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Vertical distributions of non-methane hydrocarbons and halocarbons in the lower troposphere over northeast China

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ABSTRACT

Vertical distributions of air pollutants are crucial for understanding the key processes of atmospheric transport and for evaluating chemical transport models. In this paper, we present measurements of non-methane hydrocarbons (NMHCs) and halocarbons obtained from an intensive aircraft study over northeast (NE) China in summer 2007. Most compounds exhibited a typical negative profile of decreasing mixing ratios with increasing altitude, although the gradients differed with different species. Three regional plumes with enhanced VOC mixing ratios were discerned and characterized. An aged plume transported from the northern part of the densely populated North China Plain (NCP; i.e. Beijing–Tianjin area) showed relatively higher levels of HCFC-22, 1,2-dichloroethane (1,2-DCE) and toluene. In comparison, the plume originating from Korea had higher abundances of CFC-12, tetrachloroethene (C_2Cl_4) and methyl chloride (CH_3Cl), while regional air masses from NE China contained more abundant light alkanes. By comparing these results with the earlier PEM-West B (1994) and TRACE-P (2001) aircraft measurements, continuing declining trends were derived for methyl chloroform (CH_3CCl_3), tetrachloromethane (CCl_4) and C_2Cl_4 over the greater China–northwestern Pacific region, indicating the accomplishment of China in reducing these compounds under the Montreal protocol. However, the study also provided evidence for the continuing emissions of several halocarbons in China in 2007, such as CFCs (mainly from materials in stock) and HCFCs.

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1. Introduction

Volatile organic compounds (VOCs) are an important class of chemical constituents in the atmosphere. Non-methane hydrocarbons (NMHCs) are at the center of tropospheric photochemistry involving radical (i.e. RO_x and HO_x) cycling and propagation processes, resulting in the formation of secondary species such as surface ozone (O_3). Their atmospheric oxidation products can also undergo condensed phase reactions to produce secondary organic aerosol (SOA; Kroll and Seinfeld, 2008; Hallquist et al., 2009). Long-lived halogenated hydrocarbons (halocarbons) are potent greenhouse gases and deplete stratospheric ozone, and therefore the production and consumption of many halocarbons are regulated by the Montreal Protocol and its subsequent amendments (WMO, 2002; UNEP, 2003). Consequently, information on the sources and atmospheric concentrations of VOCs is fundamental to understanding issues regarding atmospheric chemistry, regional air quality, and climate change.

China has become an important emitter for many chemically active and radiatively important air pollutants owing to the large population and fast-paced industrialization. In terms of non-methane VOCs (NMVOCs), their release from anthropogenic sources in China was estimated as approximately 23 Tg in 2006 (Zhang et al., 2009), and is expected to further increase in the following decades (Ohara et al., 2007). A number of studies based on surface measurements have been carried out in various regions of China in recent years, especially in developed areas (e.g. Liu et al., 2000,

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2008a; So and Wang, 2004; Barletta et al., 2005, 2006; Chan et al., 2006a, 2006b; Chan and Chu, 2007; Tang et al., 2007a, 2007b; Suthawaree et al., 2010; Wang et al., 2010), providing vast valuable information on the ambient concentrations, composition profiles, and temporal and spatial distributions of various VOC compounds. Some studies were conducted to apportion the VOC emission sources (Guo et al., 2004, 2006, 2007, 2009; Song et al., 2007; Liu et al., 2008b, 2008c; Zhang et al., 2008) and to quantify their potential to ozone production (So and Wang, 2004; Zhang et al., 2007; Shao et al., 2009). However, information on the vertical distribution of VOCs in the troposphere over China is very scarce, despite its important roles in understanding vertical exchange/dynamic processes and evaluating chemical transport models.

China ratified the Montreal Protocol in 1991. Since then, great effort has been made to phase out the production and use of ozone-depleting substances (ODS) (Wan et al., 2009). Although Barletta et al. (2006) reported an enhancement in ambient mixing ratios of selected halocarbons in some Chinese cities with respect to the global background, more recent studies confirmed the achievement of China in cutting emissions of primary ODS (Wan et al., 2009; Kim et al., 2010). Therefore it is interesting to investigate if the surface emission reductions are reflected by decreases in their mixing ratios in the free troposphere around China.

As part of China's National Basic Research Program (the 973 program) on acid rain pollution and control, we carried out aircraft measurements of trace gases, aerosols, and cloud water compositions over NE China in summer 2007. During the summer season, when southerly/southwesterly winds prevail, NE China frequently lies immediately downwind of North China Plains (NCP), which is home to Beijing, Tianjin, Henan, Hebei, and Shandong provinces (see Fig. 1) and is one of the most populated and industrialized areas of China. The main objectives of this study were to characterize the vertical distributions of air pollutants and to investigate the regional transport of air pollution from the upwind NCP region to NE China. This paper presents the VOC measurement results, focusing on vertical profiles as well as long-term changes of halocarbons in the free troposphere over China.

2. Experimental

From June 20 to July 13, 2007, 16 flights were conducted over Jilin Province in NE China. A twin-engine turboprop Yun-12 aircraft served as the sampling platform. The aircraft was based at an airport (125.2° E, 43.9° N, ~245 m a.s.l.) located in the northwest of Changchun, the capital of Jilin Province. An examination of global reanalysis data suggests that during the study period, NE China was impacted by a low pressure system, and the planetary boundary layer (PBL) air primarily originated from the ocean to the south and from central eastern China (including NCP) to the southwest. More details about the aircraft missions are described elsewhere (Xue et al., 2010).

Out of 16 flight missions, 6 were carried out under sunny weather conditions, during which whole air samples were taken (the rest of the flights were conducted on cloudy days during which cloud water samples were collected). Most flights lasted 2–4 h and were centered at noon, with an average VOC sampling time of 11:50 LT (±2.7 h). A total of 88 canister samples were collected during the missions, covering a large portion of Jilin province and an altitude range of 0.5–5.5 km a.s.l. Additionally, to support analyses of the aircraft data, a total of 8 surface samples were collected in both polluted areas (i.e. Changchun, Songyuan) and clean regions (i.e. Baicheng) of Jilin during the timeframe of aircraft missions. The flight tracks and sampling locations are shown in Fig. 1.

Evacuated 2-L electro-polished stainless steel canisters were used for sampling. 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 by Blake et al. (1994) and Simpson et al. (2010). A sample inlet was mounted at the bottom of the aircraft, inside which an aft-facing stainless steel tube was connected with the canisters. During sampling, a stainless steel bellows valve was slightly opened and the selected canister was filled to ambient pressure in 30 s. Considering the flight parameters of the aircraft, each air sample represents a horizontal resolution of ~2 km or a vertical scale of ~120 m. After sampling, the canisters were shipped to the UCI laboratory for chemical analysis. A 5-column multiple GC system with flame ionization detection (FID), electron capture detection (ECD) and mass spectrometer detection (MSD) was deployed to identify and quantify VOC species including NMHCs, halocarbons and alkyl nitrates. Detailed descriptions of the analysis, quality assurance/quality control, and the measurement precision and accuracy for each species are given by Colman et al. (2001) and Simpson et al. (2010).

3. Results and discussion

3.1. Vertical distributions

3.1.1. NMHCs

Table 1 documents the statistics of the most abundant NMHC species for the PBL, free tropospheric (FT), and surface samples. The PBL height was chosen as 2 km a.s.l. according to the mean altitude

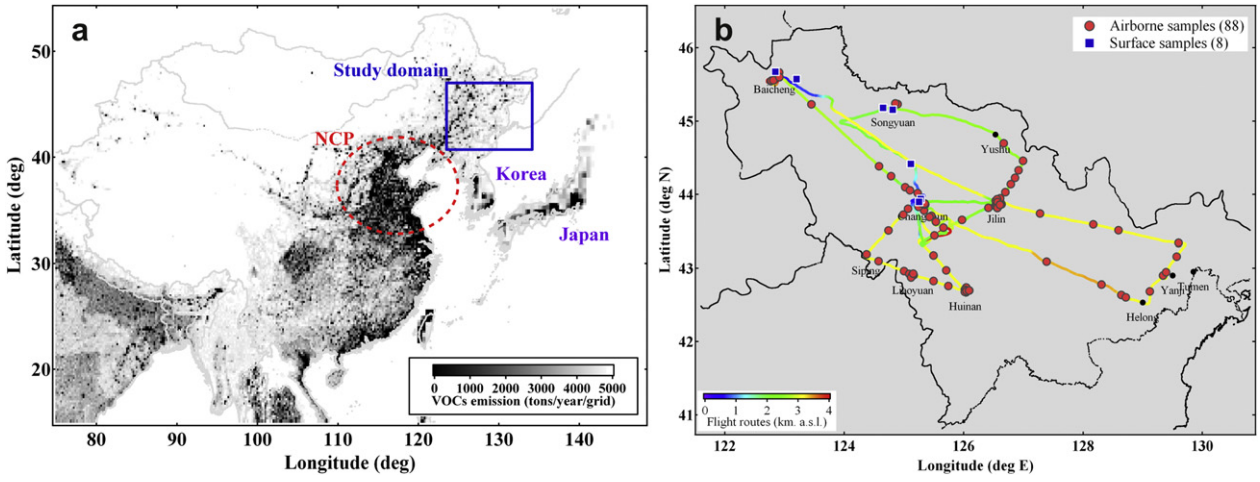

Fig. 1. Map showing the study region, flight tracks and sampling locations of VOC canisters. The NMVOC emission data was obtained from Zhang et al. (2009).

Table 1
Statistics of CO and major NMHC species measured over NE China.[a]

Name	Formula	Lifetime[b] (days)	Surface [$n = 8$][c]			PBL [$n = 34$][c]			FT [$n = 49$][c]		
			Mean	σ	Median	Mean	σ	Median	Mean	σ	Median
Carbon monoxide	CO	56.6	645	449	528	388	121	382	253	155	209
Ethane	C_2H_6	46.7	3012	1607	2784	1496	482	1362	1034	316	914
Ethene	C_2H_4	1.4	2853	2314	2288	1134	1014	864	661	407	578
Ethyne	C_2H_2	12.9	4010	5064	2818	1221	423	1134	682	367	665
Propane	C_3H_8	10.6	1883	1220	1535	503	320	357	232	155	192
Propene	C_3H_6	0.4	1125	1585	511	248	269	185	141	112	111
i-Butane	C_4H_{10}	5.5	952	690	959	146	130	108	45	44	31
n-Butane	C_4H_{10}	4.9	1004	630	963	177	139	127	61	51	49
1-Butene	C_4H_8	0.4	251	228	179	55	70	35	25	24	17
i—Butene	C_4H_8	0.2	239	161	255	65	52	45	54	47	42
i-Pentane	C_5H_{12}	3.2	1236	1131	926	154	124	119	38	37	24
n-Pentane	C_5H_{12}	3.0	511	389	430	72	60	46	24	16	19
Isoprene	C_5H_8	0.1	857	738	631	233	166	205	95	42	88
Benzene	C_6H_6	9.5	909	674	772	444	223	398	221	155	187
Toluene	C_7H_8	2.1	946	834	670	1381	957	982	923	436	728
C_2H_2/CO			5.4	2.4	5.2	3.2	0.8	3.0	2.8	1.0	2.8
C_3H_8/C_2H_6			0.59	0.24	0.58	0.31	0.10	0.27	0.21	0.07	0.20

[a] Units are pptv, except for CO which is ppbv, and for C_2H_2/CO and C_3H_8/C_2H_6 which are pptv ppbv^{-1} and pptv pptv^{-1}, respectively.
[b] The atmospheric lifetimes are calculated based on the K_{OH} values from Atkinson and Arey (2003) and an assumption of a 12-h average OH concentration of 2.0×10^6 molecule cm^{-3}.
[c] PBL = Planetary Boundary Layer, FT = Free Troposphere; the number of samples, n, is given in brackets.

profiles of other trace gases (i.e. SO_2, CO, and O_3; figures not shown). The general vertical distributions are illustrated in Fig. 2 using *i*-pentane, propene, ethyne and benzene as examples. Log scales are used here for better clarity of the variation in the altitude profiles. As is expected, all the profiles showed a peak at the surface, which then decreased with altitude. This pattern is typical and can be explained by the interplay among surface emissions, turbulent mixing, and atmospheric processing of air masses. For relatively long-lived species like ethane and ethyne (lifetimes: weeks to months), the mixing ratios in PBL and FT were about 30–50% and 12–34% of those at the surface, respectively, while for shorter-lived species such as butanes, pentanes and olefins (lifetimes: hours to days), the PBL/surface and FT/surface concentration ratios were somewhat smaller, namely 12–40% and 3–23%, respectively. Fig. 2 also shows some degree of scattering in the measured mixing ratios of NMHCs, even in the free troposphere. This is because the air samples were collected from 6 different flights, corresponding to distinct sampling locations and pollution conditions. In particular, a highly polluted plume from the northern part of NCP was sampled in the free troposphere during the flight on June 27 (Ding et al., 2009).

Examination of hydrocarbon pairs with similar sources but different removal rates is useful to evaluate the extent of atmospheric processing of air masses. In this work, we also assessed the altitude dependence of air mass aging by using the commonly employed C_2H_2/CO and C_3H_8/C_2H_6 ratios. Both ratios showed the highest values at ground level, decreasing with the height (see Table 1). This is consistent with our expectation that air masses are more processed at higher altitudes. The mean C_2H_2/CO and C_3H_8/C_2H_6 ratios (±standard deviation) for fresh air masses at the surface were 5.4 (±2.4) pptv ppbv^{-1} and 0.59 (±0.24) pptv pptv^{-1}, which reflect to some degree the emission characteristics of related sources over NE China. For comparison, Xiao et al. (2007) reported a C_2H_2/CO emission ratio of 4.8 pptv ppbv^{-1} for fossil fuel combustion sources in East Asia. The average values derived for the PBL (3.2 ± 0.8 pptv ppbv^{-1} for C_2H_2/CO; 0.31 ± 0.10 pptv pptv^{-1} for C_3H_8/C_2H_6) and FT air (2.8 ± 1.0 pptv ppbv^{-1} for C_2H_2/CO; 0.21 ± 0.07 pptv pptv^{-1} for C_3H_8/C_2H_6) were also comparable to the measurement results for the TRACE-P plumes originating from "Central" (3.9 ± 1.3 pptv ppbv^{-1} for C_2H_2/CO; 0.35 ± 0.09 pptv pptv^{-1} for C_3H_8/C_2H_6) and "Coastal" (2.5 ± 1.2 pptv ppbv^{-1} for C_2H_2/CO; 0.19 ± 0.12 pptv pptv^{-1} for C_3H_8/C_2H_6) regions of China (Russo et al., 2003).

3.1.2. Halocarbons

Statistical results of the 17 measured halocarbons are given in Table 2. Fig. 3 shows the vertical profiles of selected species, namely, CFC-12, HCFC-22, CH_3CCl_3, CCl_4, and C_2Cl_4. Fig. 3 also shows the Northern Hemispheric background values obtained from the NOAA/ESRL halocarbons in-situ program in summer 2007, except for C_2Cl_4 which was calculated as the lower 25th percentile of the INTEX-B (Intercontinental Chemical Transport Experiment – Phase B) samples not influenced by stratospheric air (Barletta et al., 2009). All of the plotted compounds generally exhibited enhanced mixing ratios compared to the background levels. Moreover, the profiles of most compounds also displayed a slight decreasing trend with altitude (see Fig. 3 and Table 2). The mixing ratios of most species in the boundary layer were evidently enhanced with respect to the PBL regional background (see Table 3), which was calculated as the median of the FT air samples not influenced by the polluted NCP plume. These results suggested that emission sources of some halocarbons still existed in NE China in 2007.

Chlorofluorocarbons (CFCs) showed elevated mixing ratios at the surface that slightly decreased with the height. Taking CFC-12 as an example, the mean surface mixing ratio (±SD) was 565 (±8) pptv, compared to 554 (±10) pptv in PBL and 547 (±12) pptv in FT. The differences are statistically significant (t-test, $p < 0.01$). CFCs are commonly used as refrigerants, and are also used in air conditioning and as foam blowing agents and aerosol propellants (Barletta et al., 2006). China has established the "country programme" within the framework of the Montreal Protocol for phasing out CFCs (State Environmental Protection Administration, 2000). By 2007, when this study occurred, the production and consumption of CFCs for many applications had been banned (see details in Wan et al., 2009). However, there were still some appliances using CFCs in stock in 2007, which would be gradually phased out in the following years (Wan et al., 2009). Therefore, the observed CFC enhancements over NE China may be due to the remaining CFC materials in storage.

In many applications, CFCs have been replaced by hydrochlorofluorocarbons (HCFCs) and more recently by hydrofluorocarbons (HFCs). Under the Montreal Protocol, the production and consumption of HCFCs in China will be frozen in 2013, with the 2009–2010 average level as a baseline, and then phased out by January 1st, 2030 (UNEP, 2008). Thus there was no effective action for controlling HCFCs and HFCs in China in 2007. Overall, the HCFC

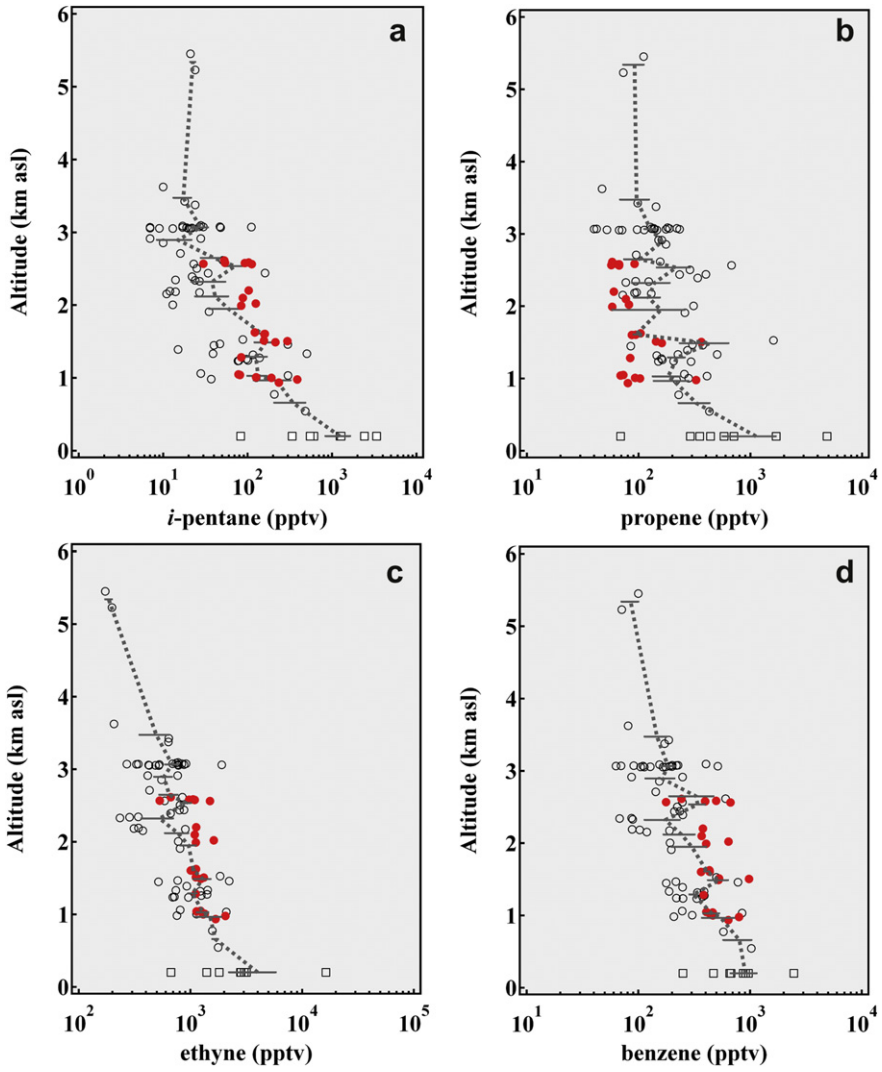

Fig. 2. Vertical profiles of (a) *i*-pentane, (b) propene, (c) ethyne and (d) benzene over NE China. The squares at the bottom represent surface samples, and red solid circles indicate the airborne samples collected on June 27 when a highly polluted plume was sampled (Ding et al., 2009). Dashed lines together with error bars indicate the mean values and standard errors for data points in 200-m bins. Log scales are used for better clarity.

Table 2
Statistics of major halocarbons measured over NE China.[a]

Name	Fomula	Lifetime[b] (years)	Surface [$n = 8$][c]			PBL [$n = 34$][c]			FT [$n = 49$][c]		
			Mean	σ	Median	Mean	σ	Median	Mean	σ	Median
CFC-12	CCl_2F_2	100	565	8	567	554	10	554	547	12	545
CFC-11	CCl_3F	45	273	13	273	265	13	268	261	12	264
CFC-113	CCl_2FCClF_2	85	82	1	81	80	1	80	79	1	79
CFC-114	$CClF_2CClF_2$	300	16	0.8	16	15	0.5	15	15	0.4	15
HFC-134a	CH_2FCF_3	14	60	14	54	53	7	53	53	9	52
HCFC-22	$CHClF_2$	12	289	90	249	315	63	302	272	41	273
HCFC-142b	CH_3CClF_2	17.9	29	10	25	40	14	37	31	7	29
HCFC-141b	CH_3CCl_2F	9.3	33	10	29	28	3	28	24	3	24
Chloroform	CHCl3	0.41	41	25	33	26	8	24	18	6	17
Methyl chloroform	CH_3CCl_3	5	18	3	17	17	2	17	17	2	16
Carbon tetrachloride	CCl_4	26	101	4	102	99	3	99	96	3	96
Tetrachloroethene	C_2Cl_4	0.27	15	11	9	10	3	10	8	3	7
Trichloroethene	C_2HCl_3	0.01	13	18	7	7	3	7	5	4	4
Methyl chloride	CH_3Cl	1	727	97	745	719	73	726	671	81	660
Methyl bromide	CH_3Br	0.7	13	4	13	13	3	12	12	2	11
Methyl lodide	CH_3I	0.02	2.6	1.8	2.0	1.4	0.5	1.3	0.6	0.4	0.7
1,2-DCE	CH_2ClCH_2Cl	0.19	91	79	55	53	24	57	33	20	27

[a] Units are pptv.
[b] The atmospheric lifetimes are taken from the Scientific Assessment of Ozone Depletion (WMO, 2007).
[c] PBL = Planetary Boundary Layer, FT = Free Troposphere; the number of samples, *n*, is given in brackets.

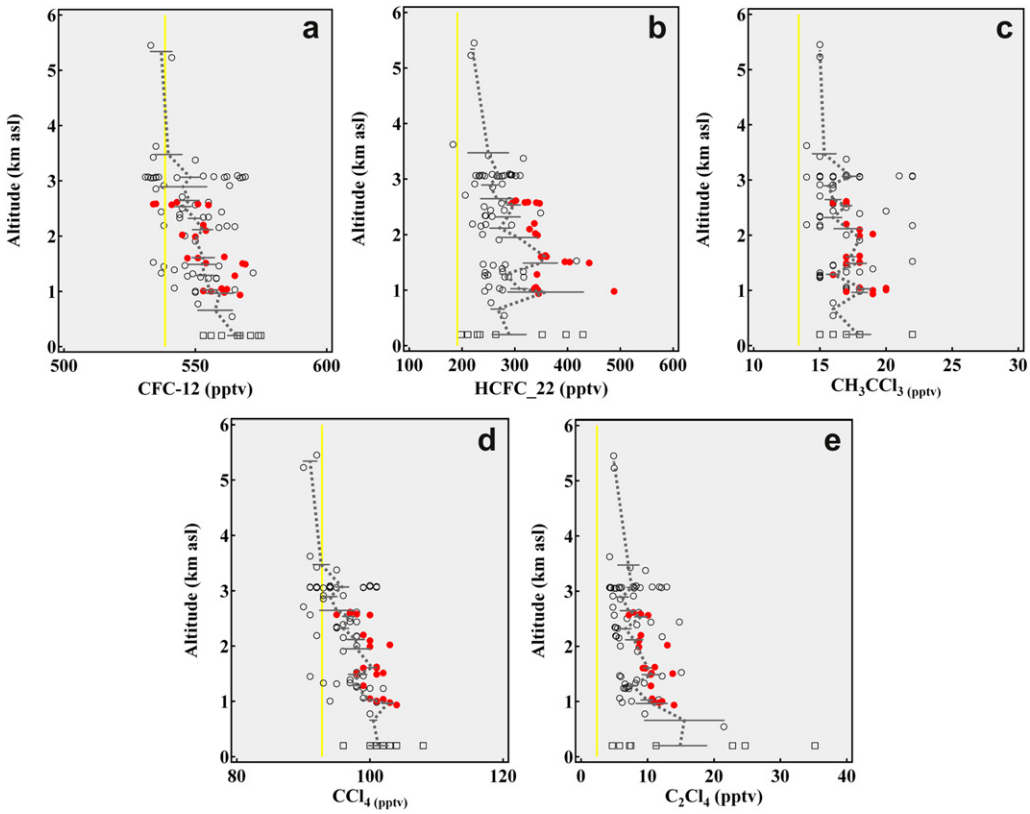

Fig. 3. Vertical profiles of (a) CFC-12, (b) HCFC-22, (c) CH_3CCl_3, (d) CCl_4, and (e) C_2Cl_4 over NE China. The squares at the bottom represent surface samples, and red solid circles indicate the airborne samples collected on June 27 when a highly polluted plume was sampled (Ding et al., 2009). Dashed lines together with error bars indicate the mean values and standard errors for data points in 200-m bins. The yellow lines indicate the Northern Hemispheric background levels (see text for their source). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

compounds exhibited higher levels in the boundary layer than in FT (Table 2), which agrees with our knowledge on the remaining emissions. However, HCFC-22 and HCFC-142b showed higher mixing ratios in the PBL than on the ground level. We examined individually the canister data and found that most samples with elevated HCFC-22 concentrations were collected during the flight on June 27, when a plume from NCP was sampled (Ding et al., 2009; see Fig. 3). The relatively lower mixing ratios of HCFC-142b at the surface may be attributed to the specific sampling locations where there was less emission of this compound.

For other halogenated compounds, general descending vertical profiles were also observed, with the gradients varied with different species. For instance, for relatively short-lived industrial markers chloroform ($CHCl_3$), C_2Cl_4, trichloroethene (C_2HCl_3) and 1,2-DCE, and biofuel/biomass burning tracer CH_3Cl, negative profiles with relatively larger gradients were obtained, suggesting extensive use of these compounds and active biofuel/biomass burning activities in NE China. For CCl_4, a slight declining trend was found. While for other species such as CH_3CCl_3 and CH_3Br, the mixing ratios showed little variation with altitude, indicating success of China in controlling these substances.

3.2. Characteristics of regional plumes

An important aim of this study was to investigate the characteristics of regional air masses transported to NE China from upwind regions, especially the populated NCP. On June 27 a target plume was encountered, with highly elevated concentrations of a variety of air pollutants observed in the free troposphere (Ding et al., 2009). To determine the source region of the collected canister air samples, we computed 72-h backward trajectories using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT, version 4.8; Draxler and Rolph, 2010) with the Global Data Assimilation System (GDAS) meteorological data. Nine FT air samples were identified as representative of "the NCP plume" as the air parcels had passed over the northern part of NCP (i.e. Beijing–Tianjin area) at low altitudes before being sampled (see Fig. 4a). A detailed analysis of the source region and transport mechanism of this plume is given by Ding et al. (2009).

On June 29, we conducted a flight mission near the border between China and North Korea. Weather forecasting analysis suggested that easterly and southeasterly winds would dominate the airflow on that day. The purpose of this flight was to explore the chemical signatures of air masses transported from Korea. Nine canister samples were taken in the free troposphere (i.e. 2600–3100 m a.s.l.) over the border area. Backward trajectories indicated that air masses had moved slowly in the PBL over the Korea peninsula before climbing quickly off the Changbai Mountain and entering NE China (Fig. 4b). Therefore, these samples can be considered as representative of "the Korea plume".

In addition, eight whole air samples were obtained within the boundary layer (<1500 m a.s.l.) around Changchun city during spirals over the base airport during the study period. Changchun is the capital of Jilin province and one of the largest cites in NE China. Such data can provide insights into the pollution features of VOCs over NE China.

Table 3 summarizes the average mixing ratios of major NMHCs and halocarbons measured in the identified regional plumes. To evaluate the enhancement of VOCs in the regional plumes, background VOC levels were estimated based on the FT air samples which

Table 3
Average mixing ratios of major VOCs measured in the regional plumes.[a]

Species	NCP Plume [$n = 9$][b]	Korea plume [$n = 9$][b]	FT[c] background	NEC plumes [$n = 8$][b]	PBL[c] background
Ethane	**1549** (250)	**941** (71)	796	**1756** (467)	891
Ethene	369 (94)	**846** (141)	285	**1583** (634)	633
Ethyne	**1088** (210)	**813** (58)	269	**1433** (595)	570
Propane	**443** (127)	**240** (52)	99	**728** (373)	156
Propene	74 (17)	**176** (35)	63	**325** (124)	131
i-butane	**115** (28)	**40** (11)	11	**266** (202)	23
n-butane	**136** (32)	**67** (16)	17	**294** (169)	32
i-pentane	**108** (35)	**32** (13)	10	**256** (172)	21
n-pentane	**47** (7)	**24** (5)	9	**116** (71)	19
Benzene	**410** (112)	**304** (163)	80	**553** (304)	161
Toluene	**1929** (331)	**790** (265)	500	**917** (480)	692
CFC-12	**550** (8)	**562** (6)	534	**560** (7)	545
CFC-11	**268** (8)	**270** (7)	244	261 (16)	264
CFC-113	79.7 (0.5)	80.7 (0.9)	78.4	80.3 (1.0)	79.0
CFC-114	15.3 (0.2)	15.4 (0.2)	14.6	15.2 (0.5)	15.2
HFC-134a	**51.6** (2.3)	**55.3** (3.4)	43.6	48.9 (6.5)	53.0
HCFC-22	**341** (18)	**285** (15)	220	**286** (21)	257
HCFC-142b	**44.9** (2.1)	**29.7** (1.3)	24.3	**36.9** (13.0)	28.0
HCFC-141b	**25.6** (2.9)	**27.7** (2.1)	20.8	26.3 (2.0)	24.0
$CHCl_3$	**23.9** (3.2)	**21.9** (4.1)	11.8	**28.3** (11.4)	16.0
CH_3CCl_3	17.3 (0.5)	18.7 (2.6)	14.7	15.9 (0.8)	16.0
CCl_4	**99** (1)	**99** (2)	91	**100** (2)	95
C_2HCl_3	**5.9** (1.1)	**10.3** (4.8)	1.1	**7.4** (4.1)	3.2
C_2Cl_4	**9.3** (0.9)	**9.6** (2.0)	4.7	**10.6** (4.9)	5.9
CH_3Cl	**751** (54)	**735** (52)	568	**706** (51)	654
CH_3Br	**12.1** (0.9)	**13.7** (2.5)	8.9	13.6 (2.6)	11.0
1,2-DCE	**63.1** (13.0)	**36.8** (10.1)	13.6	**53.0** (20.3)	22.0

[a] Units are pptv; standard deviations are given in parentheses. Mixing ratios enhanced with respect to the background are given in bold.
[b] NCP = North China Plain; NEC = Northeast China; the number of samples, n, is given in brackets.
[c] The PBL background was calculated as the median values of FT samples excluding those collected in the NCP plume the FT background levels were calculated as the averages of the lowest 25th percentile of the FT samples not influenced by the NCP pollution.

were considered to be less impacted by local emissions. Regional background for the PBL air was calculated as the median of the FT samples excluding those collected in the NCP plume on June 27, while the FT background was computed as the average of the lowest 25th percentile of the FT samples not influenced by the NCP pollution. Many species were significantly enhanced in these plumes with respect to the respective background air. These compounds include most NMHCs, selected CFCs and HCFCs (e.g. CFC-12, HCFC-22 and HCFC-142b), and some combustion and industry related halides (e.g. CH_3Cl, $CHCl_3$, CCl_4, C_2Cl_4, C_2HCl_3, and 1,2-DCE), highlighting the anthropogenic influence within these regional air masses.

Air masses that transported over large distances have undergone extensive mixing and dilution, thus the absolute mixing ratios in the pollution plumes give little information on the VOC profiles at the source regions. Enhancement ratios (ER) of VOCs with respect to relatively inert tracer such as ethyne are usually used to extract the emission profiles of the source regions (Suthawaree et al., 2010). The ER of species X relative to ethyne is given as

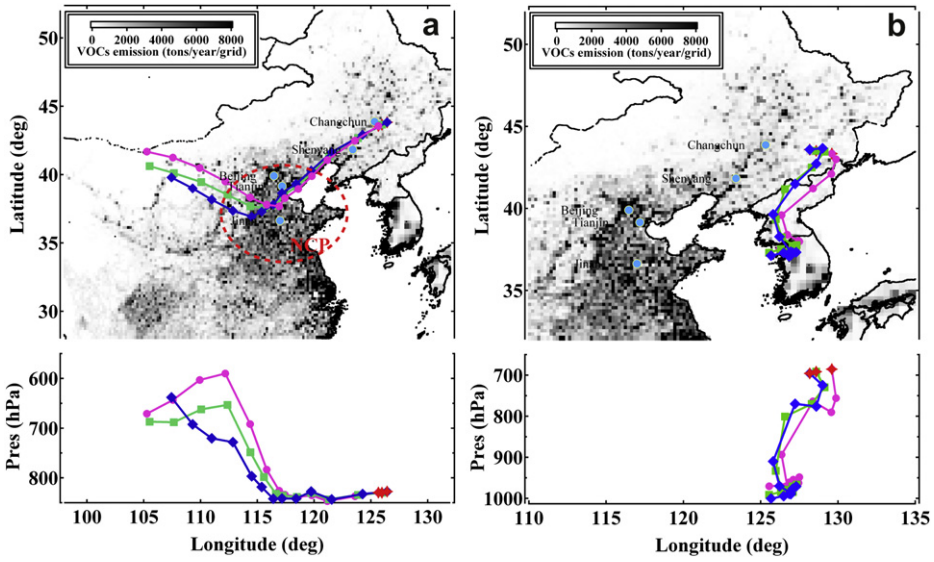

Fig. 4. 72-h backward trajectories of VOC samples representative of (a) NCP plume and (b) Korea plume. The circles on the trajectories indicate 6-h intervals. The colors of trajectories indicate different samples. The NMVOC emission data was obtained from Zhang et al. (2009). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

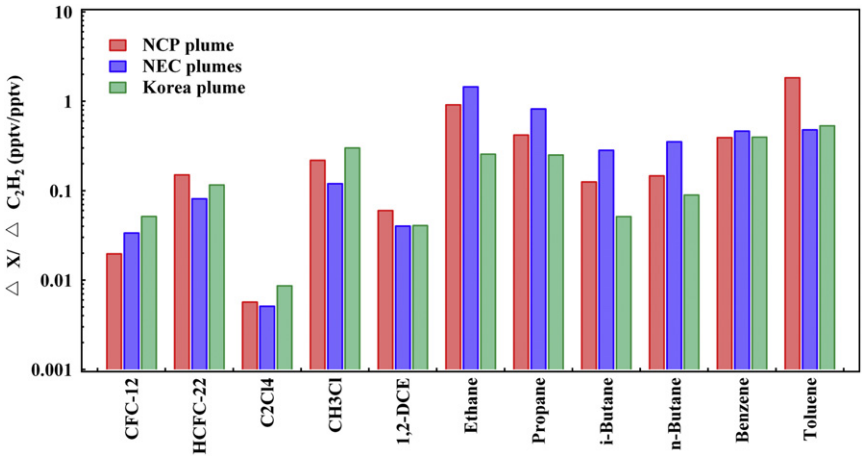

Fig. 5. VOC profiles normalized by ethyne for the regional plumes sampled over NE China.

$$\mathrm{ER(X)} = \frac{\Delta[\mathrm{X}]}{\Delta[\mathrm{C_2H_2}]} = \frac{[\mathrm{X}]_{\mathrm{ambient}} - [\mathrm{X}]_{\mathrm{background}}}{[\mathrm{C_2H_2}]_{\mathrm{ambient}} - [\mathrm{C_2H_2}]_{\mathrm{background}}}$$

where brackets indicate mixing ratios. Fig. 5 shows the normalized profiles of relatively long-lived VOCs by ethyne for the regional plumes. The three regional plumes showed varied VOC profiles, indicating different characteristics of VOC emissions in the source regions. The NCP plume contained relatively high levels of HCFC-22, 1,2-DCE, and toluene, while regional air masses from NE China had larger loadings of ethane, propane and butanes. In comparison, the Korea plume showed the highest ER values for CFC-12, C_2Cl_4, and CH_3Cl. Benzene has similar emission sources (i.e. incomplete combustion of fossil fuel and biomass) and also atmospheric lifetimes to ethyne. The ERs of Δbenzene/ΔC_2H_2 ($\pm$SD) for the regional plumes from NCP, NE China and Korea were 0.40 ($\pm$0.05), 0.47 ($\pm$0.16) and 0.41 ($\pm$0.27), respectively. These values are slightly higher than that observed at Mt. Tai (0.34) in NCP (Suthawaree et al., 2010), and also higher than those measured for urban emissions of Boston/New York (0.19–0.21) and 39 U.S. cities ($\sim$0.33) (Warneke et al., 2007 and references therein).

CH_3Cl is commonly used as a biomass/biofuel burning tracer, and the ER of CH_3Cl with respect to CO ($\Delta CH_3Cl/\Delta CO$) is usually used to elucidate the influence of biomass burning (Blake et al., 2003). Based on the emission factors summarized by Andreae and Merlet (2001), the emission ratios of CH_3Cl/CO were found to be in the magnitude of $\sim$0.62, $\sim$0.27 and $\sim$1.39 for the burning of savanna and grassland, biofuel and agricultural residues, respectively. According to an up-to-date compilation of emission factors for open and domestic biomass burning (Akaji et al., 2011), the CH_3Cl/CO emission ratio was calculated to be $\sim$0.47 for savanna fires. Suthawaree et al. (2010) reported a $\Delta CH_3Cl/\Delta CO$ ratio of 1.88 ($\pm$1.16) for the air masses influenced by the burning of agricultural residues in central eastern China. In the present study, the average $\Delta CH_3Cl/\Delta CO$ ratios ($\pm$SD) were calculated as 0.58 ($\pm$0.20), 0.35 ($\pm$0.36) and 2.08 ($\pm$1.39) for the regional plumes originating from NCP, NE China and Korea. These results implied that agricultural residue burning should be an important source of VOCs in Korea peninsula, while biofuel combustion may be more important in NE China. As there is little grassland vegetation in NCP, the NCP plume should have captured reasonably well a mixture of biofuel combustion and agricultural residue burning.

3.3. Long-term changes of halocarbons in the free troposphere around China: comparison with previous aircraft measurements

To better understand long-term trends of halocarbons in the FT above China, we compared several halocarbons with earlier measurement data collected from the PEM-West B and TRACE-P aircraft missions. PEM-West B occurred in February–March 1994, while TRACE-P took place in February–April 2001. Both campaigns were conducted over the western rim of the Pacific Ocean, closely downwind of China, and aimed to characterize the composition, transport, and chemical transformation of Asian continental outflow (Hoell et al., 1997; Jacob et al., 2003). For the comparison, we bear in mind that the survey domain in the present study is located exactly over the polluted continental regions. That means if there was no decrease of emissions over the period of 2001–2007, the mixing ratios observed in the current study should be definitely higher than those obtained from TRACE-P. It's also worth noting that the three aircraft campaigns were based on short periods of intensive sampling and limited samples, and thus the results only provide "snapshots" of the sampling domain. Finally, since some halocarbon species exhibit a pronounced latitudinal distribution, we only selected a subset of PEM-West B and TRACE-P data (i.e. 40–47.5° N, 2–8 km a.s.l.) for the comparison. The comparison of free tropospheric mixing ratios of selected halocarbons is given in Table 4.

Under the Montreal Protocol, the production and use of CFCs have been largely reduced in China in the past decade. For example, according to Wan et al. (2009), emissions of CFC-12 have been reduced by approximately 75% and 87% in 2001 and 2007, respectively, as compared to the 1995 base level. However, this is not reflected in the atmospheric mixing ratios obtained from the three aircraft measurement campaigns. The average mixing ratio of CFC-12 measured over NE China in 2007 (547 $\pm$ 11 pptv) was even higher than those obtained from TRACE-P (535 pptv) and PEM-West B (525 pptv). As for CFC-11, the mean value observed during this study (261 $\pm$ 12 pptv) was lower than that of PEM-West B (274 pptv), but comparable to that detected from TRACE-P (259 pptv). In comparison, over the 6-year interval between TRACE-P and our study, the Northern Hemispheric background levels of CFC-12 and CFC-11 decreased by approximately 5 and 14 pptv (*CFC-12 and CFC-11 data from the NOAA/ESRL halocarbons in-situ program*). The relatively higher levels of CFCs recorded in 2007 may be due to the fact that our aircraft sampled air directly over the NE China continent, where CFC emissions from materials in storage remained (see Section 3.1.2).

CH_3CCl_3 is commonly used as metal degreasing agent and in some other industrial applications (Blake et al., 2003). The Montreal protocol has since required developed countries to phase out the production of CH_3CCl_3, and developing countries to freeze the emissions in 2003 and finally phase it out by 2015 (UNEP, 1991). As its lifetime is relatively short compared to other ozone-depleting

Table 4
Comparison of free tropospheric mixing ratios of selected halocarbons measured during this study and previous aircraft measurement campaigns.[a]

Species	Lifetime (years)	This study, 2007 summer (2–6 km)	TRACE-P[b], 2001 spring (40° N–47.5° N; 2–8 km)	PEM-West B[b], 1994 spring (40° N–47.5° N; 2–8 km)	Background[c], 2007 summer Northern Hemisphere
CFC-12	100	547 (11)	535	525	539
CFC-11	45	261 (12)	259	274	248
CH_3CCl_3	5	17 (2)	41	128	13.4
CCl_4	26	96 (17)	99	107	93
C_2Cl_4	0.27	7.9 (6.7)	10.6	19.2	2.4

[a] Units are pptv. Standard deviation is given in parentheses for this study.
[b] Data from Blake et al. (2003).
[c] Background values of CFC-12, CFC-11, CH_3CCl_3 and CCl_4 are from the measurements of NOAA/ESRL halocarbons in-situ program in June–July 2007, while the background concentration of C_2Cl_4 is from the INTEX-B aircraft measurements in 2006 spring (Barletta et al., 2009).

halocarbons (~5 years), the atmospheric burden of CH_3CCl_3 has been rapidly declining in response to the Montreal protocol (Romashkin et al., 1999). The mixing ratios measured from TRACE-P (mean = 41 pptv) were only ~1/3 of those recorded during PEM-West B (mean = 128 pptv) (Blake et al., 2003). During the present study, substantially lower levels of CH_3CCl_3 (mean = 17 (±2) pptv) were measured over NE China, indicating the continuing decrease of CH_3CCl_3 in the atmosphere over the great northwestern Pacific region. Furthermore, comparable values were also observed in the boundary layer (mean = 17 pptv) and at the surface (mean = 18 pptv). These results demonstrated the accomplishment of China in regulating CH_3CCl_3 emissions.

Similar trends were also found for CCl_4 and C_2Cl_4. The main use of CCl_4 is as a feedstock to produce CFCs (Barletta et al., 2006). With the phase out of CFCs under regulation of the Montreal protocol, the global atmospheric mixing ratio of CCl_4 has been declining since 1990s (Prinn et al., 2000). From PEM-West B (1994) to TRACE-P (2001), a decrease of ~9 pptv in the CCl_4 mixing ratios was measured (Blake et al., 2003). In 2007, the CCl_4 levels in the free troposphere over NE China (mean = 96 (±17) pptv) were slightly lower than those observed from TRACE-P (mean = 99 pptv), even though the aircraft sampling was conducted immediately over the continental source region. By comparison, UCI's global trace gas monitoring data suggests a global CCl_4 decline of approximately 5 pptv between 2001 and 2007 (D. R. Blake, personal communication). Together these results suggest a continuous decreasing trend of CCl_4 in the atmosphere over this region, and also provide indirect evidence to the banning of CFC production in China. However, the slight decreasing with altitude vertical profile also indicates small levels of CCl_4 emissions still appear to exist in NE China (Fig. 3d).

C_2Cl_4 is primarily used as a dry cleaning solvent and metal degreasing agent, and has been well known as a useful tracer for urban/industrial activities (Wang et al., 1995). Simpson et al. (2004) have reported a notable decline in the global atmospheric burden of C_2Cl_4 based on the long-term measurements at the remote Pacific sites from 1989 to 2002. Consistent with this, the mean C_2Cl_4 mixing ratio measured during TRACE-P was 10.6 pptv, which was substantially lower than 19.2 pptv recorded during PEM-West B (Blake et al., 2003). In the present study, the mean C_2Cl_4 level in the FT over continental NE China was even smaller at 7.9 (±6.7) pptv. The results indicated the persistent reduction of atmospheric C_2Cl_4 levels over the China-NW Pacific region. However, several samples with significantly elevated levels of C_2Cl_4 (>20 pptv) were also collected both at the surface and in the PBL (see Fig. 3e), indicating the remaining occasional use of C_2Cl_4 in NE China.

4. Summary

Whole air samples were collected during an intensive aircraft study over Jilin province in NE China in summer 2007. NMHC and halocarbon data were analyzed to investigate the vertical distributions, characteristics of regional plumes, and long-term changes of halocarbons in the free troposphere over the great China–NW Pacific region.

Almost all of the NMHCs exhibited a vertical profile of decreasing mixing ratios with the height. Most halocarbons also displayed a negative vertical trend, although the gradients varied with different species. Some halocarbons, such as CFC-12, HCFC-22, CH_3CCl_3, CCl_4 and C_2Cl_4, were somewhat enhanced over NE China compared to the Northern Hemispheric background levels. Three types of regional air masses transported from NCP, Korea and NE China were identified, and were characterized by comparing the VOC profiles normalized by ethyne. The plume transported from northern NCP had relatively high levels of HCFC-22, 1,2-DCE and toluene, while air masses representative of NE China air pollution contained higher abundances of ethane, propane and butanes. The plume from Korea contained more abundant CFC-12, C_2Cl_4 and CH_3Cl.

To derive the long-term changes of ozone-depleting halocarbons over China, the free tropospheric mixing ratios of selected halocarbon compounds were compared with earlier measurements from the PEM-West B and TRACE-P aircraft campaigns. The results verified the continuing declining trends in the atmospheric mixing ratios of CH_3CCl_3, CCl_4, and C_2Cl_4, demonstrating the achievements of China in regulating these halogenated compounds, though with some remaining CCl_4 and C_2Cl_4 emissions. The study also provided evidence of continuing emissions of CFCs (from materials in stock), $CHCl_3$ and 1,2-DCE in NE China by 2007.

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