Supplementary Information

Experimental budgets of OH, HO_2 and RO_2 radicals and implications for ozone formation in the Pearl River Delta in China 2014

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Supplementary text

Addtional uncertainties in the budget analyses

Radical initiation by unmeasured VOCs

As pointed out in Section 4.1, unmeasured VOCs were most likely responsible for the observed missing OH reactivity. This not only considerably influences the radical chain propagation from OH to RO_2 (Fig. 3e, g), but can also affect the primary production of OH, HO_2, and RO_2 radicals. Unmeasured alkenes could form additional radicals through ozonolysis. However, the contribution to radical formation is very likely unimportant as the small amount of $RO_2^\#$ compared to RO_2 (Fig. 1), and the analysis of the RO_2 and $RO_2^\#$ budgets suggest that most of the missing reactivity is not caused by alkenes (Section 4.1). Unmeasured OVOCs could form additional radicals (HO_2, RO_2) through photolysis. Such reactions would further increase the gap between the production and destruction rate for RO_2 and disturb the closed RO_x and HO_2 budgets.

Radical initiation by Cl atoms

Gaseous nitryl chloride ($ClNO_2$) can be formed at night by heterogeneous reaction of N_2O_5 with chloride in moist particles (e.g., Osthoff et al., 2008). In the morning, $ClNO_2$ photolyzes and forms Cl atoms which react very fast with VOCs and produce additional RO_2. This mechanism can play a role for 2 - 3 hours after sunrise until the $ClNO_2$ reservoir is depleted. $ClNO_2$ was not measured in Heshan, but was reported for other places in China. Measured concentrations shortly before sunrise are typically below 1 ppbv (e.g., Tham et al., 2016; Wang et al. (2018)), but can occasionally reach a few ppb (e.g., 2.1 ppbv in Wangdu, Tham et al. (2016); 4.7 ppbv in Hong Kong,(Wang et al., 2016)). With photolytical lifetimes of 2 - 3 hours, Cl production rates rarely exceed 0.5 ppbv/h. RO_2 production with a similar rate will make only a minor contribution to the RO_2 budget (Fig. 3e), and make the balance in the ROx budget slightly worse (Fig. 2g).

Chain propagation versus termination in the reaction of RO_2 + NO

The reaction of RO_2 radicals with NO can form HO_2 (reaction R8) resulting in radical chain propagation, or produce organic nitrates (reaction R14) resulting in chain termination. As the branching ratio can be different for each RO_2 species and as most of the organic reactivity was caused by unmeasured VOCs, the branching ratios of most RO_2 species are not known. Typical yields for organic nitrates lie in the range between 1% and 35% (Atkinson et al., 1982; Lightfoot et al., 1992). For the budget analysis (Figs. 2 - 4), an organic nitrate yield of 5% is assumed. Figs. S4 and S5 show cases where higher yields (10%, 20%) are assumed. Higher organic nitrate yields compensate the slightly negative bias of D-P in the RO_x budget (Fig. S4). An average yield of 10% would lead to a perfect balance between production and destruction rate of ROx during daytime, whereas a yield of 20% would result in a slightly positive bias of up to +1 ppbv/h in D-P. For the HO_2 production rate, these changes have little impact. Thus, in all cases (80%, 90%, 95% yield of HO_2), the HO_2 budget is balanced within the experimental uncertainties.

Table S1 Measured quantities used to evaluate the radical budgets.

Measured quantity	Measurement technique	Time resolution	Detection limit [a]	Accuracy (1σ)
OH	LIF [b]	300 s	3.9×10^5cm^{-3}	±13 %
HO_2	LIF [b, c]	300 s	1.2×10^7cm^{-3}	±20 %
RO_2	LIF [b, c]	300 s	0.6×10^7cm^{-3}	±26 %
$RO_2^\#$	LIF [b, c]	300 s	1.7×10^7cm^{-3}	±32 %
k_{OH}	LP-LIF [d]	180 s	0.3 s^{-1}	±10 %, ±0.7 s^{-1}
Photolysis frequencies	Actinic flux spectroradiometry	20 s	e	±10 %
O_3	UV photometry	60 s	0.5 ppbv	±5 %
NO	Chemiluminescence	60 s	60 pptv	±20 %
NO_2	Chemiluminescence [f]	60 s	300 pptv	±20 %
HONO	LOPAP [g]	30 s	7 pptv	±20 %
CO,CH_4,CO_2,H_2O	Cavity ringdown spectroscopy	60 s	h	i
SO_2	Pulsed UV fluorescence	60 s	0.1 ppbv	±5 %
HCHO	Hantzsch fluorimetry	60 s	25 pptv	±5 %
Volatile organic compounds [j]	GC-FID/MS [k]	1 h	20 - 300 pptv	±(15-20) %

[a] Signal to noise ratio = 1; [b] Laser-induced fluorescence; [c] Chemical conversion via NO reaction before detection; [d] Laser photolysis – laser-induced fluorescence; [e] Five orders of magnitude lower than maximum at noon; [f] Photolytic conversion to NO before detection, home built converter; [g] Long-path absorption photometry; [h] CO: 1 ppbv; CH_4:1 ppbv; CO_2: 25 ppbv; H_2O: 0.1 % (absolute water vapor content).; [i] CO: ±1 ppbv; CH_4: ±1 ppbv; CO_2: ±25 ppbv; H_2O: ±5 % ; [j] VOCs including C_2-C_{11} alkanes, C_2-C_6 alkenes, C_6-C_{10} aromatics; [k] Gas chromatography equipped with mass spectrometer and a flame ionization detector.

Table S2 Measured volatile organic compounds.

Groups	VOC compounds
Alkanes	CYCLOHEXANE, CYCLOPENTANE, ETHANE, ETHYNE, I-BUTANE, METHYLCYCLOHEXANE, METHYLCYCLOPENTANE, N-BUTANE, N-DECANE, N-DODECANE, N-HEPTANE, N-HEXANE, N-NONANE, N-OCTANE, N-PENTANE, N-UNDECANE, PROPANE, 2,2,4-TRIMETHYLPENTANE, 2,2-DIMETHYLBUTANE, 2,3,4-TRIMETHYLPENTANE, 2,3-DIMETHYLBUTANE, 2,3-DIMETHYLPENTANE, 2,4-DIMETHYLPENTANE, 2-METHYLHEPTANE, 2-METHYLHEXANE, 2-METHYLPENTANE, 3-METHYLHEPTANE, 3-METHYLHEXANE, 3-METHYLPENTANE
Alkenes	CIS-2-PENTENE, CIS-BUTENE, ETHENE, I-BUTENE, I-PENTANE, N-PROPYLBENZENE, PROPENE, TRANS-2-BUTENE, TRANS-2-PENTENE, 1-BUTENE, 1-HEXENE, 1-PENTENE, STYRENE [a]
Aromatics	BENZENE, ETHYLBENZENE, I-PROPYLBENZENE, M-DIETHYLBENZENE, M-ETHYLTOLUENE, M,P-XYLENE, O-ETHYLTOLUENE, O-XYLENE, P-DIETHYLBENZENE, P-ETHYLTOLUENE, TOLUENE, 1,2,3-TRIMETHYLBENZENE, 1,2,4-TRIMETHYLBENZENE, 1,3,5-TRIMETHYLBENZENE
Biogenic	ISOPRENE

[a] Styrene is treated as alkene because its major funtional group is the C-C double bond with respect to OH reaction.

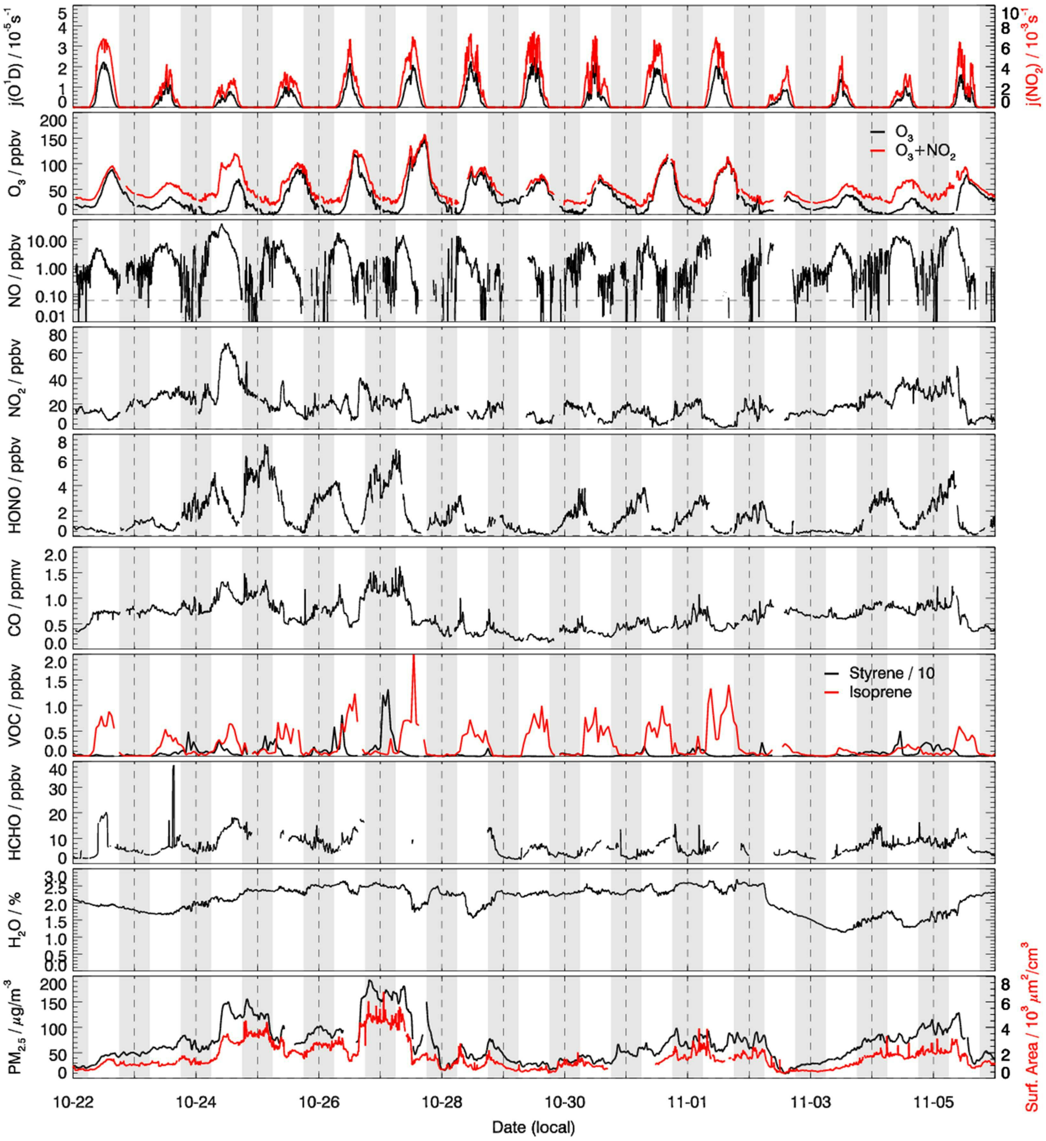

Figure S1 Time series of measured photolysis frequencies, O_3, O_x (O_3+NO_2), NO, NO_2, HONO, CO, isoprene, styrene, HCHO, and H_2O volume mixing ratios, $PM_{2.5}$ mass concentrations and surface area of particulate matter. The vertical dashed lines represent midnight and grey areas represent nighttime.

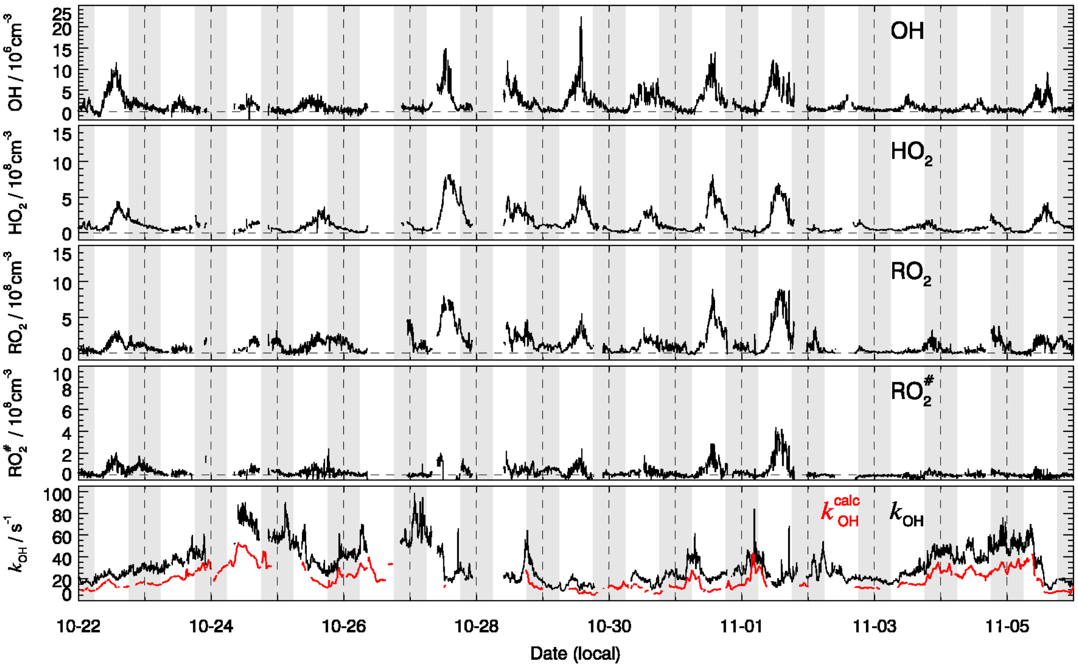

Figure S2 Time series of measured OH, HO_2, RO_2 and $RO_2^{\#}$ concentrations. The lowest panel shows the measured total OH reactivity (k_{OH}) and the calculated OH reactivity (k^{calc}_{OH}) derived from measured concentrations of CO, NO_x, CH_4, NMHCs and HCHO. The vertical dashed lines represent midnight and grey areas represent nighttime.

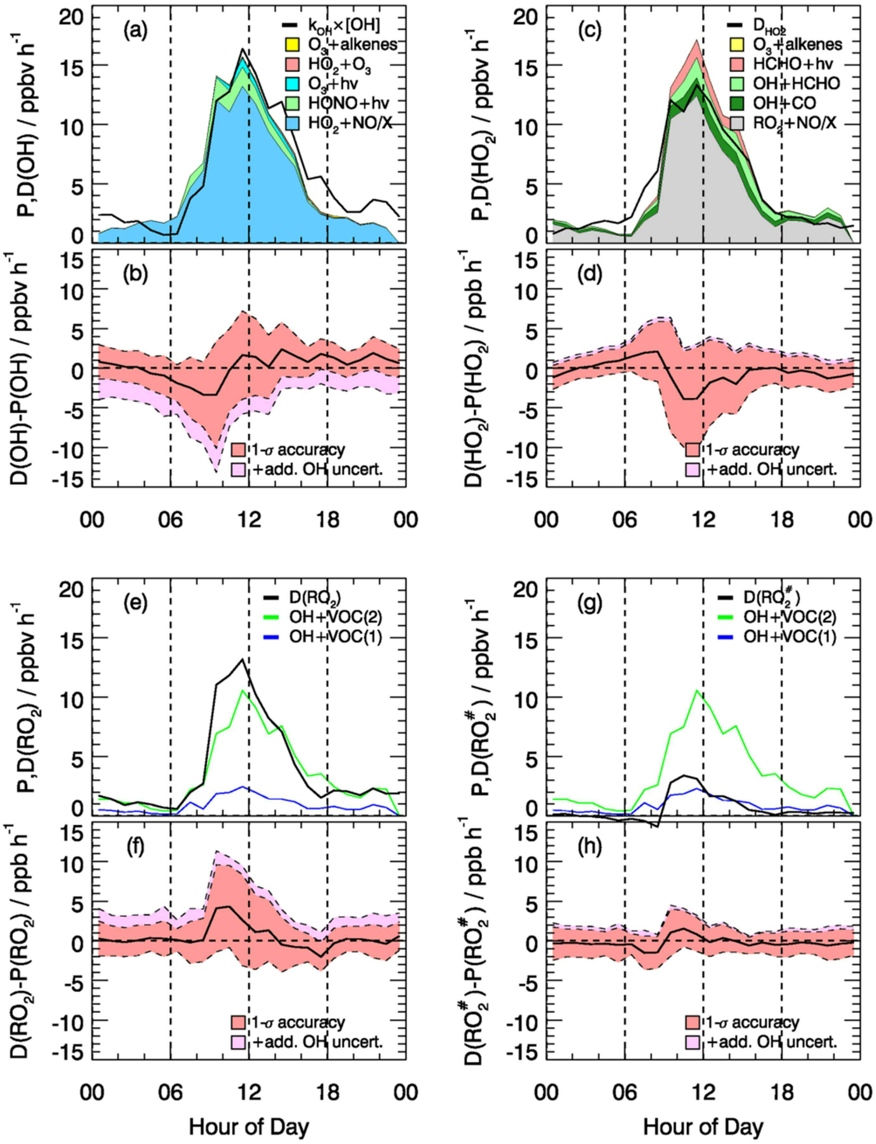

Figure S3 Same as Figure 3, but with additional OH recyling by X equivalent to 0.4 ppbv NO (RO_2 + X → HO_2, HO_2 + X → HO_2).

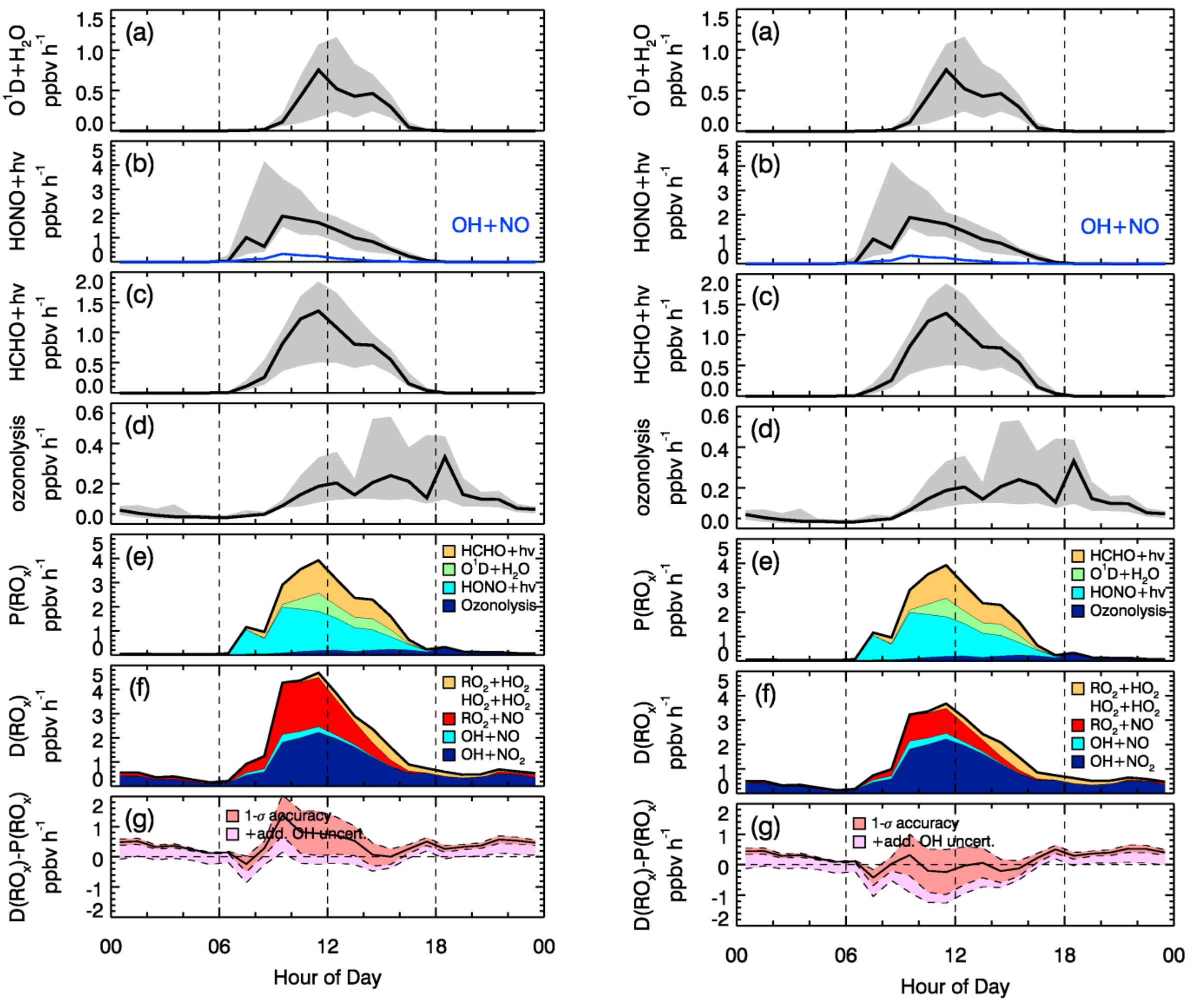

Figure S4 Same as Figure 2, but assuming a different branching ratio between reaction R8 and R14. Left: HO_2 yield is 0.8, organic nitrate yield is 0.2. Right: HO_2 yield is 0.9, organic nitrate yield is 0.1.

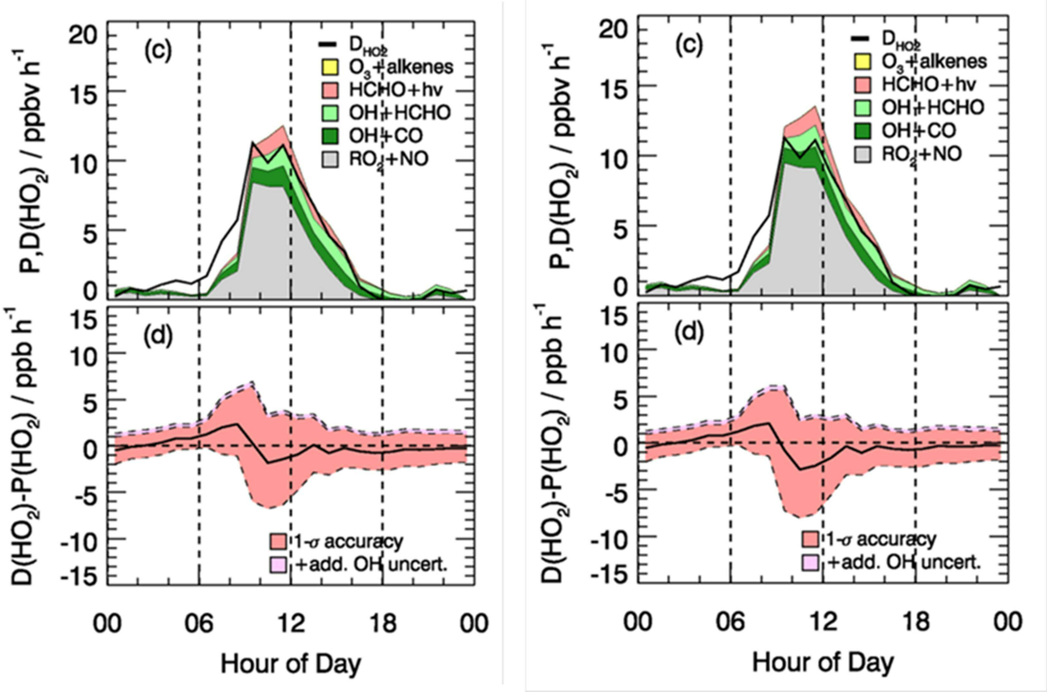

Figure S5 Same as Figure 3(c, d), but assuming a different branching ratio between reaction R8 and R14. Left: HO$_2$ yield is 0.8, organic nitrate yield is 0.2. Right: HO$_2$ yield is 0.9, organic nitrate yield is 0.1.