

Eastern Asian emissions of anthropogenic halocarbons deduced from aircraft concentration data

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Abstract. The Montreal Protocol restricts production of ozone-depleting halocarbons worldwide. Enforcement of the protocol has relied mainly on annual government statistics of production and consumption of these compounds (bottom-up approach). We show here that aircraft observations of halocarbon:CO enhancement ratios on regional to continental scales can be used to infer halocarbon emissions, providing independent verification of the bottom-up approach. We apply this top-down approach to aircraft observations of Asian outflow from the TRACE-P mission over the western Pacific (March–April 2001) and derive emissions from eastern Asia (China, Japan, and Korea). We derive an eastern Asian carbon tetrachloride (CCl_4) source of 21.5 Gg yr^{-1} , several-fold larger than previous estimates and amounting to $\simeq 30\%$ of the global budget for this gas. Our emission estimate for CFC-11 from eastern Asia is 50% higher than inventories derived from manufacturing records. Our emission estimates for methyl chloroform (CH_3CCl_3) and CFC-12 are in agreement with existing inventories. For halon 1211 we find only a strong local source originating from the Shanghai area. Our emission estimates for the above gases result in a $\simeq 40\%$ increase in the ozone depletion potential (ODP) of Asian emissions relative to previous estimates, corresponding to a $\simeq 10\%$ global increase in ODP.

Introduction

The role of halocarbons in the destruction of stratospheric ozone is well established [WMO/UNEP, 1999]. The 1987 Montreal Protocol and later amendments lay out a schedule to ultimately cease the production of these compounds. Monitoring compliance with such a protocol is difficult. Traditional approaches have relied on bottom-up emission inventories derived from annual government records of production and consumption [UNEP, 2002]. These approaches are becoming increasingly uncertain as leakage from existing stockpiles, and possibly unreported production, progressively represent a larger relative contribution to the atmospheric burden of these compounds. We show here that aircraft observations of halocarbon concentrations provide new top-down constraints for monitoring anthropogenic halocarbon emissions.

We focus on eastern Asia, a region where halocarbon emissions are particularly uncertain, by using measurements of halocarbons and CO in Asian outflow from the NASA TRACE-P two-aircraft mission in March–April 2001 [Jacob *et al.*, 2003]. The aircraft operated out of Hong Kong and Japan, providing considerable geographical coverage of the Asian outflow (Figure 1). Boundary layer flights (0–2 km) sampled fresh continental outflow. We use observed relationships between halocarbons and CO to determine the corresponding halocarbon emissions. Sources of CO from fuel consumption (fossil fuel and biofuel) are relatively well known and are in general collocated with the halocarbon sources. Loss of CO is by oxidation by OH, resulting in an atmospheric lifetime of a few months. The TRACE-P data have been used previously to evaluate and refine regional CO source estimates in eastern Asia [Carmichael

Figure 1

et al., 2003; *Heald et al.*, 2003; *Palmer et al.*, 2003; *Streets et al.*, 2003]. Provided that there is a strong correlation between CO and a particular halocarbon, one can infer the halocarbon emission from the halocarbon:CO relationship.

Methyl chloroform (CH_3CCl_3) is a halocarbon of particular interest even though it plays a relatively minor role in stratospheric ozone depletion. It is used extensively as the standard proxy for the hydroxyl radical (OH), the main atmospheric oxidant for many environmentally important gases. Long-term surface air measurements of CH_3CCl_3 concentration have been used to infer the global mean OH concentration and its trend [*Spivakovsky et al.*, 1990; *Spivakovsky et al.*, 2000; *Krol et al.*, 1998; *Montzka et al.*, 2000; *Prinn et al.*, 2001]. This requires accurate knowledge of CH_3CCl_3 emissions. Recent studies have attempted to determine emissions of CH_3CCl_3 from Europe and North America using the CH_3CCl_3 :CO correlation in long-term surface data sets [*Barnes et al.*, 2003] or by using an *ad hoc* inverse method to minimize the discrepancy between aircraft CH_3CCl_3 concentration data and modeled values [*Krol et al.*, 2003]. These studies find a significant source of CH_3CCl_3 from Europe and North America, casting doubt on studies of trends in the oxidizing capacity of the atmosphere that rely on government reports of zero emissions in these regions [*Prinn et al.*, 2001].

In the next section we use observations of CH_3CCl_3 to illustrate the general method used to determine emissions of halocarbons from measurements of atmospheric concentration. Then in the following sections we apply this methodology to carbon tetrachloride, halon 1211, and CFCs 11 and 12. We conclude the paper by discussing the implications of our results for the ozone depletion potential (ODP) of Asian emissions.

Methyl Chloroform (CH_3CCl_3)

The Montreal Protocol called for a total ban on the production and sales of CH_3CCl_3 in developed countries by 1996. Beginning in 2003, the first in a series of restrictions on consumption in developing countries takes effect. Prior to the Montreal Protocol, accurate emission estimates of CH_3CCl_3 were calculated from manufacturers' records of production and sales [Midgley and McCulloch, 1995; McCulloch and Midgley, 2001]. Now, however, emissions from developed countries are generally thought to represent slow release from legal stockpiles accumulated prior to the ban [Krol *et al.*, 2003].

We use boundary layer (0–2 km) aircraft observations taken directly downwind of the Asian continent during the TRACE-P mission. Outflow of CO below 2 km during TRACE-P was mainly anthropogenic, with minimal contribution from biomass burning [Liu *et al.*, 2003]. Analysis of five-day kinematic back-trajectories [Fuelberg *et al.*, 2003] for the highest 5% (≥ 45.9 pptv) of CH_3CCl_3 concentrations shows that they originate from South Korea and from the area around Shanghai (Figure 2).

Figure 2

CH_3CCl_3 and CO both have background latitudinal gradients, reflecting their sources at northern mid-latitudes and the higher OH concentrations in the tropics. We remove the influence of these gradients on the CH_3CCl_3 :CO relationship by subtracting background values (defined as the 20th percentile) for each 5° increment of latitude. Measurements with this background removed are denoted by Δ . Background concentrations of CH_3CCl_3 and CO over the latitude range $12\text{--}43^\circ\text{N}$ vary from 39.2 to 41.6 pptv and from 102.8 to 280.3 ppbv, respectively. We further remove statistical outliers (≥ 95 th percentile of CH_3CCl_3 and CO) so that our derived

emissions are not influenced by specific plumes but are more representative of the region. There is a statistically significant relationship between $\Delta\text{CH}_3\text{CCl}_3$ and ΔCO for the ensemble of the data (Figure 3). Table 1 gives a summary of correlation statistics.

Figure 3

Table 1

We use a bottom-up emission inventory for anthropogenic CO in eastern Asia customized for the TRACE-P period [Streets *et al.*, 2003] and refined with a formal inverse model analysis constrained by the TRACE-P CO observations [Palmer *et al.*, 2003]. The resulting *a posteriori* anthropogenic emissions from China (168 Tg CO yr⁻¹) are approximately 50% greater than the *a priori* values from [Streets *et al.*, 2003]. *A posteriori* emissions for Korea and Japan combined are not significantly higher than the *a priori* so that the *a priori* estimates are retained here (8.5 Tg CO yr⁻¹ for Korea and 9.3 Tg CO yr⁻¹ for Japan). Combining information about $\Delta\text{CH}_3\text{CCl}_3:\Delta\text{CO}$ (0.016 pptv/ppbv) calculated for the ensemble of the data (Figure 3) with the anthropogenic CO emission estimate for eastern Asia leads to a CH_3CCl_3 emission estimate for eastern Asia of 14.2 Gg yr⁻¹.

We further refine this emission estimate for eastern Asia by disaggregating contributions from China (CH), Japan (JP), and Korea (KR), using five-day kinematic back-trajectories to classify the origin of the sampled air masses. We consider only observations whose back-trajectories pass over countries at altitudes below 850 hPa. Most air masses (44%) originate from mainland China. There are instances when air passes over more than one country, which we take into account by including the additional classifications of CHKR, CHJP, and KRJP, and instances when air originates from the marine boundary layer (10% of all back-trajectories) with values typical of the global background.

Combining the $\Delta\text{CH}_3\text{CCl}_3:\Delta\text{CO}$ slope for China (0.013 pptv/ppbv; Figure 3) with the CO

emission estimate for China leads to a CH_3CCl_3 emission of 10.4 Gg yr^{-1} for that country. The $\Delta\text{CH}_3\text{CCl}_3:\Delta\text{CO}$ slopes for air masses originating from Japan (0.023 pptv/ppbv) and Korea (0.044 pptv/ppbv) are much higher than for China. From these slopes we estimate CH_3CCl_3 emissions of 1.0 Gg yr^{-1} for Japan and 1.8 Gg yr^{-1} for Korea. The $\Delta\text{CH}_3\text{CCl}_3:\Delta\text{CO}$ slopes for air masses that pass over more than one country (Figure 3) are intermediate and consistent with the values derived above. The relatively weak $\Delta\text{CH}_3\text{CCl}_3:\Delta\text{CO}$ correlation for air masses originating from Japan (Table 1) means that our corresponding emission estimate is highly uncertain.

Estimated uncertainties on our halocarbon emission estimates are given in Table 2.

Table 2

Quantifying these uncertainties is difficult. *Streets et al.* [2003] estimate uncertainties of 78% for their anthropogenic CO emissions from China, 42% for Korea, and 17% for Japan. The inverse model of *Palmer et al.* [2003] reduced these uncertainties, in particular for China, but the *a posteriori* error statistics from this analysis (typically $<5\%$) likely underestimate the actual uncertainty. We assume here an uncertainty of 20% for the regional and national CO emissions in eastern Asia. Uncertainties on the halocarbon:CO slopes (Table 1) are calculated in the standard way by assuming the linear model. There are additional errors associated with this assumption that we do not take into account. As a result, the uncertainties given in Table 2 are likely too low.

Our CH_3CCl_3 emission estimate for eastern Asia in 2001 is in good agreement with emission estimates for the ‘Far East’ (11 Gg yr^{-1}) [*McCulloch and Midgley, 2001*] constructed by extrapolating government data from the United Nations for the late 1990s (12.5 Gg yr^{-1}) [*UNEP, 2002*]. However, our CH_3CCl_3 emission estimates for individual countries are

substantially different. Past studies have assumed zero emissions from Japan in recent years, with emissions from eastern Asia due mainly to China and Korea [McCulloch and Midgley, 2001]. The value we report for China during 2001 is 40% larger than the value given by UNEP [2002]. The UN estimate [UNEP, 2002] for Korean emissions of CH_3CCl_3 is 6 Gg yr^{-1} .

Carbon Tetrachloride (CCl_4)

Emissions of CCl_4 originate primarily from its use as a chemical feedstock for the production of CFC-11. The Montreal Protocol called for a total ban of this gas in developed countries by 1996, while restrictions in developing countries are scheduled to start in 2005. The total Asian source of CCl_4 in 1999 according to the UN is 17 Gg yr^{-1} [UNEP, 2002], with India contributing more than 80% to this value. Our $\Delta\text{CCl}_4:\Delta\text{CO}$ relationships for eastern Asia and for individual countries are all highly significant (Table 1). As for CH_3CCl_3 , Δ represents the enhancement above a latitudinally dependent background. Background values of CCl_4 vary from 98.7 to 100.6 pptv over the latitude range $12\text{--}43^\circ\text{N}$. Using the same method as for CH_3CCl_3 , we estimate CCl_4 emissions from eastern Asia of 21.5 Gg yr^{-1} . Five-day kinematic back-trajectories for the TRACE-P period do not pass over India, implying that Indian emissions of CCl_4 do not influence our calculated eastern Asian signal.

Our emission estimate for individual countries, based on the statistics in Table 1, are 17.6 Gg yr^{-1} for China, 2.3 Gg yr^{-1} for Korea, and 1.3 Gg yr^{-1} for Japan. The UN report emissions of 0.1 Gg yr^{-1} for China, 1.3 Gg yr^{-1} for Korea, and 0.1 Gg yr^{-1} for Japan. It appears from our work that the CCl_4 source from China is considerably higher than previous estimates, highlighting serious shortcomings in our knowledge of the sources of this gas.

Bromofluorocarbons

Bromofluorocarbons (halons) are amongst the most effective gases in destroying stratospheric ozone. Emissions of halons from developed countries were banned in 1994, while emissions from developing countries are currently frozen at their values for 1995-1997. Three halons were measured during TRACE-P: halon 1211, halon 1301, and halon 2402. Only halon 1211 (CF_2BrCl) was correlated with CO. Halon 1211 is used as a fire retardant, and China is one of the few countries in the world that still produces this compound. Back-trajectories corresponding to the highest 5% (≥ 6.1 pptv) of halon 1211 concentrations show they originate from the area around Shanghai (Figure 2). Background values of halon 1211 vary from 4.3 to 4.6 pptv over the latitude range $12-43^\circ\text{N}$. We find that by removing the highest 5% of concentration data, in order to obtain a $\Delta\text{halon 1211}:\Delta\text{CO}$ slope more representative of the regional signal, we effectively remove any useful signal that is significantly different from background (0.003 pptv/ppbv). The $\Delta\text{halon 1211}:\Delta\text{CO}$ slope for the highest 5% of concentration data ($n=88$, $r=0.62$) is 0.023 pptv/ppbv, but we cannot adequately constrain the regional source of CO that would be appropriate for scaling to the halon 1211 emission estimate.

Chlorofluorocarbons

Traditional uses for CFCs include air-conditioning, refrigeration, and foam blowing. The Montreal Protocol imposed a total ban on production and consumption of these gases in developed countries in 1996; developing countries are subject to a series of restrictions, beginning in 2003 with a 20% reduction in production and consumption relative to 1998-2000

values. Four CFCs were measured during TRACE-P. We find statistically significant correlations with ΔCO for $\Delta\text{CFC-11}$ (CFCl_3) and $\Delta\text{CFC-12}$ (CF_2Cl_2) (Table 1). Background values for CFC-11 and CFC-12 vary from 259.1 to 264.0 pptv and from 535.0 to 541.0 pptv, respectively over the latitude range 12–43°N.

Eastern Asian emissions of CFC-11 and CFC-12, as derived from $\Delta\text{CFC}:\Delta\text{CO}$ slopes in Table 1 and the regional CO source, are 30.1 Gg yr⁻¹ and 39.4 Gg yr⁻¹, respectively. Chinese, Korean, and Japanese sources are 22.3, 2.9, and 2.3 Gg yr⁻¹, respectively for CFC-11; and 28.3, 3.6, and 3.4 Gg yr⁻¹, respectively for CFC-12. Eastern Asian emissions of CFC-11 calculated from marketing records for 2000 are 17.9 Gg yr⁻¹ [McCulloch *et al.*, 2001], representing 24% of the estimated global source of this gas; contributing emissions from China, Korea, and Japan are 7.2, 2.6, and 8.1 Gg yr⁻¹, respectively. These values are in good agreement with our estimates for Korea but are less than half of our estimates for China and are more than double for Japan. Eastern Asian emissions of CFC-12 derived from sales and production records for 2000 are 37.3 Gg yr⁻¹ [McCulloch *et al.*, 2003], representing 28% of the estimated global source for this gas; emissions from China, Korea, and Japan are 20.3, 5.6, and 11.4 Gg yr⁻¹. These results agree remarkably well with our estimates.

Implications for the Ozone Depletion Potential of Asian Emissions

The ozone depleting potential (ODP) describes the relative strength of a halocarbon gas to destroy stratospheric ozone, defined as the ratio of the net chemical destruction of ozone by a specified mass emitted of that gas to the net ozone destroyed by a similar mass emitted of CFC-11. From the top-down emission estimates in Table 2 we calculate a total ODP-weighted

source for CH_3CCl_3 (ODP=0.1), CCl_4 (ODP=1.1), CFC-11 (ODP=1.0), and CFC-12 (ODP=1.0) from eastern Asia of $94.6 \text{ ODP Gg yr}^{-1}$ for 2001, as compared to $60.0 \text{ ODP Gg yr}^{-1}$ using the previous bottom-up estimates [McCulloch and Midgley, 2001; McCulloch *et al.*, 2001; McCulloch *et al.*, 2003; UNEP, 2002]. Our ODP-weighted emission estimate for the sum of these four gases is 40% higher than previous estimates, corresponding to a $\simeq 10\%$ increase in their global ODP-weighted emissions, using published global emission estimates in Table 2 [McCulloch and Midgley, 2001; McCulloch *et al.*, 2001; McCulloch *et al.*, 2003; Simmonds *et al.*, 1998]. This global relative increase in ODP is likely a conservative estimate, owing to our use of 1995 data for the global CCl_4 emissions [Simmonds *et al.*, 1998] in the absence of more recent data (long-term trend of concentration measurements suggests that present-day global emissions are lower than 1995 emissions [Montzka *et al.*, 1999]). These four halocarbons were estimated to account for $\simeq 70\%$ of the total global ODP in 1995 [WMO/UNEP, 1999].

The method we have used to construct regional-scale emission inventories of anthropogenic halocarbons from aircraft concentration data in continental outflow does not rely on government records, and therefore can be used as an independent test of reported values for production or consumption. It has general application to monitor the magnitude and trends of emissions of a wide range of environmentally important gases.

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Figure Captions

Figure 1. Geographical distributions of **A** CH_3CCl_3 , **B** CCl_4 , **C** halon 1211, **D** CFC-11, **E** CFC-12, and **F** CO concentrations measured in the boundary layer (0–2 km) during the TRACE-P aircraft campaign (March-April 2001). Further details about the measurement of halocarbons and CO can be found in *Blake et al.* [1996] and *Sachse et al.* [1987], respectively.

Figure 2. Five-day kinematic back-trajectories indicate the origin of the highest five percent of **A** CH_3CCl_3 and **B** halon 1211 concentrations measured in the boundary layer (0–2 km) during the TRACE-P aircraft campaign (March-April 2001). Open squares represent the measurement locations and open circles along the back-trajectories denote 12-hour increments.

Figure 3. Reduced Major Axis Regression (RMAR) [*Hirsch and Gilroy*, 1984] of CH_3CCl_3 and CO enhancements over their background values ($\Delta\text{CH}_3\text{CCl}_3$ and ΔCO) for aircraft observations at 0–2 km altitude off the Asian Pacific rim during March–April 2001. **A** All available data. Green circles denote the ≥ 95 th percentiles of CH_3CCl_3 and CO concentrations, which are removed from the RMAR calculations. **B**, **C**, **D** Air masses originating from China (CH), Korea (KR), and Japan (JP), and of mixed China-Korea (CHKR), Korea-Japan (KRJP), and China-Japan (CHJP) origins.

Table 1. Halocarbon:CO relationships [10^{-3} pptv/ppbv] measured in Asian outflow during TRACE-P^a

Halocarbon X	Eastern Asia			China			Korea			Japan		
	n^b	r^c	$\Delta X:\Delta CO^d$	n	r	$\Delta X:\Delta CO$	n	r	$\Delta X:\Delta CO$	n	r	$\Delta X:\Delta CO$
CH ₃ CCl ₃	618	0.55	16±0.48 ^e	247	0.66	13±0.65	32	0.63	44±6.2	100	0.34	23±2.1
CCl ₄	620	0.60	21±0.63	239	0.64	19±0.95	36	0.59	50±6.5	101	0.47	25±2.3
CFC-11	611	0.46	33±1.7	238	0.46	27±1.62	34	0.56	69±9.7	98	0.56	50±4.0
CFC-12	613	0.38	49±2.5	246	0.43	39±2.34	33	0.56	99±16.8	97	0.44	83±7.5

^aStatistics are for the ensemble of data collected in boundary layer outflow (below 2 km) after removal of the latitudinal background (defined as the 20th percentile of the observations and denoted by Δ) and exclusion of the top 5th percentile, as described in the text for CH₃CCl₃. Kinematic back-trajectories are used to identify the source region. “Eastern Asia” refers to the continental domain of Figure 1, including China, Korea, and Japan.

^b n is the number of 1-minute average measurements used in the regression analysis.

^c r is the Pearson correlation coefficient of $\Delta X:\Delta CO$.

^dReduced Major Axis Regression slopes [10^{-3} pptv/ppbv].

^eSlope uncertainties are calculated by assuming the linear model.

Table 2. Bottom-up and top-down halocarbon emission estimates (Gg yr^{-1}) for eastern Asia.^a

	CH_3CCl_3		CCl_4		CFC-11		CFC-12	
	(ODP = 0.1)		(ODP = 1.1)		(ODP = 1.0)		(ODP = 1.0)	
	Bottom-up	Top-down	Bottom-up	Top-down	Bottom-up ^e	Top-down	Bottom-up ^f	Top-down
China	6.5 ^b	10.4±2.6	0.1 ^b	17.6±4.4	7.2	22.3±5.8	20.3	28.3±7.4
Japan	0.0 ^b	1.0±0.3	0.1 ^b	1.3±0.4	2.6	2.3±0.6	5.6	3.4±1.0
Korea	6.0 ^b	1.8±0.6	1.3 ^b	2.3±0.8	8.1	2.9±1.0	11.4	3.6±1.4
Eastern Asia	11 ^b –12.5 ^c	14.2±3.3	1.5 ^b	21.5±5.0	17.9	30.1±7.2	37.3	39.4±9.5
Global	19.7 ^c	19.6–26.2 ^g	47.0 ^d	62.0–72.0 ^g	74.6	79.6–94.0 ^g	132.9	125.5–144.5 ^g

^aBottom-up estimates rely on government reports of production and consumption. Top-down estimates are computed here using $\Delta\text{halocarbon}:\Delta\text{CO}$ relationships measured in Asian outflow during March–April 2001 (Table 1) and a top-down emission estimate of CO derived for the same period [Palmer *et al.*, 2003]. Anthropogenic emissions of halocarbons are aseasonal so we can use this methodology to quantify annual mean emissions from eastern Asia.

^bValue based on estimated consumption during 1999 [UNEP, 2002].

^cValue based on estimated emissions from 2001 [McCulloch and Midgley, 2001].

^dValue based on estimated emissions from 1995 [Simmonds *et al.*, 1998].

^eValue based on estimated emissions from 2000 [McCulloch *et al.*, 2001].

^fValue based on estimated emissions from 2000 [McCulloch *et al.*, 2003].

^gTop-down global emissions are estimated by taking the difference between bottom-up and top-down regional emission estimates for eastern Asia and adding it to the bottom-up global emission estimate.

Figures

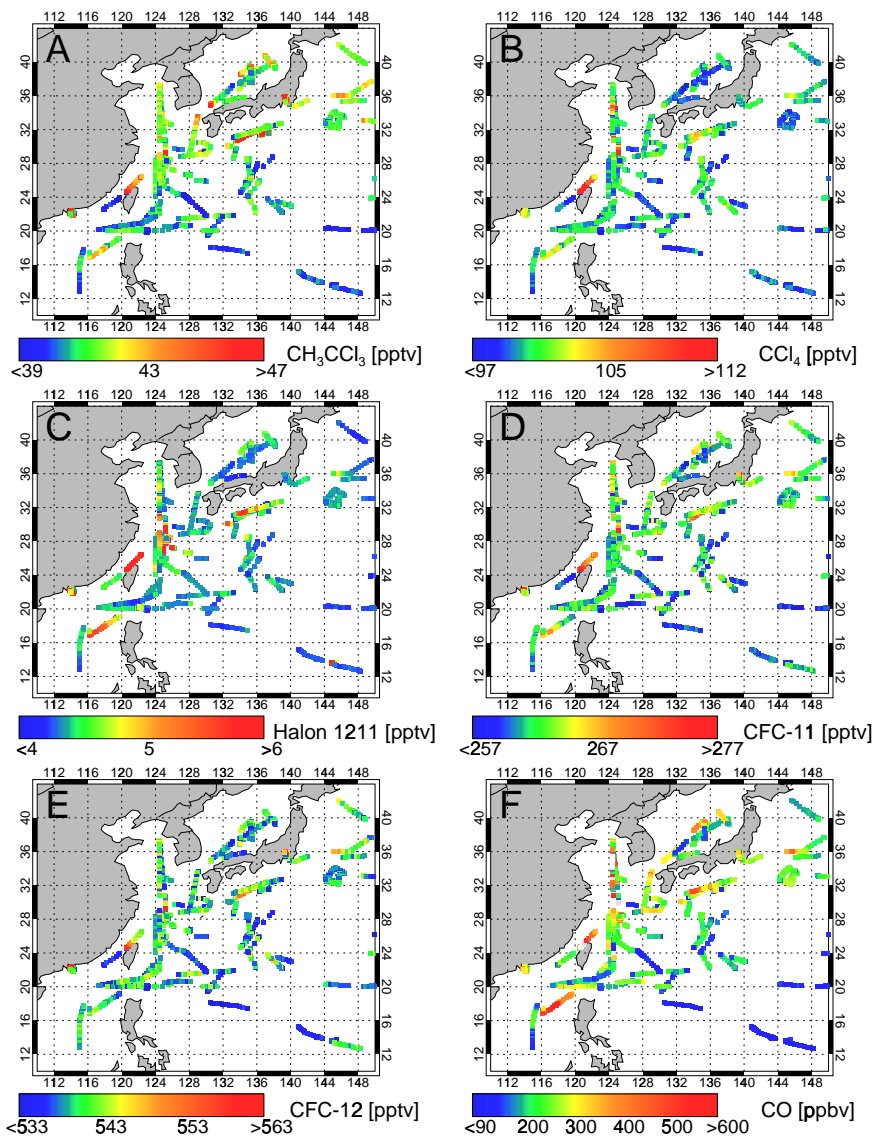


Figure 1. Geographical distributions of **A** CH_3CCl_3 , **B** CCl_4 , **C** halon 1211, **D** CFC-11, **E** CFC-12, and **F** CO concentrations measured in the boundary layer (0–2 km) during the TRACE-P aircraft campaign (March–April 2001). Further details about the measurement of halocarbons and CO can be found in *Blake et al.* [1996] and *Sachse et al.* [1987], respectively.

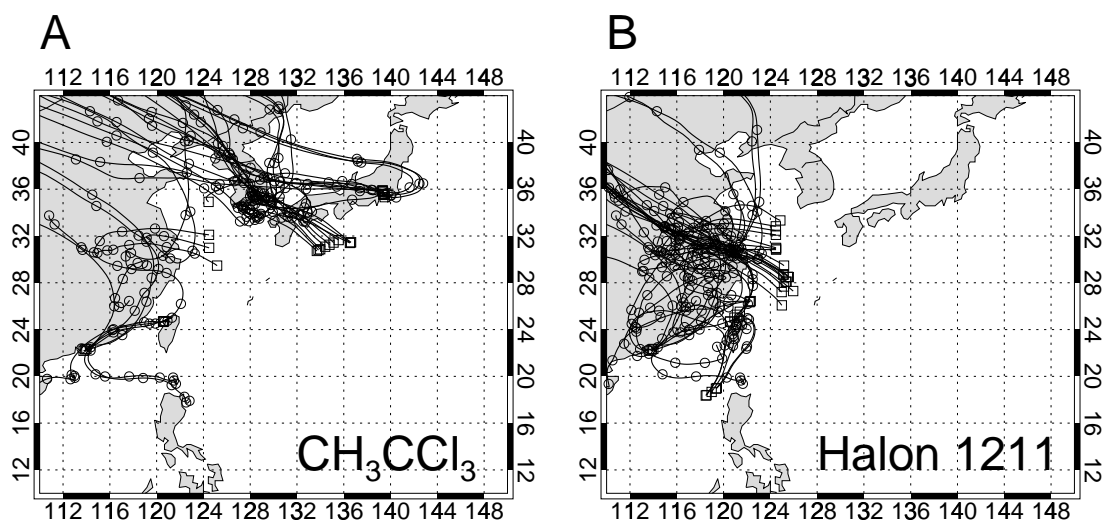


Figure 2. Five-day kinematic back-trajectories indicate the origin of the highest five percent of **A** CH_3CCl_3 and **B** halon 1211 concentrations measured in the boundary layer (0–2 km) during the TRACE-P aircraft campaign (March–April 2001). Open squares represent the measurement locations and open circles along the back-trajectories denote 12-hour increments.

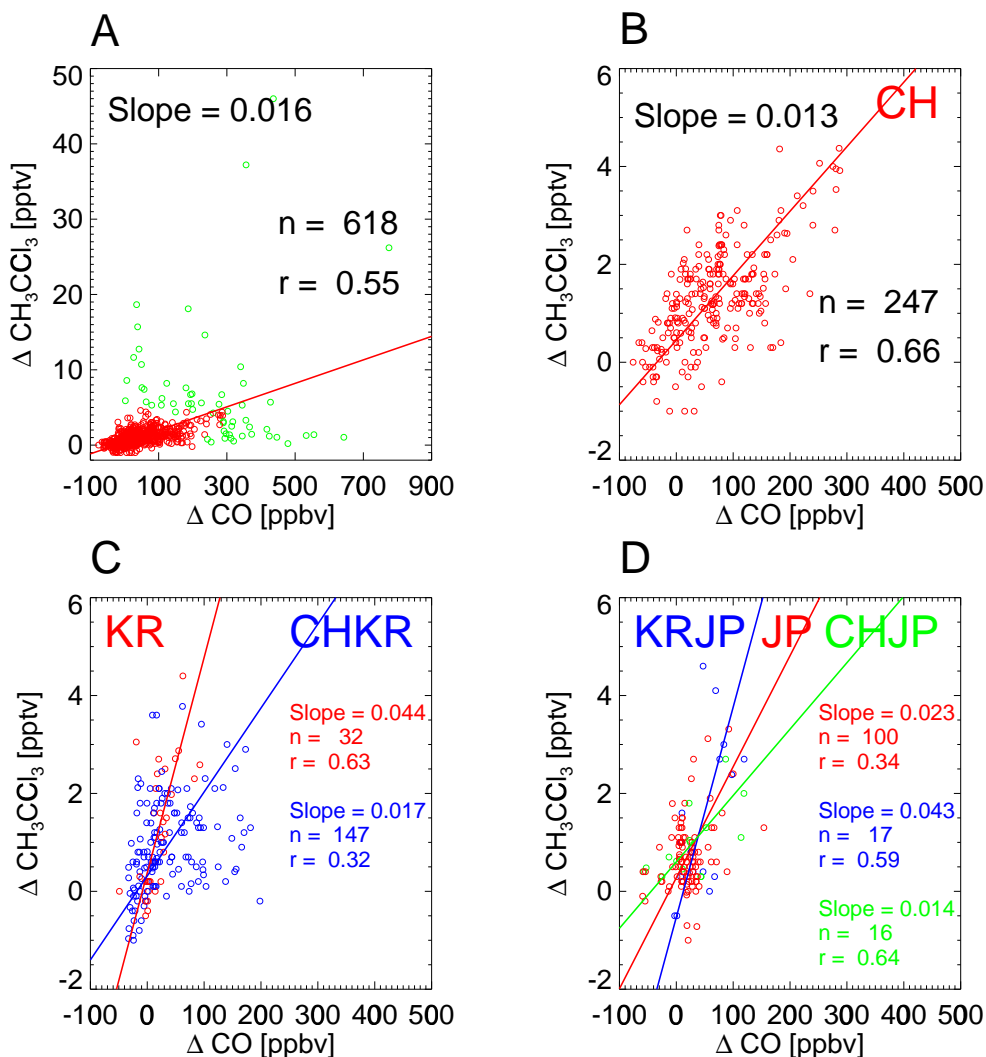


Figure 3. Reduced Major Axis Regression (RMAR) [Hirsch and Gilroy, 1984] of CH_3CCl_3 and CO enhancements over their background values ($\Delta\text{CH}_3\text{CCl}_3$ and ΔCO) for aircraft observations at 0–2 km altitude off the Asian Pacific rim during March–April 2001. **A** All available data. Green circles denote the ≥ 95 th percentiles of CH_3CCl_3 and CO concentrations, which are removed from the RMAR calculations. **B, C, D** Air masses originating from China (CH), Korea (KR), and Japan (JP), and of mixed China-Korea (CHKR), Korea-Japan (KRJP), and China-Japan (CHJP) origins.