.06	1.00
heneicosanoic acid	0.40	1.04	0.33	0.07	0.33	0.47	0.83	0.40	5.58	4.53	0.43
docosanoic acid	1.94	4.97	1.58	0.26	1.27	2.30	3.32	1.90	24.54	19.88	1.96
tricosanoic acid	1.46	3.29	1.01	0.18	0.80	1.39	2.49	1.67	16.11	17.07	1.16
tetracosanoic acid	3.98	8.77	2.75	1.09	2.13	3.32	6.50	3.74	41.00	37.79	3.02
pentacosanoic acid	1.12	2.17	0.64		0.47	0.74	1.38	1.22	9.16	10.94	0.63
hexacosanoic acid	2.83	6.07	1.72		0.97	1.94	1.99	1.54	23.77	25.75	1.63
heptacosanoic acid	1.16	2.16	0.42		0.38	0.82	1.09	0.95	7.10	9.85	0.62
octacosanoic acid	3.84	7.09	1.67	0.33	1.62	4.58	4.48	3.43	28.98	32.73	2.95
nonacosanoic acid	0.88	1.77	0.31		0.32	0.92	1.15	1.04	5.75	8.75	0.54
triacontanoic acid	3.59	6.46	1.24		1.30	7.94	5.19	4.44	31.49	38.47	4.34
9-hexadecenoic acid	1.35	3.65	0.83	1.13	1.04	0.32				6.60	
9,12-octadecanedienoic acid	0.41	0.65	0.69	0.38	0.44	0.12	0.33	0.34	1.45	2.82	0.20
9-octadecenoic acid		0.48	2.69	0.47	1.82				2.27	3.68	0.09
17*α(H)*-21*β(H)*-29-norhopane	0.42	0.43	0.49	0.25	0.09	0.32	0.39	0.55	0.88	0.35	0.49
17*α*(*H*)-21*β(H)*-hopane	0.59	0.64	0.61	0.29	0.15	0.50	0.59	0.64	1.38	0.56	0.75
22,29,30-trisnorneohopane			0.12			0.27					0.38
22,29,30-trisnorhopane			0.12								0.18
20*S,R*-5*α(H),14β(H),17β(H)*-cholestanes			0.30			0.14					

Table 2. (Continued)

Compound	TC 0325 2003	YL 0325 2003	TC-03	TC 1020 2002	YL 1020 2002	TC-10	TC 1213 2002	TC 1219 2002	YL 1213 2002	YL 1219 2002	TC -12
	D	D	M	D	D	M	D	D	D	D	M
20*R*-5$\alpha(H)$,14$\alpha(H)$,17$\alpha(H)$-cholestane			0.18								0.05
20*S*,*R*-5$\alpha(H)$,14$\beta(H)$,17$\beta(H)$-ergostanes			0.20			0.16					0.20
20*S*,*R*-5$\alpha(H)$,14$\beta(H)$,17$\beta(H)$-sitostanes	0.36	0.34	0.29		0.07	0.26	0.21	0.38	0.63	0.36	0.34
22*S*,17$\alpha(H)$,21$\beta(H)$-homohopane	0.28	0.36	0.29	0.13	0.10	0.23	0.26	0.37	0.62	0.30	0.32
22*R*,17$\alpha(H)$,21$\beta(H)$-homohopane	0.32	0.34	0.26	0.12	0.09	0.25	0.23	0.30	0.50	0.28	0.26
22*S*,17$\alpha(H)$,21$\beta(H)$-bishomohopane	0.22	0.24	0.19		0.08	0.36	0.18	0.21	0.44	0.27	0.27
22*R*,17$\alpha(H)$,21$\beta(H)$-bishomohopane	0.22	0.21	0.16		0.07		0.17	0.15	0.29	0.21	0.16
22*S*,17$\alpha(H)$,21$\beta(H)$-trishomohopane	0.17	0.16	0.11		0.06		0.09	0.18	0.23	0.23	0.22
22*R*,17$\alpha(H)$,21$\beta(H)$-trishomohopane	0.09	0.11	0.07		0.05				0.21		
nonanal	4.38	7.00	2.23	1.27	1.63	5.99	6.16	2.73	23.40	27.47	4.34
acetonylsyringol		4.88			1.16	5.09	1.90		16.50	7.90	5.18
coniferyl aldehyde											
propionylsyringol						10.64					5.61
benz(de)anthracen-7-one	5.97	23.10	9.62		4.66	14.58	15.51	5.98	109.48	47.95	16.58
cholesterol			1.03			0.31					0.92
levoglucosan	39	53	75	8	7	299	145	52	289	107	250
8,15-pimaredienoic acid					0.91						
pimaric acid	0.17	0.14	0.07	0.25	0.34	0.07	0.16	0.09	0.84		0.14
sandaracopimaric acid	0.75	0.42	0.18	1.80	0.95		0.49	0.15	2.37	2.01	0.04
isopimaric acid	1.32		0.61	4.72	1.08		0.38				
dehydroabietic acid	6.23	6.45	2.02	16.80	10.18	1.05	6.13	2.23	37.04	23.13	1.75
abietic acid			0.10	0.58	0.13		0.13		0.58		0.13
abieta-6,8,11,13,15-pentae-18-oic acid	0.10	0.21	0.09		0.04	0.27	0.24	0.10	1.76	0.78	0.36
abieta-8,11,13,15-tetraen-18-oic acid	0.04	0.12	0.03		0.03	0.13	0.10	0.04	0.67	0.49	0.17
7-oxodehydroabietic acid	1.29	2.87	0.91	0.31	1.14	0.70	1.88	0.64	13.06	8.89	0.84
1,2-benzenedicarboxylic acid	11.89	9.52	3.98	1.23	1.68	6.38	10.57	12.65	57.82	73.20	9.70
1,4-benzenedicarboxylic acid	8.14	16.93	4.09	0.44	3.96	7.86	15.23	10.66	102.35	103.81	6.85
1,3-benzenedicarboxylic acid	1.27	2.24	0.49	0.18	0.56	0.68	1.49	1.33	8.74	8.18	0.93
fluoranthene	0.27	0.40	0.47	0.05	0.09	0.38	0.45	0.20	1.91	1.50	0.49
acephenanthrylene	0.06	0.10	0.10		0.03	0.09	0.09	0.06	0.48	0.23	0.10
pyrene	0.29	0.48	0.52	0.05	0.13	0.40	0.43	0.22	1.97	1.49	0.49
retene			0.02		0.03	0.03			0.16		0.03
methyl substituted MW 202 PAH	0.43	0.57	0.45	0.13	0.24	0.42	0.50	0.42	2.18	2.06	0.48
benzo(*ghi*)fluoranthene	0.18	0.35	0.32	0.06	0.10	0.21	0.22	0.14	1.20	0.86	0.28
cyclopenta(*cd*)pyrene	0.69	1.96	2.28	0.14	0.44	2.89	1.10	0.63	6.35	4.64	2.87
benz(*a*)anthracene	0.15	0.37	0.30	0.03	0.14	0.19	0.21	0.14	1.40	1.03	0.26
chrysene/triphenylene	0.36	0.74	0.61	0.14	0.27	0.44	0.51	0.37	2.78	2.39	0.57
methyl substituted MW 228 PAH	0.39	0.75	0.41		0.34	0.40	0.53	0.33	2.34	2.85	0.55
methyl substituted MW 226 PAH	0.33	0.81	0.24		0.19	0.25	0.64	0.17	2.76	2.47	0.35
benzo(*b*)fluoranthene	0.25	0.89	0.62		0.11	0.66	0.40	0.21	3.56	2.71	0.76
benzo(*k*)fluoranthene	0.14	0.71	0.63		0.12	0.58	0.58	0.18	3.11	1.59	0.76
benzo(*j*)fluoranthene	0.03	0.10	0.11		0.02	0.13	0.06	0.02	0.39	0.25	0.13
benzo(*e*)pyrene			0.62			0.66					0.77
benzo(*a*)pyrene	0.14	0.60	0.50			0.48			2.21	1.43	0.54

Table 2. (Continued)

Compound	TC 0325 2003	YL 0325 2003	TC-03	TC 1020 2002	YL 1020 2002	TC-10	TC 1213 2002	TC 1219 2002	YL 1213 2002	YL 1219 2002	TC -12
	D	D	M	D	D	M	D	D	D	D	M
perylene		0.11	0.07			0.11			0.40	0.22	0.13
indeno(*cd*)fluoranthene	0.11	0.31	0.27		0.08	0.27	0.25	0.09	1.52	0.91	0.37
indeno(*cd*)pyrene	0.26	0.92	0.75		0.13	0.85	0.74	0.24	4.26	2.32	0.84
picene	0.03	0.09	0.10		0.02	0.08	0.08	0.03	0.47	0.16	0.06
benzo(*ghi*)perylene	0.25	0.96	0.75		0.18	0.80	0.69	0.25	4.47	2.71	0.89
coronene	0.21	0.66	0.54		0.11	0.56	0.48	0.16	3.14	2.09	0.54
propanedioic acid			5.60			18.57					16.82
methylpropanedioic acid						0.25					0.26
butanedioic acid	16.36	17.42	7.75	1.20	2.25	6.61	14.98	14.36	77.61	75.50	10.38
methylbutanedioic acid	1.80	1.66	1.13	0.22	0.47	0.56	1.32	1.41	7.00	8.93	1.03
pentanedioic acid	3.11	2.71	3.08	0.21	0.36	1.81	2.93	2.38	15.13	16.88	2.80
hexanedioic acid	1.98	1.72	1.01	0.25	0.48	1.19	1.60	1.20	9.03	6.54	1.43
heptanedioic acid	0.85	1.36	0.40		0.38	0.41	1.24	0.83	6.38	4.68	0.39
octanedioic acid	1.07	1.58	0.48	0.42	0.79	0.61	1.62	0.68	9.22	4.95	0.68
nonanedioic acid	5.08	9.88	2.31	1.15	2.83	2.38	11.65	3.95	70.17	27.66	3.32
OC	10136	13559	6873	6932	3756	7504	13732	11360	16210	13068	6716
EC	2391	2690	2137	1524	2786	2023	2458	3556	2746	3062	2560
OC_{lowvol}	7921			1229			9657	7730			
EC_{lowvol}	2980			860			2930	2730			
$PM2.5_{lowvol}$	44840			9260			37260	37760			

Notes: D, daily high volume sample; M, low volume monthly composite sample. TC, Tung Chung; YL, Yuen Long

Table 3. Summary of organic compounds that overlapped by ion peaks from 1,1,1-methylphenyl-2,2-dimethyl-3,3,3-methylphenyltrisiloxane.

Sample name	Nonacosane	Hexacosanoic acid	Benzo(e)pyrene	Benzo(a)pyrene	Perylene
Characteristic ion	m/z 57,71,85	m/z 74, 87	m/z 252	m/z 252	m/z 252
TC-10202002	Overlap	Overlap	Overlap	Overlap	Overlap
TC-12132002			Overlap	Overlap	Overlap
TC-12192002			Overlap	Overlap	Overlap
TC-03252003			Overlap	Overlap	Overlap
YL-10202002			Overlap		
YL-12132002			Overlap		
YL-12192002			Overlap		
YL-03252002			Overlap		

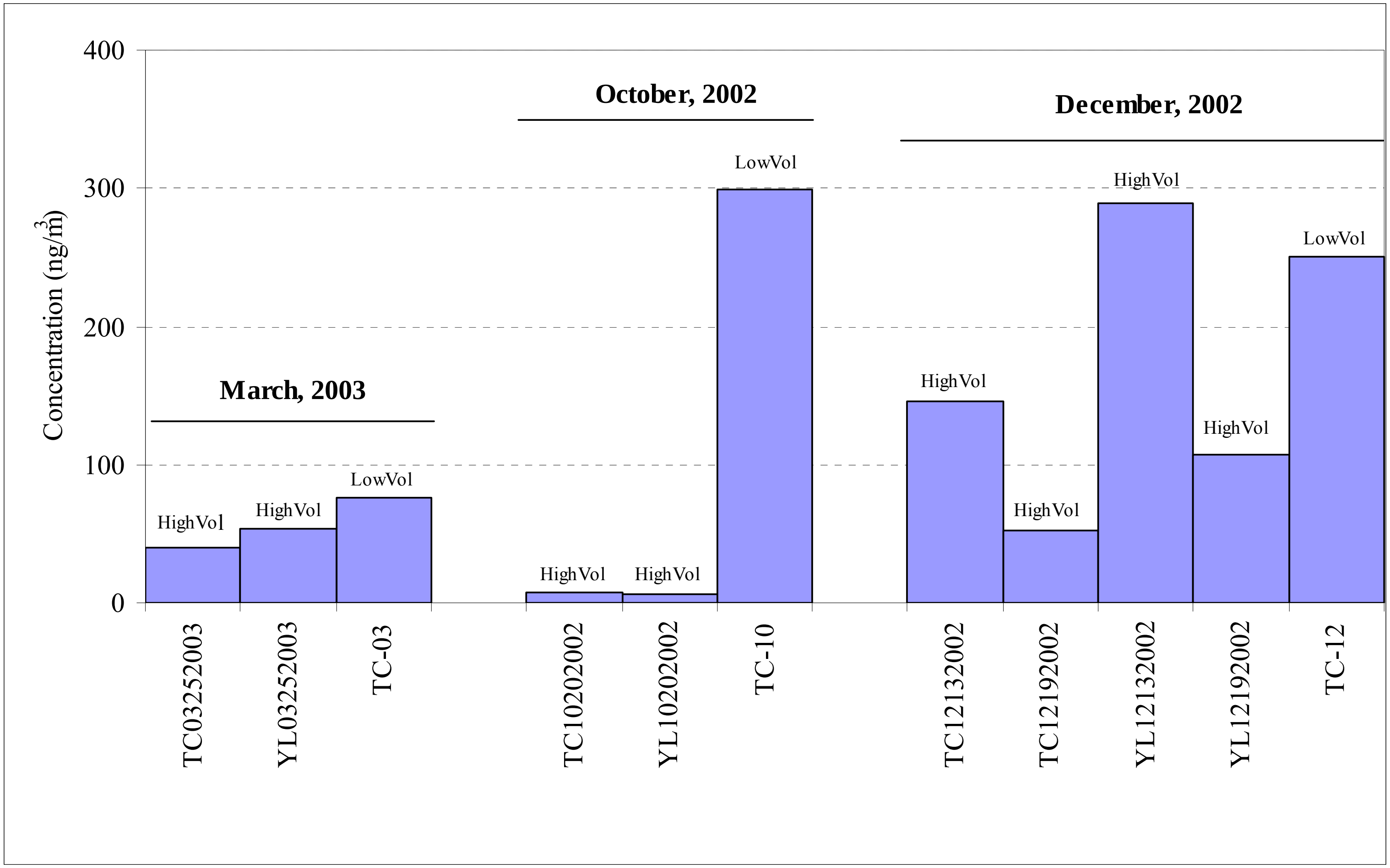

Figure 1. Distribution of levoglucosan in the high volume and low volume samples. The concentrations of levoglucosan for the low volume samples are from the corresponding low volume monthly composite samples. TC and YL stand for Tung Chung and Yuen Long sampling sites, respectively.

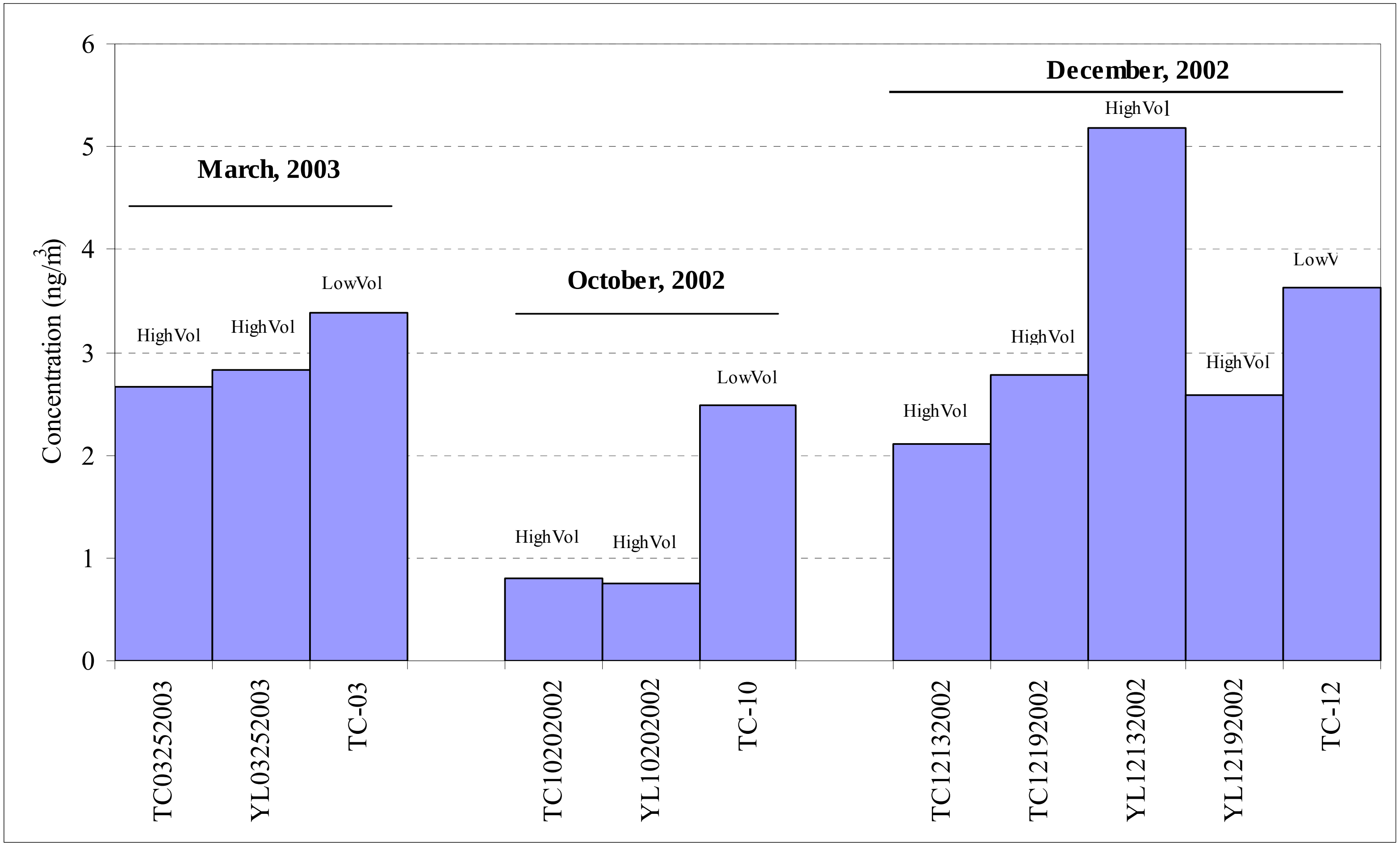

Figure 2. Distribution of the total hopanes and steranes (H+S) in the high volume and low volume samples. The concentrations of H+S for the low volume samples are from the corresponding low volume monthly composite samples. TC and YL stand for Tung Chung and Yuen Long sampling sites, respectively.

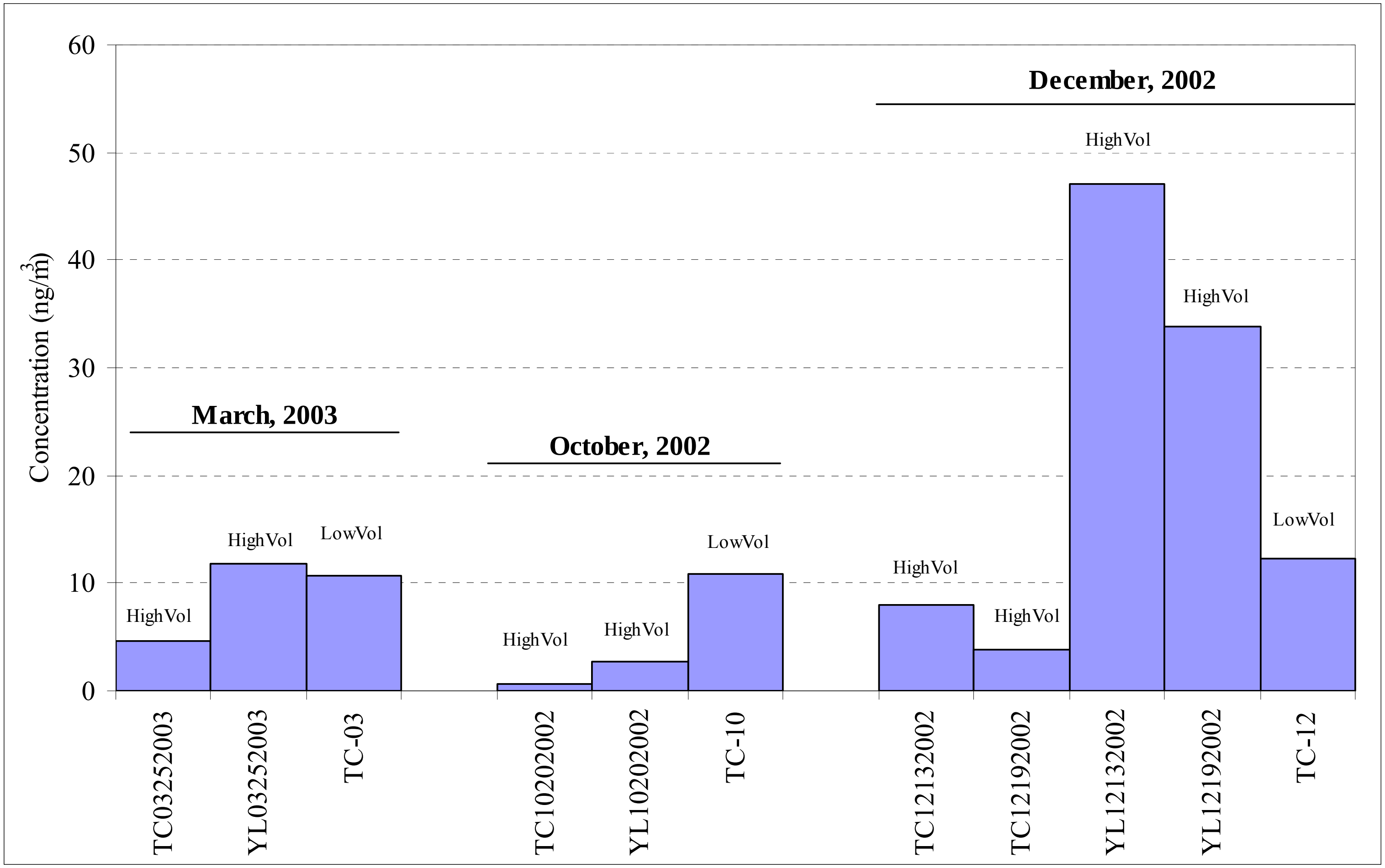

Figure 3. Distribution of the total PAHs in the high volume samples and low volume samples. The concentrations of the total PAHs for the low volume samples are from the corresponding low volume monthly composite samples. TC and YL stand for Tung Chung and Yuen Long sampling sites, respectively.

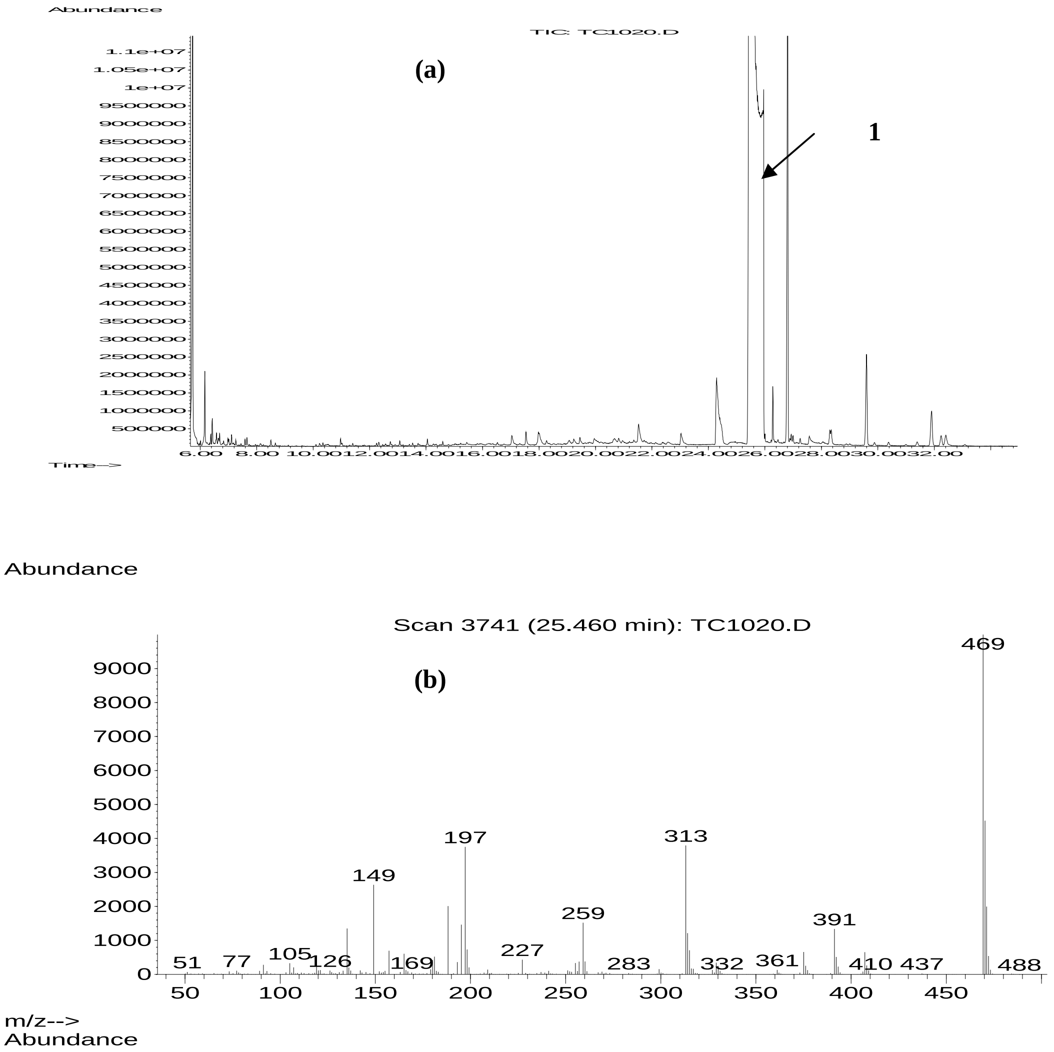

Figure 4. a) Chromatogram of Tung Chung High Volume sample showing the contaminant Peak and b) Mass spectra of contaminant

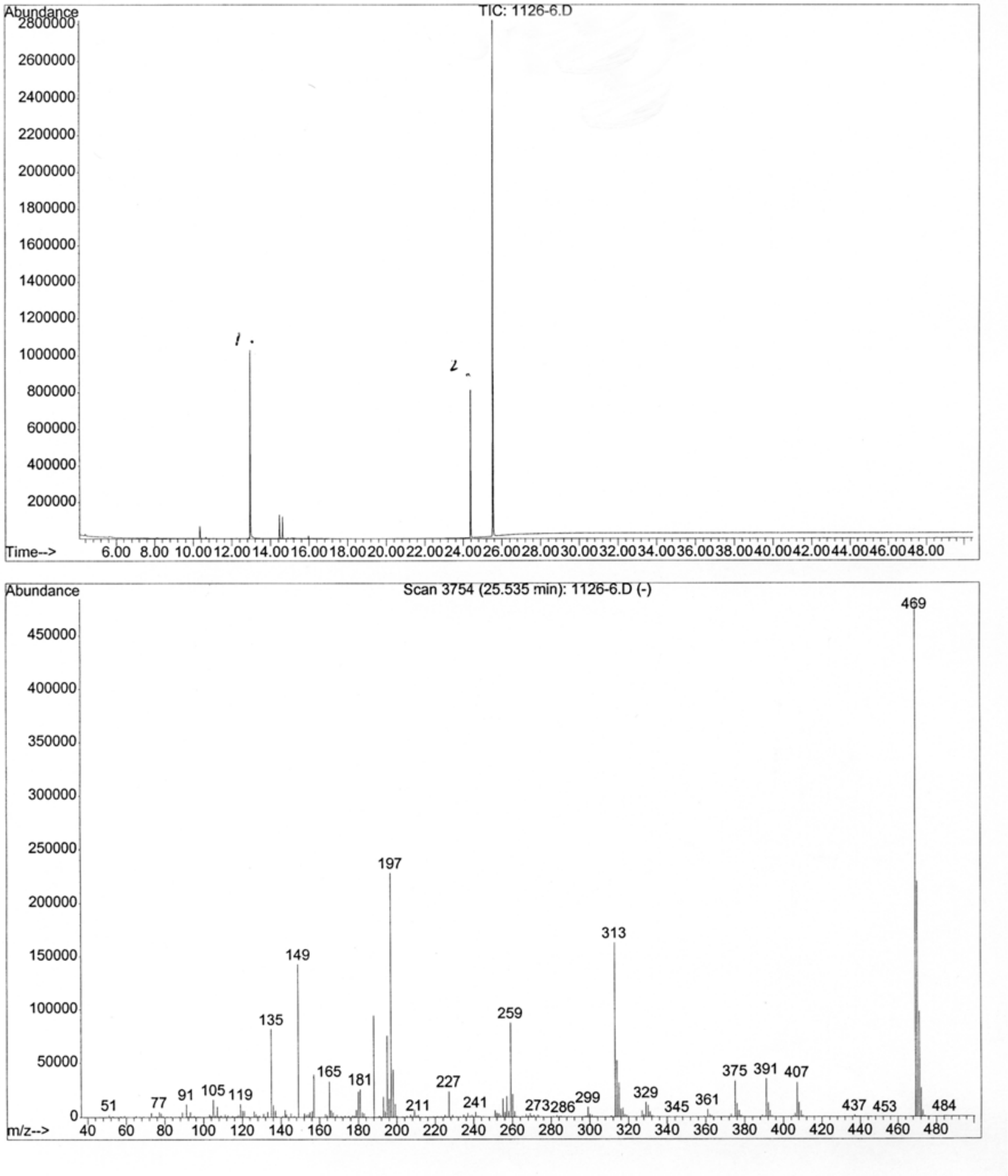

Figure 5. a) Chromatogram and b) Mass spectra of R&P WINS Impactor oil

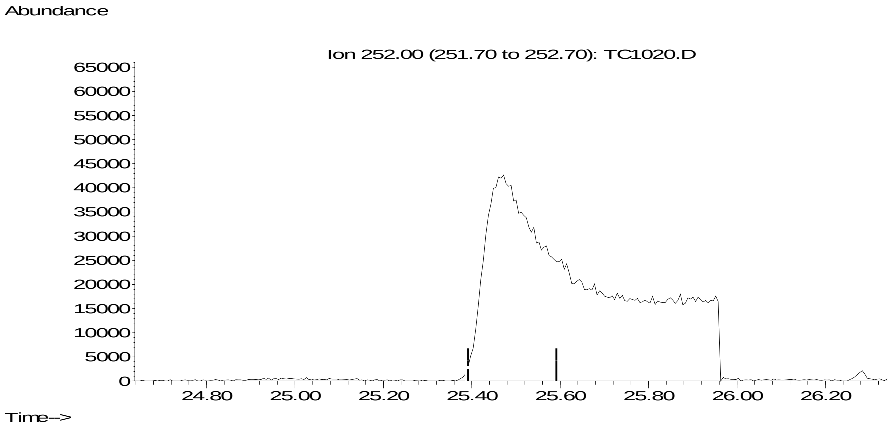

Figure 6. In TC10202002 sample, high m/z 252 ion peak from the contaminant covers all retention time intervals of Benzo(e)pyrene (BeP), Benzo(a)pyrene(BaP) and Perylene. The typical retention time of BeP, BaP, and Perylene is 25.49, 25.57, and 25.76 minutes respectively, and normally their peak width are 0.10, 0.09, and 0.07 minutes.

APPENDIX G

Chemical Characterization of Water-Soluble Organic Aerosols in the Pearl River Delta Region

Final Report

Submitted by

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Summary

As part of the overall effort to characterize the chemical properties of aerosols in the Pearl River Delta (PRD) region, we have analyzed water-soluble components of the aerosol samples collected in four sampling months spread over a year. A sampling network of seven sites across the PRD region was selected and sampling was carried out every six days in the months of October and December of 2002 and March and June of 2003. Individual daily filter samples were measured for total aerosol nitrogen (TN). The remaining filter materials in each month were combined together to yield water extracts of monthly composites. The water extract samples were analyzed for total water-soluble organic carbon (WSOC) content and individual inorganic and organic ions. This report describes our analysis results and provides preliminary data interpretation. The major observations and preliminary conclusions are summarized below.

- Aerosol organic nitrogen (ON) for individual samples was obtained as the difference of total aerosol nitrogen and the sum of two inorganic nitrogen species (NH_4^+ and NO_3^-). The ON concentration varies from non-detectable to 4 μgN/m^3, with an average value of 1.2 μgN/m^3. The ON fraction in TN was highly variable among individual samples, ranging from negligible to 60%. ON was found to be positively correlated with sulfate, suggesting that a significant fraction of ON was of secondary origin.

- Our measurements of three inorganic anions (SO_4^{2-}, NO_3^-, and Cl^-) and one cation (NH_4^+) in the monthly composite samples were compared with those computed using the concentrations of individual daily samples as measured by Lynn Salmon at CIT. The two sets of measurements were in agreement within 15%.

- The WSOC concentration varied from 1.7 to 5.2 μgC/m^3, with an average value of 3.0 μgC/m^3 for the region. This fraction accounted for 22-54% of OC, indicating that WSOC is a significant fraction of OC mass. A few lines of evidence are available from the measurement data to suggest that the WSOC fraction is mostly secondary organic carbon.

- Nine low molecular weight organic acids were quantified. They include formic, acetic, lactic, methanesulfonic, oxalic, malonic, meleanic, succinic, and glutaric acid. The sum of these acids accounted for 3.5-9.1% of WSOC on a carbon mass basis. Oxalic acid was found to be the most abundant organic acid, ranging from 182 to 481 ng/m^3. No discernable spatial contrast was found between rural and urban locations for the dicarboxylic acids, indicating the dominance of secondary sources.

- Methanesulfonic acid (MSA) is a known oxidation product of dimethylsulfide, a compound emitted from marine water. Its concentration varied from 7.5 to 28.7 ng/m^3. The principal controlling factor for the abundance of MSA in the region was found to be concentrations of atmospheric oxidants (OH and NO3). The temporal and spatial variation pattern in the atmospheric oxidants explains that higher MSA was observed in the winter than in the summer at all sites and that MSA was more abundant at two inland locations (Guangzhou and Zhongshan) than at the four coastal sites.

- A few free amino acids and aliphatic amines were detected in the aerosol samples. The sum of these two groups of amine compounds had a concentration ranging from 29-79 ng/m^3, accounting for a very minor fraction of WSOC (0.6%) or ON (1.2%).

Policy-relevant finding:
The secondary nature of WSOC implies that the effective reduction of an important fraction of PM2.5 aerosol mass (11-24%) requires identification of their precursors and their formation mechanism and rates in the atmosphere.

1. Introduction

As part of the overall effort to characterize the chemical properties of aerosols in the Pearl River Delta (PRD) region, we analyzed water-soluble components of the aerosol samples collected in the project (called the PRD project hereafter). This report summarizes our analysis results and provides preliminary data interpretation. The background information and sampling details are provided in the report by Bergin et al. (2004). Prior to the PRD project, the Hong Kong Environmental Protection Department carried out an aerosol characterization project that involved three sampling locations in Hong Kong for a period of 12 months (called the 12-month HKEPD project hereafter). Our group did similar chemical characterization work for the 12-month HKEPD project. Results of the 12-month HKEPD project are relevant to the understanding of the PRD project. As a result, we frequently cite information obtained from the first project in this report. A location map of the sampling sites in both projects is provided in Figure 1 and the site characteristics are described in Table 1.

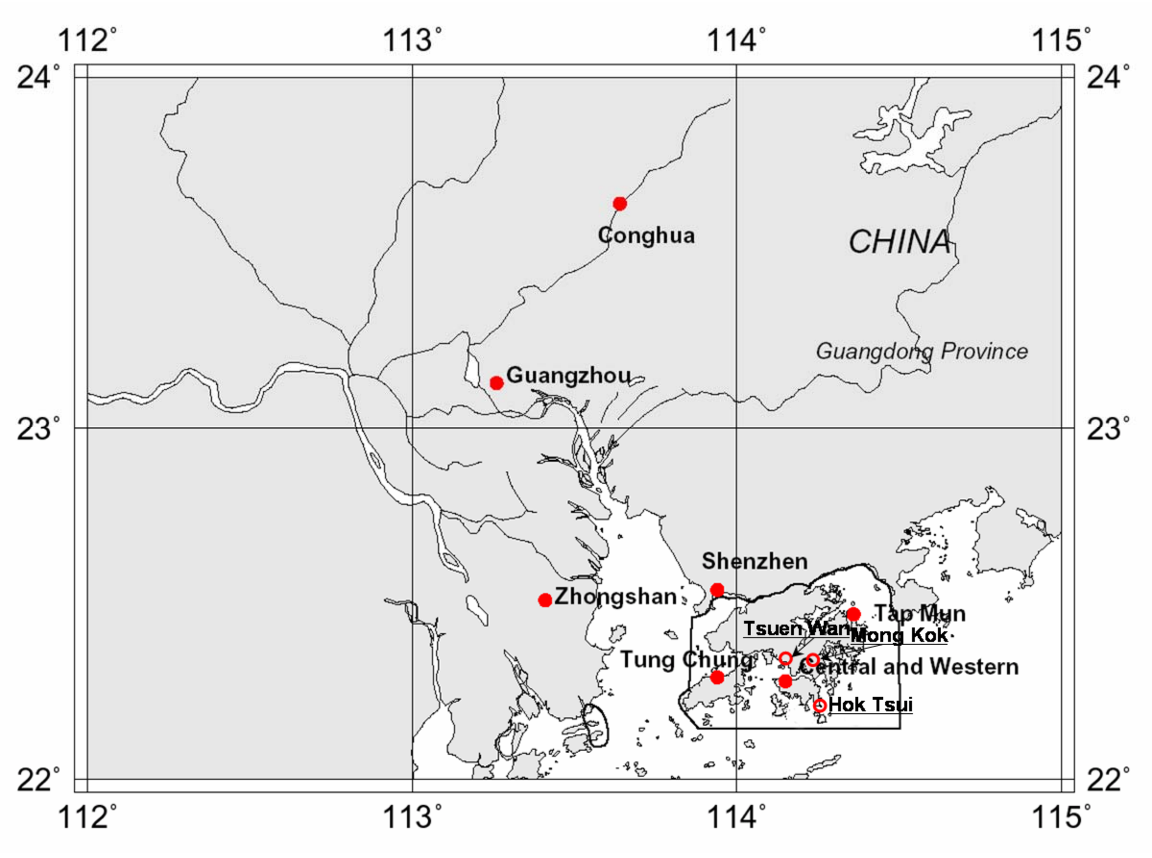

Figure 1. Location map of the sampling sites

(Solid circles are sampling sites in the PRD project; open circles represent the sites used in the 12-month HKEPD project. Credit: L. G. Salmon, G. S. Willis, M. Zheng, M. H. Bergin, Standard Operating Procedures for Sample Preparation, Handling, and Analysis during the Pilot Study in Hong Kong and the Pearl River Delta.)

Table 1. Site characteristics of the sampling locations

Location	Abbreviation	Distance to coast/Pearl River	Site characteristics
Hong Kong 12-month project study Period: November 2000 to October 2001			
Hok Tsui	HT	Within 1 km	rural area
Tsuen Wan	TW	within a few kilometers	urban area
Mong Kok	MK	within a few kilometers	Roadside in a downtown area
PRD project study Period: October 2002; December 2002; March 2003; and June 2003			
Tap Mun	TM	within 1 km	rural area, on an island without local vehicular traffic
Tung Chung	TC	within a few kilometers	residential area on Lantau Island
Central Western	CW	within 1-2 km	urban area
Shenzhen	SZ	within a few kilometers	suburban area
Guangzhou	GZ	20-30 km	urban area
Conghua	CH	50-60 km	rural area with a small village
Zhongshan	ZS	20-30 km	urban area, inside a park

2. Extraction and analysis scheme

We were allocated one quartz filter from each sampling day at each of the seven locations in the sampling network. A punch of 1x1 cm in size was removed from each filter for analysis of aerosol total nitrogen (TN). The filters in a same sampling month at each site were then combined before water extraction. Each monthly composite was extracted with 10.0 mL of ultra pure water in a sonication bath. This produced a total of 28 monthly water extracts, four extracts for each of the seven sites. The water extract samples were analyzed for the following chemical components:

- Total water-soluble organic carbon (WSOC) content
- Low molecular organic acids (formic, acetic, methanesulfonic acid, and C2-C5 dicarboxylic acids).
- Major inorganic anions (sulfate, nitrate, and chloride)
- Major inorganic cations (NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}).

2.1. Determination of aerosol total nitrogen

Aerosol TN was determined using an aerosol nitrogen analyzer developed by our group. The description of the instrument and characterization of the instrument performance are provided in the paper by Li and Yu [2004]. The instrument uses rapid thermoevolution of aerosol nitrogenous species at 800°C in a 2.5% O2/ 97.5% He carrier gas. Evolved nitrogen is oxidized to nitrogen oxides on a manganese dioxide catalyst, converted to nitrogen monoxide on a molybdenum catalyst, and quantified with a chemiluminescence detector. This system is able to provide fast (3 min per sample) and highly sensitive (a detection limit of 26 ng N) TN measurements for aerosol samples of a small size (~ 1×1 cm) without any pretreatment.

2.2. Analysis of WSOC

The standard operating procedure for determination of WSOC is given in Appendix 1 and relevant discussion on the method can be found in the paper by Yang et al. [2003]. Below is a brief description. The WSOC content in each aerosol water extract was measured by a TOC analyzer under the normal catalyst mode. The injection volume was 35 µl. The TOC has a detection limit of 0.88 µgC/ml for an injection volume of 35ul.

2.3. Analysis of cationic and anionic species

The cationic and anionic species were analyzed using ion chromatography (IC). Appendix 2 describes the detailed analysis conditions. The cationic species include NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}. The anionic species encompasses both inorganic anions (sulfate, nitrate, and chloride) and organic anions (formate, acetate, methanesulfonate, oxalate, malonate, maleate, succinate, and glutarate). The IC method could not differentiate the free acid and its dissociated ion; consequently, the concentrations reported here represent the sum of the two forms for any acidic species.

2.4. Analysis of aliphatic amines and amino acids

These two classes of compounds share a common functional group, $-NH_2$. As a result, both can be analyzed using Waters' AccQ-Tag method (Cohen *et al*., 1993). The amine group reacts with 6-aminoquinolyl-N-hydroxysuccinimidyl carbamate (AQC) to produce stable fluorescent derivatives that fluoresce strongly at 395nm (Figure 2). The resulting derivatives of various amino acids and aliphatic amines can be resolved on a HPLC column using gradient elution of three eluents: acetonitrile, water, and phosphate buffer.

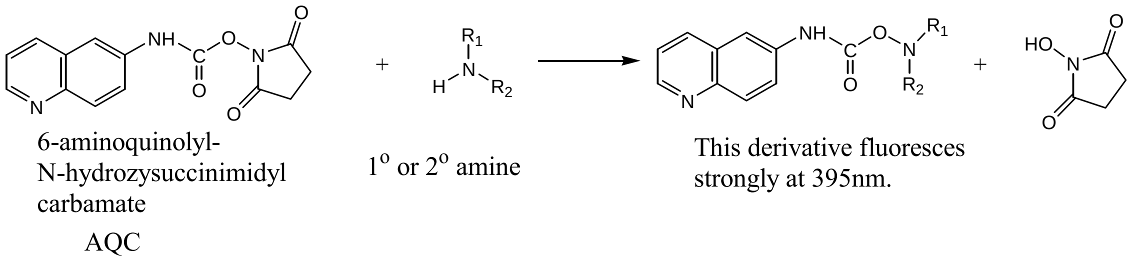

Figure 2. Derivatization reaction of –NH_2 containing compounds to form fluorescent derivatives

Besides free amino acids, proteinaceous materials, which consist of two or more amino acid units, could be present in the ambient aerosols. For example, Likens *et al* (1983) detected this kind of materials in rain samples. The proteinaceous materials can be regarded as combined amino acids and measured as their compositional amino acids through conversion to the free amino acids by hydrolysis.

The detailed procedure for analyzing the –NH_2 containing compounds is given in Appendix 3. A brief description is given below. 500 µl of aerosol water extract is transferred to a derivatization tube and evaporated to dryness under a gentle stream of N_2. To the derivatization tube, 20 µl of internal standard and 160 µl of buffer are added. N_2 is bubbled into the mixture for 50 min to remove NH_3. Otherwise NH_3 peak would interfere the determination of Histamine and Arginine if an aerosol sample contains a large amount of NH_4^+. Then 40 µl of the derivatization agent is added. The mixture is mixed with a vortex mixer for 1 min followed by heating at 55°C for 10 min. The sample is transferred to a 150 µl autosampler vial insert. Finally 10 µl is injected into a HPLC system for analysis.

3. Major inorganic ionic species

3.1. Interlaboratory comparison

Although the focus of our work is to characterize the organic fraction in the water-soluble aerosol, the water-soluble inorganic anions and cations were also measured for each monthly composite sample. Lynn Salmon at California Institute of Technology (CIT) measured a common set of three anions (SO_4^{2-}, NO_3^-, and Cl^-) and one cation (NH_4^+) in individual daily samples. She used an IC method for the determination of the three anions and a colorimetric method for the analysis of ammonium. The concentrations in the individual samples reported by Salmon were used to compute the concentrations in the monthly composite samples so that a comparison could be made with our measurements. Figure 3 plots the concentrations measured by us versus those computed from CIT's measurements. The two sets of measurements are in agreement within 15%. In addition, the data scattering of sulfate, nitrate, and ammonium is small, reflected by the high correlation coefficients (r^2>0.91). The reasonable agreement between the two labs adds to our confidence in the IC measurements from both our lab and CIT.

It is noted that chloride measurements had a lower correlation coefficient (r^2=0.83) than the other ions. The dominant source of aerosol chloride in this area is sea salt, which is known to mainly reside in coarse particles [Yao et al., 2002]. As a result, chloride concentrations in PM2.5 aerosols were present at much lower levels than either of nitrate, sulfate and ammonium. The average chloride concentration was 0.26 μg/m^3, in comparison with 1.50, 10.7, and 2.93 μg/m^3 for nitrate, sulfate, and ammonium, respectively. Ten out of 139 valid samples had chloride concentration fall below detection limit. Consequently, the chloride measurements by CIT had higher measurement uncertainties. This explains the higher degree of scattering of the chloride comparison data.

3.2. Abundance, seasonal and spatial variation

The concentrations of cationic species (NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}) and anionic species (SO_4^{2-}, NO_3^-, and Cl^-) are tabulated in Table 2. The sum of these ions accounted for 28 to 52% of the $PM_{2.5}$ mass. SO_4^{2-} was the most abundant species, varying from 6.22 to 14.18 μg/m^3. The concentration of NH_4^+ followed closely that of SO_4^{2-} ($r^2 = 0.81$). It varied from 2.00 to 6.16 μg/m^3, with an average value of 3.64 μg/m^3. The annual mean ratio of NH_4^+/ SO_4^{2-} (in charge equivalent) is 1.00 for the region, with the ratio slightly smaller than unity at the sites in Hong Kong and larger than unity at the sites in Guangdong. Nitrate also had a significant presence in $PM_{2.5}$. The annual mean of nitrate in the region was 1.23 μg/m^3. The two most abundant ionic species, SO_4^{2-} and NH_4^+, contributed to an average of 83% of the sum of all ionic mass. In comparison, Na^+ and Cl^- were less abundant, indicating the minor contribution of sea-salt particles to the overall $PM_{2.5}$ aerosol mass in the region. The annual mean concentration of Na^+ at the coastal sites and the inland locations was 0.32 and 0.29 μg/m^3, respectively. The slightly lower mass concentrations of Na^+ at the inland locations confirmed that sea salt was the dominant source of Na^+ in this coastal area.

Sulfate exhibited a consistent spatial gradient, declining from GZ, ZS to the coastal sites including SZ and the three HK sites in all seasons. Nitrate and ammonium had a similar spatial trend to that of sulfate. GZ generally had the highest sulfate, nitrate, and ammonium levels among all the seven sites. CH is a rural site further inland than GZ and ZS. The sulfate level at CH was similar to that at ZS, but the nitrate concentration was sometime more than a magnitude lower than those at ZS and GZ. The levels of sulfate, nitrate, and ammonium were similar at the three HK sites in each season, consistent with the secondary nature of these species.

Sulfate concentrations in December were generally higher than those in June with the exception of the GZ and CH sites. Higher nitrate and ammonium concentrations were observed in December than in June at all sites except for CH. Lower concentrations of air pollutants in the summer were anticipated when various meteorological factors were considered. In the summer, more frequent removal by wet deposition, high mixing height, and favorable dilution by cleaner marine air all lead to lower pollutant concentrations. It is noted that nitrate measurements in the sampling set-up used in this study are subject to negative sampling artifacts due to volatilization of ammonium nitrate after sample collection. Such negative sampling artifacts for filter-based sampling are well documented in the literature (e.g., Kim et al., 1999; Slaninas, 2004). It is also known that the magnitude of the nitrate loss is temperature dependent and more loss is expected at higher ambient temperature. A larger nitrate loss in the summer also contributed to the lower concentrations observed in this season.

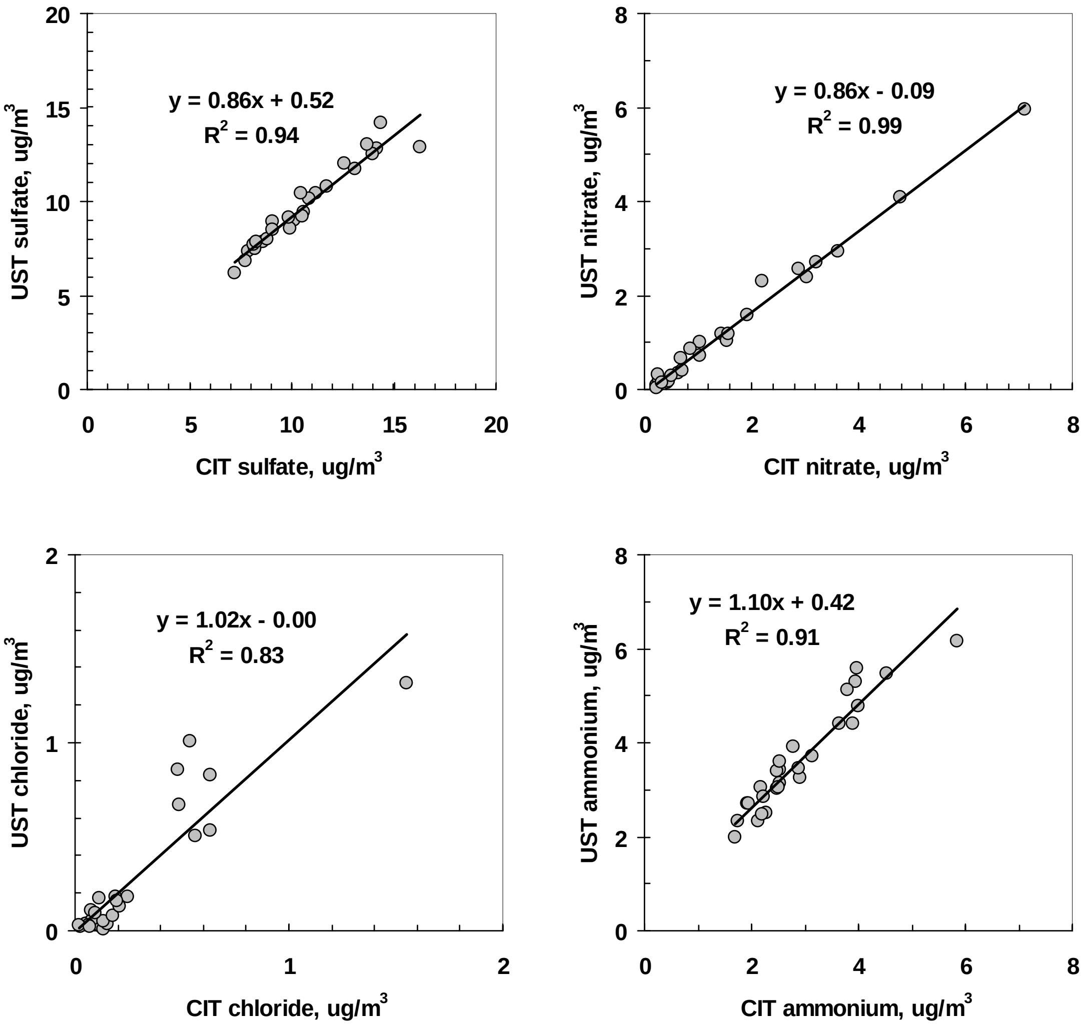

Figure 3. Comparison of three anions and one cation measurements made by UST and CIT

Table 2. Concentrations (μg/m^3) of inorganic cations and anions in the aerosol samples

Site	Sanpling month	SO_4^{2-}	NO_3^-	Cl^-	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	$PM_{2.5}$ mass	Σions/mass
TM	Oct.	7.516	0.150	0.023	0.240	2.336	0.757	0.052	0.135	23.77	47%
	Dec.	10.409	0.174	0.043	0.401	3.420	0.611	0.071	0.110	29.18	52%
	Mar.	9.027	0.339	0.033	0.368	3.238	0.365	0.048	0.107	34.39	39%
	Jun.	6.220	0.069	0.005	0.305	1.997	0.265	0.038	0.079	24.89	36%
TC	Oct.	7.355	0.291	0.033	0.204	2.498	0.741	0.044	0.155	30.76	37%
	Dec.	8.957	0.731	0.060	0.341	3.148	0.609	0.059	0.124	33.08	42%
	Mar.	9.408	1.183	0.109	0.352	3.702	0.333	0.045	0.128	41.41	37%
	Jun.	7.858	0.086	0.034	0.326	2.704	0.326	0.042	0.116	30.64	38%
CW	Oct.	7.474	0.393	0.050	0.220	2.479	0.715	0.059	0.165	28.15	41%
	Dec.	10.130	1.033	0.175	0.354	3.904	0.551	0.072	0.143	35.67	46%
	Mar.	8.533	1.176	0.171	0.369	3.445	0.305	0.048	0.171	40.85	35%
	Jun.	7.690	0.168	0.077	0.325	2.711	0.309	0.045	0.100	30.95	37%
SZ	Oct.	8.016	1.014	0.130	0.312	3.023	0.843	0.054	0.301	38.68	35%
	Dec.	12.038	2.746	0.486	0.315	5.303	0.842	0.060	0.236	45.98	48%
	Mar.	9.201	2.936	0.671	0.361	4.410	0.566	0.045	0.223	56.09	33%
	Jun.	7.853	0.857	0.183	0.397	3.063	0.358	0.047	0.159	35.88	36%
GZ	Oct.	12.781	1.617	0.159	0.300	4.406	1.571	0.042	0.373	68.27	31%
	Dec.	12.532	4.158	1.251	0.285	5.462	1.501	0.040	0.462	75.01	34%
	Mar.	12.860	5.958	0.829	0.356	6.155	1.238	0.040	0.246	80.92	34%
	Jun.	14.181	2.307	1.006	0.523	4.764	1.343	0.047	0.334	65.21	38%
CH	Oct.	9.131	0.202	0.027	0.096	2.836	1.218	0.037	0.363	34.25	41%
	Dec.	6.807	0.143	0.022	0.094	2.330	0.928	0.018	0.147	27.88	38%
	Mar.	10.244	0.480	0.013	0.235	3.928	1.309	0.033	0.235	45.79	36%
	Jun.	10.458	0.306	0.031	0.292	3.393	1.202	0.031	0.226	36.50	44%
ZS	Oct.	10.769	0.651	0.094	0.315	3.590	1.226	0.062	0.282	60.01	28%
	Dec.	12.993	2.608	0.533	0.333	5.573	1.090	0.039	0.193	81.06	29%
	Mar.	11.724	2.386	0.855	0.338	5.111	0.608	0.044	0.180	56.59	38%
	Jun.	8.464	0.143	0.024	0.314	3.050	0.184	0.034	0.108	29.56	42%
Annual mean		9.665	1.225	0.254	0.310	3.642	0.783	0.046	0.200	43.62	37%

4. Total WSOC content

WSOC concentrations varied from 1.7 to 5.2 µgC/m^3, with a mean value of 3.0 µg/m^{3}for the region (Table 3). The WSOC fraction accounted for 22-54% of OC, indicating that WSOC is a significant fraction of OC mass. The water-soluble organic aerosol mass, calculated from the concentration of WSOC by multiplying by a factor of 2.1 [Kiss et al., 2002], ranged from 2.6 to 7.9 µg/m^3, with a mean value of 4.4 µg/m^3. The mean water-soluble organic aerosol mass was more than half of the sulfate aerosol mass, demonstrating that the role of organic components in affecting hygroscopicity of ambient aerosols can not be overlooked.

A few lines of evidence are available to suggest that WSOC is mostly secondary in nature. First, the WSOC concentration levels were similar among all sites while an obvious contrast was seen in OC levels between rural and urban sites (Figure 4). Second, the WSOC/OC ratio had a similar spatial pattern to that of OC/EC, i.e., the ratios were lower in the urban locations and higher in the rural locations (Figure 5). The two rural sites, TM and CH, had a notably elevated ratio in WSOC/OC and OC/EC. The OC/EC ratio is known to increase with increased contribution of secondary OC. Third, WSOC and sulfate were positively correlated, with a correlation coefficient r of 0.75 (Figure 6). It has long been established that sulfate is a secondary aerosol component, formed from oxidation of precursor SO_2 [e.g., Seinfeld and Pandis, 1996].

The secondary origin of WSOC means that water-soluble organic compounds are largely not directly emitted from sources; instead they are mainly acquired either from oxidation of gaseous precursors or pre-existing aerosol OC materials. The reduction in this significant portion of aerosol material (11-24% of aerosol mass) requires identification of their precursors and their formation mechanism and rates in the atmosphere. Chemical characterization of the WSOC fraction at a molecular level is an essential step towards unraveling the formation mechanism. As results in the subsequent sections indicate that only a small fraction of WSOC could be identified as known chemical identities, we are far from identifying the major sources (i.e., anthropogenic versus biogenic) for WSOC.

Table 3. WSOC concentrations and relative abundance to other species

Site	Sampling month	WSOC (ugC/m3)	OC (ugC/m3)	WSOC/OC	OC/EC	2.1*WSOC/sulfate	2.1*WSOC/mass
TM	Oct.	2.76	5.74	48%	6.47	0.71	22%
	Dec.	3.00	5.53	54%	4.98	0.56	19%
	Mar.	2.23	4.79	46%	6.95	0.46	14%
	Jun.	1.71	3.52	49%	5.91	0.50	15%
TC	Oct.	3.29	7.54	44%	3.72	0.88	24%
	Dec.	2.70	6.75	40%	2.63	0.62	18%
	Mar.	2.48	6.88	36%	3.22	0.49	13%
	Jun.	1.95	4.06	48%	3.29	0.47	14%
CW	Oct.	2.80	6.44	44%	3.22	0.72	20%
	Dec.	2.13	7.87	27%	3.23	0.41	12%
	Mar.	2.48	7.48	33%	4.04	0.52	13%
	Jun.	2.07	4.69	44%	3.48	0.54	15%
SZ	Oct.	3.79	12.36	31%	3.05	0.91	19%
	Dec.	2.80	11.69	24%	2.95	0.47	11%
	Mar.	2.96	12.15	24%	3.07	0.59	11%
	Jun.	2.26	6.64	34%	2.69	0.57	14%
GZ	Oct.	5.04	20.19	25%	4.35	0.75	16%
	Dec.	4.21	19.28	22%	3.64	0.63	12%
	Mar.	4.29	16.96	25%	3.78	0.55	11%
	Jun.	3.63	13.86	26%	4.55	0.53	12%
CH	Oct.	3.06	8.88	34%	5.87	0.65	18%
	Dec.	2.25	7.81	29%	5.27	0.61	17%
	Mar.	4.48	12.54	36%	7.91	0.63	18%
	Jun.	2.82	8.12	35%	6.98	0.57	17%
ZS	Oct.	2.74	11.65	23%	5.54	0.49	14%
	Dec.	5.24	15.15	35%	3.84	0.80	19%
	Mar.	3.27	11.30	29%	4.56	0.52	12%
	Jun.	1.96	4.15	47%	2.97	0.45	14%
mean		3.01	9.43	32%	4.36	0.59	15%
SD		0.94	4.60	9%	1.45	0.12	3%
min		1.71		22%	2.63	0.41	11%
max		5.24		54%	7.91	0.91	24%

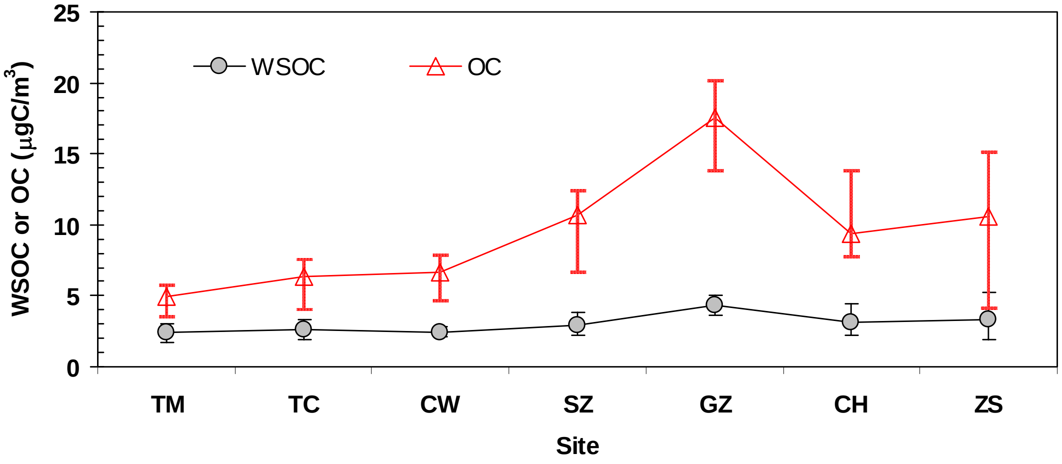

Figure 4. Spatial variation of WSOC and OC concentrations.

(The error bars represent the maximum and minimum concentrations at a given site.)

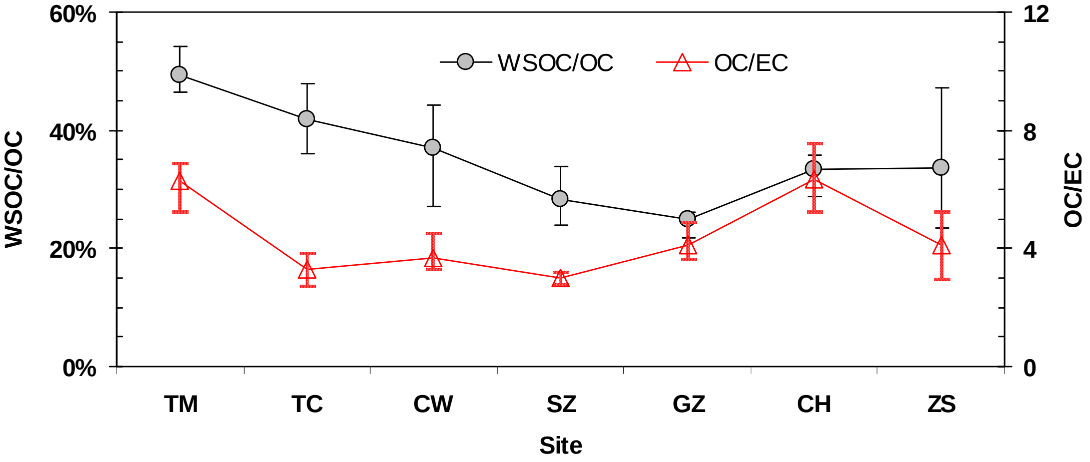

Figure 5. Spatial variation of WSOC/OC and OC/EC

(The error bars represent the maximum and minimum ratios at a given site.)

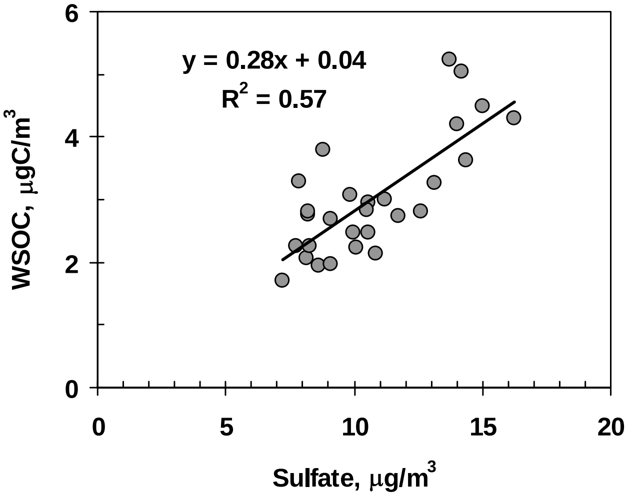

Figure 6. Correlation between WSOC and sulfate

5. Low molecular weigh organic acids

Nine low molecular weight organic acids were targeted for analysis by IC. They include lactic, formic, acetic, methanesulfonic acid (MSA), oxalic, malonic, meleanic, succinic, and glutaric acid. The IC method detects them in their ionic form. The IC chromatograms of two samples and one blank are shown in Figure 7 to illustrate their successful separation and detection by the IC method. Their concentrations in the aerosol samples are tabulated in Table 4. On a carbon mass basis, the sum of the organic ions accounted for 3.5-9.1% of WSOC.

5.1. C2-C5 dicarboxylic acids

It is noted that the low molecular organic acids are semivolatile and therefore have sampling artifact problems common to any semivolatile organic compounds when a filter-based method is used for sample collection. The sampling problem aside, we found that oxalic acid was the most abundant organic acid species, accounting for approximately half of the sum of all the organic acids mass. Its levels were similar among all sites, ranging from 182 to 481 ng/m^3. The lack of spatial contrast between urban and rural sites suggests that secondary sources dominated over primary sources. Oxalic acid had a moderate positive correlation with sulfate (Figure 8), further supporting the suggestion of the dominance of secondary formation pathways.

Abundance of C3-C5 dicarboxylic acids was one-quarter to one-tenth that of oxalic acid. Each individual dicarboxylic acid also lacked a spatial gradient from urban to rural locations. As a result, they were most likely secondary in origin. Malonate had a moderate correlation with oxalate; glutarate had a weak correlation with oxalate; however, no correlation was seen between the two C4 dicarboxylic acids and oxalate. The weak to moderate correlation indicated that oxalate, malonate, and glutarate probably had common sources for their precursors. On the other hand, the lack of correlation between C4 dicaroxylic acids was an indication of different sources for their precursors.

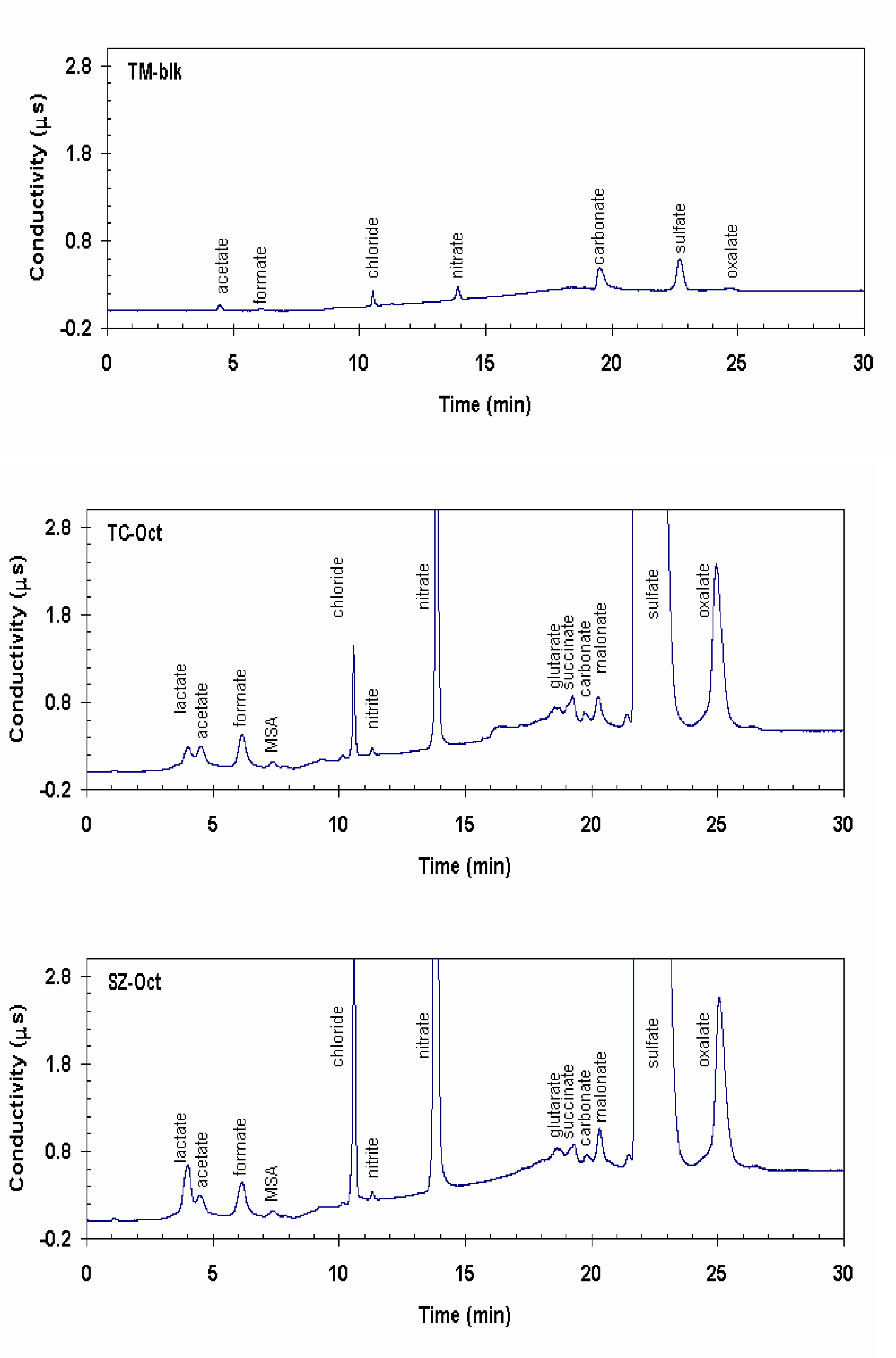

Figure 7. Example anion IC chromatograms of the aerosol water extracts

Table 4. Concentrations of low molecular weight organic anions (ng/m^3) in the aerosol samples

Site	Sampling month	oxalate	malonate	succinate	maleate	glutarate	MSA	Lactate [a]	formate	Acetate [a]	Σ(org ion) /WSOC [a]
TM	Oct.	349	53.5	47.7	12.6	38.7	13.3	41.1	40.0	43.5	7.2%
	Dec.	285	50.4	54.7	20.9	48.9	20.6	0.0	39.2	0.0	5.3%
	Mar.	290	57.9	75.0	19.8	44.5	9.1	0.0	31.7	37.0	8.1%
	Jun.	225	42.6	62.4	16.7	10.5	9.2	1.4	21.5	8.5	7.2%
TC	Oct.	336	57.9	44.4	14.5	36.9	15.3	48.7	49.3	60.2	6.4%
	Dec.	302	65.7	38.2	29.6	39.2	18.6	19.1	38.5	44.7	6.9%
	Mar.	286	62.2	76.0	42.2	35.0	13.5	0.0	29.5	10.6	7.1%
	Jun.	232	41.6	74.4	20.1	11.4	8.0	1.9	27.4	8.6	6.8%
CW	Oct.	316	62.9	56.5	8.8	35.0	14.1	43.6	39.1	71.4	7.4%
	Dec.	320	63.2	31.4	20.2	41.9	21.2	23.0	30.0	58.8	8.9%
	Mar.	283	60.9	62.0	16.9	30.4	14.8	0.6	27.2	8.6	6.3%
	Jun.	234	43.3	7.1	6.7	10.5	7.5	0.0	19.2	8.5	4.7%
SZ	Oct.	347	72.3	34.3	13.2	39.5	16.3	177.8	58.2	82.9	7.3%
	Dec.	387	89.5	45.2	19.8	49.6	19.8	54.1	47.6	87.9	9.1%
	Mar.	380	72.1	59.5	44.1	31.9	17.6	6.3	36.6	3.3	6.7%
	Jun.	290	44.5	56.8	7.3	11.5	9.6	0.0	32.8	9.1	6.1%
GZ	Oct.	481	99.9	67.0	33.9	37.0	22.2	74.5	63.7	104.1	6.2%
	Dec.	270	62.6	39.6	198.4	40.8	27.9	0.0	37.3	0.0	5.3%
	Mar.	326	65.3	68.6	0.0	43.6	16.9	0.0	34.5	31.1	4.2%
	Jun.	365	74.5	82.9	6.9	10.9	14.7	0.0	39.6	0.0	4.9%
CH	Oct.	327	86.0	20.0	38.4	40.6	13.7	55.7	39.4	70.4	7.2%
	Dec.	182	0.0	0.0	51.1	25.1	15.9	7.4	13.0	2.9	4.0%
	Mar.	316	66.7	69.9	53.4	28.6	10.7	6.7	34.4	20.0	4.3%
	Jun.	236	61.5	59.7	64.6	14.4	8.5	2.4	31.2	9.2	5.5%
ZS	Oct.	385	45.3	29.8	28.9	0.0	23.0	111.7	17.7	5.9	7.2%
	Dec.	346	43.0	0.0	87.4	46.4	28.7	24.1	14.2	0.0	3.5%
	Mar.	425	59.6	63.4	35.3	35.5	16.9	1.6	37.3	4.0	6.3%
	Jun.	345	44.5	53.3	22.4	14.6	7.9	3.7	10.5	0.1	7.7%
mean		317	58.9	49.3	33.4	30.5	15.6	25.2	33.6	28.3	6.3%
SD		65	18.7	22.6	37.8	14.2	5.8	41.1	12.5	31.9	1.4%
min		182	0.0	0.0	0.0	0.0	7.5	0.0	10.5	0.0	3.5%
max		481	99.9	82.9	198.4	49.6	28.7	177.8	63.7	104.1	9.1%

[a] Lactate and acetate partially coeluted; consequently their concentrations reported here are only for reference purpose. [b] On a carbon mass basis.

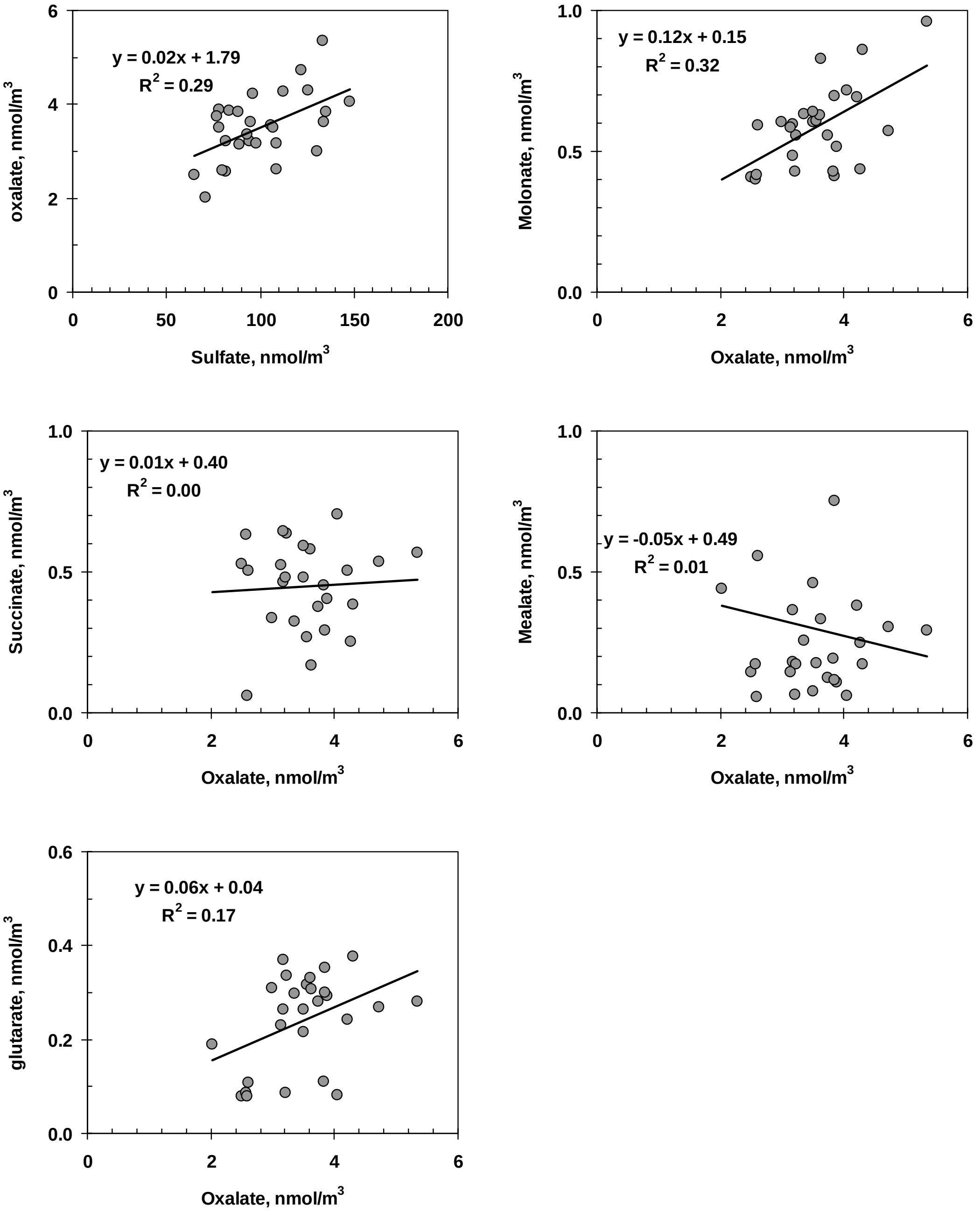

Figure 8. Correlations between various dicarboxylic acid species

5.2. Formic, acetic, and lactic acid

Lactate and acetate partially coeluted; a baseline separation of the two was usually not achieved (Figure 7). As a result, larger measurement uncertainties were associated with their quantification, which might explain the wide variation in their concentrations (from below detection to more than 100 ng/m^3) (Table 4). Because of this analytical problem, we report here acetate and lactate only for reference purpose. No further attempt is made to explain their spatial and temporal variation.

The concentration of formate ranged from 10 to 64 ng/m^3. Similar to other acid species, formic acid also lacked a spatial variation among the sites, suggesting the dominance of secondary formation pathways over primary emission sources. It had a consistent seasonal variation pattern among the four coastal sites, i.e., Oct. > Dec. >Mar.> Jun. The seasonality in the inland locations was variable and different from that at the coastal sites. For example, the highest formate concentration at ZS was observed in the March composite, and the lowest formate concentration at CH was in the December composite. The underlying cause for the different seasonal behaviors at the inland locations, is not yet clear.

5.3. Methanesulfonic acid

Table 5 lists the concentrations of MSA in the seasonal composites, along with MSA measurements made in the 12-month HKEPD project. The MSA level in the PRD project ranged from 7.5 to 28.7 ng/m^3, with an average of 15.6 ng/m^3. This level was similar to measurements made over Hong Kong by Arimoto et al. [1996]. Our measurement was lower than the average value of 29 ng/m^3 (varying from 16 to 208 ng/m^3) observed over the East China Sea, 36 ng/m^3 at Qingdao, and 66 ng/m^3 at Xiamen [Gao et al, 1996].

In the 12-month HKEPD project, the concentration levels of MSA were similar at all three sites. The seasonal trend was the same at all three sites, i.e, MSA concentration being winter > spring > summer > fall. The similar concentration levels at all three sites were consistent with its oceanic origin and photooxidation production pathway.

In the PRD project, a spatial gradient was discernable between coastal and inland locations. Higher concentrations were observed at two of the inland sites (GZ and ZS) in the October and December monthly composite samples than at the four coastal sites (TM, TC, CW, and SZ). Among the four coastal sites, TM is located on an island with little local emission, while the other three sites (TC, CW, and SZ) are in urban environments. MSA concentrations at the three urban coastal sites were similar to those at the rural coastal site, consistent with the observation in the 12-month HKEPD project. This again reflects the marine source of its precursor and the secondary nature of MSA.

The same seasonal trend was observed in the PRD project, i.e., higher MSA concentrations during the winter months than during the summer months. The MSA concentration in the winter is 1.7 times that in the summer in the 12-month HKEPD project and 2.3 times in the PRD project. Such a winter-high-summer-low seasonality contrasts most observations of seasonal variation reported in the literature. Most studies in the literature found a seasonal trend of aerosol MSA concentrations being the highest during summer and lowest in winter as a result of higher emission strength of dimethylsulfide (DMS) corresponding to increased primary productivity and enhanced photooxidation rate of DMS in the summer.

The MSA concentration in aerosols is determined by the relative strength of formation and removal processes, and gas-aerosol partitioning. The production rate of MSA is controlled by source strength of the DMS precursor and the formation rate from DMS. We examine below the various factors influencing the MSA aerosol concentrations in an effort to explain the seasonality.

Measurements of DMS air concentrations in the Pearl River Estuary and the adjacent northern South China Sea by Ma et al. [2004] indicated similar DMS levels in May and in November, with the mean DMS concentration in May 30% lower than that in November. In the summer, the prevailing wind brings more marine air mass to the PRD region.

Despite the ambiguous winter-summer variation in the input strength of DMS to the PRD, there are a number of factors that could enhance MSA abundance in aerosols in the winter.

(1) MSA production rate is enhanced in the winter due to higher atmospheric oxidant concentrations and due to cold temperatures favoring the MSA production pathway over other oxidation pathways of DMS.

MSA is one of the atmospheric oxidation productions of DMS by either OH radical or NO3 attack. A portion of DMS in the range of 5-50% is eventually oxidized to MSA [Saltzman et al., 1986]. An MSA yield of 46% from the reaction of NO3 with DMS was reported in a laboratory study [Jensen et al., 1991]. The oxidation of DMS by the OH radical proceeds by either addition or abstraction [Hynes et al., 1986; Allen et al., 1997; Seinfeld and Pandis, 1998]. Addition of the OH radical to DMS produces MSA as a major product. The abstraction route leads to formation of SO_2 as a major product and MSA as a minor product [Yin et al., 1990]. The relative importance of the abstraction and the addition pathway is temperature dependent, with the abstraction pathway favored at higher temperature. According to the rates measured by Hynes et al. [1986], a temperature decrease from 25^{o}C to 5^{o}C should result in a factor of 3.8 increase in the branching ratio of the addition to abstraction. As a result, the colder the temperature, the more favored the path to MSA formation [Seinfeld and Pandis, 1998; Berresheim, 1987; Bates et al. 1992].

The oxidation rate of DMS is clearly proportional to the concentrations of the oxidants, the OH radical and NO3. The seasonal abundance variation of the two oxidants were reflected in that of nitrate. It is known that nitric acid is mainly formed through the reaction of OH and NO2 during daytime and a heterogeneous pathway involving NOx, O3, and NO3. The nitrate has been considered a tracer of anthropogenic pollution [Savoie et al., 1992]. A positive correlation (r^2 = 0.44) was found between our measurements of aerosol nitrate and MSA (Figure 9), confirming that the production of nitrate and MSA is influenced by the same oxidants. Nitrate was consistently observed at all sites to be higher in the winter months than in the summer months (Table 2), suggesting a higher oxidant level in the winter.

It is important to note that nitrate measurements in this study were subjected to negative sampling artifacts and the artifacts were more prominent in the summer months than in the winter months. The above suggestion of higher oxidant levels in the winter could be true only if the magnitude of the sampling artifacts was not so big as to mask the seasonal difference in nitrate concentrations. Further studies, in which special sampling set-up (e.g., denude followed by a nylon filter), is adopted to minimize the sampling artifacts, are needed to verify whether nitrate has a winter-high-summer-low seasonal pattern.

(2) The removal of MSA through wet and dry deposition is reduced in the winter as a result of much lower rainfall in this season. Rainfall in this region has a stark seasonal contrast, with summer generally characterized as a wet season and winter as a dry season. The more frequent wet precipitation in the summer certainly facilitates the removal of MSA.

(3) Lower mixing height in the winter also enhances MSA concentration in this season.

(4) The lower temperatures in the winter favor the partitioning of MSA in the aerosol phase. The seasonal mean ambient temperature had a considerable variation during the sampling year from October 2002 to June 2003, varying from 17.8 to 27.9^{o}C.

The higher concentrations seen at the inland sites could be explained by the secondary nature of MSA. MSA, as a secondary pollutant, was expected to be at higher levels downwind of the marine emission source of its precursor DMS. DMS exists in the atmosphere for as long as 1 to 10 days [Berresheim et al., 1998; Chin et al., 1996; Putaud et al., 1999]. Its lifetime is sufficiently long for transport to these inland locations.

Table 5. Concentrations of MSA (ng/m^3) in PM2.5 in two field studies

	Conc.	T (^{o}C)	Conc.	T (^{o}C)	Conc.	T (^{o}C)	Conc.	T (^{o}C)
The 12-month HKEPD study								
Site	Fall/2001		winter/2000		Spring/2001		Summer/2001	
HT	13.8	26.1	27.4	18.8	22.6	23.3	17.9	27.8
TW	14.2	26.9	23.2	19.3	20.6	24.0	18.6	29.3
MK	11.1	27.7	33.4	20.1	23.2	24.7	17.8	30.0
season-mean	13.0		28.0		22.1		18.1	
annual mean	20.3							
min	11.1							
max	33.4							
The PRD study								
site	Oct/2002		Dec/2002		Mar/2003		Jun/2003	
TM	13.3	25.0	20.6	19.2	9.1	16.3	9.2	27.0
TC	15.3	26.7	18.6	20.5	13.5	18.4	8.0	28.5
CW	14.1	26.4	21.2	20.2	14.8	18.5	7.5	28.2
SZ	16.3	25.7	19.8	19.6	17.6	17.7	9.6	27.7
GZ	22.2	25.2	27.9	18	16.9	17.9	14.7	28.2
CH	13.7	-	15.9	-	10.7	-	8.5	-
ZS	23.0	-	28.7	-	16.9	-	7.9	-
season-mean	16.8		21.8		14.2		9.3	
annual mean	15.6							
min	7.5							
max	28.7							

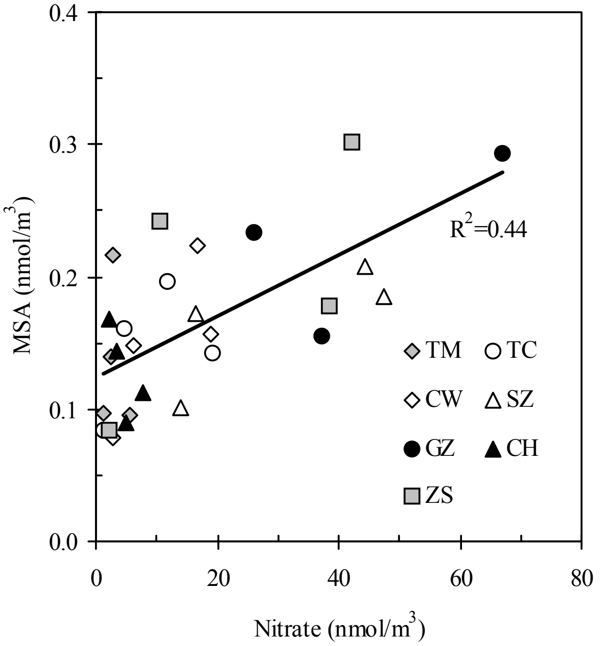

Figure 9. Correlation of MSA and nitrate

1. Aerosol organic nitrogen

The aerosol TN was directly measured by the aerosol nitrogen analyzer. The difference between TN and the sum of the two inorganic nitrogen species (NO_3^- and NH_4^+) is taken to be the aerosol total organic nitrogen (ON) concentration. Table 6 lists the ON concentrations for the individual 24-hr samples. The ON concentration varied from non-detectable to 4 µgN/m^3. The GD sites had higher mean ON concentrations than the three HK sites had. Among all the sites, ZS had the highest ON in the $PM_{2.5}$ particles. No consistent spatial variation could be discerned among the three HK sites, despite their site characteristic varying from rural to urban.

There appeared to be no discernable seasonable variation in the ON concentration, although the presence of ON in one-third of the samples collected in the summer month could not be verified due to the low concentrations. Figure 10 shows the time series of ON at each location.

Table 6. Total ON Concentrations (µgN/m^3)

Sampling date	TM	TC	CW	SZ	GZ	CH	ZS	All sites
2002/10/02	0.74	0.75	0.91	1.47	1.41	1.04	-	
2002/10/08	0.84	1.12	1.44	1.39	1.54	1.68	4.01	
2002/10/14	0.04	0.44	0.35	1.17	2.54	2.41	2.12	
2002/10/20	0.13	0.34	0.25	0.37	0.50	2.09	0.71	
2002/10/26	1.17	0.84	0.41	0.87	0.73	1.52	1.95	
2002/12/01	0.91	0.22	0.91	0.88	1.84	0.67	1.69	
2002/12/07	0.64	0.11	0.97	0.43	2.24	1.84	1.69	
2002/12/13	1.13	0.77	1.18	1.77	1.89	1.57	3.06	
2002/12/19	1.33	1.28	1.47	1.22	2.73	2.26	3.03	
2002/12/25	1.40	1.32	1.36	1.47	1.33	1.17	2.03	
2003/03/01	0.65	1.27	1.22	1.54	2.59	3.57	2.66	
2003/03/07	0.36	0.94	0.87	1.02	1.05	1.63	3.13	
2003/03/13	0.18	0.74	0.40	0.70	1.70	3.11	2.94	
2003/03/19	0.75	0.83	1.21	0.99	0.72	-	3.05	
2003/03/25	0.20	1.47	1.40	1.07	2.02	1.71	3.15	
2003/06/05	1.14	1.82	1.61	1.87	0.96	3.92	0.00	
2003/06/11	0.05	0.00	0.13	0.52	1.78	1.17	0.25	
2003/06/17	1.42	1.96	1.86	2.06	2.30	1.02	1.18	
2003/06/23	0.00	0.00	0.15	0.07	0.32	1.00	0.11	
2003/06/29	0.00	0.00	0.01	0.07	0.29	0.59	0.13	
median	0.70	0.80	0.94	1.04	1.62	1.63	2.03	1.15
mean	0.65	0.81	0.90	1.05	1.52	1.79	1.94	1.23
SD	0.51	0.60	0.56	0.57	0.77	0.93	1.24	0.89
max	1.42	1.96	1.86	2.06	2.73	3.92	4.01	4.01
min	0.00	0.00	0.01	0.07	0.29	0.59	0.00	0.00

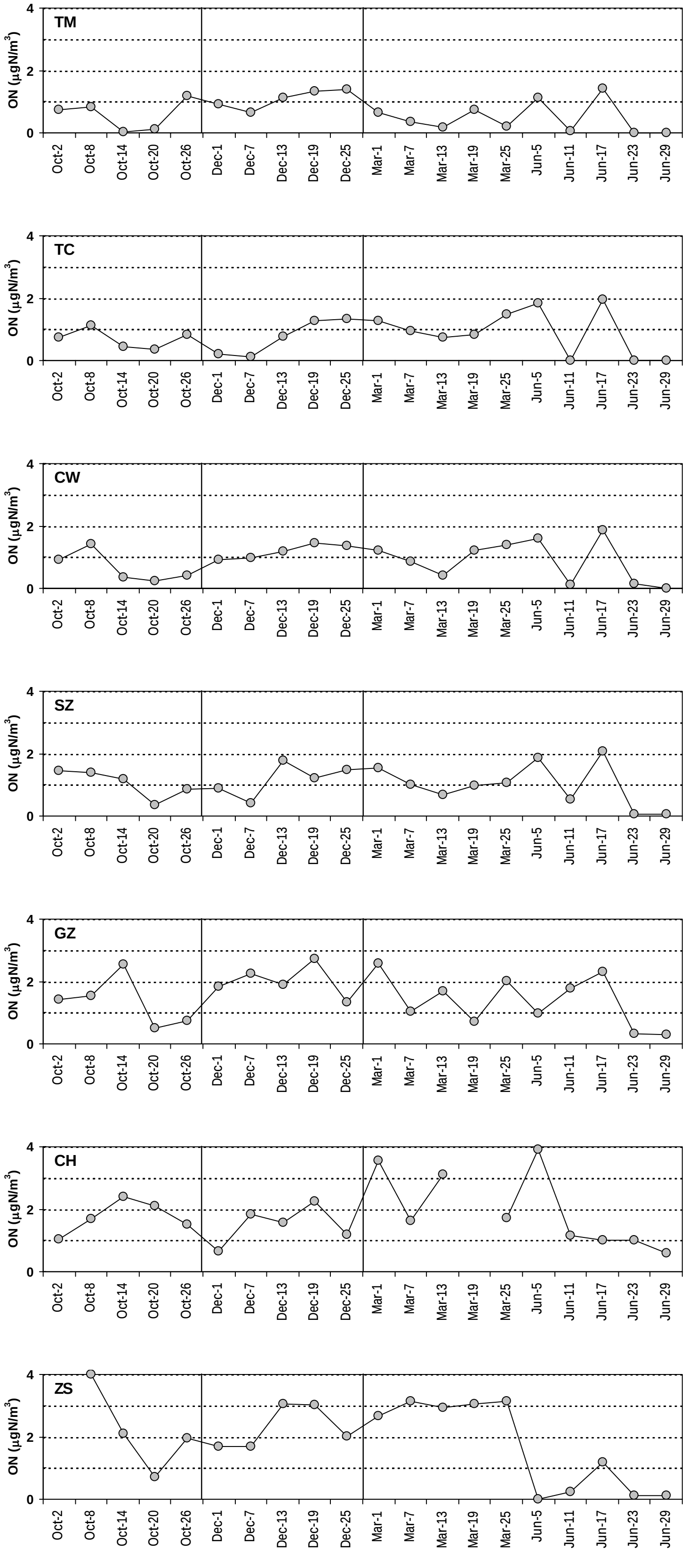

Figure 10. Time series of ON concentrations

Table 7 lists the statistics of three ratios, ON/TN, ON/aerosol mass, and ON/OC. ON accounted for on average 30% of the aerosol TN. The ON fraction was highly variable among individual samples, ranging from negligible to 60%. ON was a small fraction (~3%) of the aerosol mass. The ON/OC mass ratio was on average 0.13, and the corresponding molar ratio was 0.15. That is, in an average organic compound molecule, there were 6.6 C atoms for every N atom. The actual ratio of N:C is expected to be higher in N-containing organic molecules, since many aerosol organics do not contain N atoms.

The chemical nature of aerosol ON is little understood. A few classes of N-containing organic compounds have been reported to be present in aerosols. They include organic nitrates, nitro-PAHs, nitrophenols, urea, aliphatic amines, and amino acids [Mylonas et al., 1991; Bamford and Baker, 2003; Zhang and Anastasio, 2001; Zhang et al., 2002; Gorzelska and Galloway, 1990; Gorzelska et al., 1997; Cornell and Jickells, 1998]. The known organic N compounds have diverse sources. For example, organic nitrates and nitro-PAHs are mainly products of photoxidation of hydrocarbons and PAHs; urea and amino acids are most likely derived from biological sources.

The correlation matrix of ON with other measured aerosol species reveals that among all the species, sulfate has the highest correlation with ON (r = 0.72) (Table 8). The correlation between sulfate and ON is also plotted in Figure 11. This moderate positive correlation appears to suggest that a significant fraction of ON is secondary in origin. K, Pb, and Si also show positive correlation with ON, with a correlation coefficient (r) greater than 0.6. Currently, we do not have a good explanation for such unexpected positive correlations.

Table 7. Statistics of ON/TN, ON/aerosol mass, and ON/OC

		TM	TC	CW	SZ	GZ	CH	ZS	all sites
ON/TN	median	24%	27%	29%	24%	25%	48%	38%	30%
	mean	22%	23%	27%	27%	26%	45%	37%	30%
	max	45%	37%	41%	60%	45%	56%	59%	60%
	min	0%	0%	3%	10%	15%	0%	0%	0%
ON/Mass	median	2.4%	2.3%	2.7%	2.0%	2.2%	4.8%	4.2%	2.7%
	mean	2.0%	2.2%	2.4%	2.3%	2.2%	4.6%	3.8%	2.8%
	max	4.6%	3.7%	4.0%	4.5%	4.3%	6.5%	7.5%	7.5%
	min	0.0%	0.0%	0.1%	0.5%	0.7%	0.0%	0.0%	0.0%
ON:OC	median	0.14	0.11	0.14	0.08	0.09	0.20	0.18	0.13
	mean	0.12	0.12	0.13	0.10	0.09	0.20	0.18	0.13
	max	0.23	0.28	0.23	0.20	0.17	0.27	0.37	0.37
	min	0.00	0.00	0.01	0.03	0.03	0.11	0.00	0.00

Table 8. Correlation coefficient matrix of ON with other species in aerosols

0	ON	OC	EC	sulfate	nitrate	chloride	NH4+	Al	Si	Fe	Mn	Na	Mg	K	Ca	V	Ni	As	Pb
ON	1	**0.679**	**0.354**	**0.725**	**0.393**	**0.273**	**0.585**	**0.551**	**0.634**	**0.520**	**0.355**	-0.094	**-0.168**	**0.709**	**0.569**	**0.474**	**0.546**	**0.439**	**0.636**
OC		1	**0.748**	**0.692**	**0.662**	**0.514**	**0.724**	**0.649**	**0.826**	**0.786**	**0.685**	0.010	**-0.247**	**0.803**	**0.754**	**0.645**	**0.321**	**0.764**	**0.824**
EC			1	**0.336**	**0.637**	**0.518**	**0.498**	**0.441**	**0.587**	**0.578**	**0.544**	**0.176**	-0.116	**0.479**	**0.551**	**0.517**	0.122	**0.558**	**0.587**
sulfate				1	**0.451**	**0.252**	**0.899**	**0.518**	**0.583**	**0.491**	**0.361**	-0.070	-0.127	**0.626**	**0.530**	**0.476**	**0.367**	**0.470**	**0.574**
nitrate					1	**0.686**	**0.678**	**0.313**	**0.444**	**0.443**	**0.434**	0.128	-0.033	**0.452**	**0.418**	**0.445**	0.146	**0.605**	**0.580**
chloride						1	**0.436**	**0.282**	**0.435**	**0.585**	**0.652**	0.099	-0.096	**0.299**	**0.341**	**0.424**	0.120	**0.593**	**0.537**
NH4+							1	**0.456**	**0.565**	**0.518**	**0.439**	-0.012	-0.110	**0.551**	**0.506**	**0.477**	**0.287**	**0.531**	**0.587**
Al								1	**0.896**	**0.647**	**0.402**	-0.032	**-0.200**	**0.693**	**0.839**	**0.630**	**0.338**	**0.505**	**0.615**
Si									1	**0.819**	**0.629**	-0.067	**-0.334**	**0.810**	**0.913**	**0.622**	**0.310**	**0.650**	**0.769**
Fe										1	**0.921**	-0.064	**-0.282**	**0.671**	**0.698**	**0.506**	**0.344**	**0.735**	**0.776**
Mn											1	0.012	**-0.204**	**0.491**	**0.482**	**0.381**	0.156	**0.675**	**0.663**
Na												1	**0.410**	-0.047	-0.019	0.043	-0.074	-0.016	0.024
Mg													1	**-0.265**	**-0.296**	**-0.227**	-0.110	**-0.243**	**-0.260**
K														1	**0.785**	**0.495**	**0.334**	**0.712**	**0.886**
Ca															1	**0.543**	**0.272**	**0.578**	**0.686**
V																1	**0.478**	**0.528**	**0.589**
Ni																	1	**0.212**	**0.336**
As																		1	**0.867**
Pb																			1

In bold, significant values (except diagonal) at the level of significance alpha=0.050 (two-tailed test).

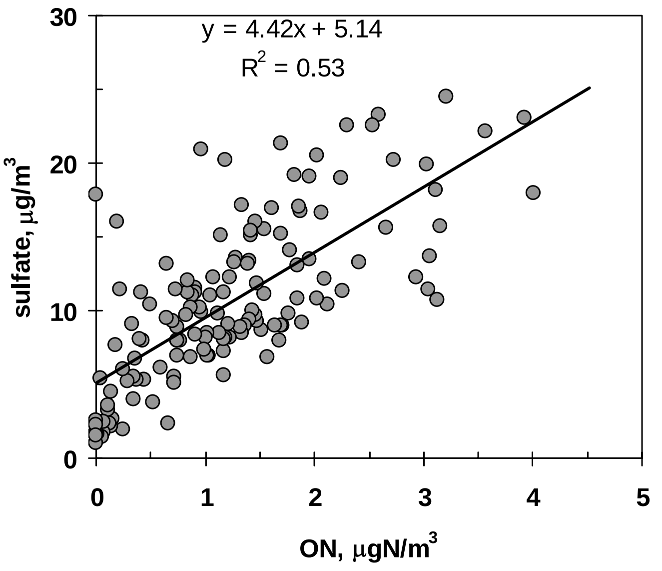

Figure 11. Correlation plot of sulfate versus ON

2. Amino acids and aliphatic amines

A total of 20 amino acids and 3 aliphatic amines were targeted for analysis. Seven amino acids were detected in more than 50% of the samples. They are Asp, Ser, Gly, Thr, 2-Ala, Ala, and Phe. Among them, Gly, 2-Ala, and Ala were present in every samples. The three target aliphatic amines, methyl amine, ethyl amine, and ethanol amine, were detected in every sample. Their concentrations are listed in Table 9. Eight FAAs (Pro, 2-Aba, Cys, Tyr, Orn, Lys, Lle, and Leu) were detected in at least one sample but in less than 50% of the samples. Five FAAs (Gal, His, Arg, Val, and Met) were included in the calibration standards, but their presence in the samples could not be detected.

The sum of all FAAs ranged from 18.9 to 62.5 ng/m^3, with an average value of 32.5 ng/m^3. The FAAs accounted for a small fraction (an average of 0.4%) of WSOC on a carbon mass basis. The most abundant FAA is glycine, ranging from 13.8 to 33.4 ng/m^3. The average level of gly was roughly one order of magnitude larger than the next two most abundant AAs (Ala and 2-Ala). Gly alone accounted for three-quarter of the total FAA mass concentration.

The sum of the three aliphatic amines ranged from 9.2 to 24.3 ng/m^3, with an average value of 15.6 ng/m^3. The contribution of the aliphatic amines to WSOC was also small, accounting for only 0.22% on a carbon mass basis. Methyl amine was the most abundant aliphatic amine. The other two aliphatic amines had similar abundance, about one-fifth that of methyl amine.

No consistent seasonal variation pattern was seen across the sampling sites. The levels of the total FAAs and the total aliphatic amines were similar in different sampling months at each site. When measurements at all sampling sites pooled together, we note that positive correlation exist among some individual species. Table 10 tabulates the correlation (r) matrix for the FAAs and aliphatic amines. Glycine showed positive correlation with Ala, Phe, methyl amine, and ethyl amines. Methyl amine had a positive correlation with ethyl amine, but not ethanol amine. The correlations may indicate a dominant common source or common sources for these species. Further inference to sources of the FAAs and aliphatic amines is not readily extractable other than that they are of biological origin.

The contributions of FAAs and aliphatic amines to total aerosol ON were also computed and listed in Table 11. The two classes of amine compounds accounted for a very minor faction of ON, approximately 0.6% each. This is in line with the earlier suggestion that ON is mainly secondary in origin.

Table 9. Concentrations of free amino acids and aliphatic amines (ng/m^3) in the aerosol samples

Site	Sampling month	Asp	Ser	gly	Thr	2-Ala	Ala	Phe	other AAs [a]	ΣFAA	Ethanol amine	M. amine	E. amine	Σ(ali-amine)	%WSOC [b]	
															FAA	ali-amine
TM	Oct.	0.0	1.2	17.1	0.0	1.4	0.8	0.0	0.3	20.8	0.2	8.6	0.9	9.8	0.25%	0.14%
	Dec.	0.0	1.3	19.9	0.5	1.2	0.7	0.3	0.0	23.9	0.3	11.7	1.1	13.0	0.27%	0.17%
	Mar.	0.0	0.3	20.8	0.5	1.4	1.3	0.4	0.0	24.6	0.4	11.6	0.9	12.9	0.37%	0.23%
	Jun.	2.6	0.0	13.8	0.4	1.9	1.6	0.4	0.8	21.5	0.7	7.8	0.7	9.2	0.44%	0.22%
TC	Oct.	0.0	1.2	22.7	0.0	1.6	1.2	1.1	0.0	27.6	4.7	9.2	1.3	15.2	0.29%	0.19%
	Dec.	1.4	1.1	17.9	0.6	1.1	1.1	0.9	0.0	24.2	1.8	10.5	1.6	13.8	0.31%	0.21%
	Mar.	0.0	0.0	27.4	0.5	1.1	1.9	0.7	0.0	31.6	2.7	10.1	1.5	14.2	0.43%	0.23%
	Jun.	2.5	0.3	26.6	0.3	2.2	1.7	0.6	0.4	34.6	1.3	10.7	1.7	13.7	0.61%	0.29%
CW	Oct.	1.6	1.1	19.9	0.0	1.5	1.2	0.8	0.3	26.4	2.1	9.7	3.1	14.9	0.32%	0.22%
	Dec.	0.0	1.2	22.4	0.0	1.5	1.7	1.5	0.0	28.5	4.1	11.7	3.3	19.2	0.46%	0.37%
	Mar.	1.7	0.4	23.7	0.4	1.3	2.6	0.9	0.2	31.2	3.1	10.7	2.0	15.9	0.43%	0.26%
	Jun.	4.5	6.6	33.4	2.2	2.0	4.6	1.5	7.7	62.5	3.5	10.4	2.5	16.4	1.11%	0.33%
SZ	Oct.	1.3	1.5	19.9	0.0	1.9	1.5	1.2	1.2	28.6	2.3	9.5	1.6	13.4	0.27%	0.14%
	Dec.	0.0	1.6	24.5	0.0	1.5	1.6	0.8	0.8	30.7	1.2	9.9	1.4	12.5	0.38%	0.18%
	Mar.	1.4	0.0	21.5	0.7	1.3	2.5	1.3	0.8	29.6	2.4	14.2	1.6	18.2	0.36%	0.25%
	Jun.	2.5	0.2	23.2	0.4	1.8	2.0	1.1	0.8	32.1	2.9	10.1	1.2	14.2	0.50%	0.25%
GZ	Oct.	1.6	1.4	28.0	0.0	1.6	3.1	2.1	3.4	41.3	2.5	18.1	3.3	24.0	0.29%	0.19%
	Dec.	0.0	1.1	26.7	0.0	1.4	3.3	2.1	6.7	41.2	2.8	15.6	4.8	23.2	0.37%	0.23%
	Mar.	0.0	0.1	32.3	0.7	1.3	4.5	2.0	3.1	44.1	2.6	18.4	3.3	24.3	0.37%	0.23%
	Jun.	1.1	0.0	28.8	0.5	1.9	3.5	2.1	4.1	42.1	3.7	16.4	3.4	23.4	0.41%	0.26%
CH	Oct.	1.6	1.4	25.9	0.0	2.1	1.8	1.1	0.0	33.9	0.2	9.8	2.4	12.4	0.38%	0.17%
	Dec.	0.0	1.6	14.7	0.0	1.1	0.9	0.6	0.0	18.9	0.2	8.2	1.8	10.2	0.29%	0.19%
	Mar.	0.0	0.0	30.8	0.6	1.6	2.6	0.7	3.3	39.5	0.6	12.5	2.0	15.0	0.31%	0.14%
	Jun.	2.0	0.3	24.2	0.6	1.8	2.4	1.4	0.6	33.2	0.9	13.4	2.9	17.2	0.41%	0.25%
ZS	Oct.	2.0	1.9	21.1	0.0	2.2	1.5	0.8	1.9	31.4	0.3	14.0	1.4	15.7	0.41%	0.23%
	Dec.	2.1	2.1	27.3	1.0	1.4	2.1	1.0	2.1	39.0	1.2	13.7	1.9	16.8	0.26%	0.13%
	Mar.	0.0	1.1	26.2	1.0	1.5	4.1	1.2	2.7	37.9	1.2	13.8	1.7	16.7	0.41%	0.21%
	Jun.	1.6	0.0	23.8	0.4	2.1	1.7	0.5	0.0	30.1	0.6	9.3	0.9	10.8	0.52%	0.22%
mean		1.13	1.03	23.7	0.40	1.60	2.13	1.04	1.48	32.5	1.81	11.76	2.02	15.6	0.40%	0.22%
SD		1.17	1.27	4.9	0.47	0.34	1.07	0.56	2.04	9.0	1.33	2.86	0.99	4.2	0.16%	0.06%
min		0.00	0.00	13.8	0.00	1.11	0.74	0.00	0.00	18.9	0.20	7.83	0.72	9.2	0.25%	0.13%
max		4.53	6.57	33.4	2.16	2.24	4.57	2.11	7.74	62.5	4.69	18.36	4.82	24.3	1.11%	0.37%

[a] Other amines include eight minor FAAs (Pro, 2-aba, cys, Tyr, Orn, Lys, Lle, Leu) that have a detection rate less than 50%. [b] On a carbon mass basis.

Table 10. Correlation matrix of various FAAs and aliphatic amines

	Asp	Ser	gly	Thr	2-Ala	Ala	Phe	other AAs	ΣFAA	Ethanol amine	M. amine	E. amine	Σ(ali-amine)
Asp	1	**0.434**	0.135	**0.458**	**0.634**	0.199	0.077	0.253	**0.400**	0.072	-0.110	-0.020	-0.058
Ser	**0.434**	1	0.218	**0.491**	0.152	0.231	0.124	**0.510**	**0.500**	0.138	-0.110	0.120	-0.003
gly	0.135	0.218	1	**0.493**	0.203	**0.787**	**0.590**	**0.647**	**0.904**	0.366	**0.577**	**0.493**	**0.631**
Thr	**0.458**	**0.491**	**0.493**	1	0.020	**0.605**	0.156	**0.512**	**0.649**	0.136	0.159	-0.011	0.150
2-Ala	**0.634**	0.152	0.203	0.020	1	0.126	0.080	0.168	0.312	-0.062	-0.056	-0.024	-0.064
Ala	0.199	0.231	**0.787**	**0.605**	0.126	1	**0.740**	**0.794**	**0.870**	**0.400**	**0.659**	**0.564**	**0.715**
Phe	0.077	0.124	**0.590**	0.156	0.080	**0.740**	1	**0.638**	**0.656**	**0.639**	**0.743**	**0.825**	**0.911**
other AAs	0.253	**0.510**	**0.647**	**0.512**	0.168	**0.794**	**0.638**	1	**0.853**	0.313	**0.532**	**0.581**	**0.604**
ΣFAA	**0.400**	**0.500**	**0.904**	**0.649**	0.312	**0.870**	**0.656**	**0.853**	1	**0.392**	**0.536**	**0.533**	**0.620**
Ethanol amine	0.072	0.138	0.366	0.136	-0.062	**0.400**	**0.639**	0.313	**0.392**	1	0.221	**0.448**	**0.578**
M. amine	-0.110	-0.110	**0.577**	0.159	-0.056	**0.659**	**0.743**	**0.532**	**0.536**	0.221	1	**0.623**	**0.906**
E. amine	-0.020	0.120	**0.493**	-0.011	-0.024	**0.564**	**0.825**	**0.581**	**0.533**	**0.448**	**0.623**	1	**0.809**
Σ(ali-amine)	-0.058	-0.003	**0.631**	0.150	-0.064	**0.715**	**0.911**	**0.604**	**0.620**	**0.578**	**0.906**	**0.809**	1

Note: Values in bold indicates statistically significant correlation (except diagonal) at the level of significance alpha=0.050 (two-tailed test).

Table 11. Contribution of FAAs and aliphatic amines to organic nitrogen

Site	Sampling month	ΣFAA	Σ(ali-mine)		%ON	
		(ng N/m^3)	(ng N/m^3)	FAA	ali-amines	total
TM	Oct.	3.7	4.2	0.6%	0.7%	1.4%
	Dec.	4.3	5.7	0.4%	0.5%	0.9%
	Mar.	4.4	5.6	1.0%	1.3%	2.4%
	Jun.	3.9	3.9	0.7%	0.7%	1.5%
TC	Oct.	4.9	5.6	0.7%	0.8%	1.5%
	Dec.	4.3	5.6	0.6%	0.8%	1.3%
	Mar.	5.7	5.6	0.5%	0.5%	1.1%
	Jun.	6.3	5.7	0.8%	0.7%	1.6%
CW	Oct.	4.7	5.8	0.7%	0.9%	1.6%
	Dec.	5.0	7.3	0.4%	0.6%	1.0%
	Mar.	5.6	6.2	0.5%	0.6%	1.2%
	Jun.	10.2	6.3	1.4%	0.8%	2.2%
SZ	Oct.	5.0	5.3	0.5%	0.5%	1.0%
	Dec.	5.4	5.2	0.4%	0.3%	0.7%
	Mar.	5.2	7.5	0.5%	0.7%	1.2%
	Jun.	5.7	5.6	0.6%	0.6%	1.2%
GZ	Oct.	7.0	9.8	0.5%	0.7%	1.3%
	Dec.	6.8	9.2	0.3%	0.5%	0.8%
	Mar.	7.6	9.9	0.5%	0.6%	1.1%
	Jun.	7.1	9.3	0.6%	0.8%	1.5%
CH	Oct.	6.1	5.2	0.3%	0.3%	0.6%
	Dec.	3.3	4.3	0.2%	0.3%	0.5%
	Mar.	6.9	6.4	0.3%	0.2%	0.5%
	Jun.	5.9	7.2	0.4%	0.5%	0.8%
ZS	Oct.	5.5	6.8	0.3%	0.3%	0.6%
	Dec.	6.8	7.0	0.3%	0.3%	0.6%
	Mar.	6.4	7.0	0.2%	0.2%	0.5%
	Jun.	5.5	4.6	1.6%	1.4%	3.0%
mean		5.7	6.4	0.6%	0.6%	1.2%
SD		1.4	1.6	0.3%	0.3%	0.6%
min		3.3	3.9	0.2%	0.2%	0.5%
max		10.2	9.9	1.6%	1.4%	3.0%

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4. Acknowledgements

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List of Appendices

Appendix 1. SOP for extraction and analysis of water-soluble organic carbon in ambient aerosols.

NOTE: The volume of water used for extraction varies depending on the amount of filter materials to be extracted. In this project, 10 ml of water was used.

Treatment of apparatus (e.g. forceps, Al foil) before doing the experiment:

1. Bake the apparatus for 12 hours at 550°C.
2. Rinse with Milli-Q water, methanol and hexane in sequence. (This step is skipped for Al foil)

Treatment of glassware (e.g. beakers) before doing the experiment:

1. Wash the glassware with detergent.
2. Rinse with Milli-Q water.
3. Soak in hydrochloric acid for one day.
4. Rinse with Milli-Q water again.
5. Finally bake for 12 hours at 550°C.

Extraction of filter samples:

The seasonal composites consist of 5 filter pieces. The water extraction procedure is as follows:

1. Use a pair of tweezers to transfer the 5 pieces of filters from their storage cassettes to an 25-ml Conical flask.
2. Add 8 ml of UV oxidized pure water (Barnstead Ultrapure Water System, Dubuque, IA, USA) to the flask. (Water used for extraction in the following steps has to be the purified water without any exception.)
3. Place the flask in an ultrasonic bath for 20 min. Ice water is placed in the ultrasonic bath to keep the water temperature below 10°C.
4. After sonication, pass the supernatant solution through a 0.2 mm pore size Teflon membrane syringe filter. (Keep the syringe filter for the next water extract of the same group of filters).
5. Discharge the filtrate into a 10.0 ml volumetric flask.
6. Add 3 ml of pure water into the filter residue and repeat steps 2-5. The filtrate is placed in the same 10.0 ml volumetric flask.
7. Fill the volumetric flask with water to the 10-ml mark. (Approximately 1 ml of water was retained by the 5 pieces of filters.)
8. Discard the filter residue in the conical flask.
9. Transfer the 10-ml water extract to a brown glass bottle with Teflon-lined cap.
10. Store the water extract in the freezer until analysis.

Analysis of WSOC using a TOC analyzer

A TOC analyzer (Model TOC-5000A, Shimadzu, Kyoto, Japan) (located in ATC) is used for the analysis. In the TOC analyzer, an autosampler (ASI-5000A) introduces aqueous samples into a combustion tube filled with platinum catalyst on alumina spherical support. Carbonaceous materials are either combusted or decompose to become CO_2. A high purity air carrier gas transports the combustion product from the combustion tube to a sample cell in a NDIR gas analyzer for the detection of CO_2. The TOC analyzer allows a maximum injection volume of 100 μl to be introduced into the instrument when operated with a normal catalyst in place. A maximum injection volume of 2000 μl is possible when a high sensitivity catalyst is used. The normal catalyst option was used in this study. An injection volume of 35 μl is typically used for our analysis.

1. Prepare three levels of potassium hydrogen phthalate solutions in the range of 0-20 μgC/ml to be used for instrument calibration.
2. Load no less than 3 mL of water extract into each autosampler tube.
3. Instrument condition: sparged by air for 2 min; 35 μl injection volume; a maximum of three injections for each sample. [For every sample, multiple consecutive injections are made until the peak areas of at least two injections achieved a standard deviation of less than a user-defined value or the specified maximum allowable number of injections, which we recommended to be 3, is reached.]

Sample pretreatment and analysis of WSOC using the Sunset Labs aerosol carbon analyzer (ACA): [This procedure was not used in the current study.]

1. Use one 5-ml and one 3-ml volumetric pipettes to withdraw 8ml water extract from its storage bottle and transfer to a 25-ml round bottom flask.
2. Connect the 25-ml flask with the rotary-evaporate. Evaporate the water extract to dryness. This step takes 20-30 min.
3. Add 500 μl water back to the 25-ml flask. Make sure to rotate the water so that the flask wall is thoroughly rinsed.
4. Use a syringe to withdraw 50 μl of the concentrated water extract and spike to a pre-baked 1.45 cm2 quartz filter punch.
5. Let the spiked filter air-dry. This takes ~30 min.
6. Place the dried filter punch on the quartz boat for the carbon analyzer and start the C analysis.
7. The conditions for the carbon analysis are as follows:
   - Purge the combustion chamber with 1% O2:99% He with the blower off for 20 sec.
   - Raise the front oven temperature to 600°C and keep at this temperature until 600 sec.
   - Raise the front oven temperature to 870°C and keep at this temperature until 120 sec has passed since the temperature ramp.

Method detection limits and precision

The limit of detection (LOD) of the methods is calculated using the following equation:

$$C_L = kS_{bl} / S$$

Where C_L is the limit of detection; k is a constant related to the confidence level and is usually set to be 3 (Miller and Miller, 1993); S_{bl} is the standard deviation of 5 measurements of blank water extracts; and S is the slope of the calibration curve. The ACA was determined to have a LOD of 0.48 μg carbon using this definition (S_{bl}= 0.16, S=0.999) whereas the TOC had a LOD of 0.88 μgC/ml for an injection volume of 35 μl (S_{bl}= 662, S=2242). These values translate to 4.8 μgC per sample in the ACA method (0.48 μgC in 50 μl of spiked water extract out of a 500 μl water concentrate) and 2.6 μgC per sample in the TOC method (0.88 μgC/ml in 35 μl of injected water extract out of a 3 ml solution).

The ACA analyzer has a linear dynamic range up to approximately 900 times its LOD (Birch and Cary, 1996). The dynamic range of the TOC is up to 25,000 μg/ml, more than 1000 times its LOD. As a result, the lower detection limits of the analyzers are more of a concern to the determination of aerosol WSOC concentrations rather than the upper limits of the linear range.

For evaluation of the measurement precision of the two carbon analyzers, the relative standard deviation (RSD) is computed using the multiple consecutive measurement results for the 6 aerosol samples. When the WSOC loading levels are 20-40 times the LOD of the TOC method and 40-75 times the LOD of the ACA method, the RSD values are better than 3% in both methods.

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Appendix 2. Analysis of cationic and anionic species in aerosol water extracts

Analysis of anionic species

Instrument: A Dionex DX500 Ion Chromatograph with a conductivity detector (CD20) and a gradient pump GP40 operating in the anion analysis mode.

Instrument analysis conditions: An IonPac AG11 guard column (4x50 mm) and an IonPac AS11 analytical column (4x250mm) are used to separate the analytes. An IonPac ATC-1 trap column (4mm, 9x24mm), and a Dionex ASRS-ultra 4mm anion self regenerating suppressor ensure the lowest possible background noise levels and detection limits. A sampling loop of 50ul is chosen for all the samples. The eluent is 0.2-5 mM NaOH (gradient) and the flow rate is 2 ml/min. The eluent gradient is as below:
Time 0 min. 6 min. 16 min. 30 min.
Conc. 0.2mM----0.2mM----5mM------5mM

Anion analysis: Water extracts of aerosol samples are loaded into autosampler vials. The anions are separated by the anion exchange column. After separation, the anions pass through an electronic suppressor to eliminate background conductivity and are then detected with a conductivity cell. The resultant peaks are identified by their characteristic retention times and quantified by reference to external standards.

Target analytes:
Inorganic anions: Sulfate, nitrate, chloride, and nitrite.
Organic anions: formate, acetate, lactate, methanesulfonate, oxalate, malonate, succinate, and glutarate. A typical IC chromatogram for anionic species in an aerosol water extract sample is given in Figure A-1.

Method detection limits (MDLs): The analytical procedure MDL is defined as the amount of an analyte that generates a response equal to the sum of the mean blank signal (Y_B) plus three times the standard deviation (SD_B) of the blank signal. Y_B is approximated with the intercept of a calibration line obtained from the analysis of a series of analytical standards in the vicinity of the blank response; and SD_B is approximated with the standard error for the Y estimate, Y being the response (i.e., IC peak area in this application) (Miller and Miller, 1993; NIOSH, 1993). The MDLs for the target anions are listed in Table A3-1.

Method precision: Replicate analyses indicate that the relative standard deviation is less than 10% for samples at a concentration level 10 times or greater than the MDL, and less than 20% for samples at a concentration level between 5 and 10 times the MDL.

Traceability: Calibration standards of the inorganic anions are prepared from commercially available standards (Alltech), concentrations of which are traceable to NIST standard reference materials. Organic acid standards that are traceable to NIST are not commercially available. They are prepared from 90-95% pure chemicals.

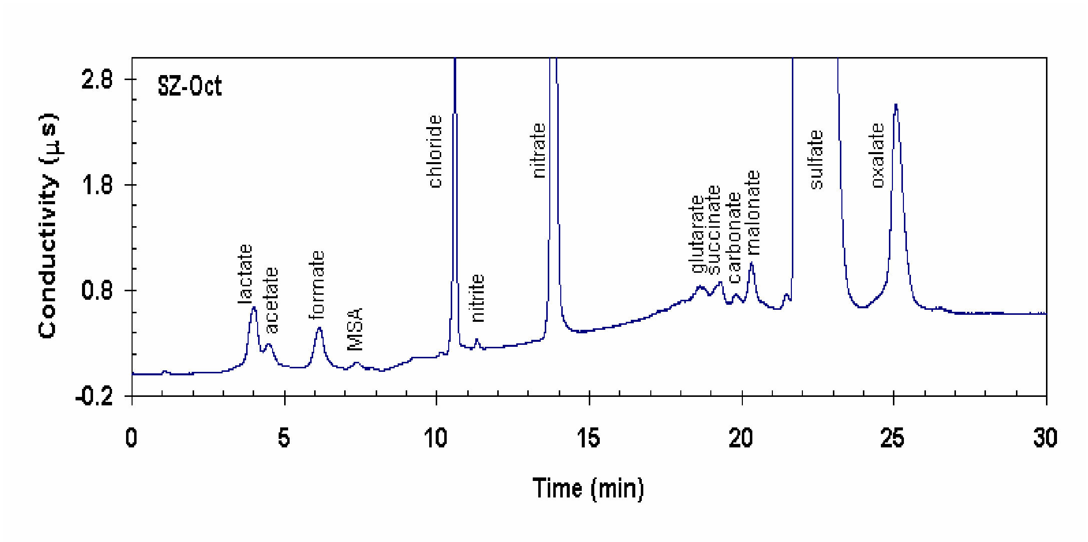

Figure A-1. Example Anion Chromatogram of a Typical Aerosol Water Extract Sample.

Table A-1. Analytical Procedure Method Detection Limits of Anions

Anion		Analytical procedure MDL
inorganic		µM
	chloride	0.67
	nitrite	0.12
	nitrate	<2.5
	sulfate	<11.7
Organic		
	lactate	0.47
	acetate	0.74
	formate	0.60
	methanesulfonate	0.07
	pyruvate	0.07
	oxalate	0.98
	malonate	0.56
	maleate	0.49
	succinate	0.28
	glutarate	0.14

Analysis of cationic species

Instrument: The cations are analyzed using a Dionex DX500 ion chromatograph with electrochemical detector ED 40 and gradient pump GP40. An IonPac CG12 guard column 4x50mm and an IonPac CS12 analytical column 4x250mm are used. Dionex CSRS-ultra 4mm is used. The sampling loop is 50ul. The eluent is 20mM methanesulfonic acid. Isocratic elution at a flow of 1 ml/min is used and each analysis lasts 12 min.

Target analytes: NH_4^+, K^+, Na^+, Ca^{2+}, and Mg^{2+}. A typical IC chromatogram for cationic species in an aerosol water extract sample is given in Figure A-2.

Sample analysis: Water extracts of aerosol samples are loaded into autosampler vials. Injection loop is 50 μL. The cations are separated by a cation exchange column. After separation, the cations pass through an electronic suppressor to eliminate background conductivity and are then detected with a conductivity cell. The resultant peaks are identified by their characteristic retention times and quantified by reference to external standards.

Method detection limits (MDLs): The analytical procedure MDL is defined as the amount of an analyte that generates a response equal to the sum of the mean blank signal (Y_B) plus three times the standard deviation (SD_B) of the blank signal. Y_B is approximated with the intercept of a calibration line obtained from the analysis of a series of analytical standards in the vicinity of the blank response; and SD_B is approximated with the standard error for the Y estimate, Y being the response (i.e., IC peak area in this application) (Miller and Miller, 1993; NIOSH, 1993). The MDLs for the target cations are listed in Table A-2.

Method precision: Replicate analyses indicate that the relative standard deviation is less than 10% for samples at a concentration level 10 times or greater than the MDL, and less than 20% for samples at a concentration level between 5 and 10 times the MDL.

Traceability: Calibration standards of the inorganic cations are prepared from commercially available standards (Alltech), concentrations of which are traceable to NIST standard reference materials.

Reference:

Miller, J. C.; Miller, J. N. *Statistics for Analytical Chemistry*, Ellis Horwood: Chichester, 3rd edn; 1993, pp. 46-51 and 115-117.

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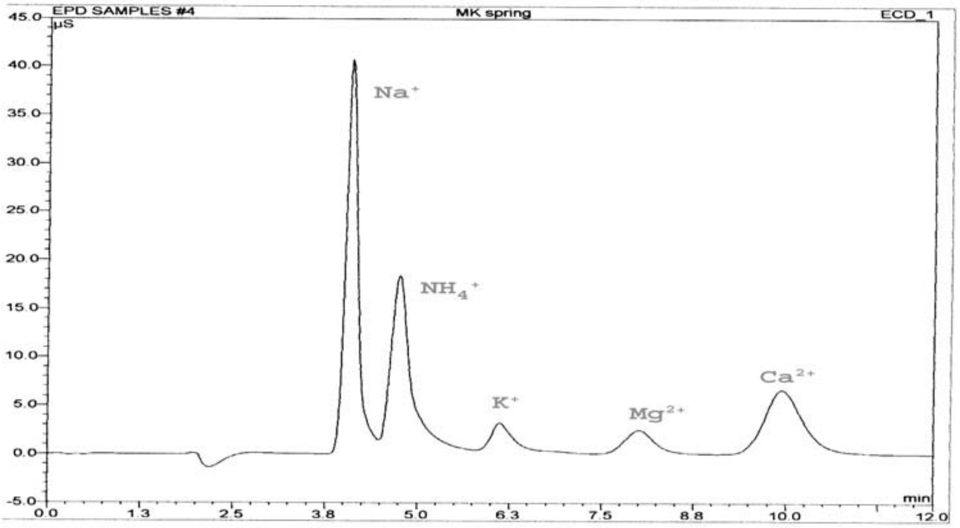


Figure A-2. Example Cation Chromatogram of a Typical Aerosol Water Extract Sample.

Table A-2. Analytical Procedure Method Detection Limits of Cations

	Analytical procedure MDL
	uM
Na^+	1.3
NH_4^+	1.1
K^+	1.3
Ca^{2+}	1.3
Mg^{2+}	1.2

Appendix 3. SOP for analysis of amino acids and aliphatic amines in aerosol water extracts

Treatment of apparatus (e.g. forceps) before doing the experiment:

3. Bake the apparatus for 12 hours at 550°C.
4. Rinse with Milli-Q water, methanol and hexane in sequence.

Treatment of glassware (e.g. beakers) before doing the experiment:

6. Wash the glassware with detergent.
7. Rinse with Milli-Q water.
8. Soak in hydrochloric acid for one day.
9. Rinse with Milli-Q water again.
10. Finally bake for 12 hours at 550°C.

Reconstituting AccQ·Fluor Reagent:

1. A heating block is preheated to 55°C.
2. Tape Vial 2A lightly before opening to ensure all AccQ·Fluor Reagent Powder is at the bottom of the vial.
3. Rinse a clean micropipette by drawing and discarding 1ml of AccQ·Fluor Reagent Diluent from vial 2B.
4. Transfer 1.0ml of AccQ·Fluor Reagent Diluent 2B to the AccQ·Fluor Reagent Powder in vial 2A.
5. Cap the vial tightly.
6. Vortex for 10 seconds.
7. Heat Vial 2A on top of the heating block at 55°C until the AccQ·Fluor Reagent Powder is dissolved. (Do not heat the reagent for longer than 10 minutes.)
8. Store the reconstituted AccQ·Fluor Reagent in desiccators at room temperature up to one week.

Preparation for the internal standard solution (DL-Norleucine):

Note: The procedure is the same if a different –NH2 containing compounds is selected as the internal standard.

1. Weigh 32.795mg DL-Norleucine into a 25ml volumetric flask and dissolve it using 20mM HCl. This is 10 µM DL-norleucine stock.
2. Pipette 1ml 10 µM DL-Norleucine to a 10ml volumetric flask and fill with 20mM HCl to the mark. This is 1 µM (1000 pmol/µl) DL-norleucine stock solution.
3. Pipette 100 µl of the 1000 pmol/µl stock solution to a 5ml volumetric flask and fill with 20 mM HCl to the mark. This is 20 pmol/µl internal standard working solution.

Internal Standard (DL-norleucine)		
Required concentration	Calculation	Mass / Volume required
10 µM	0.01M*0.025L*131.18g/mol	32.795mg
1000 pmol/µl	0.001M*10ml/0.01M	1ml
20 pmol/µl	20pmol/ µ l*5ml/1000pmol/µl	100µl

Preparation of 2.5 mM Amino Acid standard mixture (AA Std mix-1 and AA std mix-2):

1. Dissolve the following individual AA or aliphatic amine standards in a 25 ml volumetric flask to make 10 mM stock solution.

53.91mg	D(+)-Galactosamine hydrochloride,
53.91mg	D(+)-Glucosamine hydrochloride,
22.27mg	Beta-Alanine,
24.39mg	Ethanolamine hydrochloride,
16.88mg	Methylamine hydrochloride,
25.78mg	D(-)-2-Aminobutyric acid,
20.39mg	Ethylamine hydrochloride
41.41mg	L(+)-Ornithine hydrochloride

2. Pipette 1.25ml of the above 10mM standard mixture to a 5ml volumetric flask and fill with water to the mark. This is the 2.5 mM Amino Acid standard mixture (AA std mix-1).
3. The commercially available AA standard mixture from Waters is AA std mix-2. Each AA standard in this mixture is supplied at a concentration of 2.5 mM except for cystein, which is supplied at 1.25 mM. The following 17 amino acids are included in this standard mixture:

L-alanine
L-methionine
L-proline
L-threonine
L-valine
L-leucine
L-arginine
L-cystine
Glycine
L-isoleucine
Ammonia
L-phenylalanine
L-serine
L-tyrosine
L-lysine
L-aspartic acid
L-glutamic acid
L-histidine

Preparation of the 100 pmol/ul standard mixture:

1. Add 40µl AA std mix-1 into a clean autosampler vial. (The remaining 2.5mM AA standard mixture-1 can be stored at –20^{o}C for up to 3 months.)
2. Add 40µl AA std mix-2 (2.5mM Waters Amino Acid Hydrolysate Standard into the same autosampler vial.
3. Add 920µl Milli-Q water to the vial. This is 100 pmol/µl stock calibration standard mixture. It can be stored at –20 ^{o}C for up to one month.

Preparation of 0.5, 2, 5, 20, 40 pmol/µl standards

1. 5, 20, 50, 200, and 400 µl of 100 pmol/ul stock calibration standard are added into five separate clean vials.
2. Add 995, 980, 950, 800, and 600 µl water, respectively, to make the final volume 1000ul.

Standard dilution			
Concentration of diluted standards (pmol/µl)	Calculation	Volume of 100 pmol/µl standard required (µl)	Volume of water required (µl)
0.5	1000µl*0.5pmol/µl / 100pmol/µl	5	995
2	1000µl*2pmol/µl / 100pmol/µl	20	980
5	1000µl*5pmol/µl / 100pmol/µl	50	950
20	1000µl*20pmol/µl / 100pmol/µl	200	800
40	1000µl*40pmol/µl / 100pmol/µl	400	600

Procedures for derivatization of the calibration standards:

1. Pipette 10µl of calibration standard and 10µl of internal standard (20 pmol/µl) in a 6 x 50 mm sample tube.
2. Add 160µl AccQ-Tag borate buffer.
3. Vortex for 10 seconds.
4. Add 20µl of AQC reagent solution.
5. Vortex immediately for 10 seconds.
6. Wait for 1 minute.
7. Transfer the content of the sample tube to a low volume insert (LVI) and cap tightly with a silicon-lined septum.
8. Remove the bubbles in the sample tube.
9. Heat the sample vial in a heating block for 10 minutes at 55°C.
10. Inject 20µl of the solution into the HPLC for analysis. Note: The derivatives can be stored at room temperature for up to one week.

Diluted standard concentration (pmol/µl)	0.5	2	5	20	40
Final standard concentration (pmol/µl)	0.025	0.1	0.25	1	2

Analysis of water soluble free amino acid in water extracts:

6. Prepare two sample tubes for each water extract sample.
7. Transfer 0.5ml water extract to each sample tube.
8. Evaporate the water extract to dryness under a gentle stream of argon gas or nitrogen gas (ultra high pure) at 40°C. This process takes about 2.5 – 3 hours.
9. Add 10µl internal standard solution (20pmol/µl) and 170µl borate derivatization buffer into the sample tube.
10. Vortex briefly the sample tube.
11. Gently purge the reconstituted sample solutions with ultra high purity argon gas or nitrogen gas for 50 minutes. The flow rate of gas must be controlled so that the volume loss of the sample solution won't exceed 30%. The purpose is to lower the NH3 levels as a big NH3 peak would interfere the quantitation of the adjacent amino acid compounds.
12. Add 20 µl AccQ-fluorescence reagent solution into the sample tube and vortex immediately for 10 seconds.
13. After 1 minute of reaction, transfer the sample into a low volume insert (LVI) placed in an autosampler vial and cap tightly with a silicone-lined septum. The bubbles in the sample vial should be removed before heating.
14. Heat the sample vial to 55°C for 10 minutes prior to the HPLC analysis.

Analysis of hydrolysable combined amino acid:

1. Prepare two all-Teflon hydrolysis containers for each sample.
2. Add 1ml of water extract and 1ml constant boiling HCl (6N) to each Teflon hydrolysis vial.
3. Vortex for 10 – 20 seconds.
4. Seal the surface of the solution with Ultra high purity nitrogen gas for three times each for 2 minutes.
5. Screw the cap for the hydrolysis vial and place the vial in an oven at 110° for 24 hrs.

6. Cool the sample to room temperature before opening the cap.
7. Transfer 0.5 ml post-hydrolysis sample solution to a sample tube.
8. Evaporate to dryness under a gentle stream of argon gas or nitrogen gas (ultra high pure) at 40°C.
9. Follow instruction for step 4 and onwards in the free AA analysis procedure.

Calculation:

Calibration curve:

$PR = m * C_{AA} + b$

Where PR is the peak area ratio, C_{AA} is the amino acid concentration in unit of pmol/μL.

Amount of FAA & CAA in the water extract:

$C_{AA} = (PR - b) / m$

Amount of FAA (nmol) in x ml water extract = $C_{AA}*200*(x/0.5)/1000$

Amount of CAA (nmol) in x ml water extract = $C_{AA}*200*(2/0.5)*(5/1)/1000$

Amount of FAA and CAA expressed as air concentration

$$C(nmol/m^3) = C(nmol) * \frac{A_{filter}}{A_{water}} * \frac{1}{V(m^3)}$$

Where V is the sampled air volume, A_{filter} is the entire filter area, and A_{water} is the filter area used in water extraction.

Appendix 4 Responses to Review Comments

Below is a point-by-point response to three reviewers' comments on the report. For the convenience of discussion, review comments are provided and marked in a smaller font.

Review I

Comments:

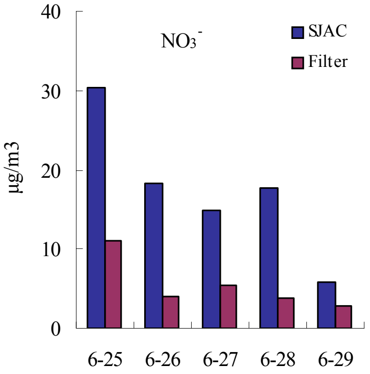
General:

As far as I can judge (never having seen the original project description), the report answers in a very straightforward manner a number of policy relevant questions such as: what is the contribution of water soluble organic compounds, is it primary or secondary and, as a consequence of origin, can it be controlled.
Data quality cannot always be judged, but as far as inorganic ions are concerned, seems to be all right indeed. It would have been nice if intercomparison data would have been available too for the organic species, as some of the analytical methodologies involve concentration steps, which could potentially introduce artifacts.
The interpretation of the data is, with one exception (see specific remarks), straightforward and based on solid science.
The report is written in a clear style.
The conclusions are justified and relevant, again with one specific remark, see below.

Specific remarks:

1. Regarding section 2. Extraction and analysis scheme.

The methods are in general quite robust, though concentration by evaporation is always a bit dangerous. There is one notable exception though. The filter methods can easily miss a lot of the nitrate in PRD; see results obtained in Guangzhou by Zhang.



Intercomparison between filter and SJAC results in Guangzhou, measured by Zhang.
The error is dependent on many factors, but generally higher in summertime, as the volatilization of ammonium nitrate is strongly temperature dependent. So the nitrate data are really a lower estimate and this has other consequences, see below.

Response:

The nitrate measurement artifact is a sampling issue, not an analytical problem. Nitrate loss occurs on the filter before water extraction takes place. In addition, I wish to clarify that concentration by rotary evaporation was not used in the current study. [We used rotary evaporation in our previous studies due to larger numbers of filter pieces that had to be extracted for each composite sample. Appendix 1 has been revised to clearly indicate that the procedure applied to the samples in this study did not involve concentration of water extracts.] I also revised the report text to indicate the sampling artifact issue for nitrate.

Comment:

2. The same problem is also relevant for semi-volatile organic compounds, e.g. oxalate.

It would depend on the chemical form, e.g. the acid is semi-volatile, the sodium salt is not. So here too filter sampling methods could show a bias.

Response:

Yes, I agree that there was a sampling artifact issue with semivolatile organic compounds (e.g., oxalic acid). The sampling set-up in this study was not designed to how to best characterize the aerosol phase concentrations of semi-volatile species. The report text on dicarboxylic acids is revised to note this sampling issue with semivolatile organic compounds.

Comment:

3. Interpretation of MSA data, in 5.3. Methanesulfonic acid.

Here some problems are encountered, in my view. The conclusion that OH and NO3 radical concentrations are highest in winter, based in nitrate data, seems questionable, especially if possible volatilization is kept in mind. The losses of nitrate will be much higher in summer, compared to winter. It is indeed true that competition is going on between different chemical pathways and that temperature is an important factor, as is pointed out in the report.

Response:

The current nitrate measurements do not allow us to quantitatively assess the magnitude of nitrate loss during sampling. I agree that the nitrate data alone, due to the sampling artifact problem, could not lead to a definitive conclusion of higher oxidant levels in the winter. To answer this question, we need carry out addition experiments that are designed to minimize nitrate sampling artifacts. The text has been revised to indicate the uncertainty in oxidants levels as inferred from nitrate measurements.

Comment:

But there is perhaps another factor which contributes. The DMS emissions in the polluted

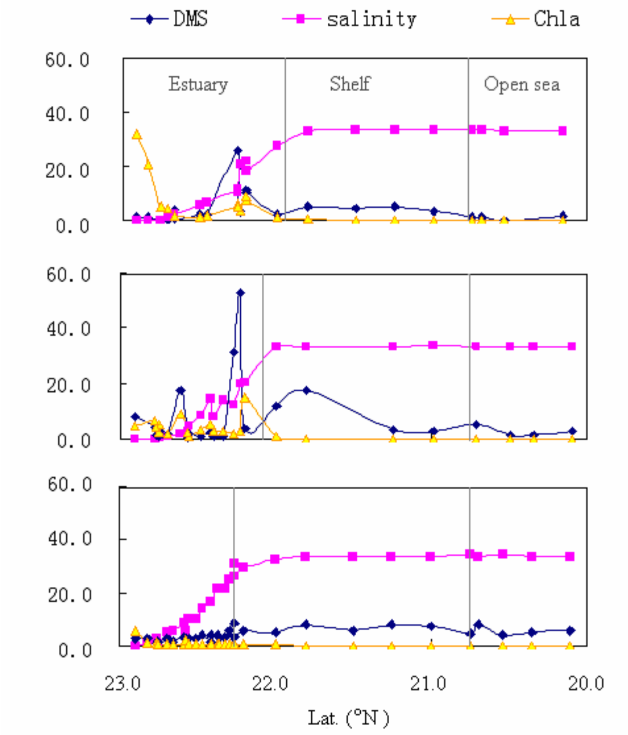


Fig. DMS, Chlorophyl a and salinity vs. latitude of (a) July 2000, (b) May 2001 (c) November 2002

Estuary region is much higher than in the open see, see data from Ma and Hu, Beida, in press. The result is that higher DMS concentrations are seen near the coast, the conversion to HMSA takes time and the end result is higher concentrations of HMSA in inland stations.

Response:

In my original report, I have made an interpretation of the spatial variation pattern that is the same as expressed by the reviewer here. Below I quote what appears in my report.

> "The higher concentrations seen at the inland sites could be explained by the secondary nature of MSA. MSA, as a secondary pollutant, was expected to be at higher levels downwind of the marine emission source of its precursor DMS. DMS exists in the atmosphere for as long as 1 to 10 days [Berresheim et al., 1998; Chin et al., 1996; Putaud et al., 1999]. Its lifetime is sufficiently long for transport to these inland locations."

Comment:

Conclusions:

This report is a valuable contribution to the PRD Pilot Project. The work is of good quality, the results are relevant and well presented. Discussion on the interpretation of some results does not really detract from the overall value of the report.

Response:

None.

Review II

Comment:

This report provides comprehensive measurements of water-soluble species in the atmospheric aerosols in the PRD area. The measurements are very useful for an assessment of the environmental impact of aerosols. The author might want to revise the report by considering the following comments and suggestions:

- ■ A complete description of the sampling method used in the work is needed.

Response:

A detailed description of the sampling method is provided in the report by Bergin et al. (2004). This is now noted in the revised report.

Comment:

- ■ The extraction of aerosol species was made after the sampling seasons. Thus, the samples might be stored for several weeks before extraction. Given that all the target compounds (WSOC, organic acids, amines) analyzed in this work are highly biodegradable, the uncertainties and bias due to the storage processes should be carefully evaluated. This reviewer did not find any description on this point in the report.

Response:

The filter samples were stored at 4^{o}C before water extraction and subsequent analysis. Biodegradation of the WSOC species was likely limited under this low-temperature storage. We will conduct work in the near future to assess biodegradation of target WSOC species at the storage temperature.

Comment:

- ■ Sulfate was used as the indicator of secondary sources and nitrate was used as the proxy of oxidants in this work. There must be concurrent measurements of ozone, why not use it?

Response:

Concurrent measurements of ozone are not available for the sites in Guangdong (SZ, GZ, ZS, and CH) since the focus of project 2 is on PM and limited resources do not permit measurements of all relevant species.

Comment:

- ■ Concentrations of MSA were plotted vs. nitrate concentration in Figure 9 and a linear regression line for MSA and nitrate with R^2 of 0.44 was obtained. However, the line in Figure 9 seems dominated by the data points for GZ and SZ. The correlation between MSA and nitrate at the other sites was not as significant as the line showed. Examining the MSA-nitrate correlation site by site might be useful.

Response:

Although there were 20 individual samples collected at each site during the project period, individual filters in the same sampling months were combined to generate one single seasonal composite to ensure sufficient material for chemical characterization. As a result, each site had only four seasonal composite samples. This limited number of samples does not permit to examine the MSA-nitrate correlation on a site by site basis. If the data points for GZ and SZ are removed, a positive correlation with $r^2 = 0.40$ still exists.

Review III

Comment:

We have some minor comments for your consideration:

1. Page vi. “Effective reduction in this portion of aerosol material requires identification of their precursors and their formation mechanism and rates in the atmosphere”. Since this part of the information is put forward as policy-relevant finding, relevant recommendations regarding sources identification and control options should be elaborated.

Response:

Our current knowledge of the sources and formation mechanism is very limited, as reflected by the fact that only a small fraction of WSOC mass (less than 10% in this study) could be identified as known chemical identities. We have a long way to go before we could make recommendation regarding sources and control options. A few sentences are added into the WSOC section to note this.

Comment:

2. Page 8. “The policy relevant implication is that an important fraction of aerosol mass (11-24%) could not be reduced simply by cutting primary emissions.” This is an important finding from Jian’s study, in general, findings from this study should be considered together along with studies conducted under Project 2 should that a more holistic view can be formed.

Response:

Integration of findings from WSOC chemical characterization work could be done once the scientific team decides that this should be the way to represent results from project 2.