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Impact of Asian continental outflow on the concentrations of O_3, CO, NMHCs and halocarbons on Jeju Island, South Korea during March 2005

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Abstract

As part of ABC-EAREX2005 experiment, numerous trace gases were measured at Gosan on Jeju Island, South Korea in March 2005 to characterize the impact of recent outflow from the Asian continent and to inter-compare measurement techniques used by participating groups. Here we present measurements of O_3, CO, and whole air samples of methane, C_2–C_8 non-methane hydrocarbons (NMHCs) and C_1–C_2 halocarbons obtained during the study. The large temporal variations in the measured trace gas concentrations at Gosan were due to the transport of background marine air and of regional pollution mainly from the Chinese subcontinent. Average mixing ratios (± s.d.) were 54.6 (±9.0) ppbv and 283 (±100) ppbv for O_3 and CO, respectively. CO showed good correlations ($r^2 = 0.62$–0.81) with combustion tracers such as ethyne and benzene but poorly correlated ($r^2 = 0.11$–0.29) with light alkanes, suggesting that the latter were contributed by non-combustion source(s). Back trajectory analysis showed that air masses mainly originated from the North China Plains and northeastern China, which together accounted for 64% of the total trajectories. The highest mean mixing ratios of O_3 and combustion-derived species were found in air masses from eastern China and Korea, indicating the significant impact of emissions from these regions. Interestingly, air masses from northeast China contained elevated levels of light alkanes and the smallest ratios of ethyne/propane and benzene/propane among the air-mass groups, suggesting contribution from natural gas leakage in the upwind region, possibly from Siberia.

Keywords: Ozone; Carbon monoxide; NMHCs; Continental outflow; Back trajectory; Nature gas leakage

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1. Introduction

East Asia is an important source region for many chemically active and radiatively important trace gases and aerosols owing to the large population and fast-paced industrialization. The emissions of major pollutants in this region have not only caused severe urban air pollution but also region-wide environmental issues such as photochemical ozone, haze and acid deposition (e.g. Wang and Wang, 1995; Chameides et al., 1999; Luo et al., 2000; Wang

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et al., 2001, 2005). There have also been concerns about the larger-scale impact of the outflow of Asian pollution on the chemistry and radiative budget over the Pacific Ocean (e.g. Hoell et al., 1997; Huebert et al., 2003; Jacob et al., 2003, and references cited therein) and North America (e.g. Jacob et al., 1999; Jaffe et al., 1999).

Besides the major aircraft campaigns PEM-West, TRACE-P and ACE-Asia, ground-based measurements have been made at coastal and island locations in the Asian Pacific rim to characterize the outflow of Asian pollution and to assess its impact on downwind regions (Akimoto et al., 1996; Wang et al., 1997, 2003; Pochanart et al., 1999; Sharma et al., 2000a,b; Kato et al., 2001, 2004). These studies confirmed that trace gas levels can be strongly influenced by the outflow of continental air masses, and that outflow in the boundary layer is often initiated by the passage of cold fronts/Asian monsoon systems (e.g. Pochanart et al., 1999; Wang et al., 2003).

Most of the previously reported studies were conducted in 2001 or before, and it is important that new measurements be carried out to examine possible changes in the chemical composition of the outflow, in view of the likely changing emissions in the region in the past five years. Indeed recent satellite data have shown a steady increase in column NO_2 concentrations over China from 1996 to 2004, implying an increase in the emission of NO_x (Richter et al., 2005). This contradicts the results from emission inventories, which suggests a moderate decrease in NO_x emissions from China from 1994 to 2000 (Streets et al., 2003). Hence, up-to-date atmospheric chemistry data at downwind locations are needed to document recent chemical characteristics and to assess the impact of the outflow plumes on the atmospheric chemistry of the western Pacific region. In March 2005 we measured ozone (O_3), carbon monoxide (CO), methane, non-methane hydrocarbons (NMHCs) and halocarbons at Gosan on Jeju Island in South Korea as part of the Atmospheric Brown Cloud's East Asian Regional Experiment 2005 (ABC/EAREX2005) (http://abc-gosan.snu.ac.kr/index.html). These gases were selected because they play important roles in atmospheric chemistry and climate change and also provide valuable information on emission sources and the age of air masses (NRC, 1991; Crutzen, 1995; Warneck, 2000).

Jeju Island is an ideal place to measure the eastward transport of Asian continental pollution, which is at a maximum in the spring season. During the ACE-Asia field campaign in 2001, the Gosan site was among the most heavily instrumented surface sites (Huebert et al., 2003). Most of the previous studies at Jeju focused on aerosols (e.g. Kim and Seinfeld, 1995; Kim et al., 1998; Huebert et al., 2003) with limited investigations on trace gases (Kim et al., 1998; Shon et al., 2004, 2005) and no publications for volatile organic compounds (VOCs). In this paper we examine the temporal variations of the measured trace gases, and we compare the observations at Gosan with other measurements in East Asia, particularly with studies conducted during the TRACE-P period. We then apply back trajectory techniques to characterize the air parcels reaching the sampling site.

2. Experiment and methodologies

2.1. The Gosan site

The field study was carried out between 26 February and 29 March 2005 at the Gosan Weather Station (126.16°E, 33.29°N) on the island of Jeju, one of the World Meteorological Organization's Global Atmospheric Watch Stations. The island is located at the northern part of the East China Sea, about 100 km south of the Korean peninsula, 500 km northeast of Shanghai, China, and 250 km west of Kyushu, Japan (Fig. 1). The Gosan site is located at the western edge of the island at the top of a 50 m cliff, facing the East China Sea. The prevailing surface winds in spring are from the seaward direction, thus isolating the site from local pollution sources and making it a good site for monitoring the long-range transport of air pollutants in the northeast Asian region.

2.2. O_3 and CO measurements

Measuring instruments were housed in Container No. 2 at the Gosan station. The sampling system, instrumentation (including measurement precision and accuracy), and calibration for O_3 and CO have been described by Wang et al. (2001, 2003), and are therefore only briefly summarized here.

Ambient air was drawn through a perfluoroalkoxy (PFA) sampling tube (outside diameter: 12.7 mm; inside diameter: 9.6 mm; length: 7.2 m) with the inlet placed 6.7 m above the ground (3.7 m above the

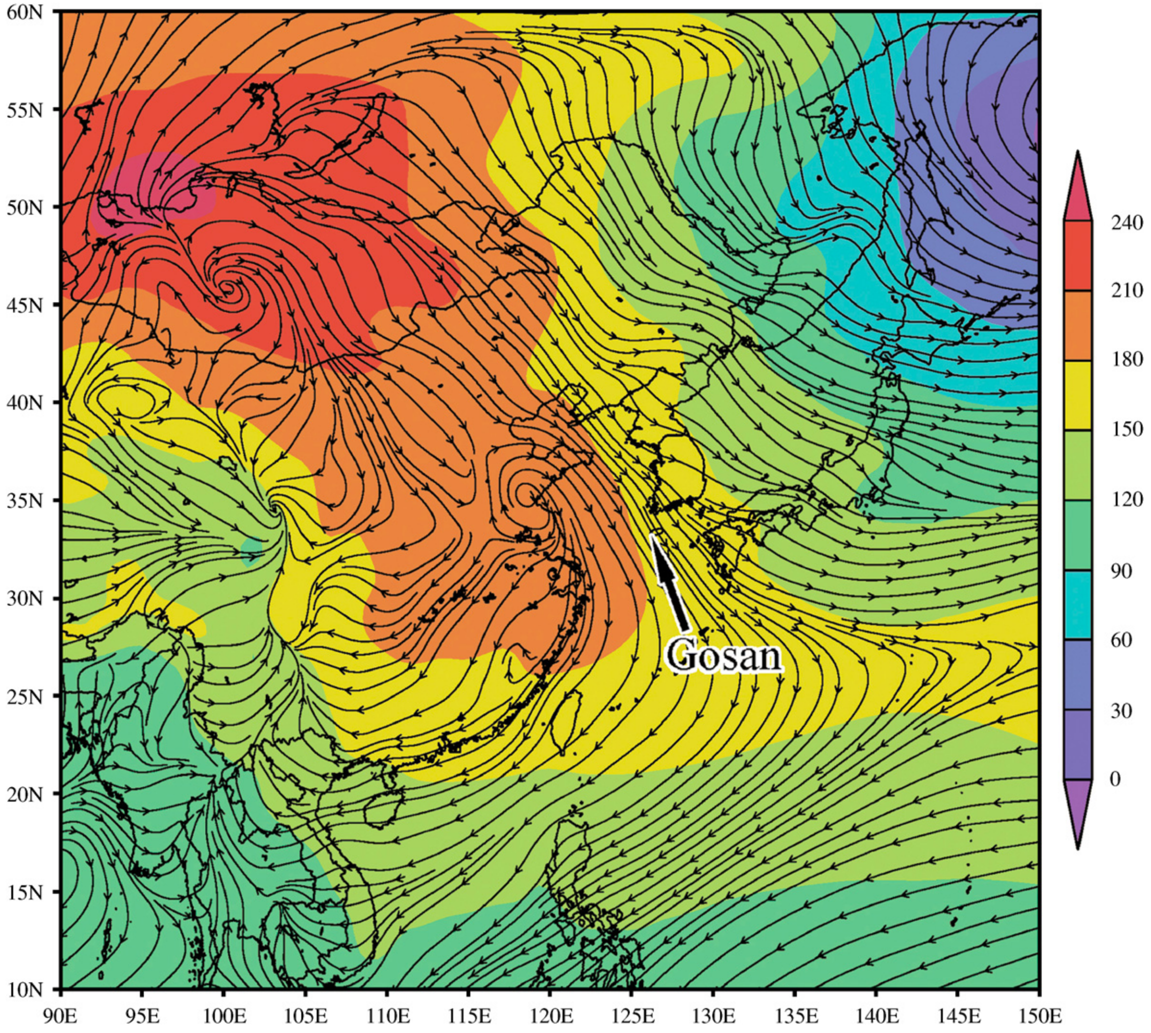

Fig. 1. Mean geopotential height and wind field on 1000 hPa over eastern Asia between 26 February and 29 March 2005.

rooftop of container). Inside the laboratory, the sampling tube was connected to a PFA-made manifold with a bypass pump drawing air at a rate of 12.1 L min^{-1} to reduce the residence time of sampled air. The intakes of the O_3 and CO analyzer were connected to the manifold.

Ozone was measured using a commercial UV photometric analyzer (Thermal Environmental Instruments (TEI), Model 49C). The analyzer was calibrated by a transfer standard (TEI 49PS) prior to the study and was checked by another transfer standard (TEI 49CPS) during the campaign. Both transfer standards were calibrated by the National Institute of Standards and Technology (NIST) Standard Reference Photometer (SRP) prior to the campaign. Carbon monoxide was measured with a gas filter correlation and non-dispersive infrared analyzer (Advanced Pollution Instrumentation (API), Model 300) with a heated catalytic scrubber for baseline determination. The CO analyzer was calibrated on a daily basis by injecting scrubbed ambient air (produced from TEI, Model 111) and a span gas generated by diluting a NIST traceable standard containing 153.8 ppmv CO (±2%), which was purchased from Scott-Marrin Inc., California. The baseline for CO was determined by passing ambient air to the internal scrubber every 2 h for 20 min. The CO concentrations were also separately determined during the analyses of 22 canister samples at the University of California, Irvine using gas chromatography (GC) (see below). The canister data set agreed to within 5% of the data determined by our NDIR analyzer $[CO]_{canister} = 0.98\,([CO]_{NDIR} - 15,\ r = 0.90,\ n = 22)$.

A data logger (Environmental Systems Corporation, Model 8816) was used to control the calibrations and to collect data, which were averaged over 1-min intervals. The data presented in this study are hourly averaged values.

2.3. Sampling and analysis of VOCs

Twenty-four whole air samples were collected for the analysis of VOCs via a separate stainless steel tube (inside diameter: 5.3 mm; length: 8.6 m) which was installed next to the main sample inlet above the rooftop of container. The air samples were drawn at a flow rate of $4\,L\,min^{-1}$ by a bypass pump and pressurized into 2-L conditioned and evacuated stainless steel canisters (to about 5 psig) by a metal bellows pump. From 3rd to 28th of March 2005 the canister samples were collected daily (except for 4th and 5th) from 12:30 to 13:30 local time. The canisters were later sent to the University of California, Irvine (UCI) for chemical analysis. The concentrations of methane, C_2–C_8 NMHCs, C_1–C_2 halocarbons and C_1–C_4 alkyl nitrates were determined using a combination of GC with flame ionization detection (FID), electron capture detection and quadrupole mass spectrometers. Carbon monoxide was quantified from the canister samples by first reducing CO to methane, followed by determination with GC/FID. Details of the preparation and preconditioning of the canisters are described in Blake et al. (1994) and 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).

2.4. Calculation of back trajectories

Backward air trajectories were calculated and used to segregate the sampled air masses according to their origin and path. Four times a day (0300, 0900, 1500, 2100 GMT) 5-day backward trajectories were calculated, with an endpoint altitude of 500 m above sea level, using the online version of the HYSPLIT model and the final analysis data (FNL), accessed via the NOAA ARL Real-time Environmental Applications and Display System website (http://www.arl.noaa.gov/ready/open/hysplit4.html).

3. Results and discussion

3.1. Meteorological conditions and temporal variations of trace gases

The mean geopotential height and wind on 1000 hPa for East Asia is shown over the whole sampling period in Fig. 1. The plot was made using FNL data with a horizontal resolution of $1^\circ \times 1^\circ$. Fig. 2 gives the temporal variations of O_3 and CO, together with some meteorological parameters measured at Gosan during this period. Fig. 1 shows that over the Asian continent there was an intensive high-pressure system, with the center located over Mongolia but extending southward to northern and eastern China, causing movement of the inner-continental cold air masses. Both figures indicate that the Gosan site was affected by strong north/northwest winter monsoons (mean speed $= 11.3\,m\,s^{-1}$) during the period. Except occasionally rainy or cloudy days (e.g. 11, 17, 22 and 27 March), the site was generally dominated by sunny weather under high-pressure system.

Inspection of the daily weather plots indicates that the moving high-pressure system controlled the transport pathways of air masses to the site, giving rise to large day-to-day variations of trace gases with hourly values from 32.7 to 84.4 ppbv for O_3 and from 122 to 1012 ppbv for CO. There were two general types of movements. In the first type, the high pressure crossed the ocean from northern China to the Korean peninsula and moved easterly (e.g. 28 February, 17, 20–21 and 25–27 March). NW → N → E winds were predominant, and the site was affected by air masses from northern China (NW winds), northeastern China and Korea (N winds), and Japan (E winds). The Gosan site often observed a sharp rise in the level of CO, associated with a variable O_3 concentration. On some days (e.g. 28 February, 25–27 March), the O_3 level increased with that for CO indicative of ozone production in photochemically aged air masses (Parrish et al., 1998); but on other days (e.g. 11 and 17 March) a sharp decrease in the O_3 level with an increase of CO suggests fast transport of fresh plumes from Korea (e.g. 11 and 17 March).

In the second type, the high pressure moved much more southerly and then proceeded eastward to the Pacific from central/southern China (e.g. 5–10, 14–16, 25–28 March). Under such synoptic conditions, Gosan experienced winds of NW → W → SW → S, and the air masses generally

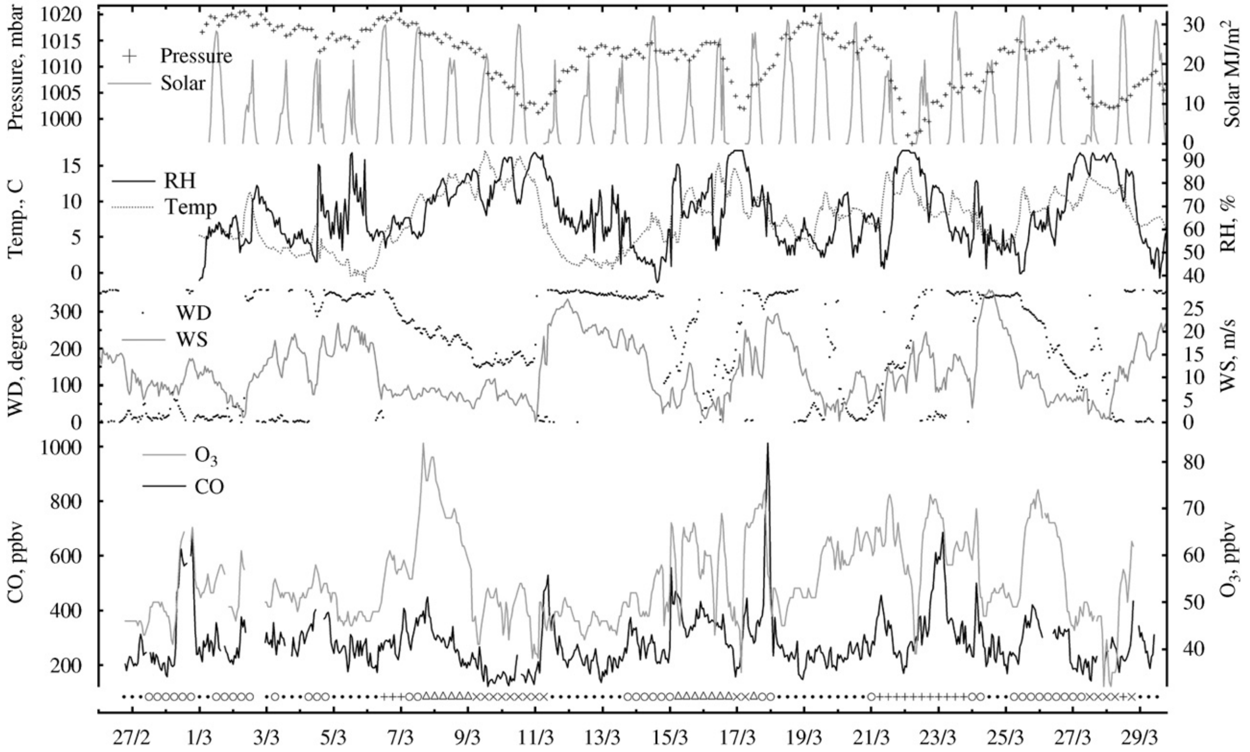

Fig. 2. Time series of O_3, CO and meteorological parameters measured at Gosan. WS = wind speed; WD = wind direction; Temp. = temperature; RH = relative humidity. At the bottom of the figure, the periods corresponding to the five different trajectory categories (refer to Fig. 5) are marked: marine (cross), Korea (plus), northeast China (dot), north China plains (open circle) and eastern China (triangle).

came from northern China (NW winds), eastern China (W and SW winds) and marine environments (S winds). O_3 often showed a large rise in concentration associated with a moderate increase in the CO concentration. For the entire period, a weak overall positive O_3–CO correlation ($r^2 = 0.22$) (figure not shown) was observed, indicating mixing of air masses of different ages. The source regions of these air masses will further be discussed in the later sections.

3.2. Overall statistics and comparison with other studies

3.2.1. Overall concentrations and source characteristics of trace gases

Table 1 summarizes the means and standard deviations of O_3, CO and selected VOCs measured at Gosan. The average hourly mixing ratios of O_3 and CO (mean ± s.d.) were 55 ± 9 and 283 ± 100 ppbv, respectively. The most abundant NMHC was ethane (2500 ± 545 pptv), followed by propane (930 ± 350 pptv), ethyne (800 ± 260 pptv), *n*-butane (270 ± 140 pptv), ethene (260 ± 220 pptv) and benzene (195 ± 75 pptv). The dominant halocarbon measured was methyl chloride (680 ± 60 pptv). By comparison, background levels of ethane at comparable latitudes in the NH during March are around 1800 pptv (Blake, 2005), whereas ethane mixing ratios can reach over 100 ppbv in cities. Here, the generally low levels of these trace gases indicate that the site was not significantly affected by local pollution. An examination of scatter plots of NMHCs and halocarbons with CO (not shown) revealed that combustion related species such as ethyne, benzene and methyl chloride were well correlated with CO ($r^2 = 0.62-0.81$), suggesting their common source origin. In contrast, light alkanes (i.e. ethane, propane and *n*-butane) had little/poor correlations with CO ($r^2 = 0.11-0.29$) indicating that there were contributions of light alkanes from sources other than combustion. This topic will be investigated more detailed in Section 3.3.3.

From the calculated trajectories, the number of hours to Gosan taken by an air parcel from the last

Table 1
Comparison of the March 2005 Gosan results with other studies

Species	Gosan[a]	TRACE-P[b]	Lin'an[c]	Hok Tsui [d]	Okinawa[e]		Chichijima[f]	Happo[g]
					Coastal	SD		
O_3 (ppbv)	55 (9)	64	34	45	~43		48	
CO (ppbv)	283 (100)	303	677	404	248	179		
Ethane	2497 (547)	2695	3189	2368	1896	1397	1576	1741
Ethene	257 (222)	396	1679	498			166	208
Ethyne	803 (258)	1465	2475	1402	845	523	452	696
Propane	927 (353)	1010	1250	814	749	576	542	613
n-Butane	267 (142)	290	453	326	233	184	171	223
n-Pentane	131 (99)		140	85	79	67		81
i-Pentane	118 (67)		345		102	96		112
Benzene	194 (76)	437	851	492	191	116	119	
Toluene	131 (83)		1529	540	109	125	78	
Tetrachloroethene	12 (6)	18	26	26				
Methyl chloride	678 (62)	654	1108	821				
ΔEthyne/ΔCO (pptv ppbv^{-1})	3.8		5.0	5.3				
ΔBenzene/ΔCO (pptv ppbv^{-1})	1.2		2.6	2.0				

Notes: All data are mean values in pptv unless otherwise specified.

[a] This study—mean (standard deviation).

[b] Russo et al. (2003) (spring 2001, "Central" (30–60°N, 80–130°E) <2 km).

[c] Wang et al. (2004) (spring 2001).

[d] Wang et al. (2003) (spring 2001).

[e] Kato et al. (2004) (November–December 2000, Coastal: Chinese coastal area, SD: Shandong peninsula).

[f] Kato et al. (2001) (December 1999, March 1998 for O_3).

[g] Sharma et al. (2000b) (spring 1998).

contact with the continent was determined daily at GMT 0300 (i.e. near to the time when VOC canister samples were taken). This value was defined as the "transport time" from the source region (Kato et al., 2004). The concentrations of ethane, ethyne, propane and *n*-butane observed at Gosan were then plotted against the transport time to show the dependence of hydrocarbon concentrations on the residence time over the clean marine surface (Fig. 3). It can be seen that the concentrations of these species exhibited an exponential decrease with the transport time, and that the slope of the decay was larger for more reactive hydrocarbons (e.g. *n*-butane = 0.0167) compared to less reactive species (e.g. ethane = 0.0066). These features suggest that the abundances of light alkanes at Gosan were largely determined by emissions from distant sources, followed by chemical reactions with OH radicals and/or mixing processes. The slopes in Fig. 3 are hence an indicator of the degree of atmospheric processing (chemical and mixing) in the spring season.

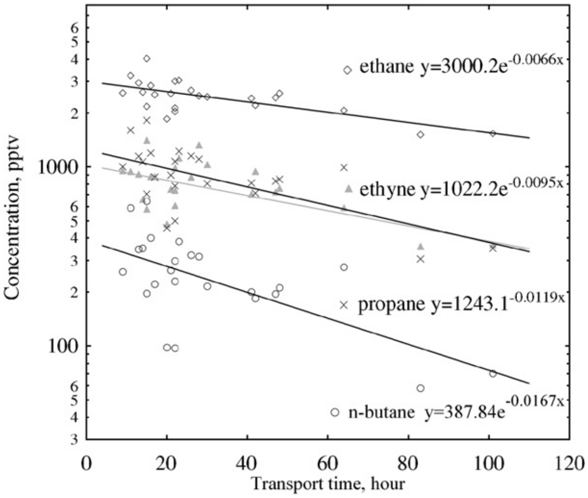

Fig. 3. Relationship between hydrocarbon mixing ratios and transport time from land.

The negligible local impact on the trace gases measured at the Gosan site can be further illustrated by examining the dependence of trace gas variability

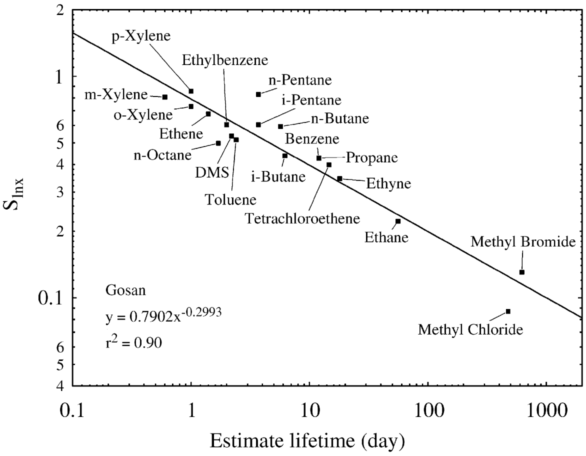

Fig. 4. Atmospheric variability versus the lifetime of selected VOCs.

on atmospheric lifetime for a variety of VOCs (Fig. 4). This relationship (also called the "Junge relationship") has previously been used to evaluate the remoteness of a sampling site (e.g. Jobson et al., 1998) and is expressed as $S_{\ln x} = A\tau^{-b}$, where $S_{\ln x}$ is the standard deviation of the natural logarithm of the mixing ratio x, τ is the atmospheric lifetime of the selected trace gas, and A and b are fit parameters. The selected species in Fig. 4 are collectively associated with various urban/industrial/combustion emissions such as vehicle exhaust, solvent use and industrial processes, and biomass burning. According to the fitted line, the b value at Gosan was 0.30, which was nearly identical to that of continental outflow from southern China (0.31; Wang et al., 2005); in between values reported at Okinawa and Ogasawara (0.25 and 0.43, respectively; Kato et al., 2004); and smaller than that over the northwest Indian Ocean (0.40; Warneke and DeGouw, 2001). The similarity of b values between Gosan and "continental outflow" air mass rather than maritime air shows the influences from continental sources at Gosan and the selected species were not strongly affected by local sources.

3.2.2. Comparison with other studies

We compared the Gosan data with previous results from other remote sites in East Asia and from the TRACE-P aircraft campaign in spring 2001 (Table 1). O_3, CO and VOC mixing ratios at Gosan were generally higher than those obtained at Okinawa, Chichi-Jima (a remote island in the western Pacific) and Happo (a remote site in Japan). When compared to data collected in or near Asian source regions such as Lin'an, eastern China (Wang et al., 2004) and Hok Tsui, southern China (Wang et al., 2003), the average O_3 mixing ratio sampled at Gosan was enhanced by about 10–20 ppbv in the spring season, which is consistent with the photochemical production of O_3 during downwind transport from the source regions. In contrast, the concentrations of combustion and vehicular tracers (e.g. CO, ethyne, benzene, methyl chloride) were lower at Gosan, while light alkanes (i.e. ethane and propane) were comparable. Similar results are obtained in the comparison between Gosan and the TRACE-P aircraft data for "Central" (30–60°N, 80–130°E) air masses sampled below 2 km (Russo et al., 2003), except for a reduced concentration of O_3 at Gosan and a comparable level of methyl chloride. One interesting observation was that while the ethyne–CO slope at Gosan (3.8 pptv ppbv^{-1}) was about 25% smaller than the near-source values in Hok Tsui and Lin'an (5.0–5.3), the benzene/CO slope was much smaller (1.2 versus 2.0–2.6, or 40–50% smaller), suggesting that Gosan received air masses with some different chemical characteristics than the southern and eastern Chinese sites.

3.3. Influences of long-range air-mass transport

3.3.1. Air-mass categorization

To identify the source regions of air masses arriving at Gosan, each calculated trajectory was examined and categorized into one of the following five groups according to the origin of the trajectory, distance/time of travel, and pathway over the geophysical regions with different emission characteristics. These five air-mass groups are: northeast China (NE-C), North China Plains (NCP), east China (E-C), Korea (KR) and marine (MR). Fig. 5 shows the five source regions and an example of trajectory in each source region. The air masses in the three Chinese groups (NE-C, NCP and E-C) originated in Russia, Siberia and Mongolia, but later traveled over different source regions in China: NE-C over the northeast region mainly Liaoning Province; NCP over the region including the Beijing metropolitan area, Hebei Province and Shandong peninsula; and E-C over the eastern region including the Shanghai metropolis and Jiangsu and Zhejiang Provinces. The air masses in the KR group mainly came from northeastern China but traveled or circulated over the Korean peninsula.

MR represents a collection of maritime trajectories that traveled over the Bohai Sea, Yellow Sea and East China Sea with a residence time longer than 80 h (~3 days) before reaching Gosan.

The NE-C, NCP, E-C, KR and MR groups account for 34%, 30%, 11%, 12% and 13%, respectively, of all the trajectories ($n = 122$) in the study period. Because of the rather limited number of trajectories, we do not further stratify whether the air masses came from the boundary layer or the free troposphere.

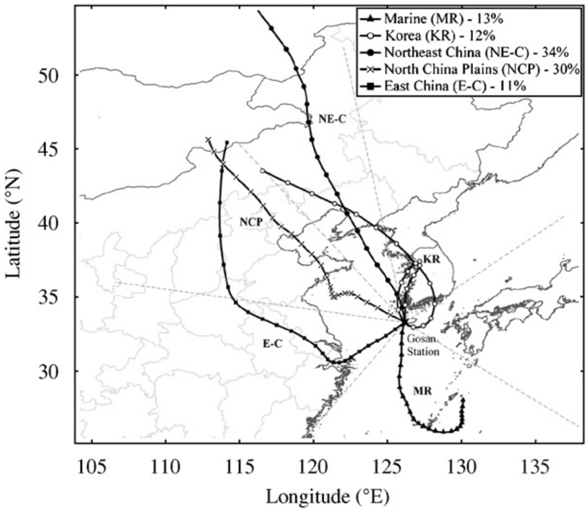

Fig. 5. Source regions for the five air-mass groups.

3.3.2. *Chemical characteristics of air masses*

Table 2 shows the statistics of mixing ratios of 6-h averaged O_3 and CO as well as of selected NMHC and halocarbons and their ratios in different air-mass groups. The center times of the 6-hourly O_3 and CO averages are the ending times of the trajectories (i.e. 0300, 0900, 1500, 2100 GMT). The E-C group had the highest level of O_3 (65 ± 9 ppbv), CO (335 ± 57 ppbv) and other combustion tracers such as ethyne, benzene, and methyl chloride. This is reasonable because the highly industrialized Yangtze River delta (including the largest Chinese city, Shanghai) is located in this source region. Air masses in the E-C group were sampled mainly during 7–8 March and 15–16 March, as indicated in Fig. 2. In comparison KR air mass contained comparable levels of O_3, CO and other combustion tracers. (Although the levels in KR were slightly lower than those in E-C, statistical

Table 2
Mixing ratios of trace gases in different air mass groups

	NE-C		NCP		E-C		KR		MR	
	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.
Continuous										
O_3 (ppbv)	15	5	56	8	65	9	61	6	48	6
CO (ppbv)	246	40	318	102	335	57	331	101	219	71
Canister										
Methane (ppbv)	1873	16	1865	13	1862	12	1870	15	1828	12
Ethane	2844	576	2471	277	2292	208	2603	481	1704	312
Ethyne	850	246	788	195	918	275	870	239	433	130
Propane	1165	367	879	215	787	253	925	290	550	384
n-Butane	369	161	253	99	198	90	252	105	134	122
n-Pentane	128	57	216	146	135	127	117	90	44	45
Benzene	199	76	198	63	240	73	212	66	86	22
Toluene	91	31	116	78	184	111	177	123	113	13
CH_3CCl_3	22	1	22	1	23	1	24	3	22	0
CCl_4	93	2	94	2	97	5	93	3	94	1
CH_2Cl_2	47	10	57	14	102	53	80	37	43	3
C_2Cl_4	11	6	10	2	12	4	17	10	8	1
CH_3Cl	653	50	682	36	725	112	701	50	640	11
CH_3Br	10	0	12	1	12	1	13	2	11	0
Ethyne/propane (pptv pptv^{-1})	0.74	0.10	0.91	0.24	1.20	0.26	0.95	0.06	0.93	0.30
Benzene/propane (pptv pptv^{-1})	0.17	0.02	0.23	0.08	0.31	0.05	0.23	0.02	0.19	0.07

Notes: All data are in pptv unless otherwise specified.

t-tests show that their differences are not significant.) Air masses in the KR group originated from northeast China, but could be significantly influenced by Korean emissions. We notice that the mean CH_3CCl_3 and CH_3Br level in the KR group (23.5 and 13.2 pptv, respectively) appears to be relatively high (see Table 2), though the differences between KR and other groups are not significant according to *t*-tests. Blake et al. (2003) observed enhanced ratios of the two species relative to CO during TRACE-P in air samples collected near Japan (particularly when the trajectories passed over the Seoul region in South Korea), and they suggested that the enhanced CH_3Br levels could be caused by quarantine and preshipment uses from Inchon port, located in the Seoul–Inchon–Suwon triangle delta area (the largest industrial zone in South Korea).

The NCP group also contained elevated levels of CO and other combustion tracers. Fig. 2 shows that several plumes arriving at Gosan were from NCP. The synchronic rises of O_3 and CO in these plumes indicate the transport of photochemically aged air masses from the North China Plains with an O_3–CO regression slope of 0.087 ppbv $ppbv^{-1}$ (scatter plot not shown), which is comparable to the slope of 0.084 recorded at Mount Tai, the highest mountain in the North China Plains, in July 2003 (Gao et al., 2005). (The O_3–CO correlation is less obvious in other air-mass groups.) For the NE-C group, although the mean CO level was significantly lower than that in E-C, KR, and NCP, the mixing ratios of light alkanes, such as methane, ethane and propane, were comparable or slightly larger (see Table 2). The likely source of these relatively enhanced alkanes will be discussed in detail in the following section. As expected, the MR group had the lowest levels of O_3, CO and most VOCs due to photochemical processing and mixing with clean maritime air during air-mass transport.

3.3.3. *Sources of light alkanes*

As previously mentioned, the mixing ratios of light alkanes (i.e. methane, ethane and propane) observed at Gosan were comparable to or even higher than those at source regions in China, although the levels of combustion and vehicular tracers were clearly reduced at Gosan. Back trajectory analysis has also indicated enhanced levels of light alkanes in the air masses from northeast China. Hence it is of interest to investigate the potential source(s) of these species. It is well known that ethane is predominantly emitted from biomass burning and natural gas leakage. Rudolph (1995) estimated that biomass burning and natural gas loss contribute 6.4 and 6 Tg yr^{-1}, respectively, to the global ethane emission, and the few minor sources (e.g. oceans, soils, wetlands and other industrial sources) could add up to about 1 Tg yr^{-1}. Although the global emissions of the two main sources are of similar, at mid-northern latitudes (35–90°N), the geogenic sources of ethane (i.e. natural gas leakage) are greater than the contributions from biomass burning by about a factor of five (Rudolph, 1995). Similar to ethane, propane is mainly derived from geogenic sources and from petrochemical industries (Mayrsohn and Crabtree, 1976), while methane is the principal component of natural gas.

In our study, the combustion sources did not appear to contribute significantly to the observed ethane and propane levels, as indicated by a lack of overall correlation between these species and CO (Section 3.2.1). In addition, the level of methyl chloride, a biomass burning tracer (Blake et al., 1996), in the NE-C group was comparable to that in the marine group (Table 2). More insights into the source(s) contributing to the observed ethane and propane levels can be obtained by examining the ratios of ethyne and benzene to propane. Ethyne and benzene are emitted from vehicular exhaust in urban areas and from biofuel/biomass burning in rural areas (Warneck, 2000; Streets et al., 2003). They have a similar chemical lifetime of 12–18 days from reaction with hydroxyl radical (Warneck, 2000), and are inefficiently removed by wet removal processes. Therefore the ratios of ethyne and benzene to propane can be used to indicate the relative importance of combustion and geogenic sources, where a small ratio indicates a large contribution of the geogenic source. As shown in Table 2, the mean ethyne/propane and benzene/propane ratios in the NE-C group (0.74 ± 0.10 and 0.17 ± 0.02 pptv $pptv^{-1}$, respectively) were indeed lower than those in other groups. In particular, the ratios in the NE-C group are significantly lower (at a 95% confident interval in *t*-tests) than those in the most polluted E-C air mass group, which had respective ratios of 1.20 ± 0.26 and 0.31 ± 0.05 pptv $pptv^{-1}$. This result suggests a significant contribution from natural gas leakage in the upwind region of the NE-C group.

Further examination of the latitudinal data collected during TRACE-P (Blake et al., 2003), showed that the ethyne/propane and benzene/propane ratios decrease from 3.58 and 0.74 to 0.88 and 0.19, respectively, as the latitude changed from 7.5°N to 42.5°N over the western Pacific troposphere (west of 165°E). This provides additional evidence for an increased impact of natural gas leakage in the northern mid-latitude region of the western Pacific. Given that Russia is the world's largest gas reserve—accounting for 27.8% of the world total as of 1 January 2005 (Anonymous, 2004)—and that natural gas loss in the former Soviet Union alone has been estimated to be 25 ± 10 Tg yr^{-1} (Craig et al., 1993), it is possible that the natural gas signature in our data set was contributed by leakages from gas fields in Siberia. This attribution is also supported by the emission inventory for methane developed by Fung et al. (1991), which was adopted in GEIA (Global Emissions Inventory Activity, http://www.geiacenter.org), indicating significant contribution to methane due to leakages of natural gases from pipelines in the Northeast China and East Siberia. Our observations at Gosan provide direct evidence of the impact of this source on atmospheric composition in downwind regions. However, it is difficult to quantify, using the measurement data alone, the contribution of natural gas loss to the observed levels of light alkanes. Additional studies are needed that make use of chemistry-transport models and detailed emission inventories that include an accurate account of emissions from natural gas leakage.

4. Summary and conclusions

Ozone, CO, hydrocarbons, and halocarbons were measured on Jeju Island, South Korea in March 2005 to characterize the chemical composition of recent outflow from the Asian continent and to intercompare the measurement instrumentation from participating groups. Average mixing ratios (±s.d.) were 54.6 (±9.0) ppbv for O_3 and 283 (±100) ppbv for CO. The most abundant NMHC was ethane (mean ± s.d. = 2497 ± 547 pptv), followed by propane (927 ± 353 pptv), ethyne (803 ± 258 pptv), *n*-butane (267 ± 142 pptv), ethene (257 ± 222 pptv) and benzene (194 ± 76 pptv). Carbon monoxide showed a good correlation with combustion tracers such as ethyne, benzene and methyl chloride ($r^2 = 0.62-0.81$), but was poorly correlated with light alkanes such as ethane, propane and *n*-butane ($r^2 = 0.11-0.29$). This suggests that light alkanes were significantly contributed by non-combustion source(s).

Analysis of 5-day back trajectories and chemical data revealed elevated concentrations of measured trace gases of combustion origin in air masses transported from eastern China ($O_3 = 65 \pm 9$ ppbv, CO = 335 ± 57 ppbv) and the Korean peninsula ($O_3 = 61 \pm 6$ ppbv, CO = 331 ± 101 ppbv), compared to springtime marine background air ($O_3 = 48 \pm 6$ ppbv, CO = 219 ± 71 ppbv). In comparison, air masses from the northeastern sector (originating from Siberia and passing over northeastern China) contained a relative abundance of light alkanes, including reduced ratios of ethyne and benzene to propane. This, together with the lack of correlation between light alkanes and CO in the overall data set, suggests a significant contribution from natural gas leakages in the upwind region, possibly from Siberia. Further studies are needed to quantify the contribution of natural gas leakage to the total emissions of light alkanes and its implications for atmospheric chemistry in the western Pacific region.

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