Eastern Asian emissions of anthropogenic halocarbons deduced from aircraft concentration data

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[1] 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. *INDEX TERMS:* 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* anthropogenic, halocarbon emissions, troposphere, TRACE-P

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1. Introduction

[2] The role of halocarbons in the destruction of stratospheric ozone is well established [*World Meteorological Organisation/United Nations Environmental Programme* (*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 [*United Nations Environmental Programme* (*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.

[3] 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 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.

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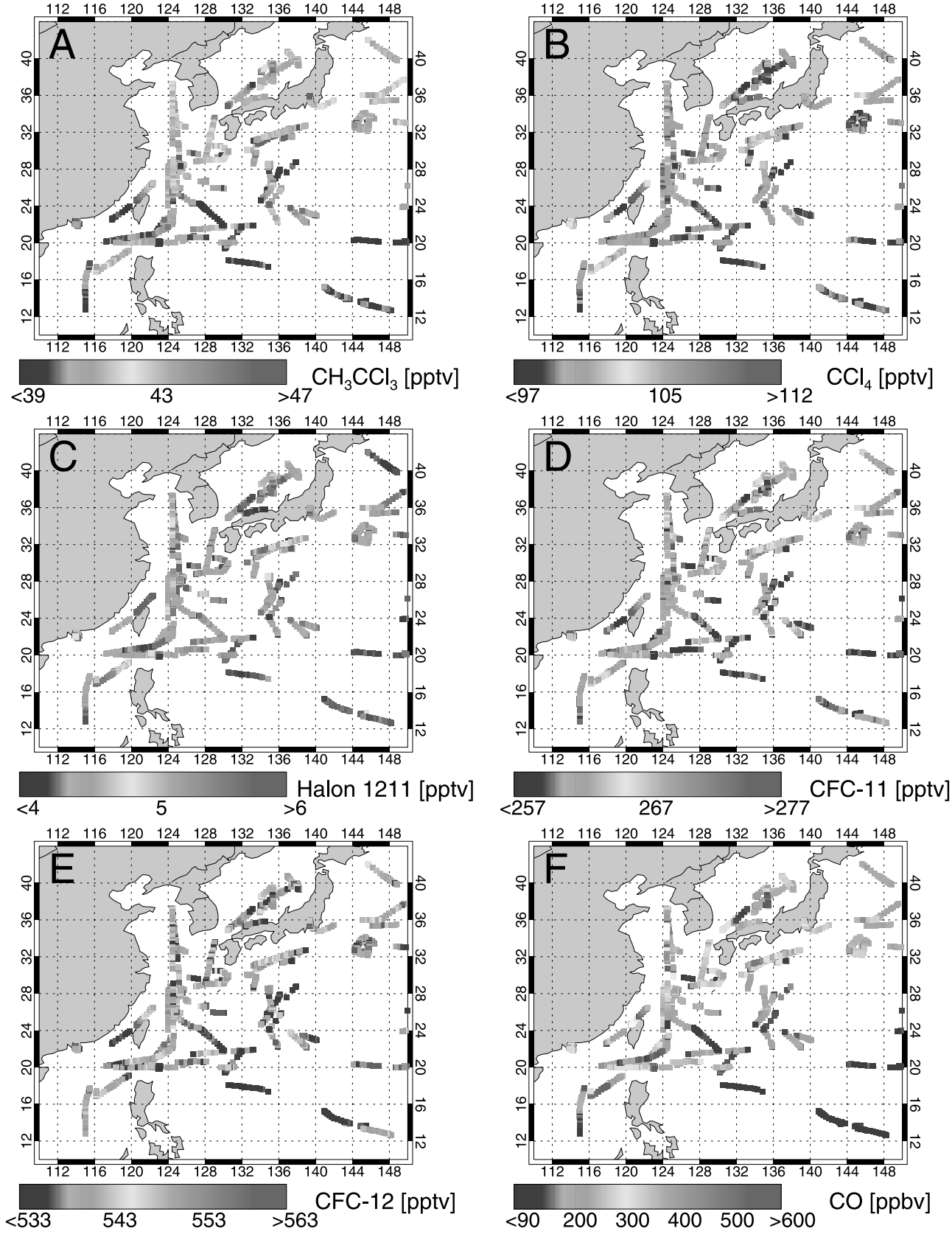

Figure 1. Geographical distributions of (a) CH_3CCl_3, (b) CCl_4, (c) halon 1211, (d) CFC-11, (e) CFC-12, and (f) CO concentrations measured in the boundary layer (0–2 km) during the TRACE-P aircraft campaign (March–April 2001). Further details about the measurement of halocarbons and CO are given by *Blake et al.* [1996] and *Sachse et al.* [1987], respectively. See color version of this figure at back of this issue.

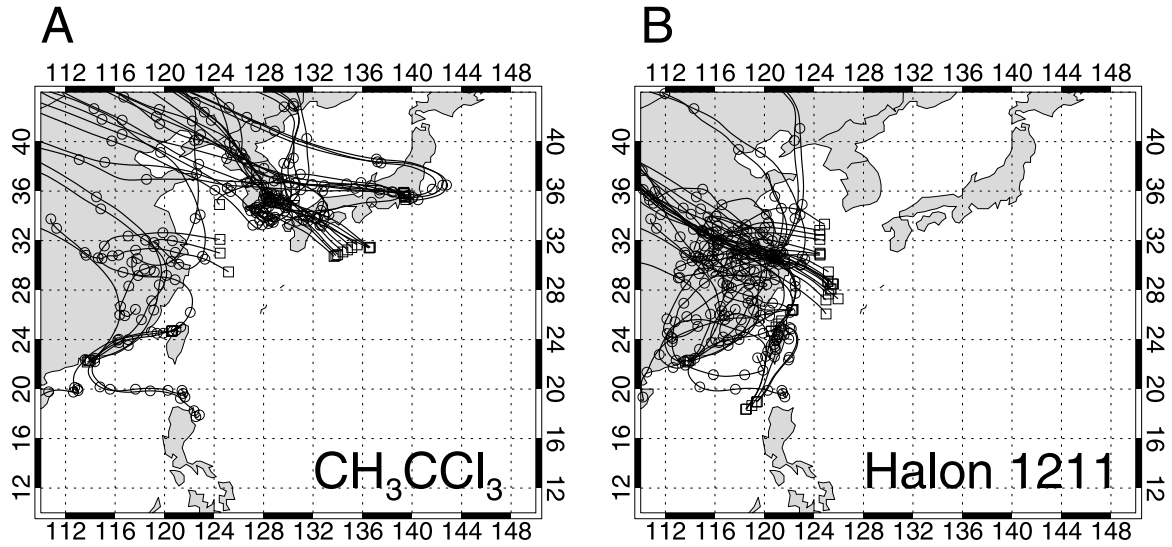

Figure 2. Five-day kinematic back trajectories indicate the origin of the highest five percent of (a) CH_3CCl_3 and (b) halon 1211 concentrations measured in the boundary layer (0–2 km) during the TRACE-P aircraft campaign (March–April 2001). Open squares represent the measurement locations, and open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

[4] 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, 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 (J. W. Elkins, NOAA CMDL, personal communication, 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].

[5] In section 2 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 sections 3–5 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.

2. Methyl Chloroform (CH_3CCl_3)

[6] 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].

[7] 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 5-day kinematic back trajectories [*Fuelberg et al.*, 2003] for the highest 5% ($\geq$45.9 pptv) of CH_3CCl_3 concentrations shows that they originate from South Korea and from the area around Shanghai (Figure 2).

[8] CH_3CCl_3 and CO both have background latitudinal gradients, reflecting their sources at northern midlatitudes 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 12–43°N vary from 39.2 to 41.6 pptv and from 102.8 to 280.3 ppbv, respectively. We further remove statistical outliers ($\geq$95th 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 $\Delta CH_3CCl_3$and ΔCO for the ensemble of the data (Figure 3). Table 1 gives a summary of correlation statistics.

[9] 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

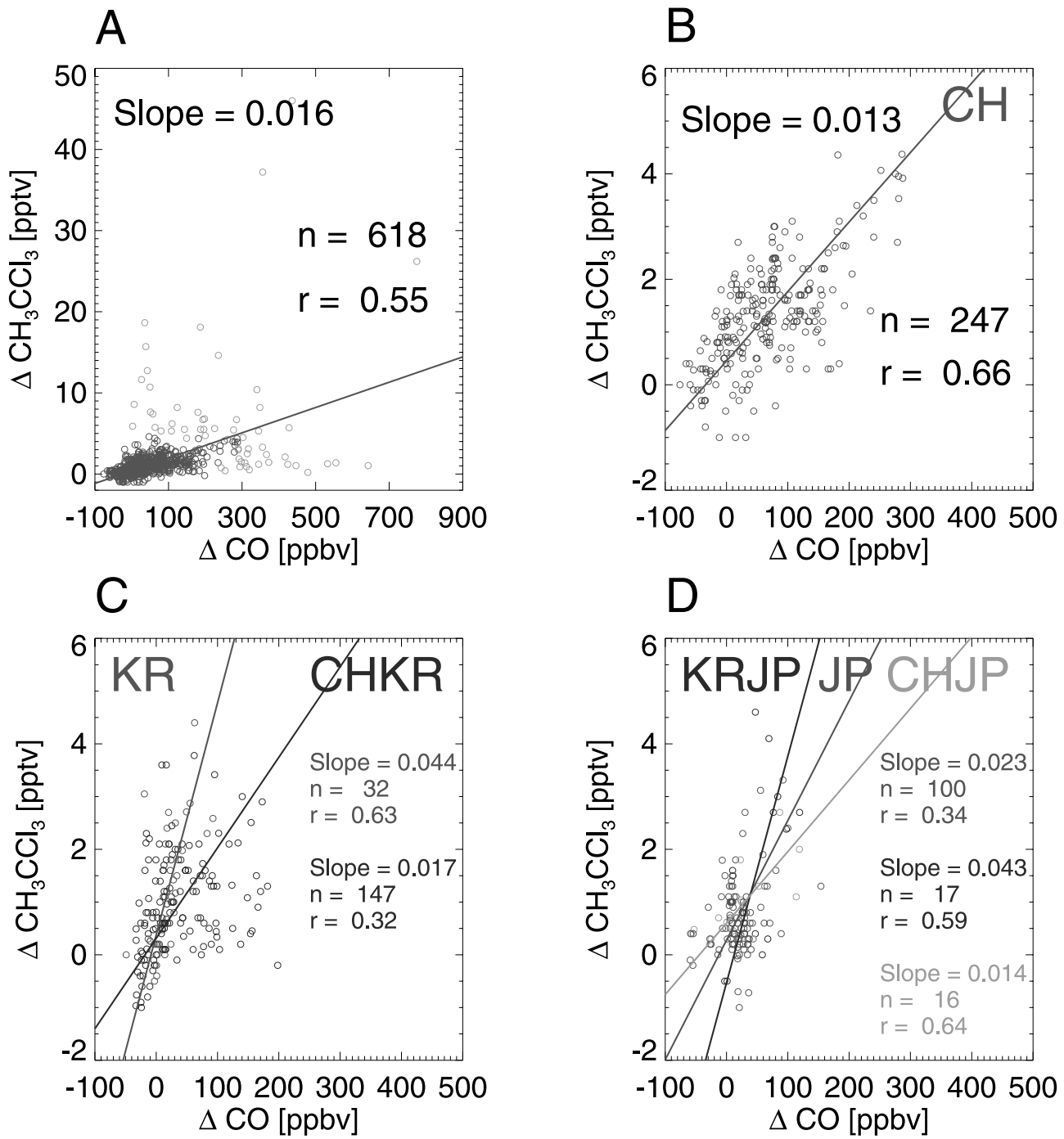

Figure 3. Reduced major axis regression (RMAR) [*Hirsch and Gilroy*, 1984] of CH_3CCl_3 and CO enhancements over their background values (ΔCH_3CCl_3 and ΔCO) for aircraft observations at 0–2 km altitude off the Asian Pacific rim during March–April 2001. (a) All available data. Green circles denote the $\geq$95th 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. See color version of this figure at back of this issue.

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 ΔCH_3CCl_3:ΔCO (0.016 pptv/ppbv) calculated or 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}.

Table 1. Halocarbon:CO Relationships Measured in Asian Outflow During TRACE-P[a]

	Eastern Asia			China			Korea			Japan		
Halocarbon X	*n*	*r*	ΔX:ΔCO	*n*	*r*	ΔX:ΔCO	*n*	*r*	ΔX:ΔCO	*n*	*r*	ΔX:ΔCO
CH_3CCl_3	618	0.55	16 ± 0.48[b]	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

[a]Statistics 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 CH_3CCl_3. 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. The parameter *n* is the number of 1-min average measurements used in the regression analysis; *r* is the Pearson correlation coefficient of ΔX:ΔCO; ΔX:ΔCO is the reduced major axis regression slopes (10^{-3} pptv/ppbv).

[b]Slope uncertainties are calculated by assuming the linear model.

[10] We further refine this emission estimate for eastern Asia by disaggregating contributions from China (CH), Japan (JP), and Korea (KR), using 5-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.

[11] Combining the ΔCH_3CCl_3:ΔCO 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 ΔCH_3CCl_3:ΔCO 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 ΔCH_3CCl_3:ΔCO 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 ΔCH_3CCl_3:ΔCO correlation for air masses originating from Japan (Table 1) means that our corresponding emission estimate is highly uncertain.

[12] Estimated uncertainties on our halocarbon emission estimates are given in 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.

[13] 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}.

3. Carbon Tetrachloride (CCl_4)

[14] Emissions of CCl_4 originate primarily from its use as a chemical feedstock for the production of CFC-11. The

Table 2. Bottom-Up and Top-Down Halocarbon Emission Estimates for Eastern Asia[a]

	CH_3CCl_3 (ODP = 0.1)		CCl_4 (ODP = 1.1)		CFC-11 (ODP = 1.0)		CFC-12 (ODP = 1.0)	
	Bottom-Up	Top-Down	Bottom-Up	Top-Down	Bottom-Up[b]	Top-Down	Bottom-Up[c]	Top-Down
China	6.50[d]	10.4 ± 2.6	0.1[d]	17.6 ± 4.4	7.2	22.3 ± 5.8	20.3	28.3 ± 7.4
Japan	0.0[d]	1.0 ± 0.3	0.1[d]	1.3 ± 0.4	2.6	2.3 ± 0.6	5.6	3.4 ± 1.0
Korea	6.0[d]	1.8 ± 0.6	1.3[d]	2.3 ± 0.8	8.1	2.9 ± 1.0	11.4	3.6 ± 1.4
Eastern Asia	11[d]–12.5[e]	14.2 ± 3.3	1.5[d]	21.5 ± 5.0	17.9	30.1 ± 7.2	37.3	39.4 ± 9.5
Global	19.7[e]	19.6–26.2[f]	47.0[g]	62.0–72.0[f]	74.6	79.6–94.0[f]	132.9	125.5–144.5[f]

[a]Bottom-up estimates rely on government reports of production and consumption. Top-down estimates are computed here using Δhalocarbon:ΔCO 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. Estimates are in units of Gg yr^{-1}.

[b]Value based on estimated emissions from 2000 [*McCulloch et al.*, 2001].

[c]Value based on estimated emissions from 2000 [*McCulloch et al.*, 2003].

[d]Value based on estimated consumption during 1999 [*UNEP*, 2002].

[e]Value based on estimated emissions from 2001 [*McCulloch and Midgley*, 2001].

[f]Top-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.

[g]Value based on estimated emissions from 1995 [*Simmonds et al.*, 1998].

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 ΔCCl_4:ΔCO 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 12–43°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.

[15] 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.

4. Bromofluorocarbons

[16] Bromofluorocarbons (halons) are among 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% ($\geq$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°N. We find that by removing the highest 5% of concentration data, in order to obtain a Δhalon 1211:ΔCO slope more representative of the regional signal, we effectively remove any useful signal that is significantly different from background (0.003 pptv/ppbv). The Δhalon 1211:ΔCO 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.

5. Chloroflurocarbons

[17] 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 ΔCFC-11 ($CFCl_3$) and ΔCFC-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.

[18] Eastern Asian emissions of CFC-11 and CFC-12, as derived from ΔCFC:ΔCO slopes in Table 1 and the regional CO source, are 30.1 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.

6. Implications for the Ozone Depletion Potential of Asian Emissions

[19] 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 ODP Gg yr^{-1} for 2001, as compared to 60.0 ODP Gg yr^{-1} using the previous bottom-up estimates [*McCulloch and Midgley*, 2001; *McCulloch et al.*, 2001, 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, 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].

[20] 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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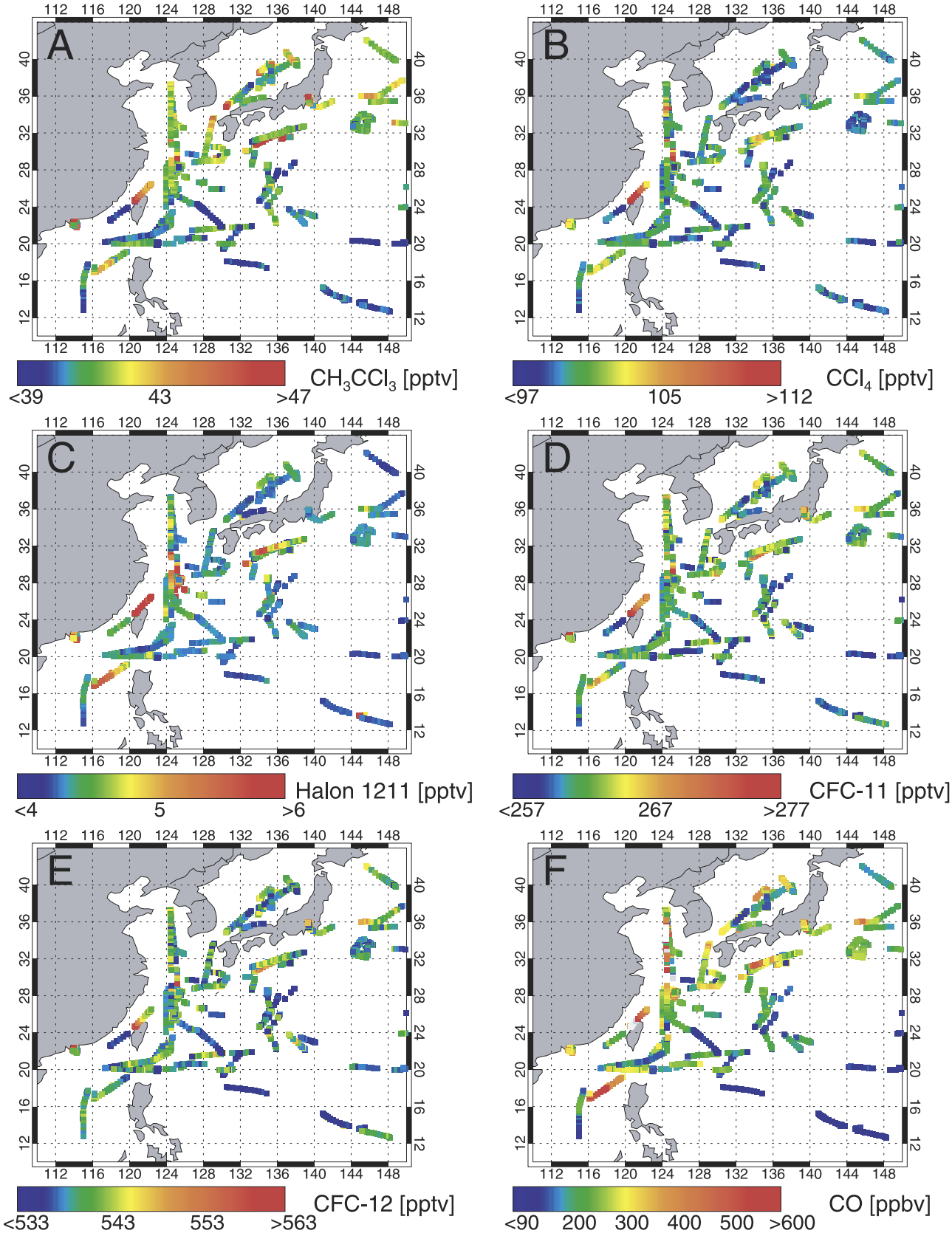

Figure 1. Geographical distributions of (a) CH_3CCl_3, (b) CCl_4, (c) halon 1211, (d) CFC-11, (e) CFC-12, and (f) CO concentrations measured in the boundary layer (0–2 km) during the TRACE-P aircraft campaign (March–April 2001). Further details about the measurement of halocarbons and CO are given by *Blake et al.* [1996] and *Sachse et al.* [1987], respectively.

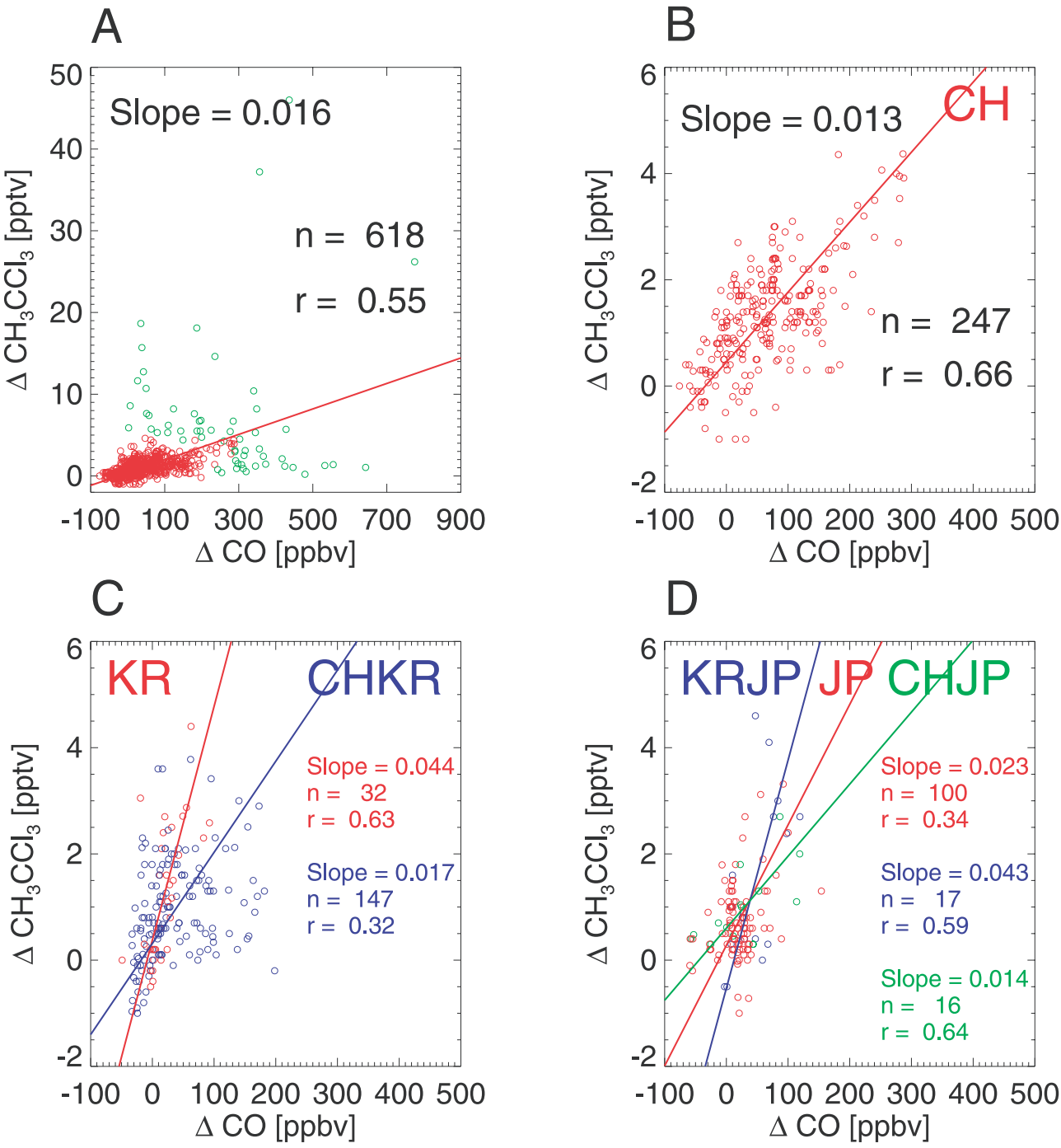

Figure 3. Reduced major axis regression (RMAR) [*Hirsch and Gilroy*, 1984] of CH_3CCl_3 and CO enhancements over their background values (ΔCH_3CCl_3 and ΔCO) for aircraft observations at 0–2 km altitude off the Asian Pacific rim during March–April 2001. (a) All available data. Green circles denote the ≥95th 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.