Reply to the Anonymous Referee #2

General comments of Anonymous Referee #2: This is a very useful and important paper. It provides an observationally based estimate of halocarbon emissions from the Pearl River Delta region of China, an issue that has attracted significant interest. However, there are shortcomings of the paper that must be corrected before publication in ACP.

Response: I would like to thank the referee for the careful review and the valuable comments, which provided insights for us to improve the paper.

Relatively major concerns include the following:
1. The method of estimating emissions that is developed Eq. (1) and applied in Section 3.2 implicitly assumes that the emissions of the halocarbons are correlated with the emissions of CO. The relatively low correlation coefficients presented in Table 4 indicate that the halocarbons and CO are not necessarily emitted from the same sources, or even uniformly enhanced proportional to their emissions in polluted air masses. Nevertheless, the method can still give a useful (although uncertain) estimate for the halocarbon emissions if the line fit to the data pass through a point that represents the global backgrounds of both CO and the halocarbon. Figure 2 suggests that this situation holds for many of the halocarbons, but in other cases the intercept of the CO background (approximately 100 ppbv) is at a halocarbon concentration that is elevated above its background (e.g. HCFC 22, CHCl3, CH2Cl2 and CCl2=CCl2). This behavior suggests that halocarbon concentrations can be elevated by local emissions even when CO is close to the global background (i.e. not elevated by local emissions). In such cases a more accurate emission estimate would be obtained from a linear fit that is forced to pass through the point that represents the global backgrounds of both CO and the halocarbon. The authors must clearly consider their estimates of the background concentrations, whether the lines fit to the data are consistent with the background estimates, and clearly discuss the implications for the uncertainty of their emissions estimates.

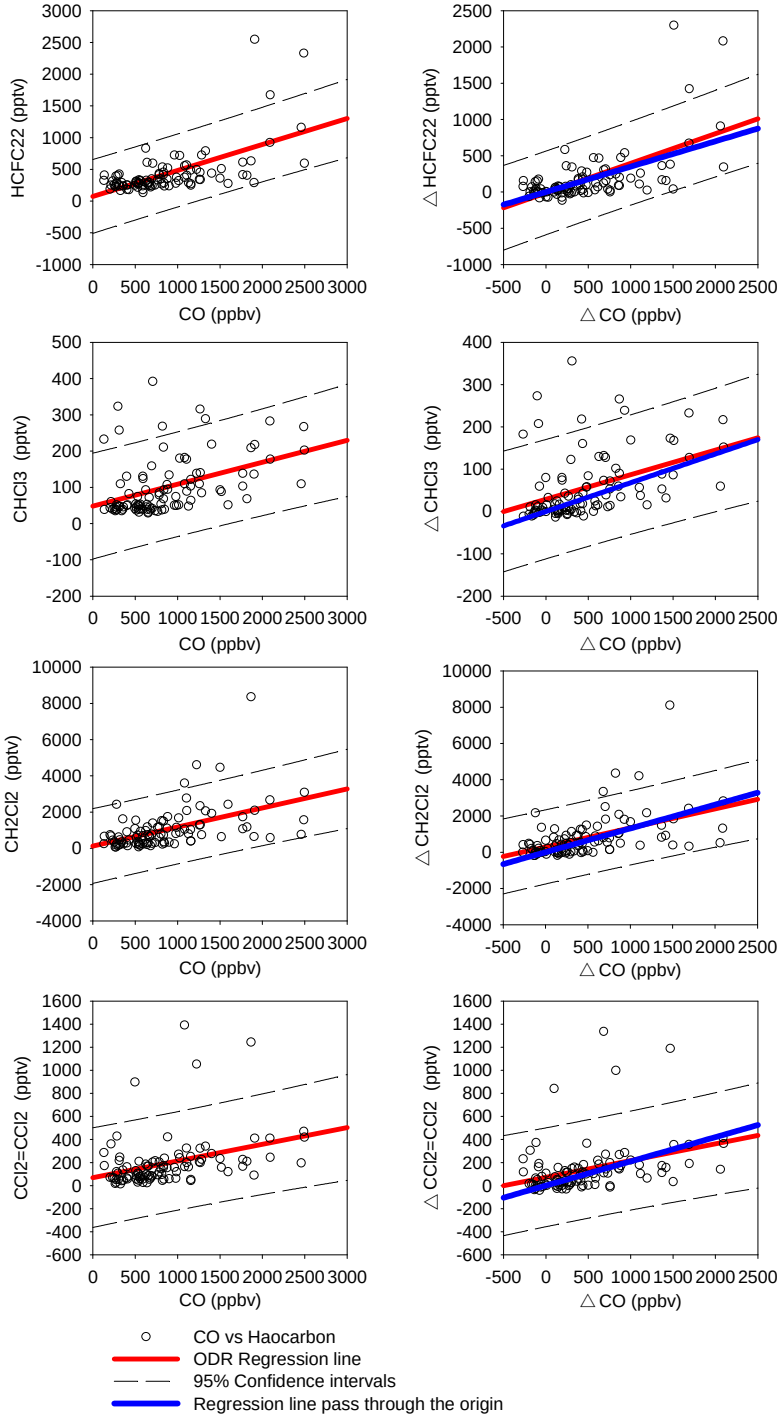
Response: This is an important point and quite intensively discussed at the ACPD stage. We agree with the reviewer's suggestions. The global backgrounds of CO and the halocarbons contribute to the ambient mixing ratios, a fit curve pass through a point that represents the regional backgrounds of CO and the halocarbons would possibly lead to a more accurate emission estimate. In fact, the statistical approaches to derive a reasonable slope of halocarbons to CO were very seriously considered:
(1) As both the ambient CO and halocarbons have measurement errors and actual ambient variation, to get a reliable slope for the linear regression, the orthogonal distance linear regression (ODR) method was selected in this work;
(2) We think that the samples were collected over a short enough period of time, the background concentrations did not change much, therefore the lowest 20th percentile[*Blake et al.*, 2003] of CO and halocarbons collected in Xinken (a regional background site, shown in Table 1) as the" regional background", and the enhancement of mixing ratios of CO and halocarbon were calculated by subtracting the background concentrations. Then , 3 different results (slope from measured mixing ratios, slope from enhanced mixing ratios, and the one from the reviewer's suggestion, regression forced to pass backgrounds) of the linear regression slopes can be compared as shown in "Comment Figure 1".
(3) The orthogonal distance linear regression (ODR) results showed that the slopes are the same weather or not the background concentration was considered. And the regression line passing through the origin point

(ΔCO=0,ΔX=0) were very close to the ODR line (Comment table 1). Actually 13 species out of 16 in "comment Table 1" gave the differences of the slopes between passing and non-passing the backgrounds were lower than 30%, generally within 20%. The three outliners were CH_3Cl, CH_3Br, and CH_3CH_2Cl. At present, we were not capable to evaluate the accuracies of the background concentrations we obtained from our measurements, especially for those species with very low mixing ratios, therefore we think that we need also to be careful when the background levels were used in the emission estimate.

From the comparison above, we think it was acceptable to use both slopes. We feel more comfortable to use only the measured mixing ratios. However, we kept the discussion on background concentrations (as table1) for distinguishing the influence of regional scale pollution and local emissions. The detailed explanations were present in 2.2.1. in revised section. As to the figure 2, the absolute concentrations were plotted according to the suggestion of the former anonymous reviewers.

Comment Table 1. (unit in pptv/ppbv)

Halocarbons	ODR line non-pasasing the origin		ODR line passing the origin	
	X/CO	Uncertainty	ΔX/ΔCO	Uncertainty
CFC-11	0.0222	0.0048	0.0292	0.0078
CFC-12	0.1100	0.0199	0.1380	0.0249
CFC-113	0.0015	0.0020	0.0012	0.0220
CFC-114	0.0010	0.0008	0.0014	0.0028
HCFC-22	0.3480	0.0430	0.3390	0.0730
CH3CCl3	0.0228	0.0028	0.0278	0.0048
CCl4	0.0588	0.0165	0.0591	0.0263
CHCl3	0.0604	0.0133	0.0682	0.0196
CH2Cl2	0.7090	0.1280	0.7870	0.1680
CH3Cl	0.0962	0.0370	0.1992	0.0470
CH3Br	0.0121	0.0047	0.0301	0.0057
CCl2=CCl2	0.1180	0.0212	0.1380	0.0309
CHCl=CCl2	0.4380	0.0699	0.5240	0.0549
CHCl2CH2Cl	0.0381	0.0042	0.0391	0.0067
CH3CH2Cl	0.0036	0.0038	0.0124	0.0068
CH3CHClCH2Cl	0.0309	0.0056	0.0387	0.0076
CO	---	---	---	---



Comment Figure 1

2. The English language use in this paper must be improved throughout the paper. There are many minor misusages of English, and in some places the content of the paper is unclear. I suggest copy editing by a native English speaker.

Response : Accepted. The English in this document has been checked by at least two professional editors, both native speakers of English. For a certificate, please see:

http://www.textcheck.com/certificate/67GZor

Less significant concerns include:

Specific comments:

1. I do not understand the significance of the rectangle inset in Fig. 1. It is never discussed, so I suggest that it be removed.

Response: Accepted and the rectangle inset in Fig. 1 has been removed.

2. The authors employ an orthogonal distance linear regression (ODR). However, the slope, intercept and their confidence limits derived from such a regression is strongly dependent upon the weighting elected for each of the variables. This weighting should be clearly discussed.

Response: The calculations assume an inherent relationship between target species X and CO. The measured CO and halocarbons are due to both actual ambient variation and the instrumental errors. Therefore, an orthogonal distance regression (ODR) was used to calculate the regression slope, in which residual distance between the measurement data and orthogonal regression line is minimized[*Barnes et al.*, 2003]. the algebraic manipulation for the slope, intercept and their confidence limits was discussed in the literature[*Cantrell*, 2008] , Indeed, the slope and intercepts were dependent upon the weights of CO and halocarbons.

However, one can perform bivariate fits without weighting, therefore, this is done by making the weights of CO and halocarbon to be the same in this study.

3. The notation in Eq. (2) is inconsistent with that in Eq. (1). CO^2 under the square root should be E_{CO}^2. Also the sentence following the equation has the definitions of the two uncertainties switched.

Response: Sorry for this error, and the notation changed in revised version as:

$$\sigma_x = \sqrt{\sigma_{E_{CO}}^2 * (X/CO)^2 + E_{CO}^2 * \sigma_{X/CO}^2} \times (M_x / M_{CO}) \times 10^{-3} \qquad (2)$$

where σ_x is the uncertainty for the estimated halocarbon emission, $\sigma_{E_{CO}}$ and $\sigma_{X/CO}$ are the uncertainties of E_{CO} and the X/CO slope respectively.

4. Line 25 and elsewhere: Inventory numbers should be reported with a number of significant figures consistent with their uncertainty; e.g. 5900 Gg (in 2000), 8700 Gg (in 2006). A similar comment applies to the estimated emission ratios; e.g. on pg 2965 the X/CO ratios, should be reported as 0.71±0.13, 0.12±0.02, and 0.44±0.07 pptv ppbv−1 for DCM, PCE and TCE, respectively.

Response: Thanks, this issue has been checked throughout the whole manuscript, and the number of significant digits in 5900 Gg (in 2000), 8700 Gg (in 2006) is at least two, to avoid uncertainty, use scientific notation to place significant zeroes behind a decimal point as:

5.9×10^3 Gg (in 2000), 8.7×10^3Gg (in 2006) on pg 2958 line 25

the same errors on pg 2959 line 15 and 20 were also revised, and other same errors on pg 2961 line 24 was replaced by "…the CO inventory emission from the PRD region in 2004."

5. In lines 25-27 on pg. 2958, the specification of the confidence limits of the CO emissions are poorly

described. The term ±185% makes no sense to me, as that would include large negative emissions, which are not physically reasonable. It would be better to indicate the uncertainty by a factor, e.g. uncertain within a factor of 1.85, if that is indeed the uncertainty that the authors wish to convey. This same approach should be taken for the other uncertainty estimates given in this section.

Response: Accepted and changed accordingly. As the suggestion by the referee, lines 25-27 on pg. 2958 was revised as "……range from 5.9×10^3Gg (uncertain within a factor of 1.9, in 2000) to 8.7×10^3Gg (uncertain within a factor of 0.7, in 2006)……"

This same approach has been taken for the other uncertainty estimates given in this section for line 15 and pg 2959.

6. Line 11 on pg. 2960: I think that the relevant statistical results are given in both Table 1 and Table 2.

Response: Accepted and the Line 11 on pg. 2960 was revised as

"The statistical results given in both Table 1 and Table 2 showed that……"

7. Lines 16-20 on pg. 2960: The magnitudes of relative standard deviations (RSD) are a function of loss processes as well as emissions. Very long-lived species have very small RSDs, other factors being equal (see for example, Jobson et al., Trace gas mixing ratio variability versus lifetime in the troposphere and stratosphere: Observations,Journal of Geophysical Research, 104 (D13), 16091-16113, 1999.) The sentence on these lines is incorrect as written.

Response: Accepted and the line 16-20 on pg. 2960 was changed as

"The large concentration variability in those halocarbons suggested substantial usage and emissions in PRD region, while the variability of CFC-11and CFC-113 were rather small using the flask sampling technique. Jobson et al. [1999] reported that the magnitudes of RSD for halocarbons species are a function of loss processes as well as emissions, but both the pollution enhancements and the large variability of the halocarbons confirm that there are some unexpected sources, such as emissions stockpile leakage and unknown production or usage[C Y Chan et al., 2006; L Y Chan and Chu, 2007; Wang et al., 2000]."

8. Line 29 on pg. 2960: In the Sentence "Moreover, the median emission values of . . ."I think the authors mean ".. median measured concentrations of . . ."

Response: Sorry for this error, and changed accordingly. the sentence of Line 29 on pg 2960 was changed as "Moreover, the median measured concentration of HCFC-22…"in revised version.

9. Line 2 on pg. 2961: In the Sentence ". . .. suggesting long-term sources of emissions for . . ." is not correct. The greater concentrations certainly suggest emission sources,but do not indicate that they are "long-term".

Response: Accepted, the sentence of Line 2 on pg. 2961 was changed as" …suggested that there are some sources emission of the two halocarbons… "

10. Line 20 on pg. 2961: The phrase "statistically positive relationships" is not clear. Do the authors mean "statistically significant"? If so, this statement should be supported by statistical significance tests, which are not given. Do the authors mean "positive correlations", i.e. the halocarbon increases with increasing CO concentration? The wording needs to be clarified.

Response: Accepted. We means that the halocarbon increases with the increasing CO concentration as the positive correlations, the statistical significance test was conducted in Table 4 , level of significance for Pearson's Correlation coefficient were also showed in this table. Here, sentence of Line 20 on pg. 2961 was

revised as ” ……The positive relationships between X and CO were shown in Figure 2 and the significance level for Pearson's Correlation coefficient (r) were also showed in Table 4.…… ”

Reference:

Barnes, D. H., S. C. Wofsy, B. P. Fehlau, E. W. Gottlieb, J. W. Elkins, G. S. Dutton, and S. A. Montzka (2003), Urban/industrial pollution for the New York City–Washington, D. C., corridor, 1996–1998: 1. Providing independent verification of CO and PCE emissions inventories, *Journal of Geophysical Research-Atmospheres*, *108*(D6, 4185), doi:10.1029/2001JD001116. .

Blake, N. J., et al. (2003), NMHCs and halocarbons in Asian continental outflow during the Transport and Chemical Evolution over the Pacific (TRACE-P) Field Campaign: Comparison With PEM-West B, *Journal of Geophysical Research-Atmospheres*, *108*(D20,8806), doi:10.1029/2002JD003367.

Cantrell, C. A. (2008), Technical Note: Review of methods for linear least-squares fitting of data and application to atmospheric chemistry problems, *Atmos Chem Phys*, *8*(17), 5477-5487.

Chan, C. Y., J. H. Tang, Y. S. Li, and L. Y. Chan (2006), Mixing ratios and sources of halocarbons in urban, semi-urban and rural sites of the Pearl River Delta, South China, *Atmospheric Environment*, *40*(38), 7331-7345.

Chan, L. Y., and K. W. Chu (2007), Halocarbons in the atmosphere of the industrial-related Pearl River Delta region of China, *Journal of Geophysical Research-Atmospheres*, *112*(D04305), doi:10.1029/2006JD007097.

Jobson, B. T., S. A. McKeen, D. D. Parrish, F. C. Fehsenfeld, D. R. Blake, A. H. Goldstein, S. M. Schauffler, and J. W. Elkins (1999), Trace gas mixing ratio variability versus lifetime in the troposphere and stratosphere: Observations, *J. Geophys. Res.*, *104*(D13), 16091-16113.

Wang, J.-L., W.-C. Lin, and T.-Y. Chen (2000), Using atmospheric CCl4 as an internal reference in gas standard preparation, *Atmospheric Environment*, *34*(25), 4393-4398.