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Measurements of Trace Gases in the Inflow of South China Sea Background Air and Outflow of Regional Pollution at Tai O, Southern China

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Abstract. We present a 16-month record of ozone (O₃), carbon monoxide (CO), total reactive nitrogen (NO_y), sulphur dioxide (SO₂), methane (CH₄), C₂–C₈ non-methane hydrocarbons (NMHCs), C₁–C₂ halocarbons, and dimethyl sulfide (DMS) measured at a southern China coastal site. The study aimed to establish/update seasonal profiles of chemically active trace gases and pollution tracers in subtropical Asia and to characterize the composition of the 'background' atmosphere over the South China Sea (SCS) and of pollution outflow from the industrialized Pearl River Delta (PRD) region and southern China. Most of the measured trace gases of anthropogenic origin exhibited a winter maximum and a summer minimum, while O₃ showed a maximum in autumn which is in contrast to the seasonal behavior of O₃ in rural eastern China and in many mid-latitude remote locations in the western Pacific. The data were segregated into two groups representing the SCS background air and the outflow of regional continental pollution (PRD plus southern China), based on CO mixing ratios and meteorological conditions. NMHCs and halocarbon data were further analyzed to examine the relationships between their variability and atmospheric lifetime and to elucidate the extent of atmospheric processing in the sampled air parcels. The trace gas variability (*S*) versus lifetime (τ) relationship, defined by the power law, $S_{\text{mix}} = A\tau^{-b}$, (where *X* is the trace gas mixing ratio) gives a fit parameter *A* of 1.39 and exponent *b* of 0.42 for SCS air, and *A* of 2.86 and *b* of 0.31 for the regional continental air masses. An examination of ln[*n*-butane]/ln[ethane] versus ln[propane]/ln[ethane] indicates that their relative abundance was dominated by mixing as opposed to photochemistry in both SCS and regional outflow air masses. The very low ratios of ethyne/CO, propane/ethane and toluene/benzene suggest that the SCS air mass has undergone intense atmospheric processing since these gases were released into the atmosphere. Compared to the results from other polluted rural sites and from urban areas, the large values of these species in the outflow of PRD/southern China suggest source(s) emitting higher levels of ethyne, benzene, and toluene, relative to light alkanes. These chemical characteristics could be unique indicators of anthropogenic emissions from southern China.

Key words: background air, inflow, outflow, Pearl River Delta, South China Sea, trace gases

1. Introduction

The impacts of continental air pollution on the remote maritime atmosphere have been a focus of global tropospheric chemistry and climate change research. Studies carried out in North America, Europe, Africa, and Asia have shown that human activities can significantly alter the chemical composition of the atmosphere over oceanic regions and thereby modify the oxidizing capacity and the radiative balance of the atmosphere on both regional and global scales (Fehsenheld *et al.*, 1996; Hoell *et al.*, 1996, 1997; Stuart *et al.*, 1998; Propero *et al.*, 2001; Ramanathan *et al.*, 2001; Jacob *et al.*, 2003; Huebert *et al.*, 2003; Akimoto, 2004; and references cited therein). A focus of recent international research is Asia, in which there have been a rapid pace of industrialization and urbanization and a sharp increase in emissions of chemically active and radiatively important trace gases and aerosols (e.g., Akimoto and Narita, 1994; Van Aardenne *et al.*, 1999; Streets and Waldhoff, 2000; Streets *et al.*, 2003).

The South China Sea (SCS) is bounded to the north by the rapidly developing Pearl River Delta (PRD) region situated in the southern region of the Chinese subcontinent (see Figure 1). The PRD is home to around 40 million inhabitants and is also the most important industrial base in southern China. Meteorological conditions over this region and a large part of Asia are strongly influenced by Asian monsoon circulations. During the winter, prevailing surface winds are northerly and northeasterly. By contrast, southerly and southwesterly winds are predominant in the summer. Such meteorological conditions make the coastal region of southern China an ideal place to measure the chemical composition of polluted continental outflow in the winter and clean SCS air during summer.

A number of studies have been carried out in Hong Kong to characterize the outflow of continental pollution and the inflow of SCS background air (e.g., Kok *et al.*, 1997; Wang *et al.*, 1997, 2001a, 2003a,b; Cheng *et al.*, 2000; Lam *et al.*, 2001; Cohen *et al.*, 2004). Most of the ground-based measurements were made at Hok Tsui, a coastal site situated in the southeast part of Hong Kong and upwind of the PRD region under prevailing northeasterly wind conditions (Figure 1). These studies provided valuable information on the long-range transport of trace gases and aerosols to southern China from central and eastern regions of China, the island of Taiwan, and northeast Asia. However, there are limited studies of pollution generated within the PRD and its effects on the chemistry and radiative budget of the SCS background air. There is also a need for data on the seasonal variations in ambient concentrations of many chemically active trace gases, such as SO₂, NO_y, and NMHCs.

From August 2001 to December 2002, we measured a suite of trace gases and fine aerosols at Tai O, a rural/coastal site on the remote Lantau Island (Figure 1). During the experiment, O₃, CO, NO, NO_y, and SO₂ were measured continuously, and whole air samples were collected in canisters for the analysis of organic compounds. In addition, fine aerosols (PM_{2.5}) were collected for analyses of chemical composition

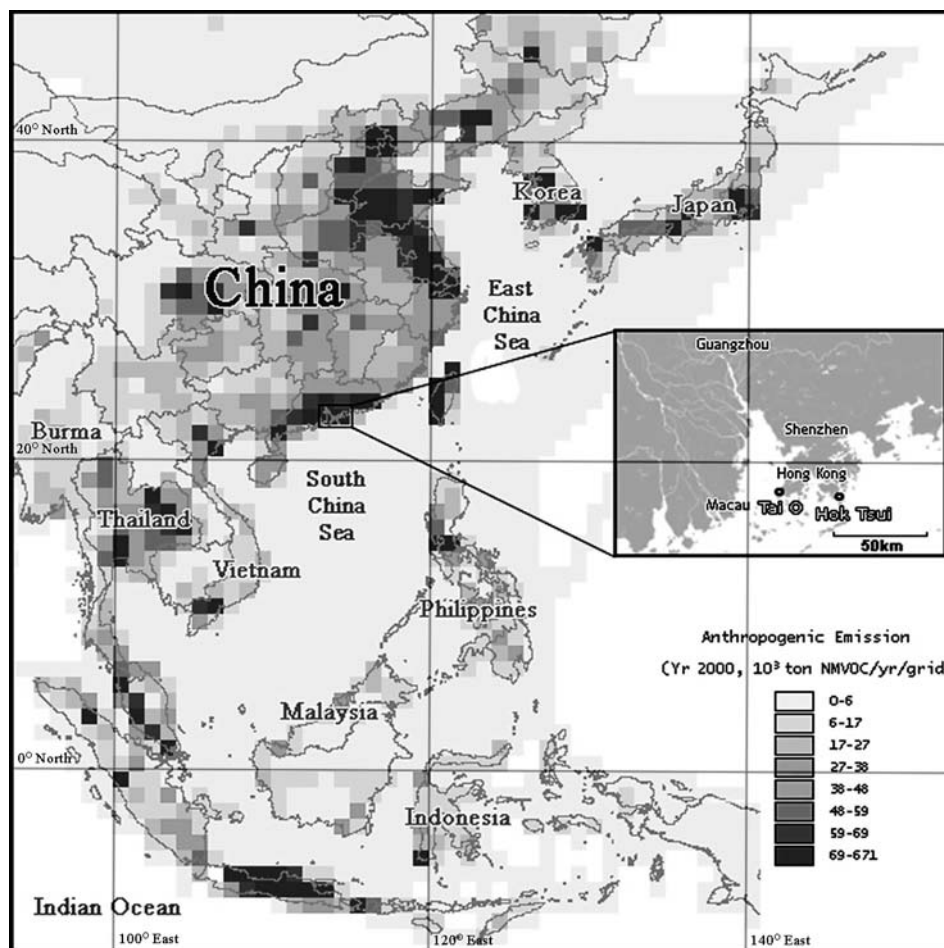


Figure 1. Map showing the study site, Pearl River Delta of China, East Asia and $1^\circ \times 1^\circ$ emission intensity of non-methane volatile organic compounds (NMVOC) (Streets *et al.*, 2003).

during intensive sampling periods. These measurements were made in a non-urban area situated over the Pearl River Estuary roughly along the north-south centerline of the PRD, and thus provide unique data for characterizing the outflow of pollution plumes from the PRD including Hong Kong under northerly and northeasterly winds, and for determining SCS background mixing ratios when southerly winds prevail. Wang and Kwok (2003) analyzed data collected at this site during an O_3 pollution episode in September 2001, and Wang *et al.* (2003a) examined O_3 , CO, NO_y and SO_2 data collected during October-December 2001. These studies were aimed to understand the short-term temporal variations and relationships of these gases, and they have revealed rapid changes in ambient concentrations and distinctly different ratios of CO/NO_y and SO_2/NO_y in air masses originating from Hong Kong versus the inner PRD region.

In the present study, we analyze O₃, CO, NO_y, SO₂, CH₄, C₂–C₈ NMHC, C₁–C₂ halocarbon, and DMS mixing ratios obtained during the entire 16-month study. The focus of this work is the seasonal concentration variations of the measured gases, and the chemical characteristics of the polluted regional outflow and the SCS background air. We first examine the seasonal trends of selected trace gases and compare the results with those obtained from other global locations. We then focus on the NMHC data to examine their concentrations and the indicators of chemical and/or transport processes that shape the distribution of these important gases. The results of this study are expected to be useful for assessing the atmospheric oxidizing capacity, elucidating the transport and chemistry of air pollution, and validating chemical transport models.

2. Experimental

2.1. THE TAI O SITE

The sampling site was Tai O, a rural/coastal area on the western coast of Lantau Island in southwest Hong Kong (22.25°N, 113.85°E, 80 m above sea level) (Figure 1). A detailed description of the site is provided in Wang *et al.* (2003a). Briefly, it is 32 km to the west of the Hong Kong urban center and 32 km east of Macau. Major anthropogenic emission sources in the PRD are located to the east, north and southwest. The three largest population centers in the PRD are Guangzhou (10 million), Hong Kong (6.8 million) and Shenzhen (4 million). The power plants, airports and seaports are mainly located along the two sides of the Pearl Estuary.

The study site is located on a hill 80 m above sea level, overlooking the Pearl Estuary to the west and north, the SCS to the south, and the Hong Kong urban center to the east. Local anthropogenic emissions are small due to a sparse population and light traffic in the village of Tai O. Immediately surrounding the site are many deciduous trees which can be the sources of biogenic hydrocarbons. The site is characterized by prevailing northeasterly winds in the winter when it is frequently impacted by urban pollution plumes originating from PRD, including Hong Kong, and by southerly winds during summer when the site receives cleaner air from the tropical Pacific Ocean and SCS.

2.2. MEASUREMENT TECHNIQUES

2.2.1. *Continuously Measured Trace Gases*

Measurement instruments were housed in a laboratory situated on the cliff. Ambient air samples were drawn through a 10 m long PFA Teflon tube (outside diameter: 12.7 mm; inside diameter: 9.6 mm). The sampling tube inlet was located 3 m above the rooftop of the laboratory. The other end of the sampling tube was connected to a PFA-made manifold with a bypass pump drawing air at a rate of 15 L/min. Descriptions of the measurements of O₃, CO, SO₂, NO and NO_y can be found in

Wang *et al.* (2003a). Briefly, O₃ was measured using a commercial UV photometric instrument (TEI, Model 49). SO₂ was measured by pulsed UV fluorescence (TEI, Model 43S). CO was measured with a gas filter correlation, non-dispersive infrared analyzer (API, Model 300) with a heated catalytic scrubber to convert CO to carbon dioxide (CO₂) for baseline determination. NO and NO_y were detected with a modified commercial MoO/chemiluminescence analyzer (TEI, Model 42S). These analyzers were calibrated daily by injecting scrubbed ambient air (TEI, Model 111) and a span gas mixture. A NIST-traceable standard (Scott-Marrin, Inc.) containing 156.5 ppmv CO ($\pm 2\%$), 15.64 ppmv SO₂ ($\pm 2\%$), and 15.55 ppmv NO ($\pm 2\%$) was diluted using a dynamic calibrator (EnviroNics, Inc., Model 6100). The NO_y conversion efficiency on MoO was checked using a 5 ppm *n*-propyl nitrate standard (Scott-Marrin, Inc.). A data logger was used to control the zero/span calibration and to collect 1-s data, which were averaged to 1-min values.

2.2.2. Sampling and Analyses of VOCs

Whole air samples were pressurized into evacuated 2-L electro-polished stainless steel canisters using a metal bellows pump. The canisters were cleaned and evacuated at the University of California, Irvine (UCI). Details of the preparation and pre-conditioning of the canisters are described in Blake *et al.* (1994). During sampling the canister valve was slightly opened, allowing about one minute for the collection of the "integrated" samples. The canisters were then shipped to UCI's laboratory for chemical analysis. A 6-column multiple GC-MS system was used to identify and quantify VOCs. Detailed descriptions of the analysis, relevant quality assurance/quality control, and the measurement precision and accuracy for each species are given by Colman *et al.* (2001).

Between August 2001 and December 2002, a total of 186 canister samples were taken. The number of samples collected each month varied from 1 to 32. Many (92 out of 186) were acquired between October and December of 2001 and 2002, a season during which high levels of pollution occurred in the region in both years. Normally, one sample was collected per day, but when an O₃ episode was anticipated, 4–7 samples were collected to determine the diurnal variation of the VOCs during the episodes. 75% of the samples were taken in the afternoon and 25% in the morning.

2.2.3. Other Data

To obtain more background samples from inflow air from the SCS, samples collected at our Hok Tsui (Cape D'Aguilar) research station, 40 km from Tai O, were used (Figure 1). A detailed description of this site can be found in Wang *et al.* (2003b). Additionally, several meteorological parameters were simultaneously measured during the study period at Tai O, including wind speed, wind

direction, temperature, relative humidity, total ultraviolet radiation (320–400 nm), and global solar radiation.

3. Results and Discussion

3.1. SEASONAL VARIATIONS

The seasonal trend of a trace gas is determined by the seasonal changes in source strength (direct emission or chemical reactions), sinks (chemical reactions and deposition), and atmospheric dynamics that influence the convection and air-mass transport climatology. Asian monsoon circulation, which brings in dry and cold continental air in autumn and winter and wet oceanic air in late spring and summer, has been found to have a profound impact on the seasonal profiles of O₃, CO and aerosols observed in subtropical Hong Kong (Chan *et al.*, 1998; Lam *et al.*, 2001; Wang *et al.*, 2001a; Cohen *et al.*, 2004). Figures 2–3 show monthly variations of the measured trace gases at Tai O for the period of October 2001 to December 2002. Among these, the seasonal profiles of SO₂, NO_y, NMHCs and halocarbons are reported for the first time for the non-urban atmosphere in southern China, although So and Wang (2004) presented the C₃–C₁₂ NMHC profiles based on limited samples ($n = 20$) from Hok Tsui.

O₃: At Tai O, mean monthly O₃ mixing ratios showed a maximum value of 45 ppbv in October 2001 and a minimum value of 17 ppbv in December 2002 (error bars are shown in Figure 2a). The autumn O₃ maximum on the southern China coast is attributed to the transport of precursor-laden air masses, coupled with sunny and dry weather with subsidence of air, favoring photochemical formation of O₃ (Lam *et al.*, 2001; Wang *et al.*, 2001a, 2003b). The lowest mean monthly O₃ concentration was due to the more frequent impact of less aged continental plumes in December with limited O₃ formation. Ozone levels also decreased in summer although occasionally very high O₃ concentrations could occur (e.g., a maximum hourly O₃ mixing ratio of 189 ppbv was observed in July 2002). The low average O₃ concentration in summer is the result of inflow of clean oceanic air masses from the tropics and of unstable rainy weather.

The seasonal trend of O₃ at this rural southern China site is different from those observed in rural areas of mid-latitudes in eastern China (Wang *et al.*, 2001b), the United States, and Europe (Logan, 1989), where monthly O₃ levels tend to be the highest in late spring/early summer. In comparison, a spring peak of O₃ is a common phenomenon observed at more remote locations in the mid- to high-latitude regions in the northern hemisphere (Monks, 2000).

CO, NO_y, and SO₂: In contrast to O₃, CO, SO₂ and NO_y exhibited a maximum in winter and a minimum in summer (Figure 2). The observed high winter levels were attributed to the transport of polluted air masses from the PRD and southern China, and weaker vertical mixing and slower chemical destruction rates in the winter. The seasonal trend of these pollutants on the southern China coast is similar

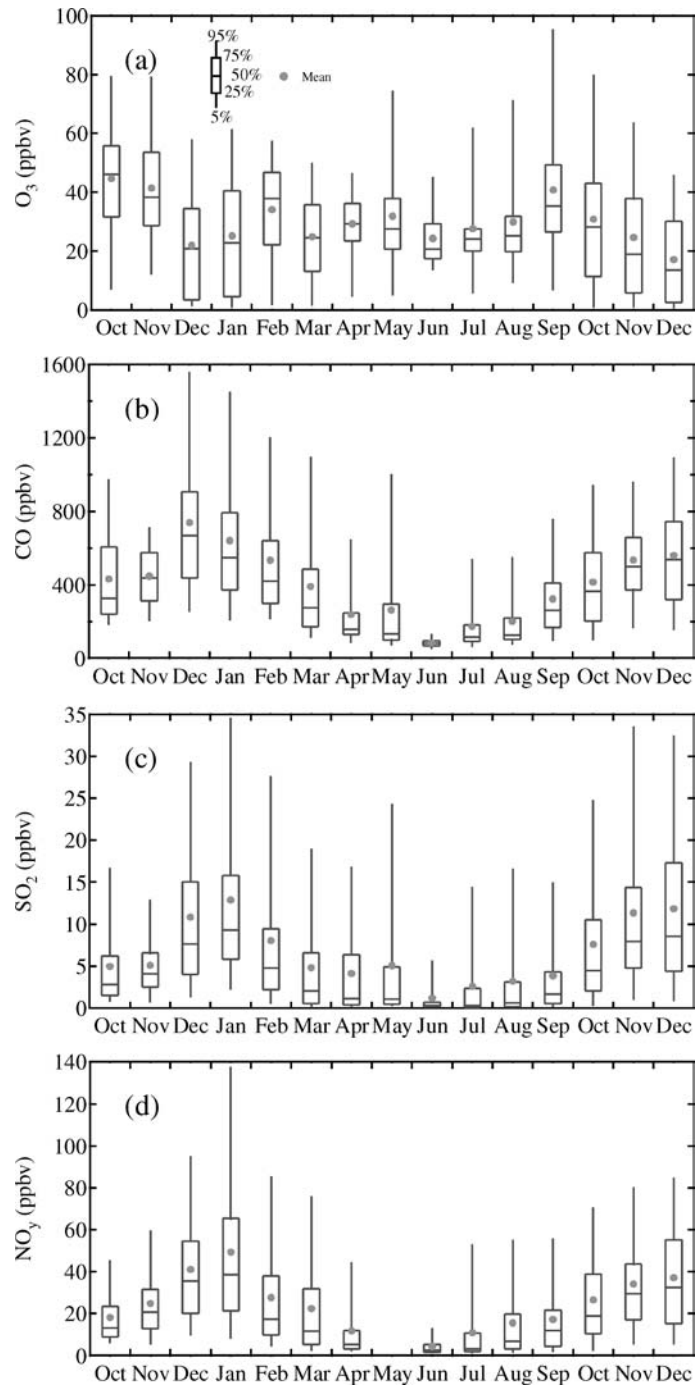


Figure 2. Monthly variations of the mixing ratios of: (a) O_3 , (b) CO, (c) SO_2 , and (d) NO_y from October 2001 to December 2002.

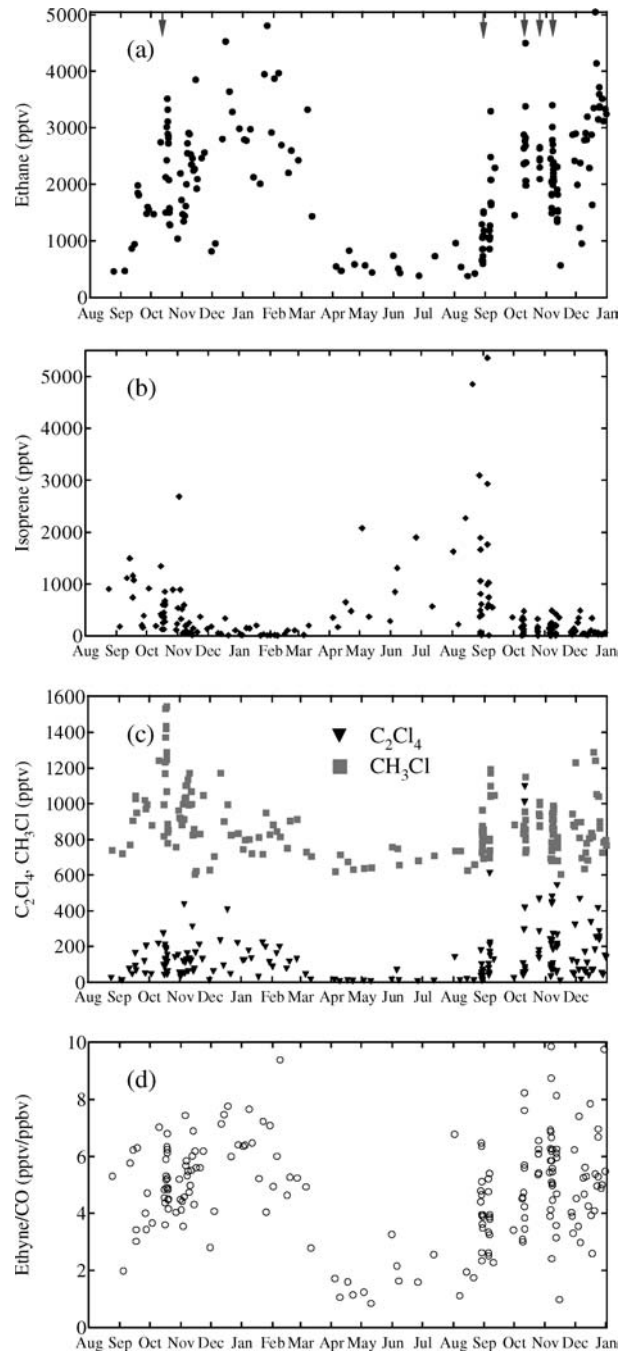


Figure 3. Seasonal variations of the mixing ratios of (a) C_2H_6 , (b) isoprene, (c) CH_3Cl and C_2Cl_4 , and (d) C_2H_2/CO ratios from August 2001 to December 2002 (Periods when multiple samples were collected are indicated by the arrows.).

to that observed in rural eastern China (Wang *et al.*, 2001b). Some differences in the abundances at the two sites are worth mentioning. The CO and SO₂ concentrations at the eastern China site were much higher (Wang *et al.*, 2001b, 2002). In contrast, the mean NO_y concentrations at Tai O were approximately twice the levels in rural eastern China, except in the summer. The higher abundance of NO_y relative to CO and SO₂ at the southern China site results from the use of low sulfur-content coals and more efficient combustion (emitting smaller amounts of CO relative to NO_y) in southern China, particularly in Hong Kong (Kok *et al.*, 1997, Wang *et al.*, 2003a).

VOCs: Figure 3 illustrates the annual profiles of ethane, isoprene, methyl chloride (CH₃Cl) and tetrachloroethene (C₂Cl₄). Similar to CO, ethane and C₂Cl₄, which are largely emitted from anthropogenic sources, showed a maximum in autumn-winter and a minimum in summer. Other measured hydrocarbons and halocarbons such as ethyne, benzene, and carbon tetrachloride had the same seasonal trend as ethane and C₂Cl₄ (not shown here). A cluster of samples with elevated concentrations in October/November 2001 and August/November 2002 were collected during O₃ episodes when urban emissions in the region strongly affected the site (see periods marked in Figure 3). More frequent sampling of VOC during these O₃ events may have contributed to an apparent peak in autumn. Isoprene mixing ratios larger than 5000 pptv were observed during O₃ pollution episodes in September 2002.

Methyl chloride is emitted in large quantities from the burning of biomass (bio-fuel, agricultural waste, etc). At Tai O CH₃Cl showed a seasonal maximum in autumn/winter. Superimposed on this seasonal trend were very high concentrations which were measured during the pollution episodes. High values of other trace gases of anthropogenic origins such as ethane and CO were also enhanced with CH₃Cl during these episodes. The enhanced levels of these species on the episode days are a result of poor dispersion due to light winds (Wang and Kwok, 2003). Biomass burning is not expected to be a major source of air pollution within the industrialized PRD, but it could be important in rural areas surrounding the PRD during the dry autumn/winter season. In contrast, the CH₃Cl mixing ratio in summer was low and much more stable (~680 pptv), which is representative of the abundance in the background SCS air.

The ratio of C₂H₂ to CO is used to indicate the degree of atmospheric processing within an air mass (McKeen and Liu, 1993) because of the difference in lifetime of these two species with respect to OH (with C₂H₂ shorter-lived than CO). Figure 3 presents seasonal variations of C₂H₂/CO ratios. As expected, C₂H₂/CO ratios were highest in winter (~7 pptv/ppbv) and lowest in summer (~1 pptv/ppbv), indicating the dominance of 'fresh' regional emissions in winter and the aged maritime air masses in summer. The propane/ethane and toluene/benzene ratios also showed a similar seasonal trend (results not shown).

In summary, the Asian monsoon circulation has a profound impact on the seasonal cycles of many anthropogenic trace gases, contributing to elevated

concentrations in autumn/winter season and lowest levels in summer. In the following sections we further analyze the canister samples in order to better understand the characteristics of carbon-containing compounds in background SCS and polluted regional air masses.

3.2. CHEMICAL CHARACTERISTICS OF NMHCs AND HALOCARBONS IN SCS AIR AND POLLUTED OUTFLOW

3.2.1. *Air-Mass Classification*

To compare the composition of background air versus polluted regional air, it is necessary to segregate bulk data into groups representing air masses from different source regions. Back trajectories and/or surface winds are widely used to trace the origin and transport pathway of an arriving air mass. However, in view of complex boundary-layer flow caused by sea-land breezes and the effect of topography in the study area, we adopt here a simple approach for the segregation of data, which is based on CO mixing ratios and meteorological parameters.

The lowest monthly mean CO mixing ratio of the study was 81 ppbv in June (Figure 2b). By examining the chemical data and the surface winds at Tai O, we found that air samples with CO mixing ratios ≤ 125 ppbv were indicative of large-scale inflow of 'pristine' background air from the SCS and the tropics. Consequently, the 186 air canister samples were classified into two groups: one ($n = 10$) with CO ≤ 125 ppbv representing least perturbed SCS air and the other with CO > 125 ppbv ($n = 176$) representing regional outflow (PRD plus southern China) including both fresh urban plumes and 'aged' continental air masses. It should be noted that this segregation method was aimed to contrast the very clean air largely associated maritime inflow in summer with the air masses in other seasons receiving varying influences of continental emissions. For the SCS group, we also included 10 samples with CO ≤ 125 collected in the same year at Hok Tsui on the eastern side of Hong Kong to increase the sample size. Analysis of variance (ANOVA) suggests that most of the VOC species measured at Tai O did not show a significant difference from those at Hok Tsui for the SCS group. Of the 20 SCS air samples, 98% were collected during late April - early September and 90% were associated with southwesterly and southeasterly winds.

Table I gives the statistics of canister samples for the two air mass groups. As expected, the average mixing ratios of selected NMHCs and halocarbons with anthropogenic sources were significantly ($\rho < 0.01$) higher in the outflow air masses (CO > 125 ppbv) than those in the inflow samples (CO < 125 ppbv). By contrast, compounds with dominant biogenic (isoprene) or oceanic (DMS) sources showed higher values in the maritime air masses. In the case of isoprene, its high concentrations in SCS air masses are most likely due to local emissions from trees surrounding the study site.

Table I. Comparison of South China Sea background air and regional pollution outflow (pptv)

Compound	SCS air (<i>n</i> = 20)			Regional outflow (<i>n</i> = 176)		
	Mean	Median	SD	Mean	Median	SD
Carbon monoxide (ppbv)	97	98	16	551	508	316
Methane (ppbv)	1784	1762	96	2069	1964	300
Ethane	467	452	114	2225	2263	927
Propane	93	80	71	2171	1593	2167
<i>n</i> -Butane	46	37	42	1737	1036	2159
<i>i</i> -Butane	29	24	29	852	564	936
<i>n</i> -Pentane	23	14	28	475	274	661
<i>i</i> -Pentane	56	31	97	850	503	1474
<i>n</i> -Hexane	23	9	46	532	323	684
2-Methylpentane	25	5	59	491	312	589
3-Methylpentane	33	4	64	431	305	458
<i>n</i> -Heptane	16	11	24	353	206	509
<i>n</i> -Octane	9	3	13	61	44	59
Ethene	142	126	87	1770	1224	1691
Propene	56	53	36	235	118	301
<i>i</i> -Butene	20	9	26	114	53	176
1-Butene	10	7	9	73	39	103
cis-2-Butene	5	3	7	26	4	69
trans-2-Butene	5	3	6	28	5	81
1,3-Butadiene	3	3	1	30	11	57
Isoprene	837	348	1179	370	157	627
Ethyne	142	139	61	2935	2662	1945
Benzene	49	42	28	921	776	926
Toluene	70	40	71	6010	3883	7212
<i>o</i> -Xylene	31	18	47	397	212	577
<i>m</i> -Xylene	36	17	68	602	216	1162
<i>p</i> -Xylene	30	13	50	427	159	747
Ethylbenzene	21	12	28	926	523	1244
Cyclohexane	7	3	9	160	99	262
Dimethyl sulfide	36	26	25	32	21	42
Carbon tetrachloride	111	112	6	123	121	14
Tetrachloroethene	5	5	3	164	114	183
Methyl chloride	680	671	46	897	860	178
Methyl bromide	10	10	1	17	16	7

3.2.2. Relationship of Variability of Trace Gases with Lifetime

The relationship between trace gas variability and atmospheric lifetime has been used to evaluate overall hydrocarbon data sets for consistency, the remoteness of a sampling site, average OH concentrations, and the presence of halogen radicals (e.g. Jobson *et al.*, 1998; Warneke and de Gouw, 2001). This relationship (also called the “Junge relationship”) is expressed as follows:

$$S_{\ln x} = A\tau^{-b}$$

Here, $S_{\ln x}$ is the standard deviation of the natural logarithm of the mixing ratio X , τ is the atmospheric lifetime, and A and b are fit parameters. The above equation was established based on the following assumptions: 1) the organic data set can be approximated as measurements of an ensemble of air parcels with the same initial concentration but varying the time between emission and sampling; 2) the lifetime of each individual species is constant; and 3) the species are long-lived with small variances so that their relative standard deviation is equivalent to $S_{\ln x}$ (Jobson *et al.*, 1998). The constant b is related to the source-receptor distances and lies between 0 and 1: $b = 0$, which has been observed in urban areas (Jobson *et al.*, 1998) and over source regions (Ehhalt *et al.*, 1998), means that the trace gas variability is caused by differences in the strengths of local sources that are in proximity to the sampling site. The limit of $b = 1$ indicates the chemical kinetic limit where the variability is dominated by chemical loss alone. The farther away the sampling site is from the trace gas sources, the larger the exponent b (Ehhalt *et al.*, 1998). In the present study, the lifetimes of the selected species were adopted from Warneck (2000) for the maritime air, and we assume hydrocarbon lifetimes are determined only by the OH radical. Since there is a large seasonal variation in atmospheric lifetime due to changes in OH concentration and the temperature dependence of the rate constants, the lifetimes for the continental outflow were assumed to be 5 times those for the summer inflow. Spivakovsky *et al.* (2000) used a factor of 10 for data collected at a high-latitude site.

Figure 4 illustrates the dependence of variability on lifetime for C_2 – C_8 alkanes, ethyne, C_2Cl_4 , aromatics, and CH_3Cl for the background air and the outflow. These species are collectively associated with various urban/industrial/combustion emissions such as vehicle exhaust, solvent use and industrial processes, and biomass burning. The b values were 0.42 for the SCS air and 0.31 for the outflow, indicating that the species were not strongly affected by local sources. The smaller b value in the outflow group reflects the fact that the sampling site was more frequently impacted by urban emissions. The b value in the inflow air was comparable to that (0.40) over the northwest Indian Ocean (Warneke and de Gouw, 2001) and those (0.43–0.53) for the NARE, ABLE 3B, TRACE-A and PEM-West B aircraft campaigns (Jobson *et al.*, 1998, 1999). Within the general trend, the variability increased with increasing carbon number for C_2 – C_5 alkanes and aromatics, in

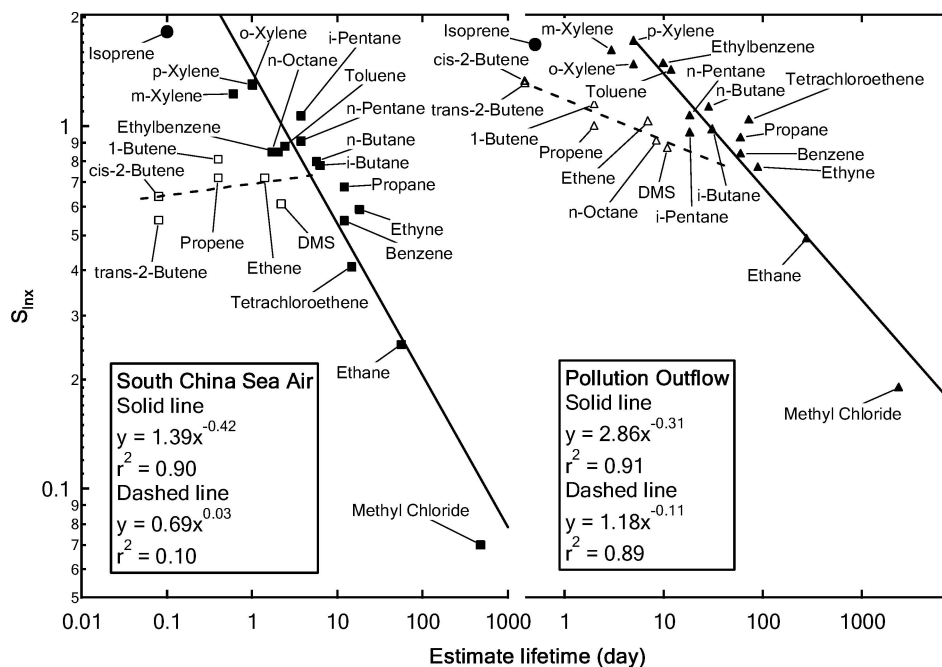


Figure 4. Atmospheric variability versus the lifetime of the VOCs for the South China Sea background air and the pollution outflow. The solid lines represent a linear fit of C_2 – C_8 alkanes, ethyne, C_2Cl_4 , aromatics, and CH_3Cl (labelled as filled triangles and squares). The dashed lines represent a fit to light alkenes and DMS (and n -octane for the outflow) labelled in open triangles and squares. Isoprene (filled circle) was not included in either fit.

accordance with their decreasing lifetimes. In addition, the most reactive species (such as the xylenes) displayed the greatest variability.

However, short-lived species such as light (C_2 – C_4) alkenes and DMS showed a different trend with a b exponent close to zero in the SCS inflow, suggesting significant influence by nearby sources, i.e. oceanic and biogenic emissions (Guenther *et al.*, 1994; Warneke and de Gouw, 2001). For the outflow air, the light alkenes and DMS points were also below the general trend, as was n -octane. Considering the longer lifetimes of light alkenes and DMS in winter, long-range transport of these species is possible. Thus, light alkenes and DMS in the outflow could be affected by both the transport of regional pollution and local (oceanic and biogenic) emissions. Previous studies have shown that light alkenes are emitted from oceans and vegetation, in addition to their anthropogenic sources (see Warneck, 2000). For DMS, although it is emitted in large quantity from oceans, anthropogenic sources and vegetation also release it in the continental atmosphere (e.g. Kesselmeier *et al.*, 1993). It is interesting to see that n -octane did not follow the general trend in the outflow, perhaps suggesting the impact of relatively near source(s) of this species under outflow conditions.

Isoprene is another outlier in the SCS air and polluted outflow showing a lower variability than the general trend (Figure 4). As the most reactive species shown in Figure 4, isoprene had the largest variability in the SCS air, and was among the most highly variable species (together with the xylenes) in the outflow air. Considering its very short lifetime (hours), the variability of isoprene mixing ratios at Tai O is expected to be dominated by local biogenic emissions (i.e., from trees) as opposed to vehicular emissions as has been observed in some urban areas, including Hong Kong (e.g., Barletta *et al.*, 2002; So and Wang, 2004). This conclusion is supported by the lack of correlations between isoprene and combustion tracers such as ethyne and benzene at Tai O (not shown).

3.2.3. Atmospheric Processing

The concentration ratio of [*n*-butane]/[ethane] versus [propane]/[ethane] is plotted in log scale in Figure 5. The slope of the plot gives information about photochemistry and atmospheric transport (McKeen and Liu, 1993; Warneck, 2000). If hydrocarbons are emitted into the atmosphere from a common source, their mixing ratios would change with time because of chemical reactions and mixing with air masses having different concentrations of these compounds. If the concentrations of NMHCs decrease only by OH oxidant chemistry, the slope would be, in this case, equal to $(k_{n\text{-butane}} - k_{\text{ethane}})/(k_{\text{propane}} - k_{\text{ethane}})$, which is about 2.56 (here k is the rate constant for reaction with OH). If, in contrast, only atmospheric mixing is important, the slope would have a much lower value. The extreme case is that the original air parcel is mixed with air masses having negligible concentrations of the compounds of interest. In this case the relative concentrations of these compounds would not change as the air parcel moves away from its source, and the slope would be 1.00. Such idealized mixing will be referred to as dilution. In this

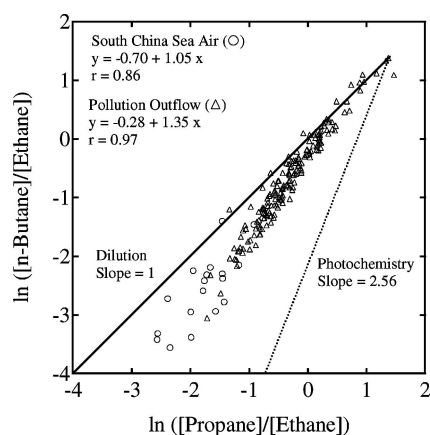


Figure 5. The log-log plots of hydrocarbon pairs.

study, the slopes for the SCS background air and the regional outflow were 1.05 ($r = 0.86$) and 1.35 ($r = 0.97$), respectively. The slope for the outflow is similar to values reported during other rural studies (e.g. Parrish *et al.*, 1992; Jobson *et al.*, 1994). The much smaller slope than that calculated using the kinetic data suggests that decreased concentrations of C₂–C₄ hydrocarbons in our study were predominantly due to mixing with background air.

It should be noted that the above discussion has assumed a NMHC source with constant emission ratios of butane/ethane and propane/ethane, which may not be true in reality. Further studies are needed to evaluate the impact of the presence of multiple sources of NNHC on the relationship between the two pairs of ratios.

3.3. COMPARISON WITH OTHER OBSERVATIONS

Table II shows mixing ratios of selected VOCs and their ratios in the SCS air samples and at other coastal sites, while Table III compares the results for the

Table II. Comparison of South China Sea air with other marine atmospheres (pptv)

Site	Northwest	Western North	Atlantic	Northeast	South
	Indian Ocean ^a	Pacific and Eastern Indian Ocean ^b			
Ethane	183	610	727	1771	467
Propane	35	240	90	468	93
<i>n</i> -Butane	20	120	43	118	46
<i>i</i> -Butane	–	70	51	76	29
Ethene	223	420	83	139	142
Propene	95	600	103	80	56
Ethyne	22	170	68	306	142
Benzene	–	–	36	148	49
Toluene	9	–	48	178	70
Methyl chloride	530	–	–	541	680
Ethyne/Propane	0.6	0.9	0.7	0.7	1.9
Benzene/Propane	–	–	0.2	0.3	0.7
Ethane/Propane	5.2	2.7	8.2	3.8	7.3
Toluene/Benzene	–	–	1.4	1.2	1.4

– Not available.

^aWarneke and de Gouw (2001) (April 2000).

^bSaito *et al.* (2000) (December 1996/February 1997).

^cBoudries *et al.* (1994) (June 1992/August 1992).

^dJaffe *et al.* (2001) (March 1997/April 1997).

^eThis Study (August 2001–December 2002).

Table III. Comparison of Southern China regional outflow with air masses at various urban (U) and polluted rural (R) sites (ppbv)

Site	Eastern Asia ^b		Sweden ^c	TRACE-P ^d	Eastern China ^e		Sapporo ^f	London ^g	Osaka ^h	Karachi ⁱ	U.S. cities ^j	Tai O ^k
	France ^a	Asia ^b			China ^e	China ^e						
Ethane	1.79	1.58	3.00	1.68	3.04	3.04	3.20	4.20	4.80	93.00	11.70	2.22
Propane	1.08	0.54	1.60	0.46	1.24	1.24	6.00	2.00	4.10	41.00	7.80	2.17
<i>n</i> -Butane	0.54	0.17	0.87	0.22	0.47	0.47	3.30	3.20	3.70	19.80	10.10	1.74
<i>i</i> -Butane	0.35	0.10	0.48	0.15	0.42	0.42	1.90	1.40	1.50	11.00	3.70	0.85
<i>n</i> -Pentane	1.58	0.05	0.24	-	0.15	0.15	0.50	0.60	1.00	13.40	4.40	0.48
<i>i</i> -Pentane	0.45	0.08	0.46	-	0.31	0.31	0.90	2.60	2.40	12.10	9.10	0.85
Ethene	0.83	0.17	0.65	0.05	1.98	1.98	4.20	3.40	5.50	19.00	10.70	1.77
Propene	0.29	-	0.11	-	0.33	0.33	1.70	1.40	0.60	5.50	2.60	0.24
Ethyne	0.87	0.45	1.10	0.50	2.54	2.54	2.00	4.60	4.10	18.00	6.50	2.94
Benzene	0.24	0.12	-	0.12	1.01	1.01	-	1.10	-	5.20	-	0.92
Toluene	0.31	0.08	-	-	1.81	1.81	-	2.20	-	7.10	-	6.01
Tetrachloroethene	-	-	-	0.01	0.03	0.03	-	-	-	0.07	-	0.16
Methyl Chloride	-	0.80	-	0.56	1.29	1.29	-	-	-	2.72	-	0.90

(Continued on next page)

Table III. (Continued)

Site	Eastern Asia ^b		Sweden ^c	TRACE-P ^d	Eastern China ^e		Sapporo ^f	London ^g	Osaka ^h	Karachi ⁱ	U.S. cities ^j	Tai O ^k
	France ^a	0.8			0.7	2.2						
Ethylene/Propane	0.7	0.8	0.7	1.1	2.2	0.3	2.3	1.0	0.4	0.8	1.7	
Benzene/Propane	0.2	0.2	–	0.3	0.7	–	0.6	–	0.1	–	0.7	
Ethane/Propane	1.7	2.9	1.9	3.6	2.7	0.5	2.1	1.2	2.3	1.5	1.6	
Toluene/Benzene	1.5	0.7	–	–	1.8	–	2.0	–	1.4	–	5.4	

– Not available

^aBoudries *et al.* (1994) (France: February 1992–February 1993).^bKato *et al.* (2001) (Eastern Asia: December 1999).^cMowrer and Lindskog (1991) (Sweden: February–April 1989).^dRusso *et al.* (2003) (TRACE-P: February–April 2001).^eGuo *et al.* (2004) (Lin'an: Oct 1999, March–June 2001).^fSaito *et al.* (2000) (Sapporo: April 1998).^gDerwent *et al.* (2000) (London: 1996).^hMorikawa *et al.* (1998) (Osaka: October 1992–December 1993).ⁱBarletta *et al.* (2002) (Karachi: Winter 1998–1999).^jSeinfeld (1989) (29 U.S. Cities: 1984–1986).^kThis Study (Tai O: August 2001–December 2002).

southern China outflow group with data from other urban and rural sites. Because it is often difficult to make an unambiguous comparison of concentration levels measured in different studies, due to differences in the sampling sites, sampling periods, nearby anthropogenic activities, and meteorological conditions, we will focus on the ratios of species as they give more robust results on the type and proximity of emission sources and on the atmospheric processes that affect their ratios in the atmosphere.

Ratios of ethyne and benzene to propane: Ethyne and benzene are general combustion tracers that are products of vehicular emissions and biomass/biofuel burning, while propane is mainly released from the use of natural gas, liquefied petroleum gas and car exhaust (Goldan *et al.*, 2000). Benzene can also be released from the evaporation of solvents. The three species have similar loss rates against reaction with OH, with an atmospheric lifetime of about 12 – 18 days, and are inefficiently removed by wet removal processes. Thus, the ambient concentration ratio of between them is expected to reflect emission ratios of the two gases in the upwind source region.

Table III shows that, except for London and Lin'an (eastern China), the ratios of ethyne/propane (1.7) and benzene/propane (0.7) in the outflow were higher than values at other rural and urban sites. This implies source(s) in PRD emitting abundant ethyne and benzene relative to propane. Burning of biomass/biofuel is known to give off large amount of ethyne and benzene (Carmichael *et al.*, 2003). An examination of a sample we collected during burning of dry grass at the rural site in the central PRD showed very high ratios of ethyne/propane (8.3) and benzene/propane (1.6). These values are almost four times of the respective ratios in the outflow air mass. By comparison, the ratios in the outflow group measured at Tai O were comparable to those in samples collected at roadsides in the inner PRD cities (ethyne/propane: 1.7 (Guangzhou)-2.6 (Zhuhai), benzene/propane = 0.5 (Guangzhou and Zhuhai)) (Dr. L. Y. Chan, Personal Communication, 2005). This together with the high-degree urbanization in PRD suggests that the ethyne and benzene to propane ratios in the outflow measured at Tai O were largely dominated by vehicle/industrial emissions in the PRD.

The ethyne and benzene rich feature is also indicated in the SCS inflow. As shown in Table II, the mean ethyne/propane and benzene/propane ratios were approximately twice of those observed over the Indian Ocean, Atlantic Ocean, and the Northeast Pacific, suggesting the influence of benzene and ethyne-rich sources in the source regions upwind.

Ethane/propane: Ethane is emitted from various anthropogenic sources such as natural gas and car exhaust in urban areas (e.g. Rudolph, 1995). Given the long lifetimes of ethane (~2 months) and propane (~12 days), the variations of ethane/propane in the outflow air masses should largely reflect the changes in emission characteristics rather than the difference in photochemical ageing. The mean ethane/propane ratio was 1.6 in the outflow air, which is comparable to ratios observed in many other areas shown in Table III, suggesting similar emission

ratios for ethane and propane in these areas. In contrast, a much larger value of 7.3 was measured in the SCS air, which is comparable to that observed over the Atlantic Ocean (8.2), but higher than other maritime observations shown in Table II (2.7–5.2). The large ethane/propane ratio reinforces the notion that the SCS air mass has undergone intense atmospheric processing (chemical reactions and mixing).

Toluene/benzene: The major sources of toluene and benzene in urban areas are vehicular emissions and solvent use. Toluene has a shorter life time (~3 days) than benzene (~12 days). Table III shows that the toluene/benzene ratio in the outflow air was 5.4 pptv/pptv, which is much larger than ratios that have been reported in other cities (0.7–2.0). The large toluene/benzene ratio may be attributed to use of aromatic-rich unleaded fuels and solvents in southern China, in particular a high toluene content in unleaded gasoline (Sin *et al.*, 2000; So and Wang, 2004). For the SCS background air, this ratio is 1.4, which is comparable to that observed in the Atlantic (1.4) and the northeast Pacific (1.2). The much reduced ratios compared to those in urban areas again reflect strong atmospheric processing after the two species were emitted into the atmosphere.

4. Summary and Conclusions

We presented trace gas data obtained from a comprehensive measurement program conducted at a rural/coastal site in southern China from August 2001 to December 2002. These gases included O₃, CO, NO_y, SO₂, CH₄, C₂–C₈ NMHCs, C₁–C₂ halocarbons and DMS. Most of the anthropogenically emitted gases showed a maximum in winter and a minimum in summer due to the influence of Asian monsoon systems. In contrast, O₃ concentrations peaked in autumn and showed a minimum in winter with a sharp decrease in summer. Chemical ratios such as C₂H₂/CO, propane/ethane, and toluene/benzene were much higher in winter and lower in summer, reflecting the impact of the outflow of urban/industrial emissions in winter and the dominance of aged maritime air masses in summer.

The bulk data were segregated into two groups representing the SCS background air and the outflow of regional pollution (PRD plus southern China), based on CO mixing ratios and meteorological conditions. Analysis of the variability versus lifetime relationship for carbon-containing species, defined by the power law, $S_{\text{inx}} = A\tau^{-b}$, yielded a fit parameter A of 1.39 and b exponent of 0.42 for SCS background air, and A of 2.86 and b value of 0.31 for the polluted regional outflow. The change in relative abundance of light alkanes (C₂–C₄) was mainly determined by mixing processes rather than photochemistry, and an analysis of selected ratios of NMHCs indicates that the southern China air mass had undergone intense atmospheric processing.

Compared to the results with other rural sites and urban areas, the polluted outflow from southern China contained enhanced ratios of ethyne/propane, benzene/propane, and toluene/benzene, suggesting a relatively large emission of ethyne and benzene from mobile sources and of toluene from the use of toluene-rich

gasoline and solvents. These chemical characteristics could be unique indicators of anthropogenic emissions from southern China. The data presented here are arguably the most comprehensive trace gas record obtained to date in southern China, in terms of time span and the number of species measured. They can be used for assessing the impact of anthropogenic pollution on the chemistry of the marine atmosphere over the SCS and for studying urban and regional pollution in the PRD.

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