Comment by Rainer Volkamer and Roman Sinreich on the paper by Li et al., entitled 'MAX-DOAS measurements of NO_2, HCHO and CHOCHO at a rural site in Southern China' as published in ACPD.

The paper shows a very interesting data set. We performed measurements witha device of the same kind (Mini-DOAS) at the same time and at the same location (pointing at a perpendicular azimuth angle to the reported instrument). Unlike the instrument used by Li et al.,our Mini-DOAS included a spectrometer which was optimized for CHOCHO as the wavelength range observed includes the stronger CHOCHO absorption cross section band near 455nm that is inaccessible to the instrument used by the authors of Li et al, and free of overlapping water bands. The data of our Mini-DOAS, which were presented at the DOAS workshop 2008 in China by R. Sinreich, showed much lower CHOCHO differential slant column densities (dSCD) (factors 3-4), as evaluated in the optimized wavelength range of 420-460nm.

Triggered by this and the high CHOCHO/HCHO ratios reported in this study, as raised in the reviews, we have looked into ourdata again and performed a quick sensitivity test using the same analysis wavelength range as reported in the paper (416-441nm). We used the following cross sections: CHOCHO (Volkamer et al., 2005), NO_2 (Vandaele et al., 1997), ozone at 223K (Bogumil et al., 2003), O_4 (Greenblatt et al., 1990) with manual adjustments of the wavelength axis (A. Richter, personal communication), and H_2O (Rothman et al., 2005). We also included a Ring spectrum (Graigner and Ring, 1962), a polynomial of degree 5 and a quadratic offset for correcting for straylight in the spectrometer. The analysis was performed using a zenith Fraunhofer reference spectrum and a Ring spectrum which is chosen close in time for every spectrum (as it was done in Li et al.).
Figure 1 shows the dSCDs (2° elevation angle) of the smaller wavelength range versus the dSCDs from the larger wavelength range including the strong absorption band at 455nm. Only data of the nine cloud free days discussed by Li et al. are used here (12-14, 19-21 and 23-25 July 2006). A 1:1 line illustrates where the points would be expected if the evaluation wavelength range did not have an impact on the dSCD value. However, an average increase of more than 60% could be observed. While this does not explain the factor of 3-4 between the two data sets, it clearly shows that not using the strong absorption band at 455nm can lead to significant high bias in the data.

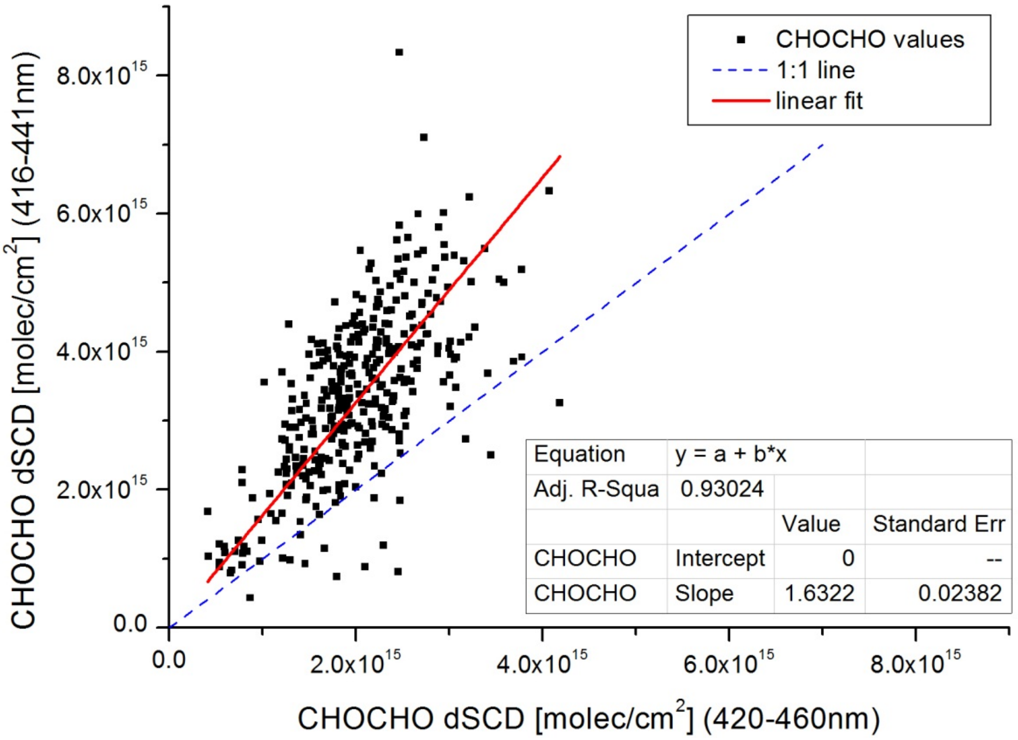


Figure 1: CHOCHO dSCDs (2° elevation angle) of the smaller wavelength range larger one for the nine days shown in the paper (12-14, 19-21 and 23-25 July 2006). The smaller wavelength range shows more than 60% higher values in average.

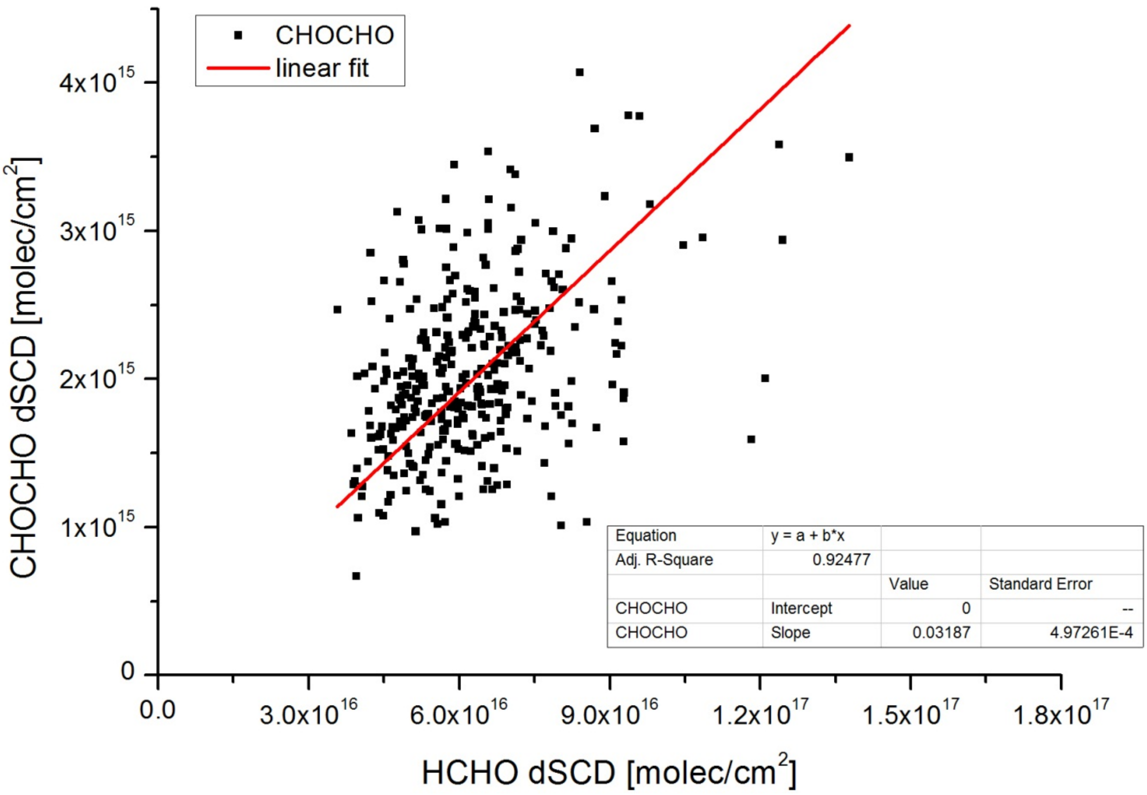
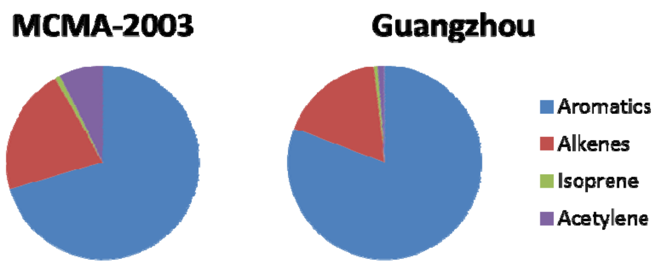


Figure 2: CHOCHO dSCDs versus HCHO dSCDS for 2° elevation angle and the nine days shown in the paper (12-14, 19-21 and 23-25 July 2006). The ratio found is 0.032.

Also, we compared the CHOCHO to HCHO ratio (RGF) reported by Li et al. with ours.Figure 2 depicts the CHOCHO dSCDs versus the HCHO dSCDs (for 2° elevation angle and the chosen 9 days mentioned above). The RGF based on our optimized, and simultaneous MAX-DOAS measurements at the BG site is 3.2%. This is on average about 4 times lower than the RGF of 0.135 reported by Li et al. Our RGF compares well with the RGF of 2.8% observed in Mexico City (Volkamer et al., 2005), and also recent measurements in Los Angeles, CA 3.2%, Bakersfield, CA 3.0% (Fig. 7 in DiGangi et al., 2012). Our value is further in reasonably good agreement with satellite measured ratios of ~ 0.04 in Southern Asia (Vrekoussis et al., 2010). Thus there is a strong indication that there is a measurement artifact in the CHOCHO data reported by Li et al..

In fact, the VOC distribution in Guangzhou, PRD does not appear to vary much from that in Mexico City (Figure 3). It seems difficult to rationalize an RGF > 0.05based on this VOC distribution.

Parameter	MCMA-2003[a]	Guangzhou[b]
Aromatics	72.40%	76.9%
Alkenes	21.80%	16.65%
Isoprene	0.90%	0.55%
Acetylene	7.50%	5.8%



[a] Volkamer et al., 2005, 2007; [b] Volkamer et al., 2006

Figure 3: Relative contributions of speciated VOC to secondary glyoxal formation. Data from Guangzhou are based on Chan et al. (2006) JGR 111, D11304, as described in Volkamer, Kurosu, Chance, Li, Zhang, Brauers, Wahner (2006), Eos Trans. AGU, 87(52), Fall Meet. Suppl., Abstract A31B-0897.

Additional comment:

Quote: 'Moreover, given CHOCHO is usually the higher generation oxidation product of primary VOCs, in the condition of higher HOX turnover rates, more CHOCHO can be produced leading to higher RGF.'

Comment: The statement makes the assumption, unsupported by the authors, that formaldehyde does form less efficiently as a higher generation oxidation product as glyoxal on a molar basis. What is the basis for such a statement? Most VOCs (e.g., aromatics, alkenes) form glyoxal primarily as a first generation oxidation product (Volkamer et al., 2001; Calvert et al., 2000; 2002; Volkamer et al., 2007, Table 1), suggesting that in fact the opposite is expected. Can the authors support the statement based on the actually observed VOC distribution at BG site?

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