Bromine explosion in smog chamber experiments above a model salt pan

Joelle Buxmann, Robert Holla,
Ulrich Platt, Karsten Kotte,
University of Heidelberg, Germany

Natalja Balzer, Sergej Bleicher,
Cornelius Zetzsch
University of Bayreuth, Germany

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BrO above salt lakes and salt pans

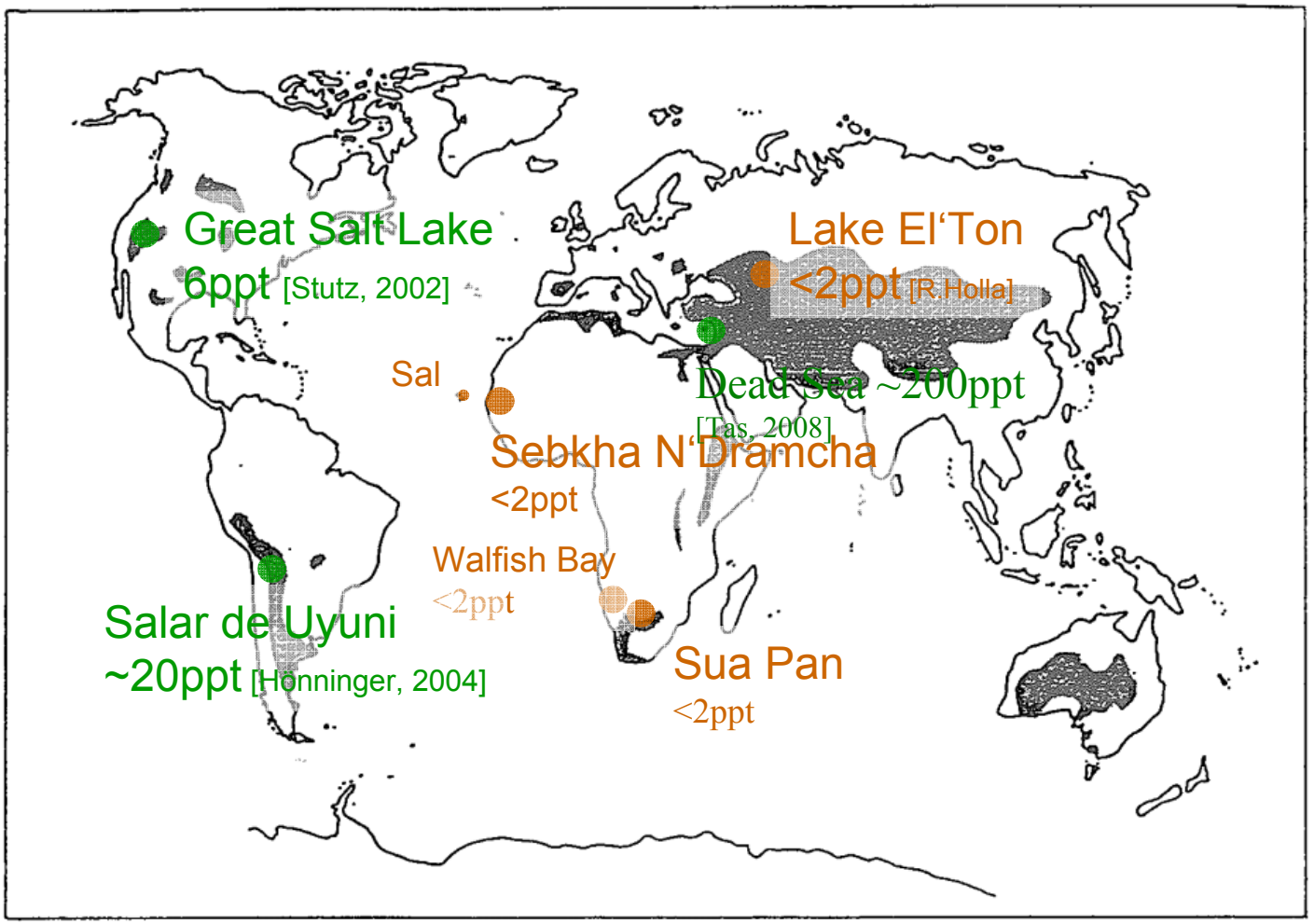
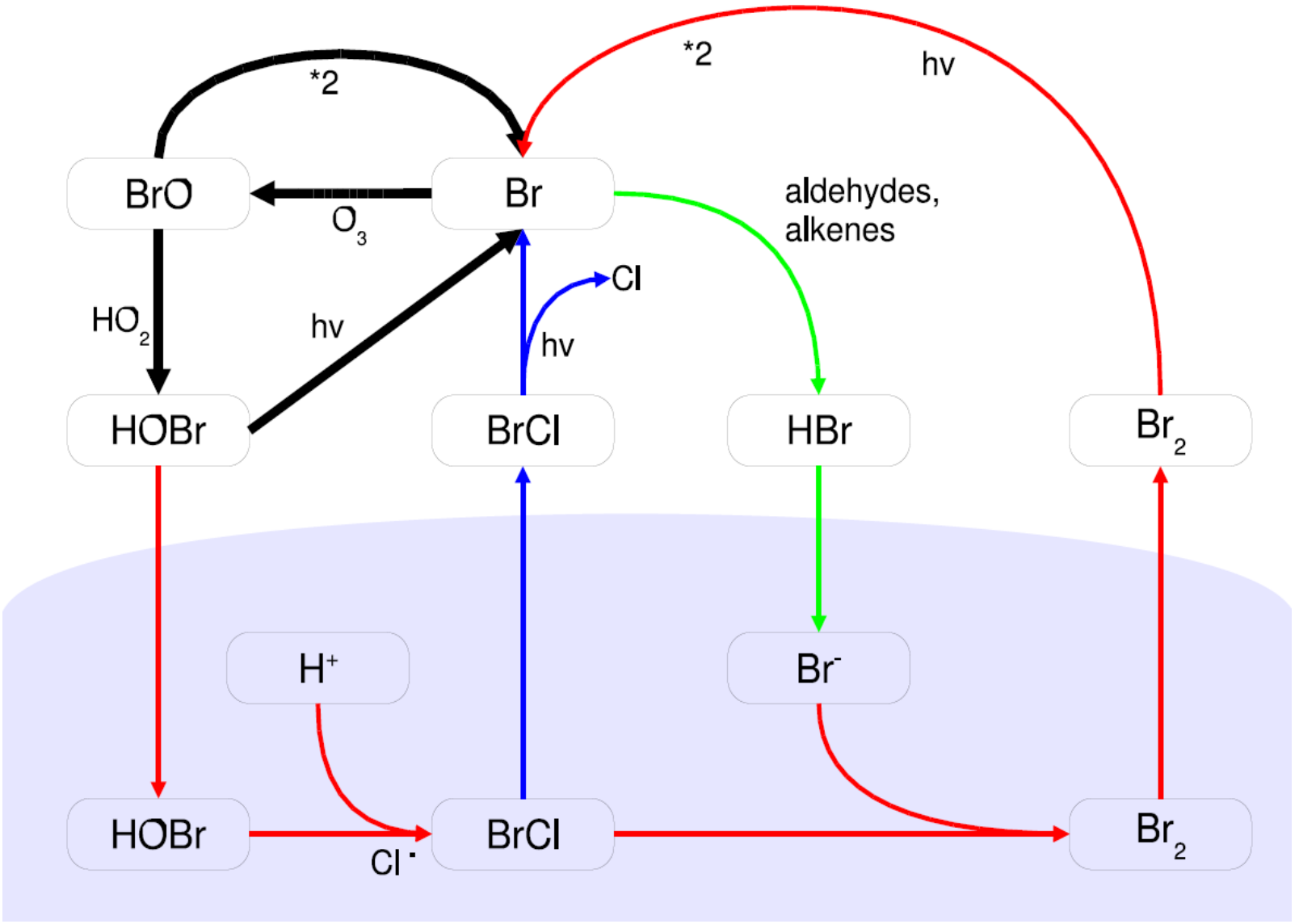


Fig. 1.1 Geographical distribution of major areas with salt lakes. Note: salt lakes occur outside these areas, but not as frequently.

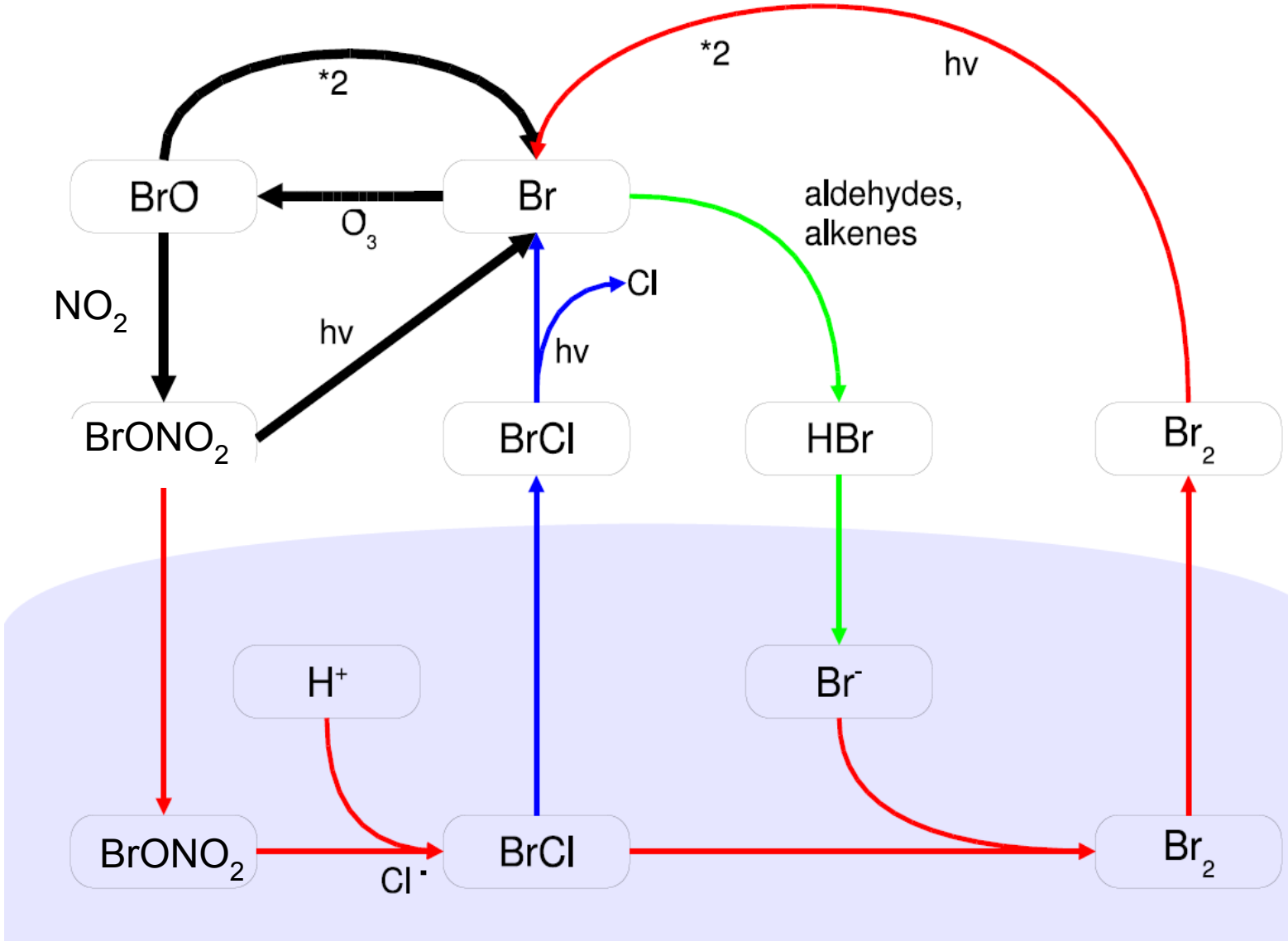
[Williams, 2002]

Bromine chemistry on salt surfaces



[Simpson 2007]

Bromine chemistry on salt surfaces



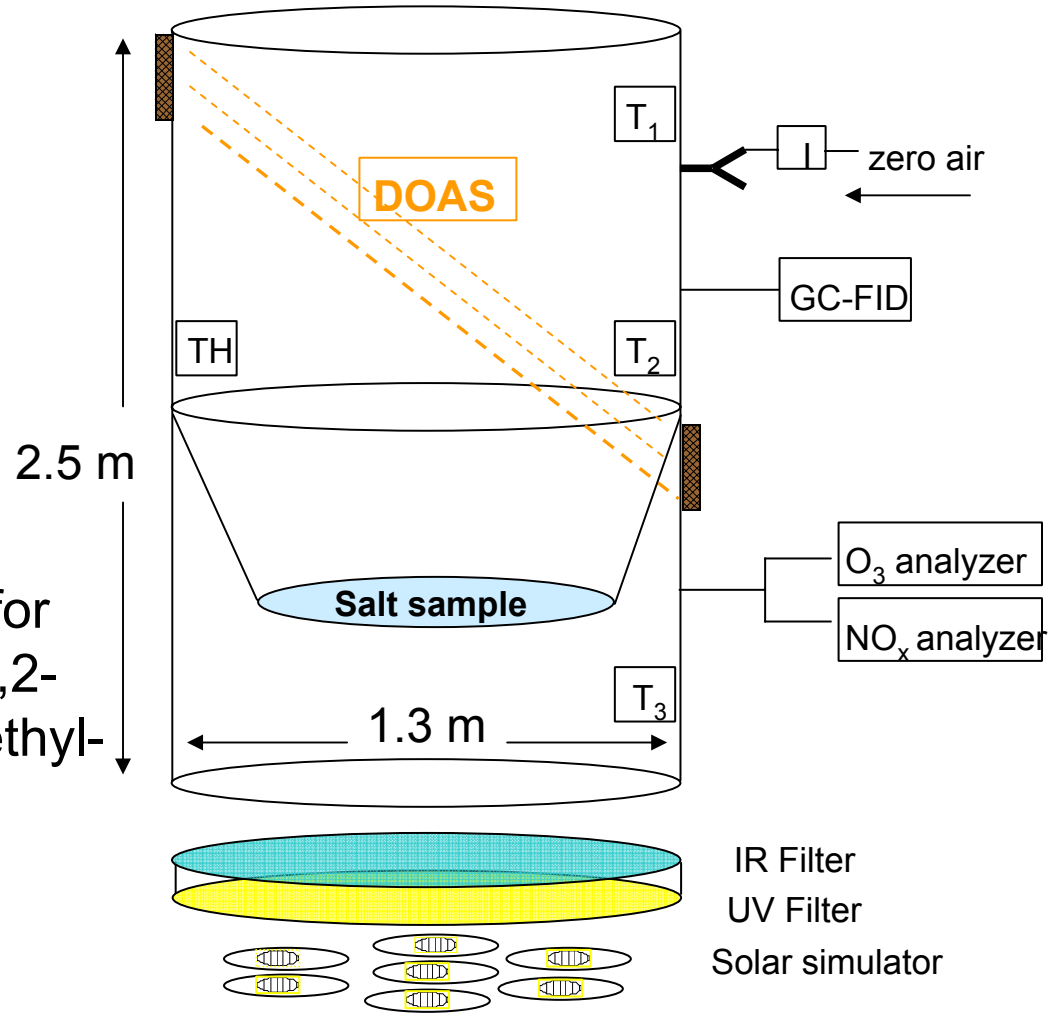
[Simpson 2007]

Experimental setup

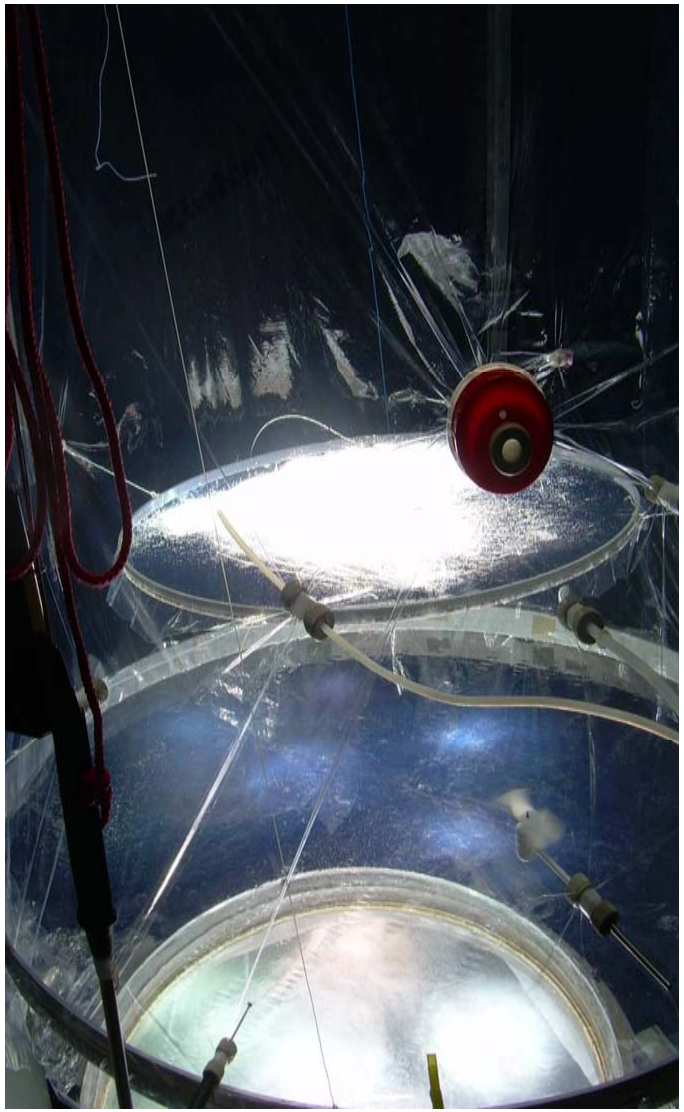
Analytical instruments:

- Multireflection system for DOAS detection of Br
- O_3 analyzer
- NO_x analyzer
- GC-FID with preconcentrator for toluene, n-butane, n-pentane, 2,2-dimethylbutane, 2,2,3,3-tetramethyl-butane, and n-perfluorohexane

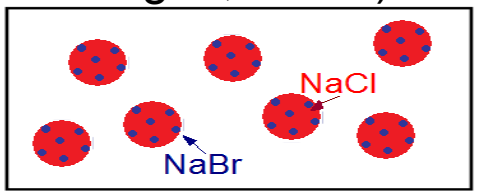
→ indirect determination of OH and Cl



Experimental preparation

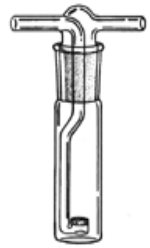


• Preparation of salt sample:
artificial salt samples
NaCl/NaBr = 300/1(similar to sea water)
internal mixture
(dissolved in water, dried over night , milled)



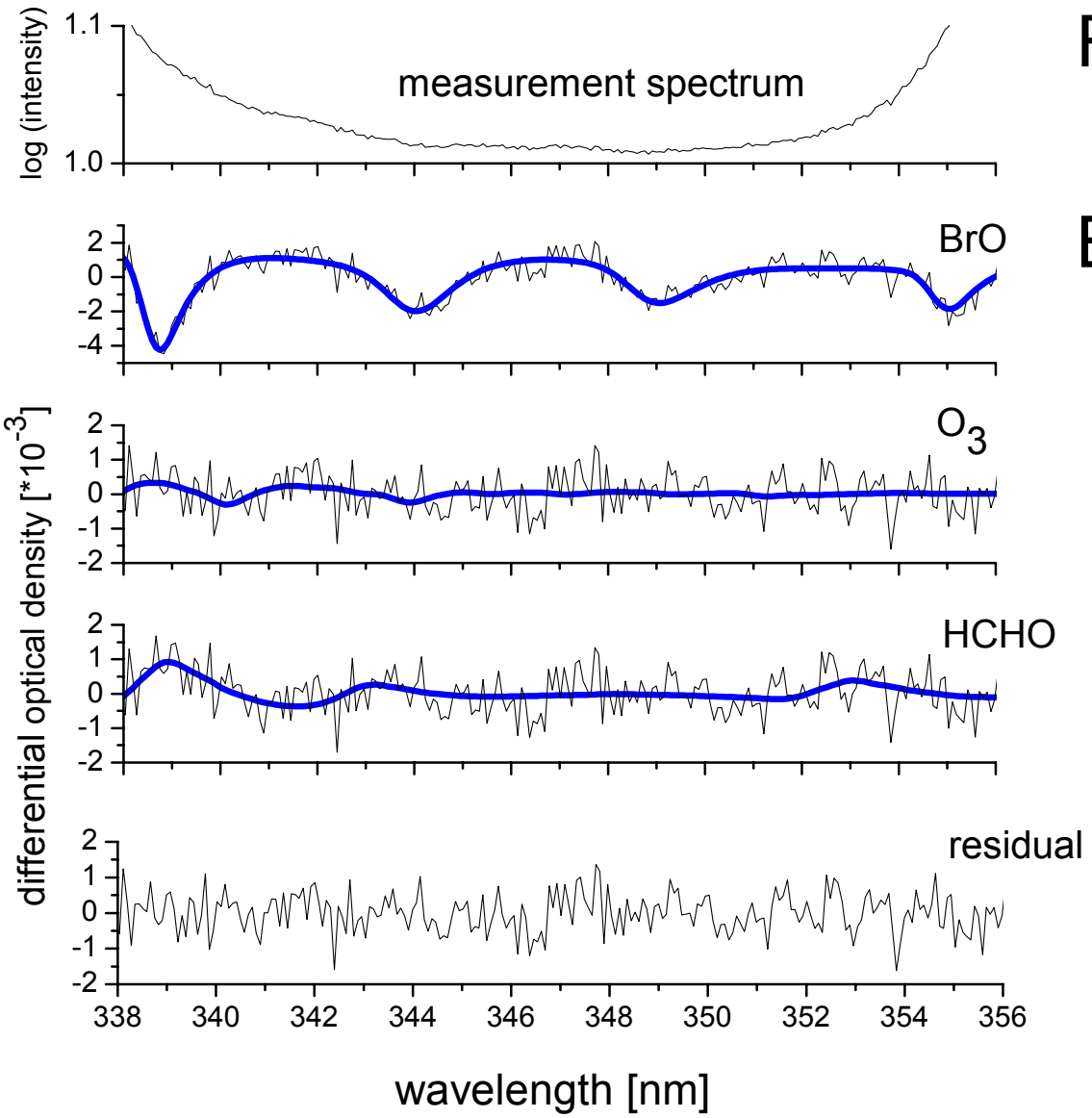
• Flush chamber over night with zero air by distilled water to „adjust“ relative humidity

• T=20°C (temperature controlled)



• Add O_3(O_2+UV light) and hydrocarbons
• Switch solar simulator on

DOAS spectra



RH = 37%

BrO: 498 ±70 ppt

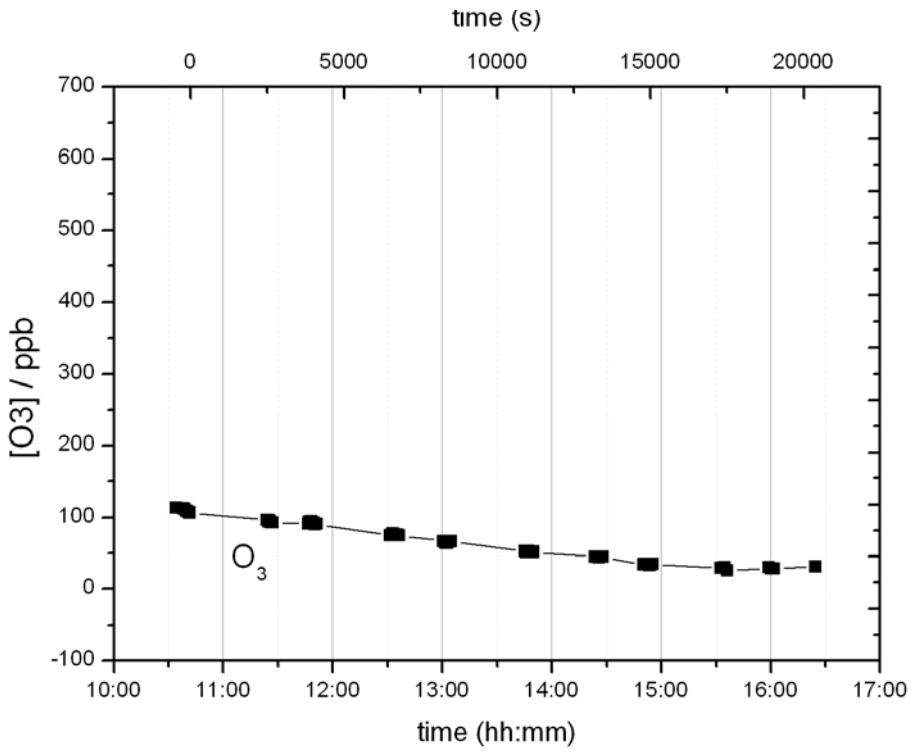
O_3: 585 ppb

(below detection limit)

HCHO: 52 ppb

(below detection limit)

Experimental conditions: RH=2%, NaCl/NaBr=300/1



$BrO + BrO \rightarrow Br + Br + O_2$ (rate determining)

$2\ (Br + O_3 \rightarrow BrO + O_2)$

net: $2\ O_3 \rightarrow 3\ O_2$

$\frac{-d}{dt}[O_3]$ ("simple model") $= 2\ k\ [BrO][BrO]$
$= 0.005 ppb/s$

$\frac{-d}{dt}[O_3](measured) = 0.005 ppb/s$

with:
$k = 2.7 * 10^{-12}\ cm^3\ molec^{-1}\ s^{-1}$ [*Atkinson, 2007*]
and [BrO]=200 ppt

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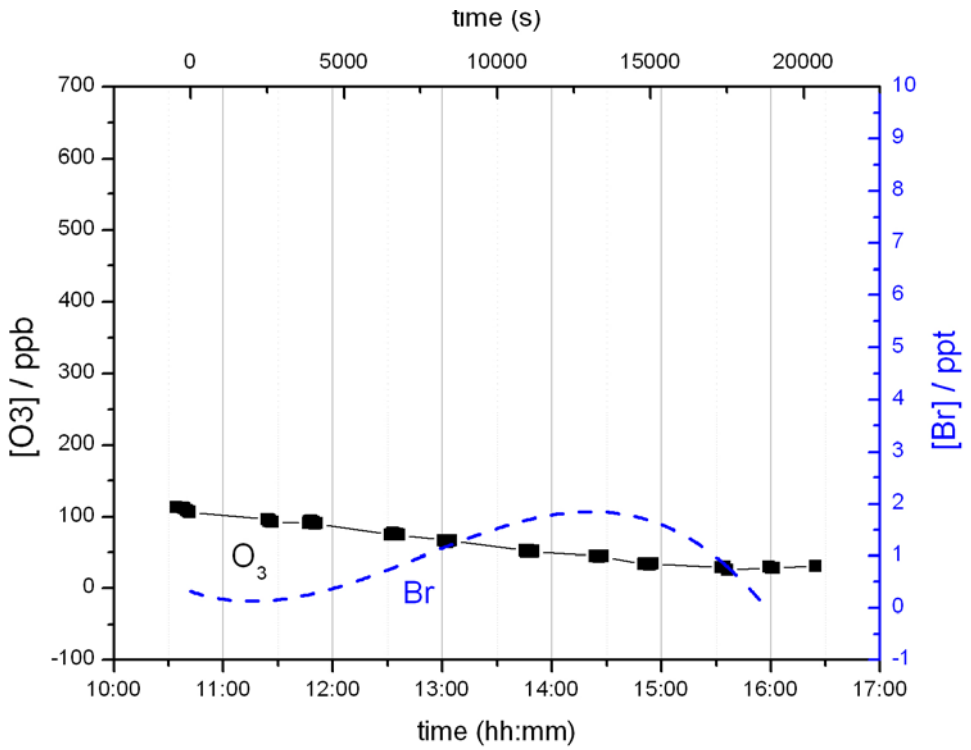

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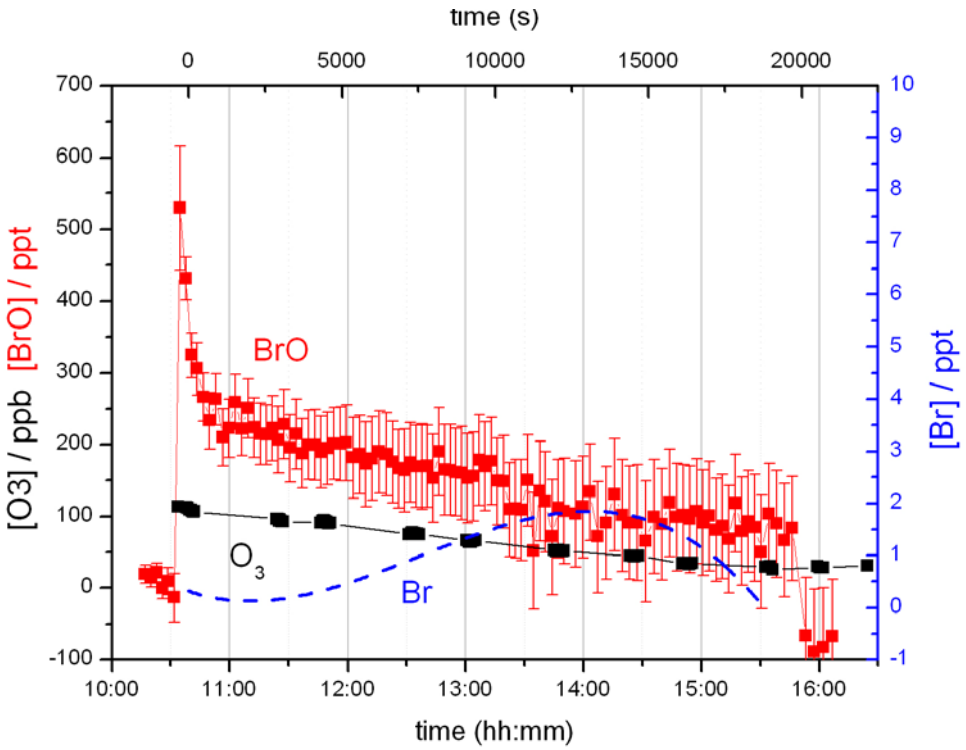

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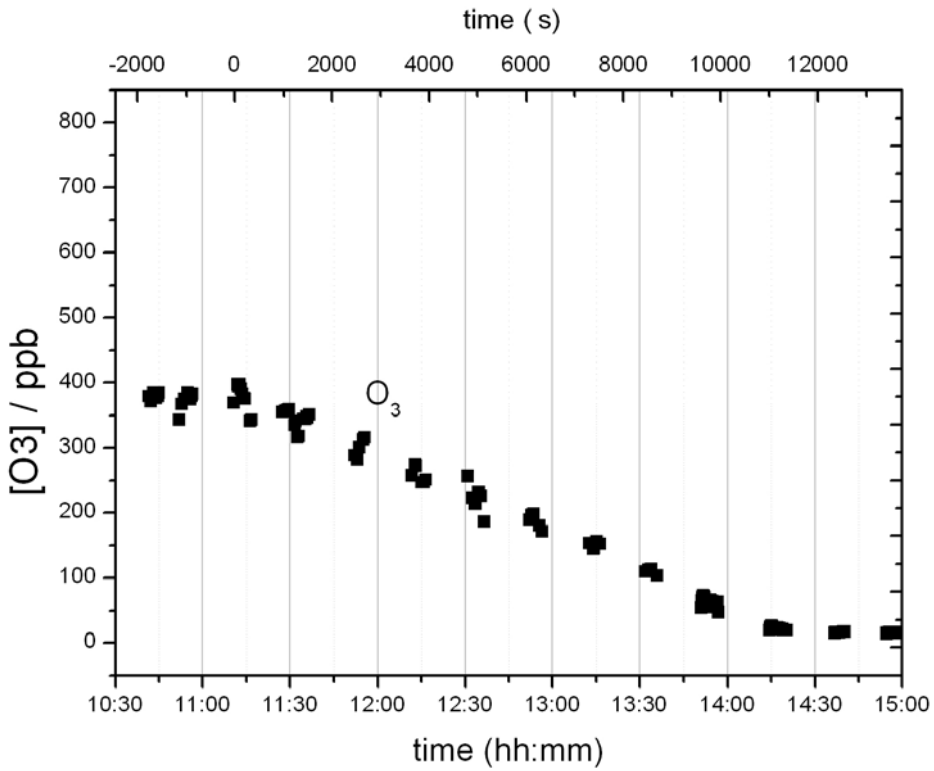

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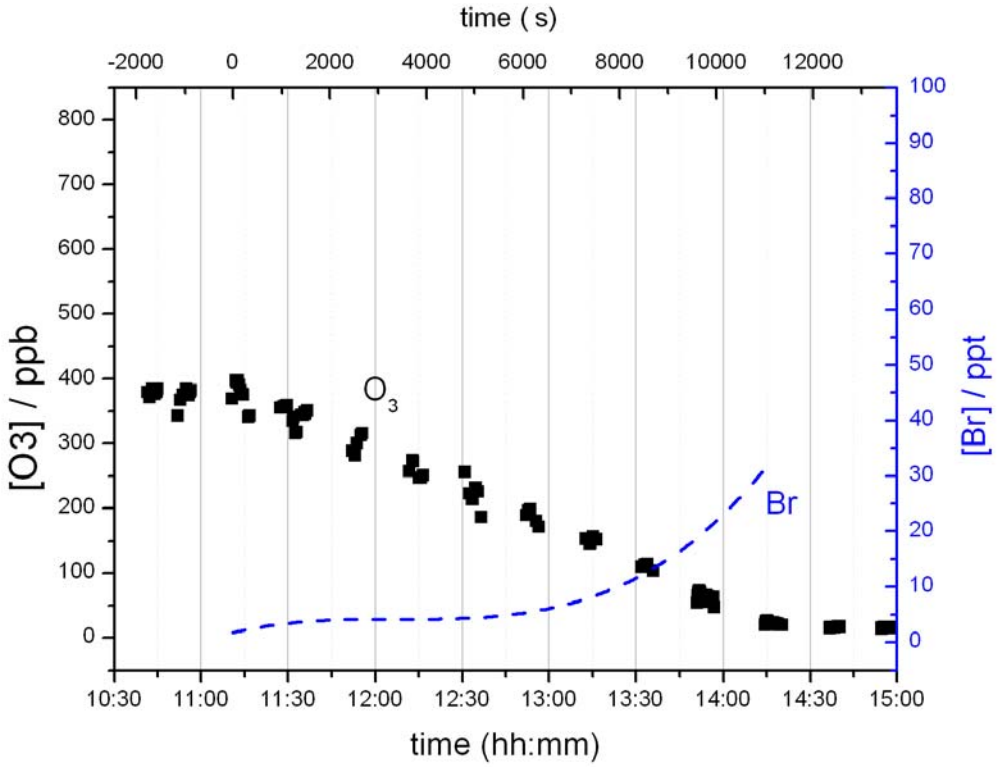
= 0.04ppb/s

$\frac{-d}{dt}[O_3]$(measured)=0.03ppb/s

with:
$k=2.7 * 10^{-12}$ cm³ $molec^{-1}$ s^{-1} [*Atkinson, 2007*]
and [BrO]=500 ppt

Experimental conditions: RH=37%, NaCl/NaBr=300/1



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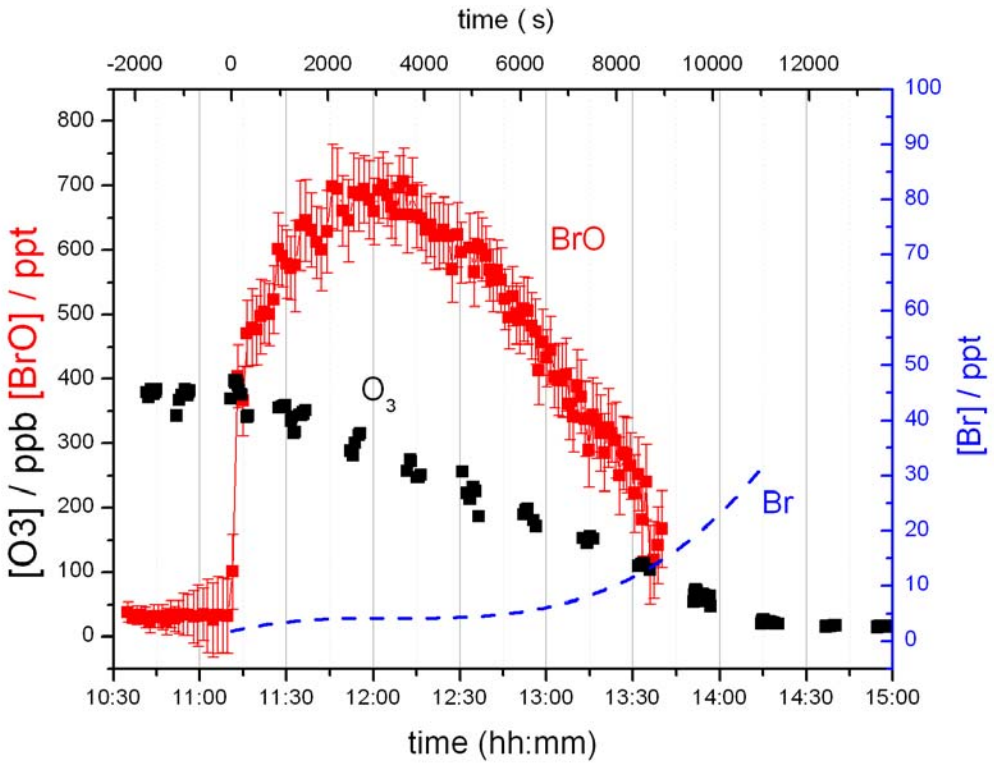

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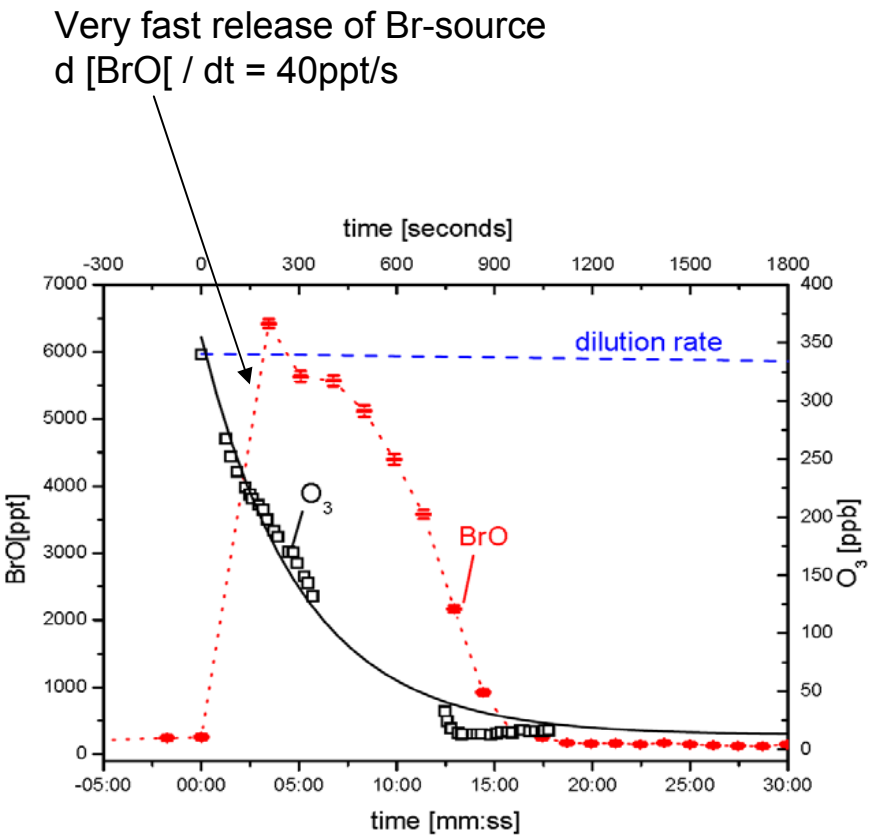
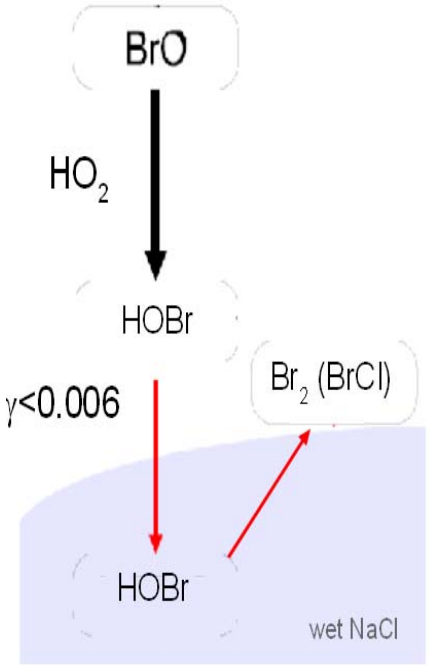
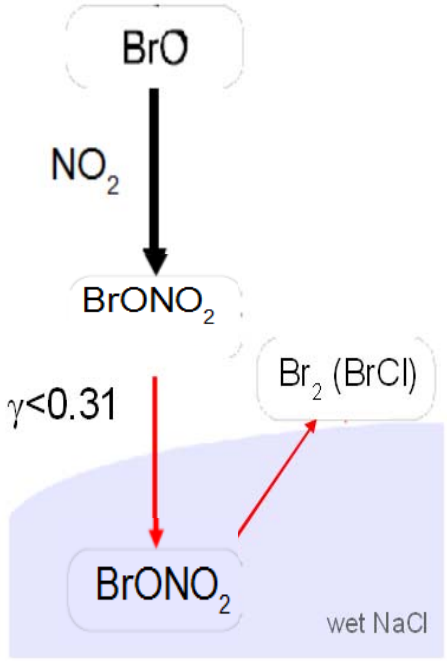
Role of HO_2 and NO_2







RH=60%, NaCl/NaBr=300/1

Rate= 0.09 s^{-1}

→ τ=11s

Rate= 5 s^{-1}

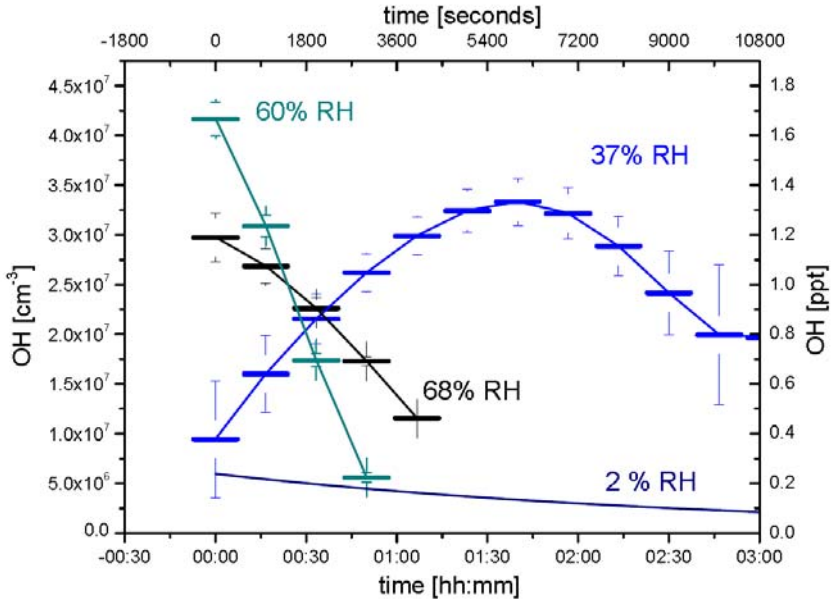
→ τ=200ms

BrO_{max}= 6420 ppt

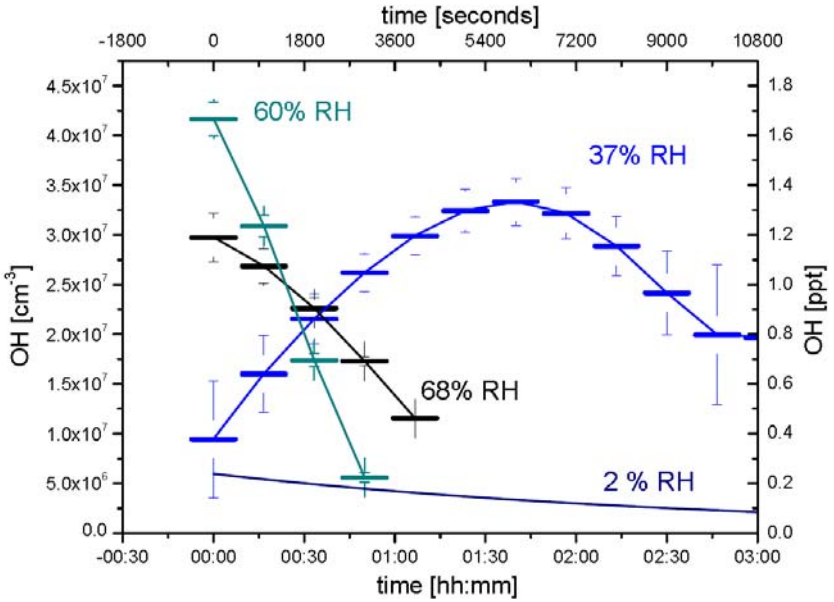
rate coefficient R= ¼ ·γ ·v ·A ,v~220m/s, A= effective surface~$1m^2/3{,}5m^3$

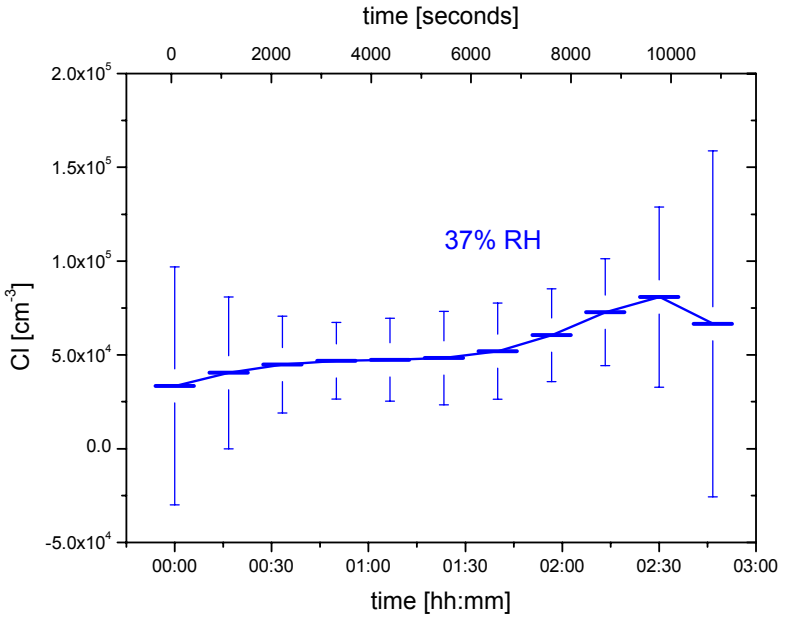
[Mochida et al., 1998],[Aguzzi and Rossi 1999]

OH


time [seconds]
-1800
0
1800
3600
5400
7200
9000
10800
4.5x10^7
4.0x10^7
3.5x10^7
3.0x10^7
2.5x10^7
2.0x10^7
1.5x10^7
1.0x10^7
5.0x10^6
0.0
OH [cm^-3]
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
OH [ppt]
60% RH
37% RH
68% RH
2 % RH
-00:30
00:00
00:30
01:00
01:30
02:00
02:30
03:00
time [hh:mm]

OH and Cl



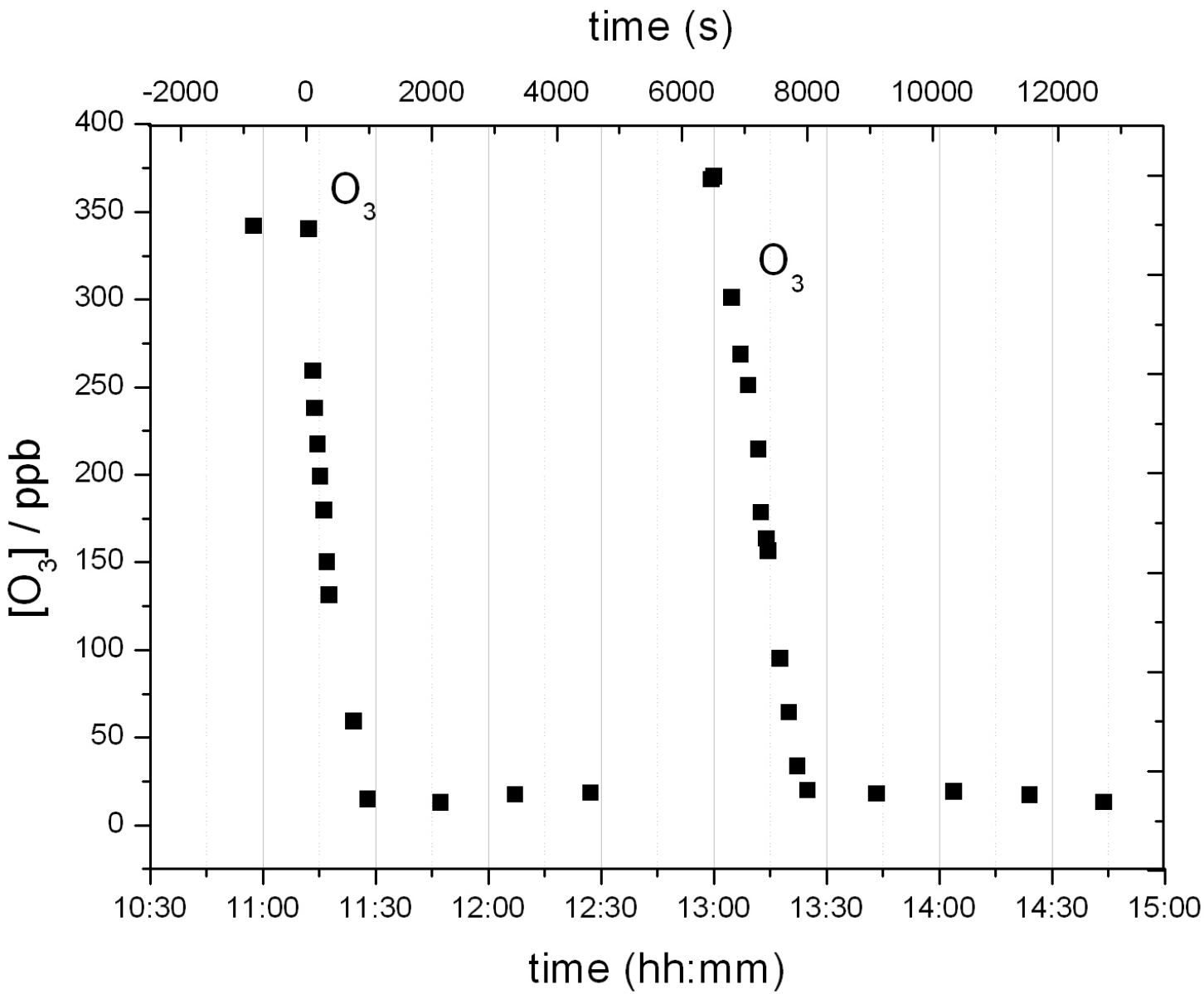


at 37% RH:

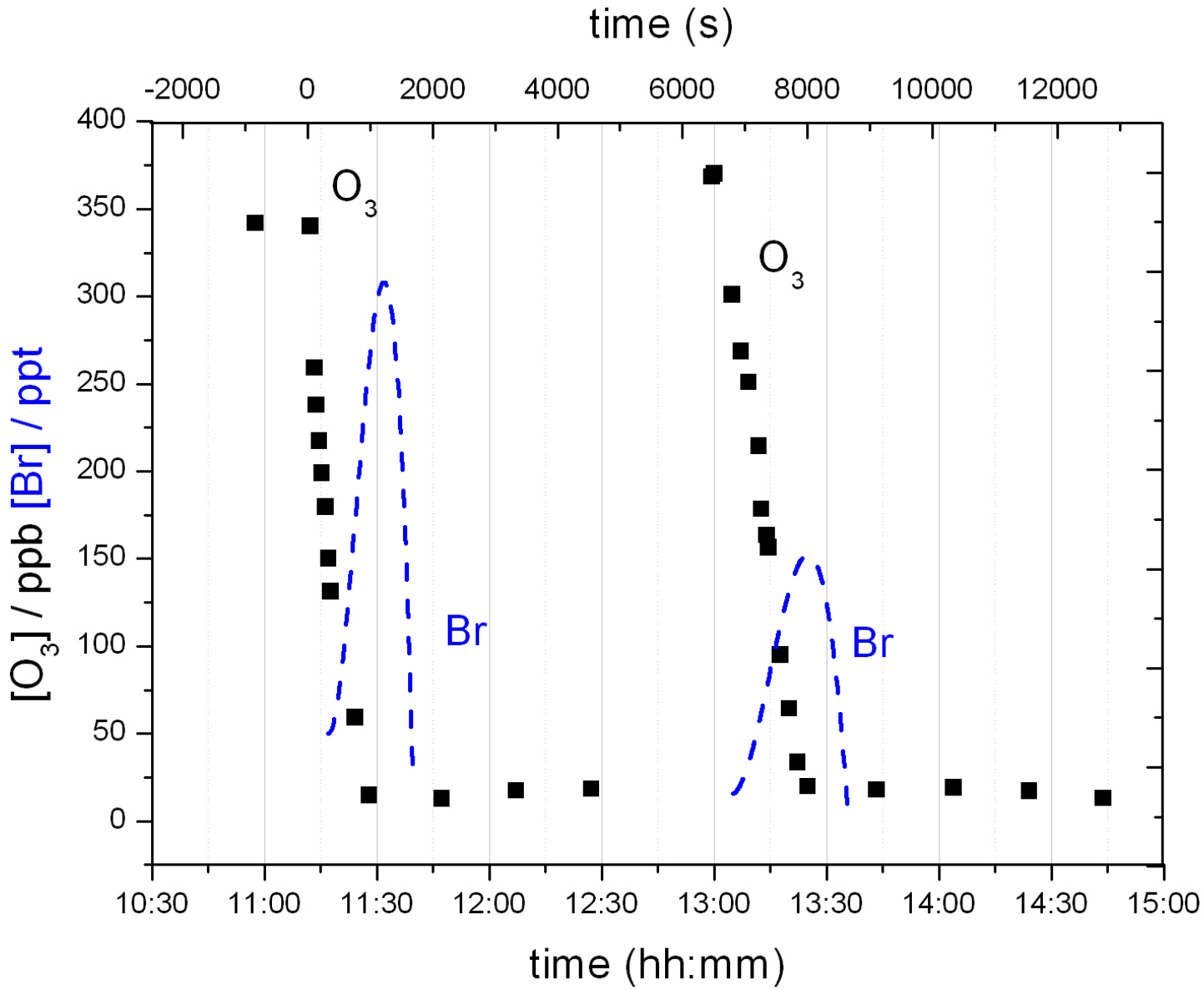
$[Cl]_0 \approx 3.5 \times 10^4$ cm^{-3}

=> $[ClO] \approx 3.3 \times 10^6$cm^{-3}

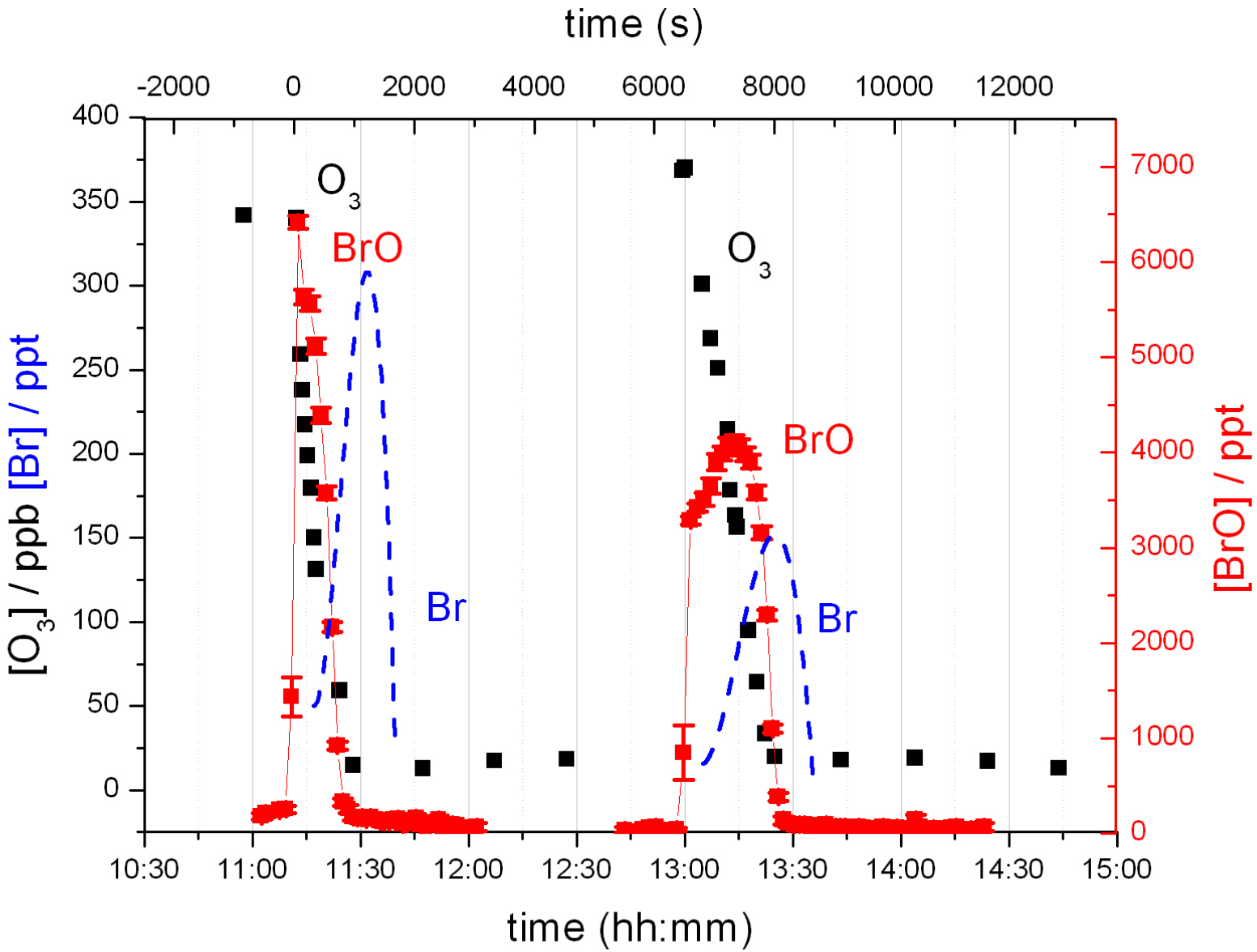
Repeated exposure of salt pan at 60% RH: O_3



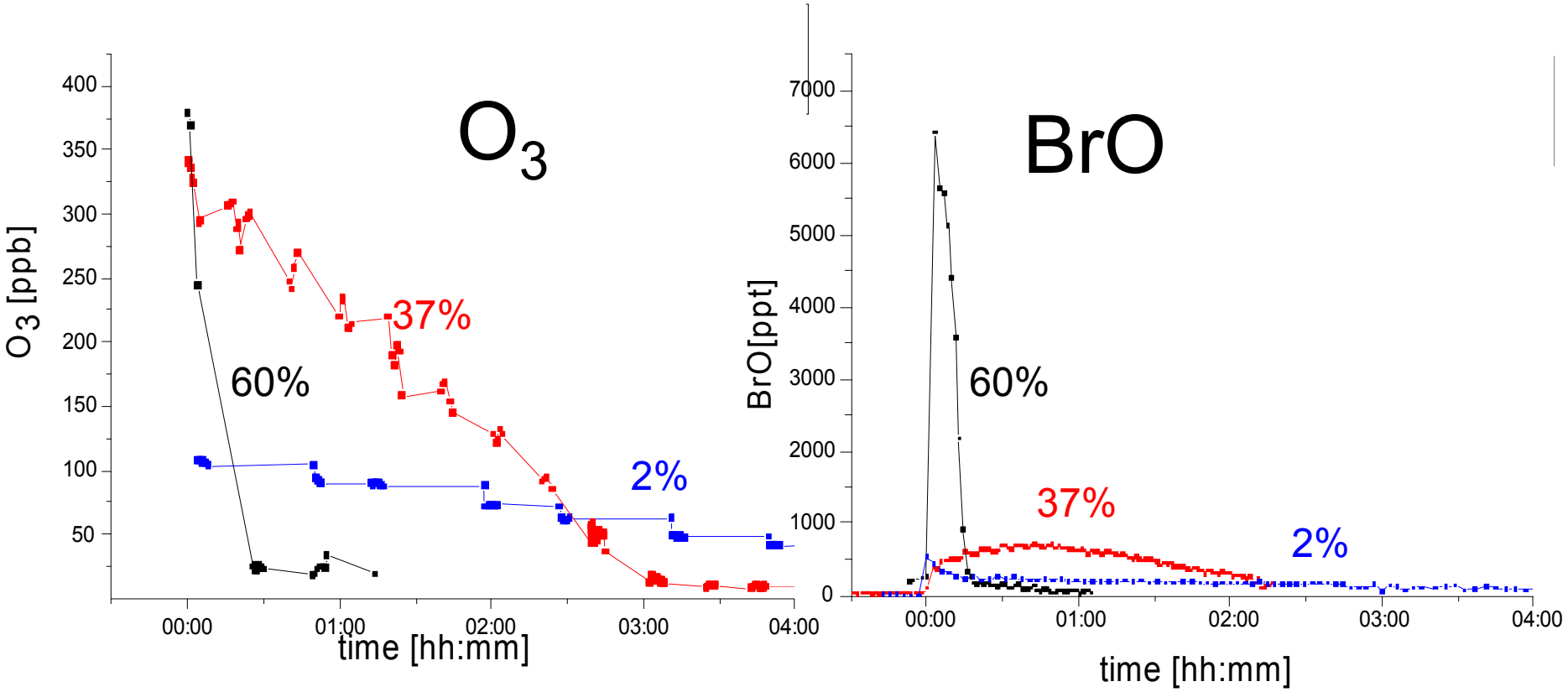
Repeated exposure of salt san at 60% RH: Br



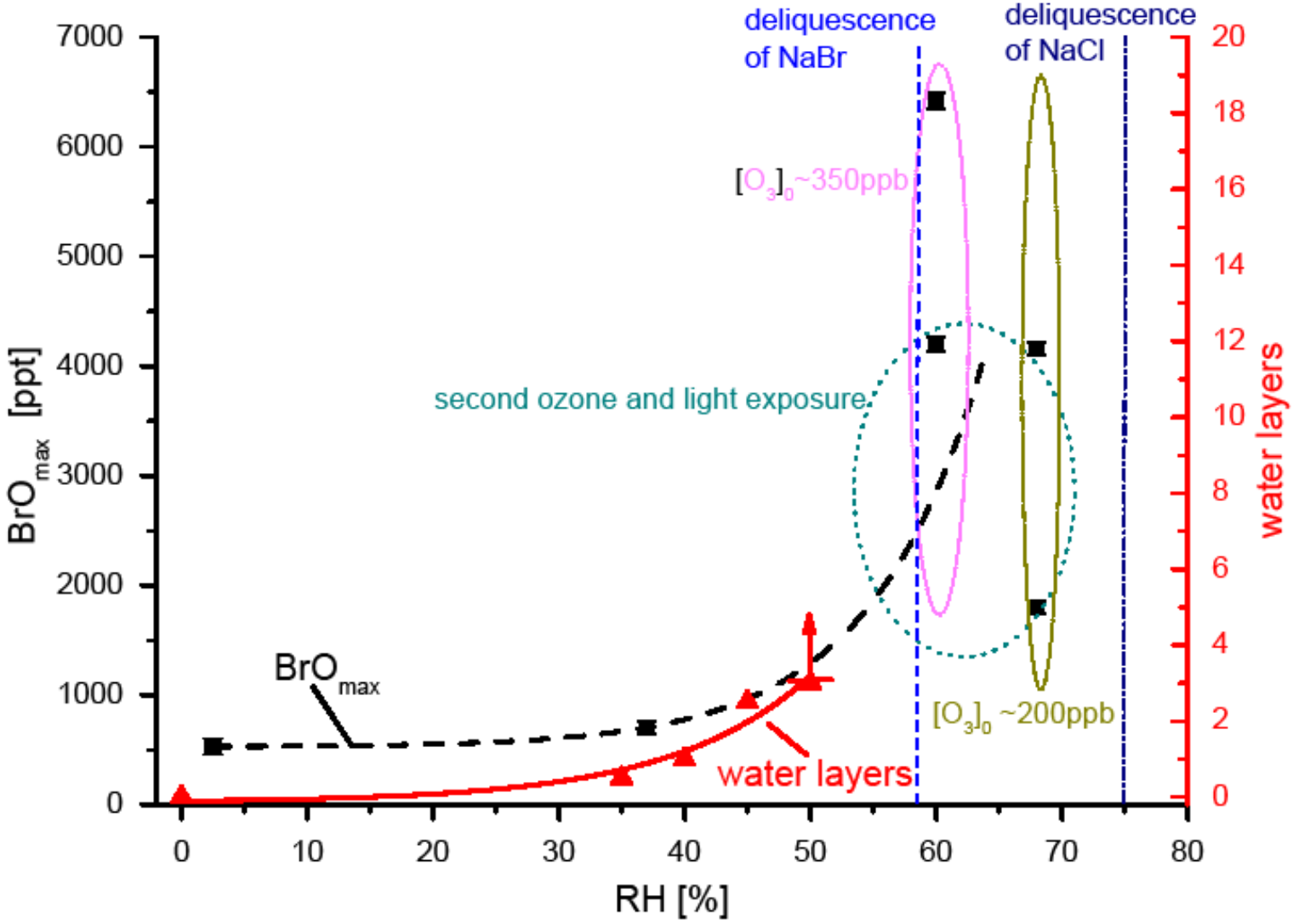
Repeated exposure of salt pan at 60% RH: BrO



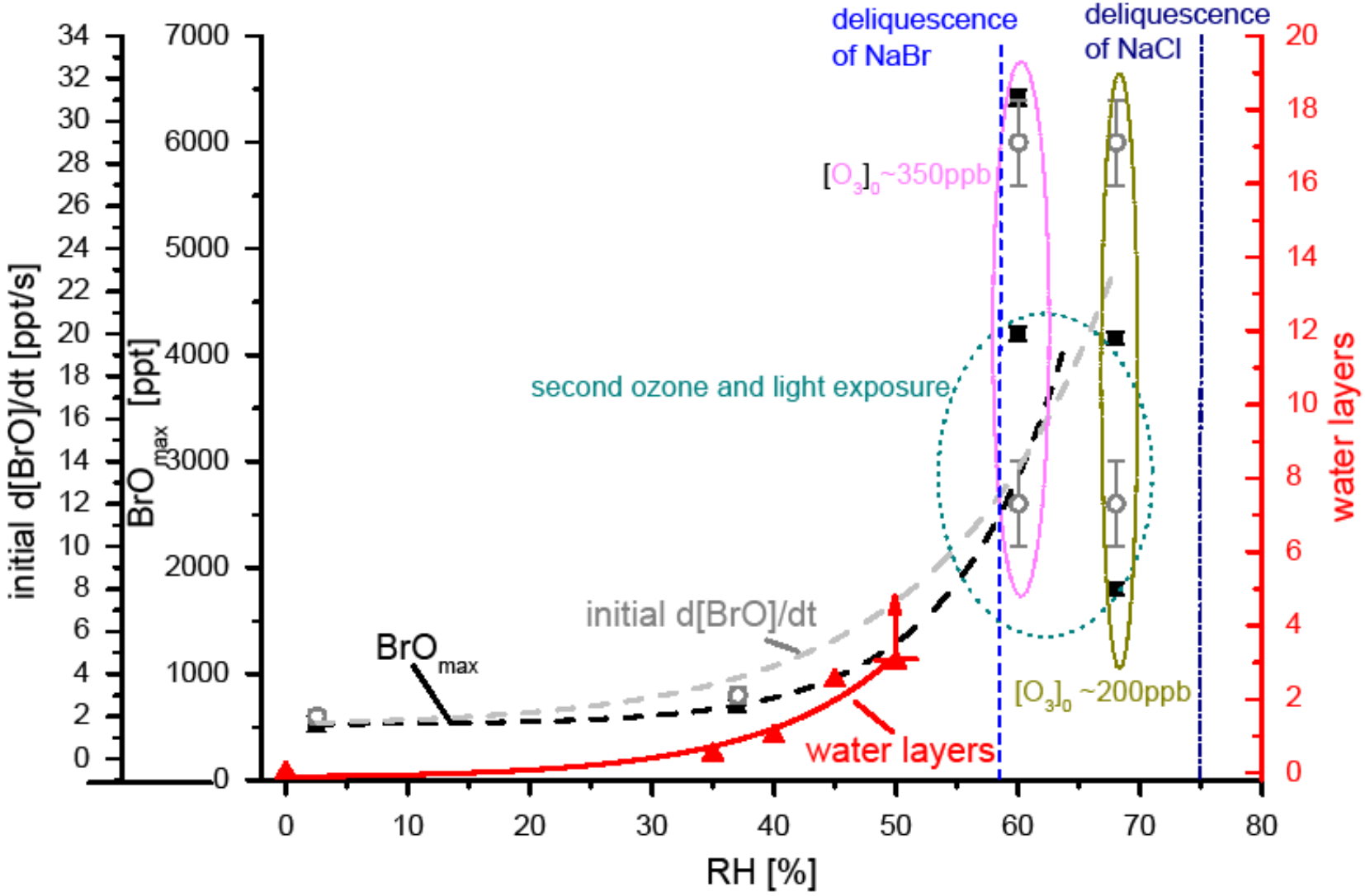
Three “bromine explosions”: Comparison



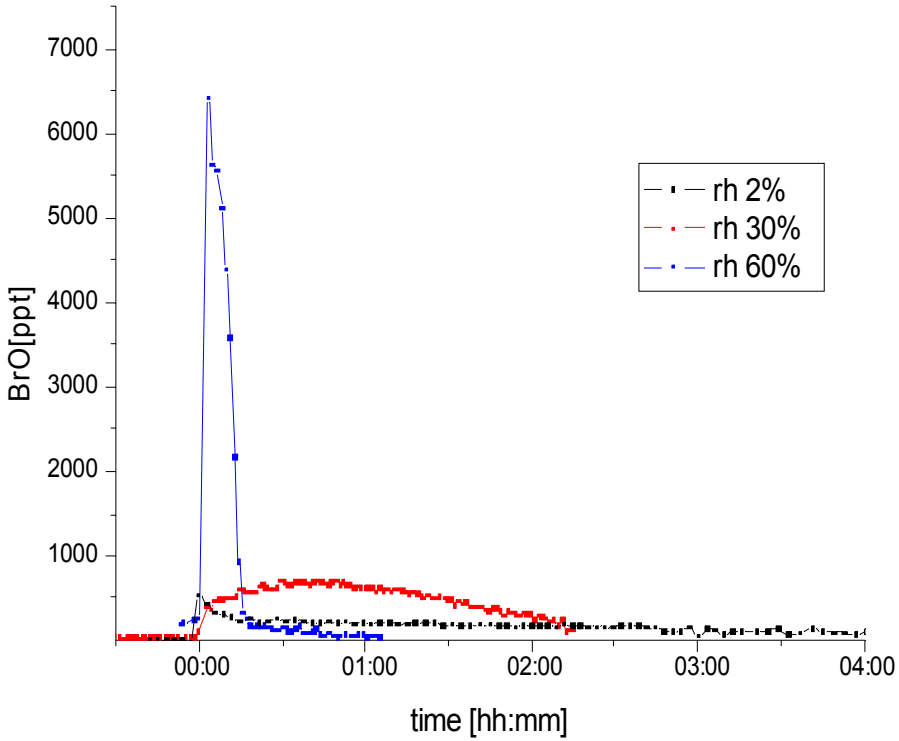
Discussion of humidity dependence: $[BrO]_{max}$



Discussion of humidity dependence: d[BrO]/dt



Summary and Conclusions



- First direct observation of “bromine explosion” in laboratory
- BrO up to 6000ppt
- Strong dependence on relative humidity
- Controlled by thickness of quasi liquid microlayer?
- Fast Br-release for 60%rh is not explained by reaction with HO_2 alone.
- NO_2 might play a key role in „bromine explosion“

Scattering by aerosol in the light path

Thank you for your attention!