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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Volatile Organic Compound (VOC) measurements in the Pearl River Delta (PRD) region, China" *by* Y. Liu et al.

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General Comments This manuscript presents results from a VOC study in the Pearls River Delta, China. It is important to know more about sources and concentrations of air pollutants in this region. Variations of VOC concentrations at different locations are discussed in detail and compared well with earlier VOC data and other air quality and meteorological data available. In addition to this some major sources are identified. The results are generally well presented and discussed adequately. Main concern was that usually stainless steel canisters are used only for measuring light C2-C6 hydrocarbons. In this study even trimethylbenzenes, MTBE and monoterpenes were measured. For these higher VOCs (C6-C10) losses to the walls of the canisters is usually a problem. Have this been taken into account? Maybe it has been tested in some earlier study and a reference could be added? If not, some tests should be conducted to

show the performance of the canisters, for example by running calibration gas from the stainless steel canisters several days after filling.

Response: Thanks a lot for the encouragements. The stabilities of VOC compounds is one of the key questions for the canister-based method, some previous studies reported that the canisters were quite satisfactory for C2-C6 hydrocarbons when ambient O3 is removed (Greenberg et al., 1992; Blake et al., 1994). Ochiai et al. (2002) observed the stabilities of 58 VOCs in canisters, including alkanes, alkenes, aromatics, halogenated hydrocarbons, alcohols, ketones, esters, ethers, nitriles, and thiols, under different humidified conditions. All measured hydrocarbons (C4-C9) had good recoveries of $>$85% in canisters under all examined conditions. The similar tests have been conducted in our laboratory. Most of target compounds showed good stabilities under dry and humid (RH$>$30%) conditions over 30 days. The presence of water enhanced the stabilities of VOC species due to the competitive adsorption of water vapor and VOC vapor on inner surfaces of canisters. After 30 days of filling of calibration gas, the recoveries of trimethylbenzenes, MTBE and α-pinene were 87%, 84% and 73% under dry conditions, respectively; and these recovers increased to 93%, 94% and 81% under the conditions of RH$>$30%, respectively. The tests on the performance of canisters are described briefly in the Section 2.2 of revised manuscript.

Supplemented references: Blake, D.R., Smith, T.W., Chen, T.Y., Whipple, W.J., Rowland, F.S., (1994): Effects of Biomass Burning on Summertime Nonmethane Hydrocarbon Concentrations in the Canadian Wetlands, Journal of Geophysical Research, 99 (D1): 1699-1719

Greenberg, J.P., Zimmerman, P.R., Pollock, W.F., Lueb, R.A. and Heidt, L.E. (1992): Diurnal Variability of Atmospheric Methane, Nonmehtane Hydrocarbons, and Carbon-Monoxide at Mauna-Loa, Journal of Geophysical Research, 97 (D10): 10395-10413

Batterman, S.A., Zhang, G.Z., Baumann, M. (1998) Analysis and Stability of Aldehydes and Terpenes in Electropolished Canisters, Atmospheric Environment, 32 (10): 1647-

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Ochiai, N., Tsuji, A., Nakamura, N., Daishima, S., Cardin, D.B. (2002): Stabilities of 58 Volatile Organic compounds in fused-silica-lined and SUMMA polished canisters under various humidified conditions, Journal of Environmental Monitoring, 4 (6): 879-889

Specific Comments from Reviewer #1: Section 2.2: How canisters were cleaned? Were they pre-evacuated?

Response: All the canisters were cleaned and pre-evacuated prior to sampling. Details of the cleaning processes and preparation of canisters are described in EPA-TO 15, including several cycles of evacuation and refilling with high purity nitrogen. The canisters are evacuated to $<$100 mtorr, and then are pressurized to ˜30psi with humid nitrogen at 95℃. After three cycles of filling and evacuation, the canisters are prepared for sample collection, with final vacuums of $<$50 mtorr.

Section 2.3: What compounds were used as internal standards (line 15)? Were there all quantified compounds in the calibration gas? If not, how they were quantified?

Response: Three VOC compounds were used as internal standards in our calibration, namely bromochloromethane, 1,4-difluorobenzene and 1-bromo-3-fluorobenzene, recommended by EPA TO-15. All quantified compounds were in the calibration gas.

Section 2.4, line 16: Table 2 should be Figure 2.

Response: Accepted. Sorry for the mistake.

Section 3.3.1: You state that evening peak coincided with heavy traffic, but VOC concentration is high already at 18:00. Do you have any explanation for that? Why it is much higher than during morning rush hour? As shown in figure 8 especially CO and VOCs are higher, but not NOx that much. Is it possible that there could be some other combustion source than traffic? For example in wood/vegetative/biomass burning emissions there are lots of CO and VOCs and not that much NOx.

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Response: VOC level elevated at 18:00 because the off-duty hours for most companies, industries and government functionaries of GZ started at about 17:00˜18:00. The peak in the late afternoon (˜18:00) was much higher than during morning rush hour (9:00˜10:00), probably explained by additional traffic for nighttime activities, the daytime VOC oxidation by OH and the daily variation of boundary layer height. In figure 8, NO increased with a factor of 4 from 16:00 to 18:00, which was quite consistent with CO and VOCs. And no corresponding enhancement in SO2, indicating coal burning emissions from industries, occurred at 18:00. This suggests that elevated CO, VOCs and NO were mostly attributed to traffic emissions. While, the statement “CO and VOCs seemed to be higher” is likely to be misled by the different left and right axes.

Section 3.5.: Acetylene is also found in wood combustion and biomass burning emissions. In addition to exhaust of gasoline-powered vehichles, evaporation of gasoline (from motors or from gasoline stations) may be a source of MTBE.

Response: You are quite right. The statements about sources of acetylene and MTBE have been modified.

Page 14720, line 4: Maybe you could add that these tunnel measurements are local and therefore really describe the local traffic emissions. There can be significant differencies between different regions, because of different gasolines used and differencies in car fleet.

Response: Yes, there are some distinct discrepancies in vehicle exhaust signatures between our work in China and previous studies in USA or Europe. The tunnel measurement cited in this study was conduct at Guangzhou city in September of 2004, as the statement in the revised version “…compared to the results obtained from the Guangzhou Pearl River Tunnel samples in Sep. 2004”

Page 14722, line 2: I would say that also traffic may be contributing. In my opinion traffic can not be ruled out based on these correlations.

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Response: Agree. The current correlations are not sufficient enough to rule out the contributions of vehicle exhaust emissions. The last sentence in Section 3.5 has been modified to “the ambient data falling on the vicinity of the regression line from tunnel samples were probably due to vehicle exhaust, and the data points above the line with higher isoprene concentrations were likely attributed to biogenic sources.”

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 14707, 2007.

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Interactive Comment