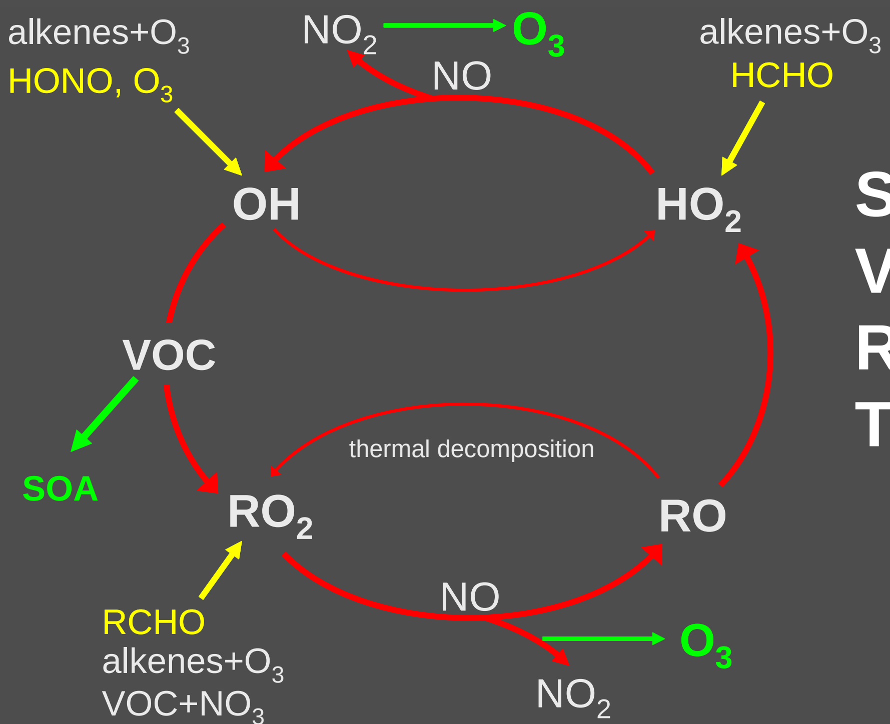
Radical sources and SOA

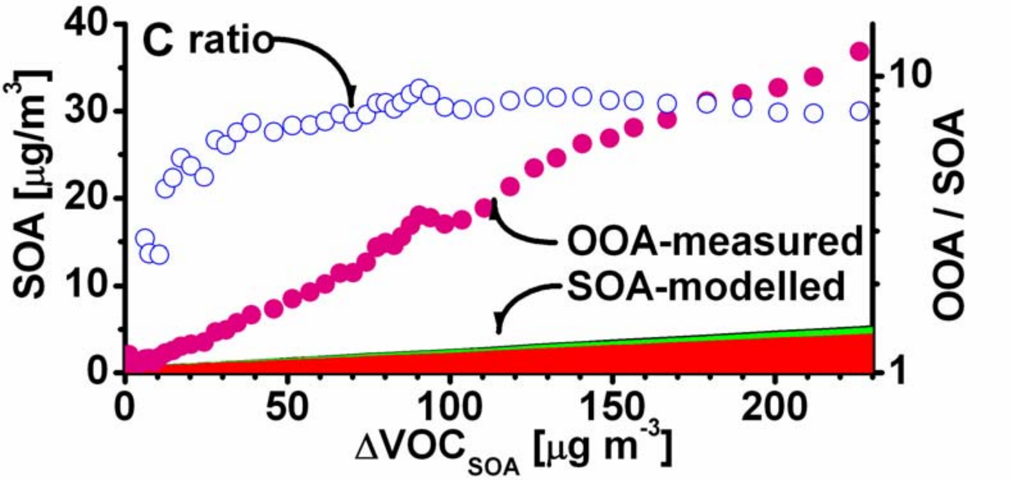
Rainer Volkamer, UCSD



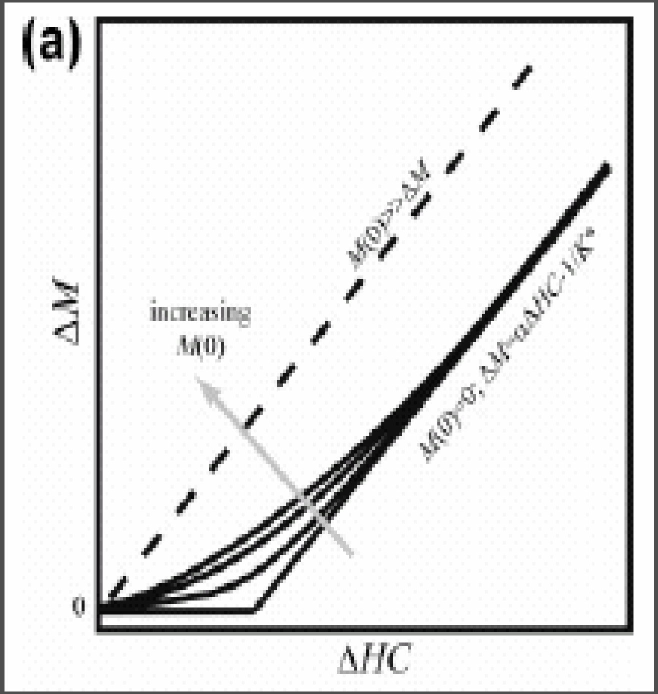
SOA formation
VOC Precursors + Oxidant fields
Radical sources (time resolved)
Test our understanding of HOx

Alexander von Humboldt
Stiftung/Foundation

Missing SOA source in urban air



⬛ Alkanes (4%) -> 0.2 - 0.5 %
🟩 Alkenes (16%) -> 0.8 – 2 %
🟥 Aromatics (80%) -> 4 – 10%



Missing SOA precursors:
SVOCs, IVOCs – what are those ?
Missing mechanisms ?

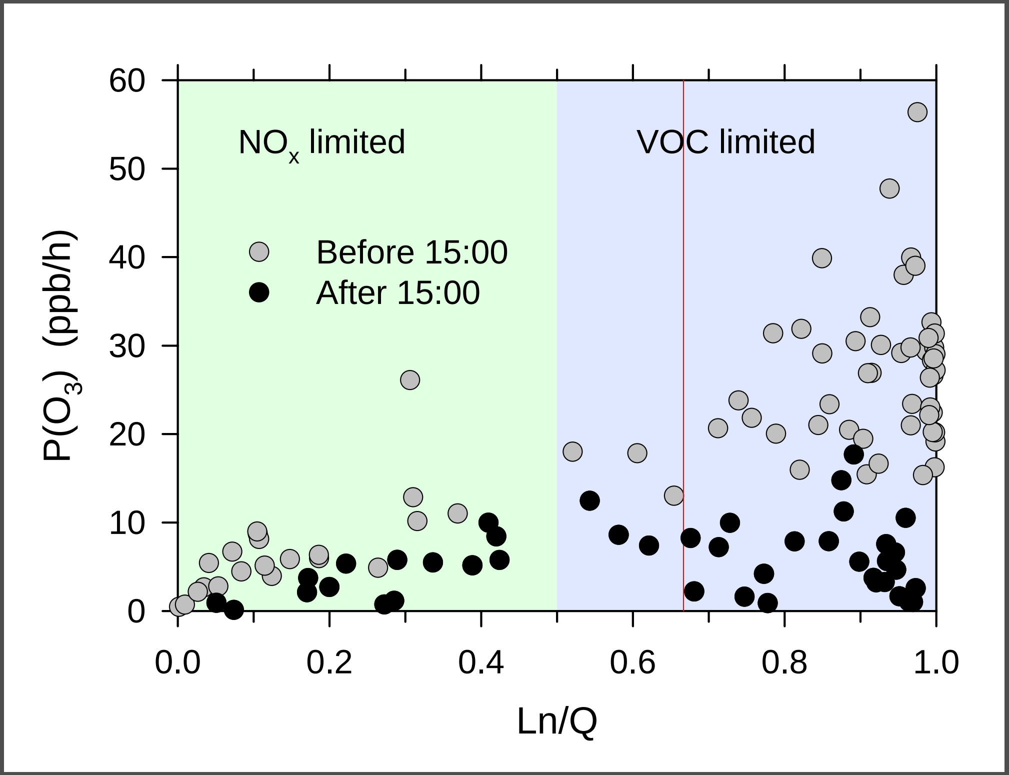
Oxidant fields:
What controls those ?

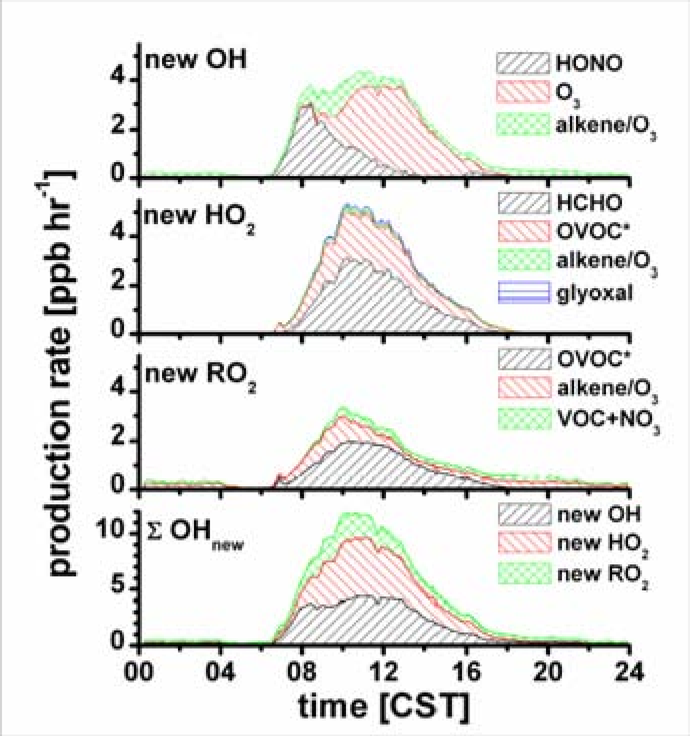
Very little curvature is observed in field studies!

Can models simulate the fast SOA formation that is observed ?

Volkamer *et al.* (2006) GRL

Highest $P(O_3)$ from VOC Limited Conditions





$P(O_3)$ = Y ☟ Q ☟ $(VOC/NO_2)_{reactivity}$

$P(O_3)$ variability mostly due to Q

More than O_3 and HCHO for Q

Volkamer et al., ACPD, 2007

Larry Kleinman

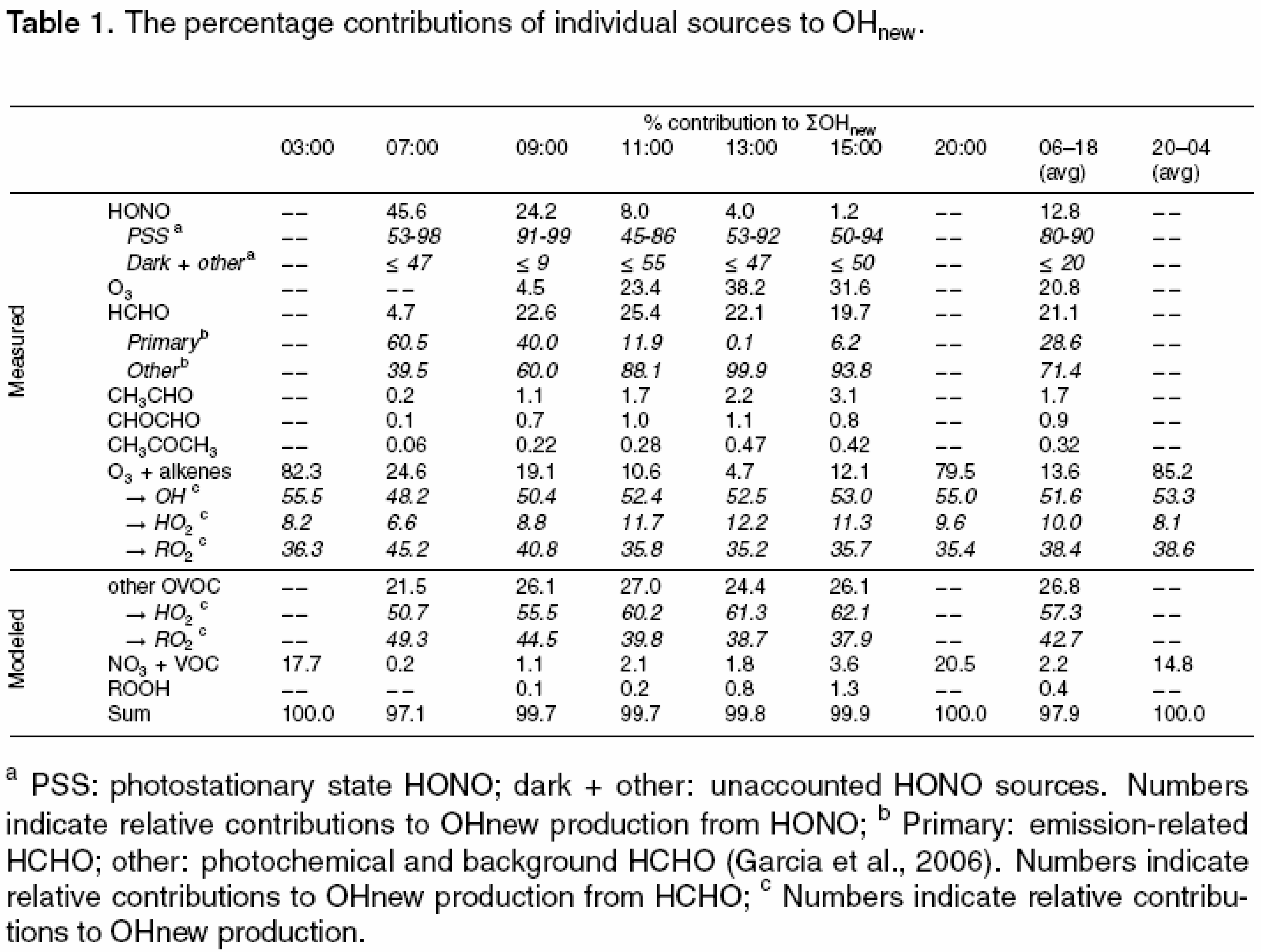


Table 1. The percentage contributions of individual sources to OH_{new}.

		% contribution to ΣOH_{new}								
		03:00	07:00	09:00	11:00	13:00	15:00	20:00	06–18 (avg)	20–04 (avg)
Measured	HONO	--	45.6	24.2	8.0	4.0	1.2	--	12.8	--
	PSS[a]	--	*53-98*	*91-99*	*45-86*	*53-92*	*50-94*	--	*80-90*	--
	Dark + other[a]	--	*≤ 47*	*≤ 9*	*≤ 55*	*≤ 47*	*≤ 50*	--	*≤ 20*	--
	O_3	--	--	4.5	23.4	38.2	31.6	--	20.8	--
	HCHO	--	4.7	22.6	25.4	22.1	19.7	--	21.1	--
	Primary[b]	--	*60.5*	*40.0*	*11.9*	*0.1*	*6.2*	--	*28.6*	--
	Other[b]	--	*39.5*	*60.0*	*88.1*	*99.9*	*93.8*	--	*71.4*	--
	CH_3CHO	--	0.2	1.1	1.7	2.2	3.1	--	1.7	--
	CHOCHO	--	0.1	0.7	1.0	1.1	0.8	--	0.9	--
	CH_3COCH_3	--	0.06	0.22	0.28	0.47	0.42	--	0.32	--
	O_3 + alkenes	82.3	24.6	19.1	10.6	4.7	12.1	79.5	13.6	85.2
	→ *OH*[c]	*55.5*	*48.2*	*50.4*	*52.4*	*52.5*	*53.0*	*55.0*	*51.6*	*53.3*
	→ HO_2[c]	*8.2*	*6.6*	*8.8*	*11.7*	*12.2*	*11.3*	*9.6*	*10.0*	*8.1*
	→ RO_2[c]	*36.3*	*45.2*	*40.8*	*35.8*	*35.2*	*35.7*	*35.4*	*38.4*	*38.6*
Modeled	other OVOC	--	21.5	26.1	27.0	24.4	26.1	--	26.8	--
	→ HO_2[c]	--	*50.7*	*55.5*	*60.2*	*61.3*	*62.1*	--	*57.3*	--
	→ RO_2[c]	--	*49.3*	*44.5*	*39.8*	*38.7*	*37.9*	--	*42.7*	--
	NO_3 + VOC	17.7	0.2	1.1	2.1	1.8	3.6	20.5	2.2	14.8
	ROOH	--	--	0.1	0.2	0.8	1.3	--	0.4	--
	Sum	100.0	97.1	99.7	99.7	99.8	99.9	100.0	97.9	100.0

[a] PSS: photostationary state HONO; dark + other: unaccounted HONO sources. Numbers indicate relative contributions to OHnew production from HONO; [b] Primary: emission-related HCHO; other: photochemical and background HCHO (Garcia et al., 2006). Numbers indicate relative contributions to OHnew production from HCHO; [c] Numbers indicate relative contributions to OHnew production.

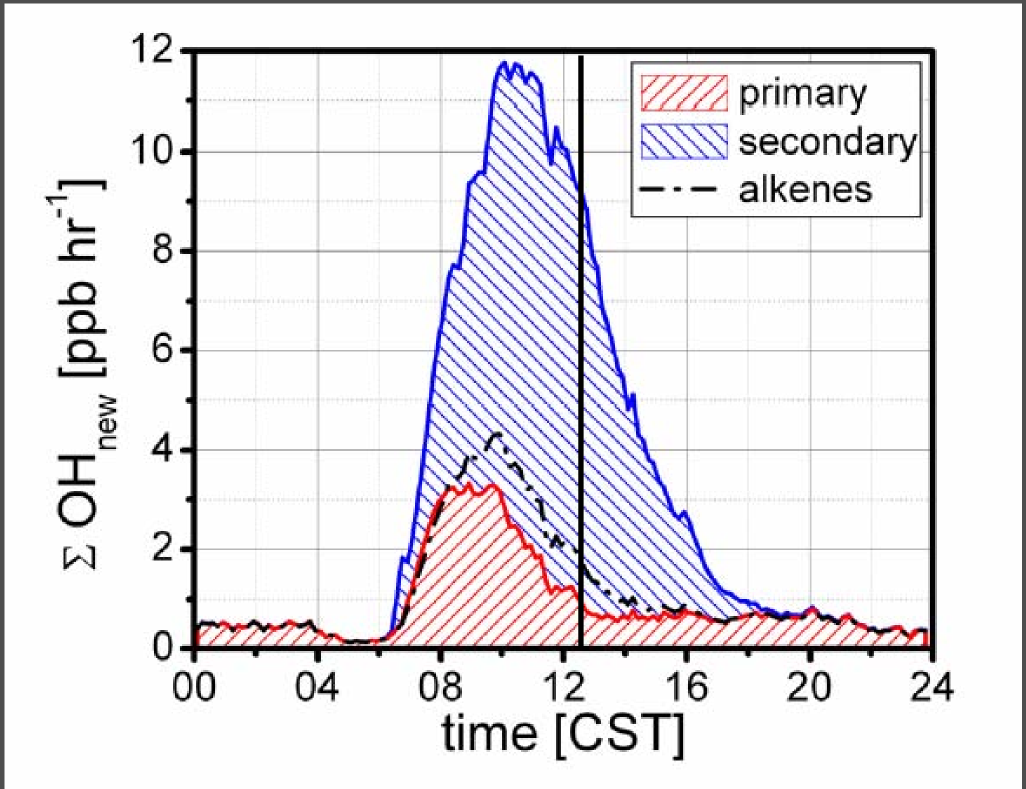
Volkamer et al., ACPD, 2007

Feedbacks of reductions in VOC emissions

(1) lowering the rate of VOC oxidation as a result of a lower VOC/NOx ratio
(effect of a lower radical re-cycling efficiency)

(2) by slowing down the 20 formation of secondary pollutants
(effect of a lower radical production rate during the day and at night)

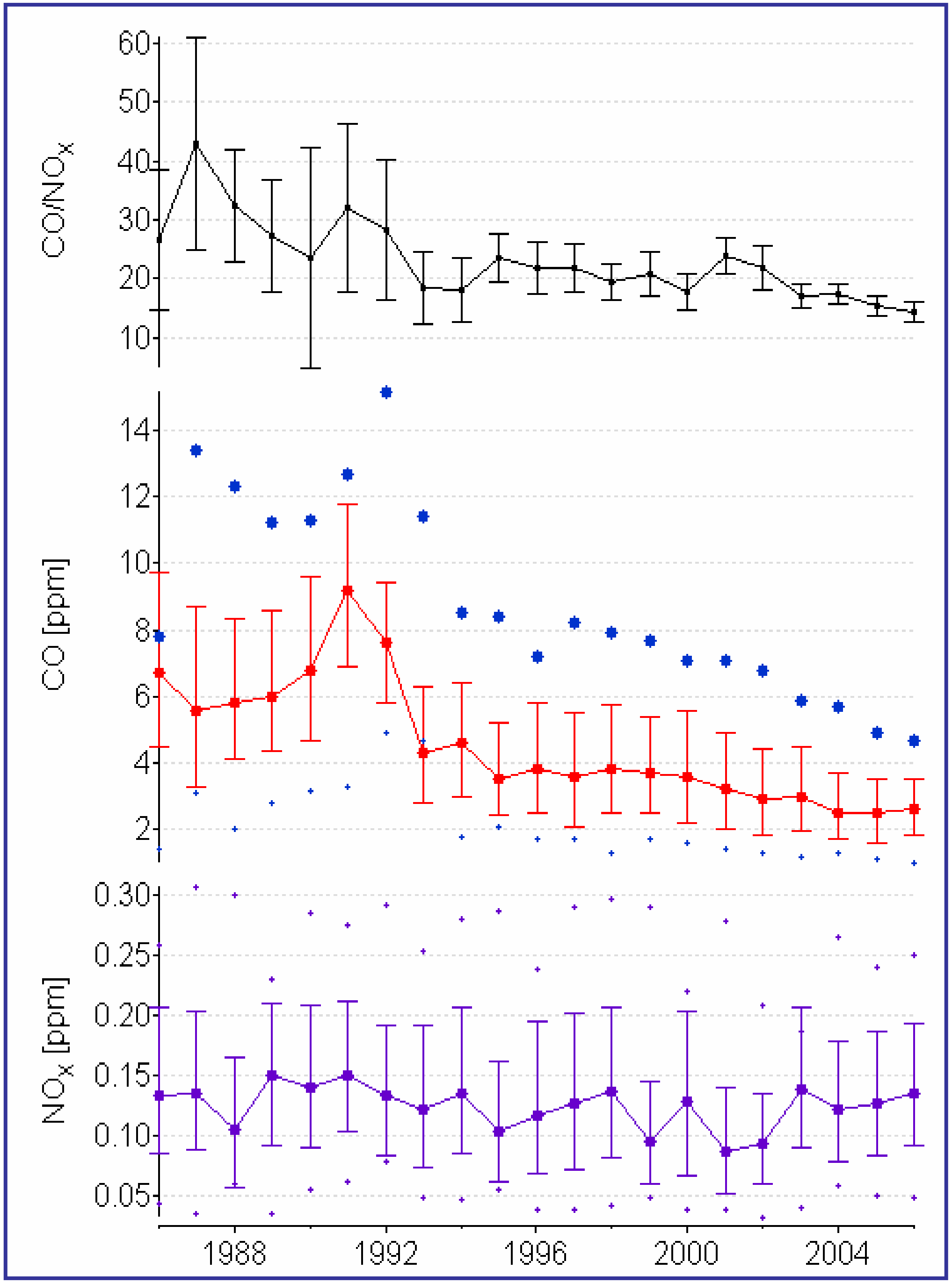
(3) by delaying the onset of photochemical processing; peak concentrations of secondary pollutants are capped by pollution export from the MCMA
(effect of reducing the time available to produce secondary pollutants).



Whether models capture these feedback effects depends on whether the radical sources are represented well.

Do they ??

Volkamer et al., ACPD, 2007



6 to 9 AM CO and NOx measurements

No Holidays, no weekends

Implications for
Mobile emission sources:

- **Downward CO/NOx**
- **Downward VOC/NOx**
- **Little or not change in NOx emissions**
- **Reduced CO variability**
- **No change in NOx variability**

Miguel Zavala

Master Chemical Mechanism (MCMv3.1)

- Near-explicit mechanism
  - limited chemical lumping
- 4500+ species, 13500+ reactions
- Updated oxidation schemes

Model constraints (radical perspective)

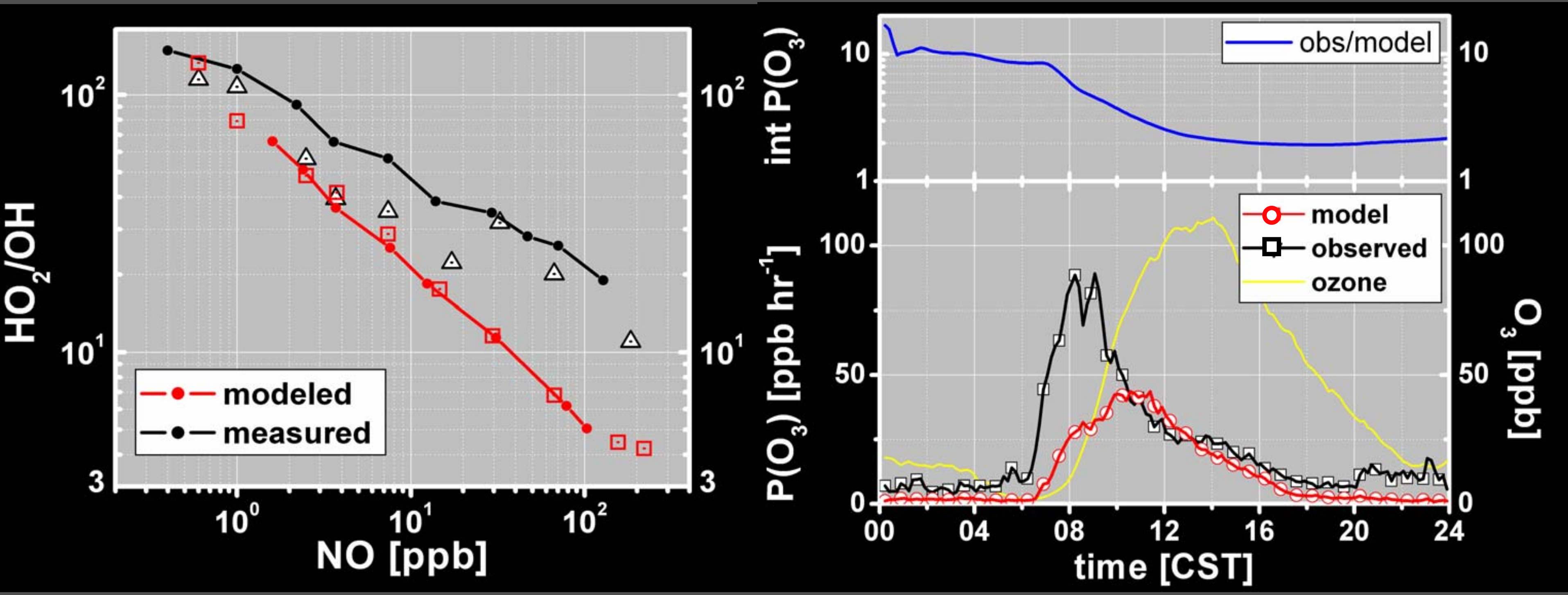
- Sources - HONO, HCHO, O_3
- Sinks - VOCs, NOx, J-values
- 1-D model, with flexible top/sides (dilution)
- 80-99% of OH loss is constrained

Oxidation capacity

What does this “missing reactivity” mean in terms of oxidative capacity of the atmosphere?

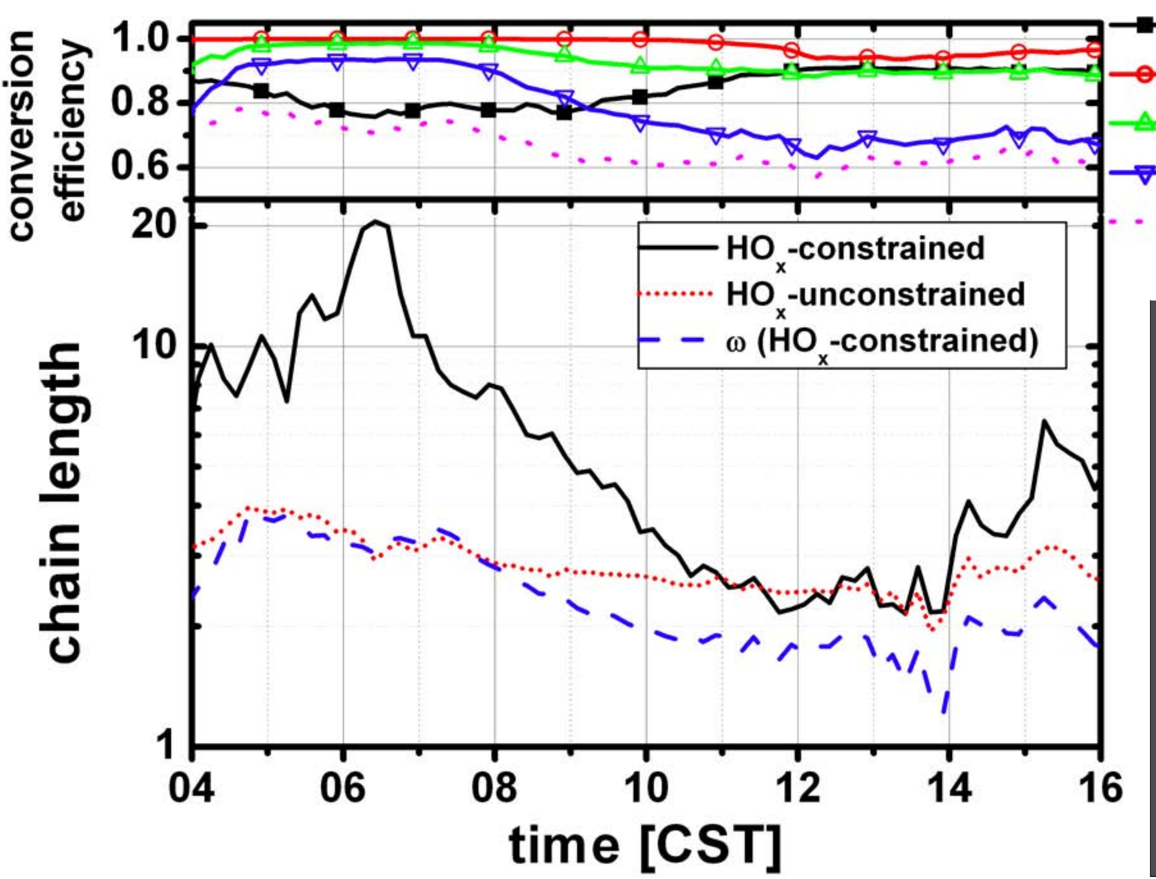
$P(O_3)$, ozone production:

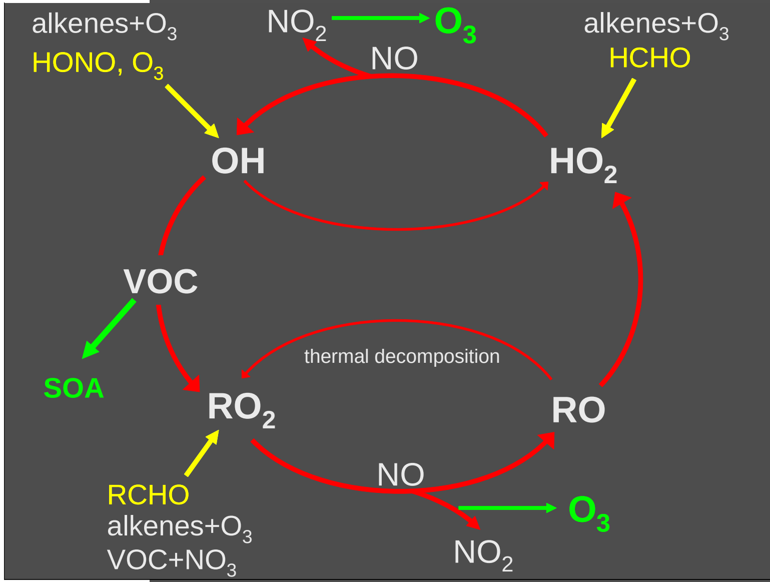
$NO \rightarrow NO_2$ conversions via rxn with HO_2 + RO_2



Sheehy, Volkamer, et al, 2007

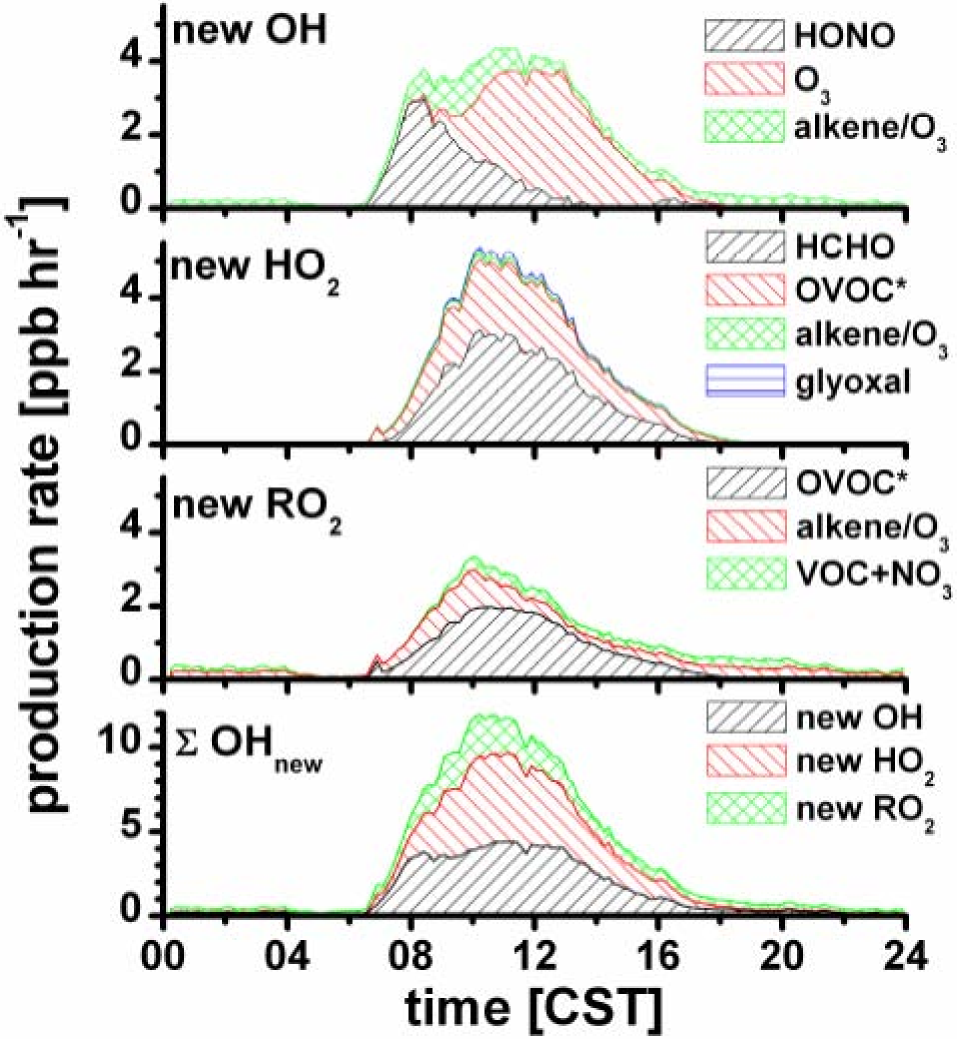
Missing reactivity expressed in chain length



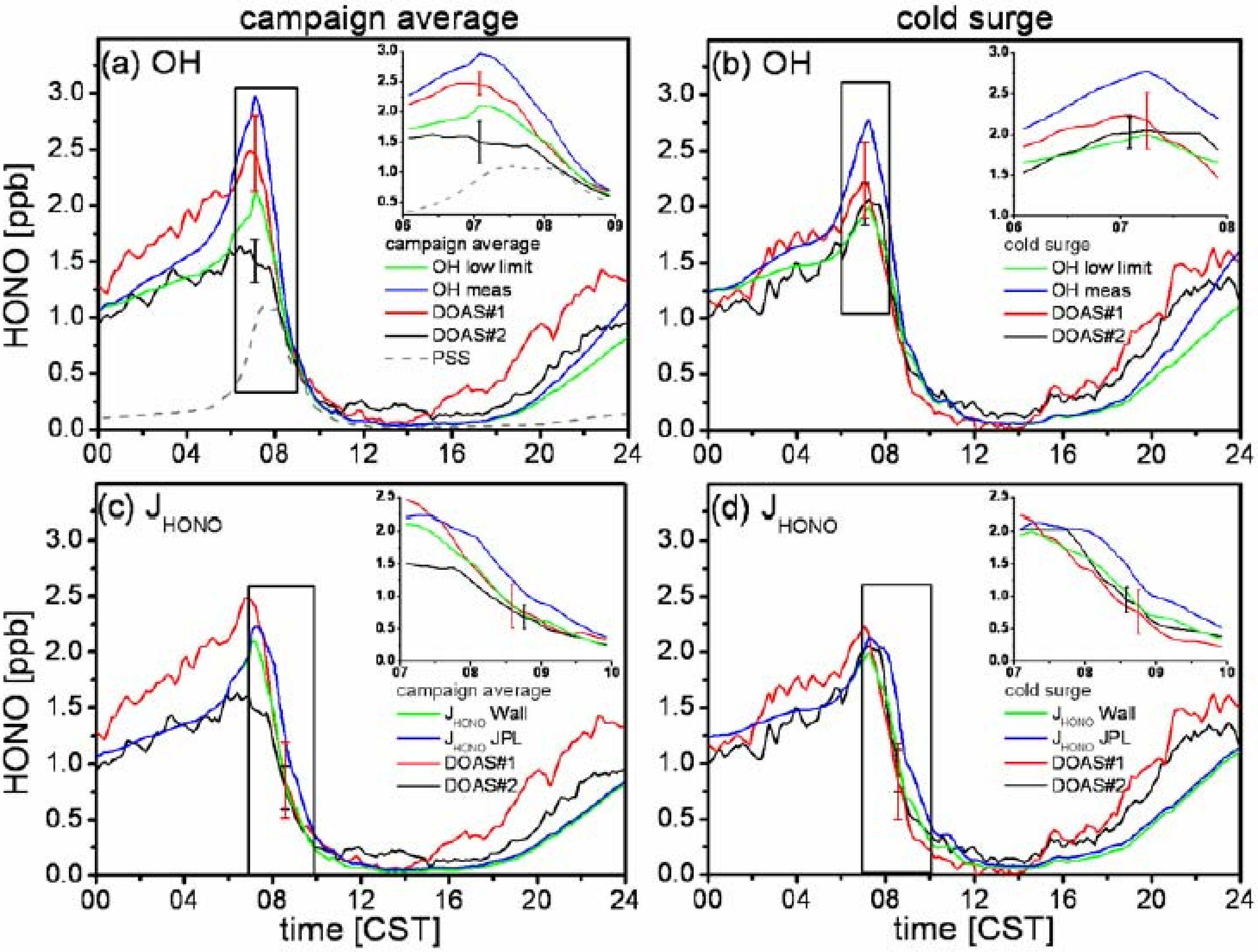


1) n = new OH + recycling / new OH (source oriented)
2) -ln (1/gamma ROx) (cycling oriented)

Sheehy, Volkamer, et al, 2007



new OH
HONO
O_3
alkene/O_3
new HO_2
HCHO
OVOC*
alkene/O_3
glyoxal
new RO_2
OVOC*
alkene/O_3
VOC+NO_3
Σ OH_{new}
new OH
new HO_2
new RO_2
production rate [ppb hr^{-1}]
0
2
4
0
2
4
0
2
4
0
5
10
00
04
08
12
16
20
24
time [CST]


campaign average
cold surge
(a) OH
(b) OH
(c) J_HONO
(d) J_HONO
HONO [ppb]
time [CST]
0.0
0.5
1.0
1.5
2.0
2.5
3.0
00
04
08
12
16
20
24
campaign average
OH low limit
OH meas
DOAS#1
DOAS#2
PSS
cold surge
OH low limit
OH meas
DOAS#1
DOAS#2
campaign average
J_HONO Wall
J_HONO JPL
DOAS#1
DOAS#2
cold surge
J_HONO Wall
J_HONO JPL
DOAS#1
DOAS#2
06
07
08
09
10

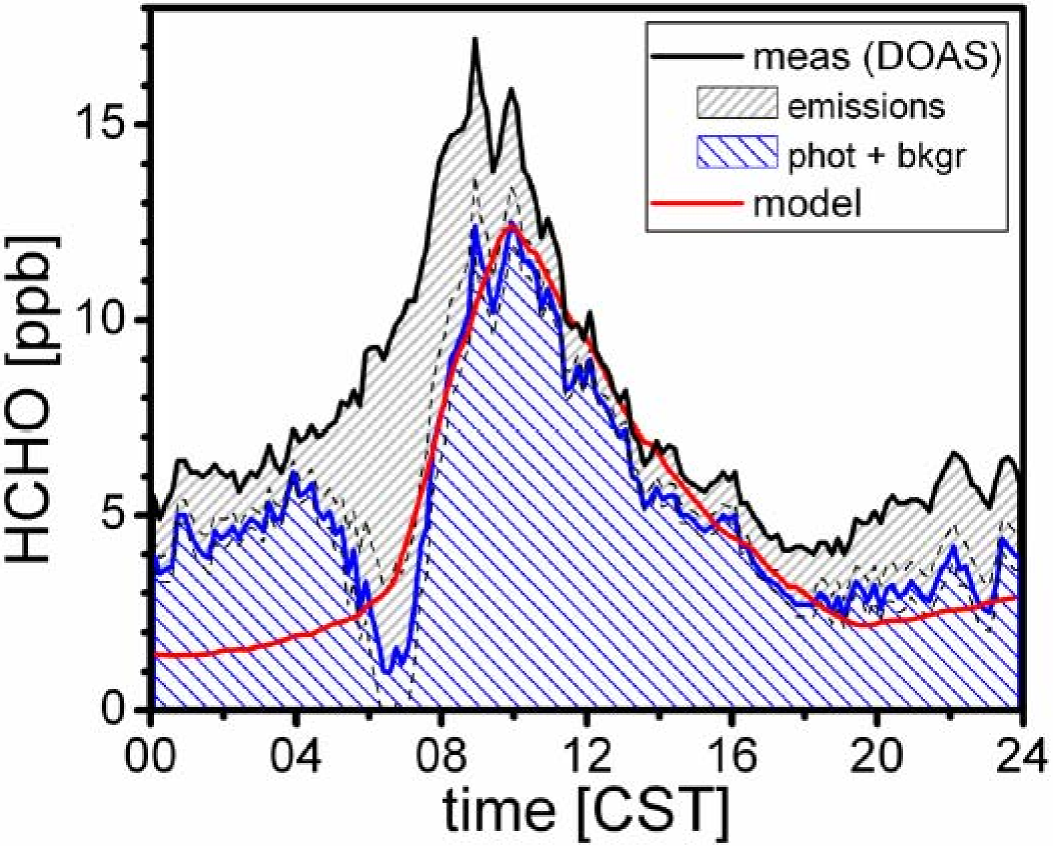
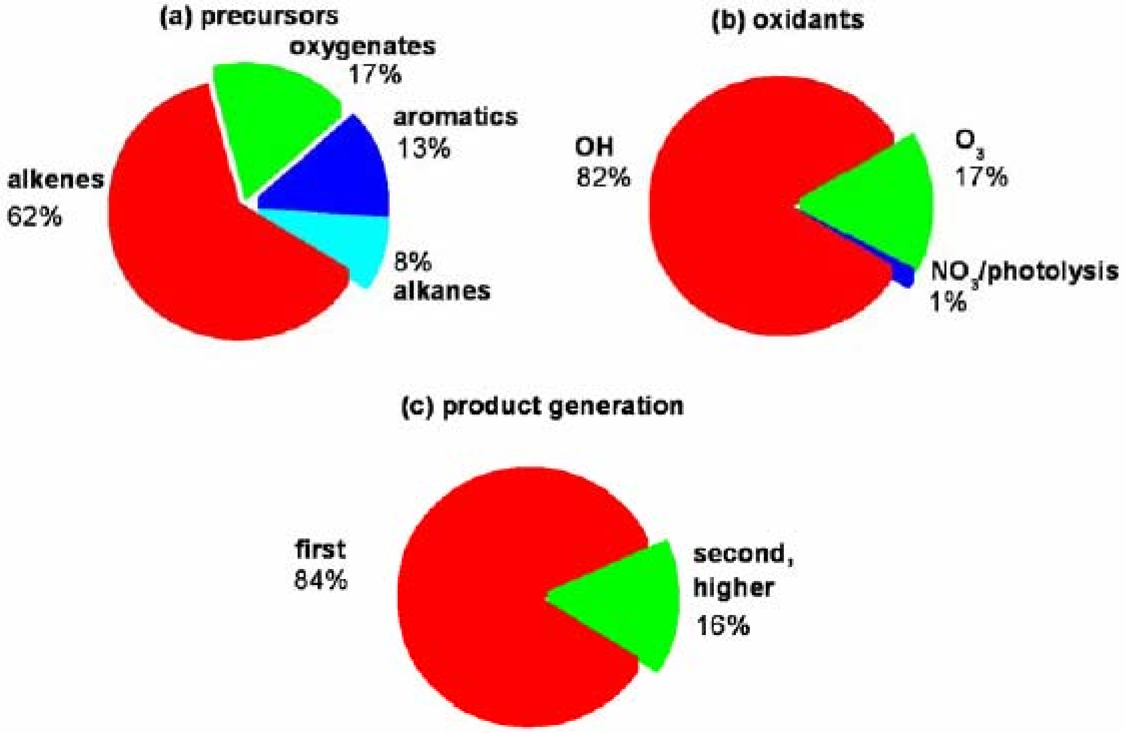


Fig. 5. HCHO observations (black line) are compared to the portion of HCHO produced from photochemical sources and background sources (blue line, shaded blue area), and from emissions (shaded gray area); the dotted lines represent the upper and lower limits of subtracting out emissions sources according to the procedure described by (Garcia et al., 2006). Modeled HCHO concentrations (red line) are shown in which dilution was adjusted to match the blue line (after 10:00 a.m., see Sect. 2.2).


(a) precursors
oxygenates 17%
aromatics 13%
alkenes 62%
8% alkanes
(b) oxidants
OH 82%
O_3 17%
NO_3/photolysis 1%
(c) product generation
first 84%
second, higher 16%