

5.2 Halogen radicals and hydrogen chloride

5.2.1 Cl atom

5.2.1.1 Sources

5.2.1.1.1 Cl sources in the gas-phase

5.2.1.1.2 Heterogeneous Cl sources

5.2.1.2 Chemistry of Cl

5.2.1.2.1 Significance for hydrocarbon chemistry

5.2.1.2.2 Methodology

5.2.1.2.3 Cl chemistry in the aqueous phase

5.2.2 Br atom

5.2.2.1 Sources

5.2.2.2 Chemistry of Br

5.2.3 HCl

5.2.3.1 Sources

5.2 Halogen radicals and hydrochloric acid

5.2.1 Cl atom



For at least most organics it applies: $k_{\text{Cl}} > k_{\text{OH}\cdot}$.

→ What is the contribution of Cl atoms to tropospheric chemistry ?

5.2.1.1 Sources

5.2.1.1.1 Cl sources in the gas-phase

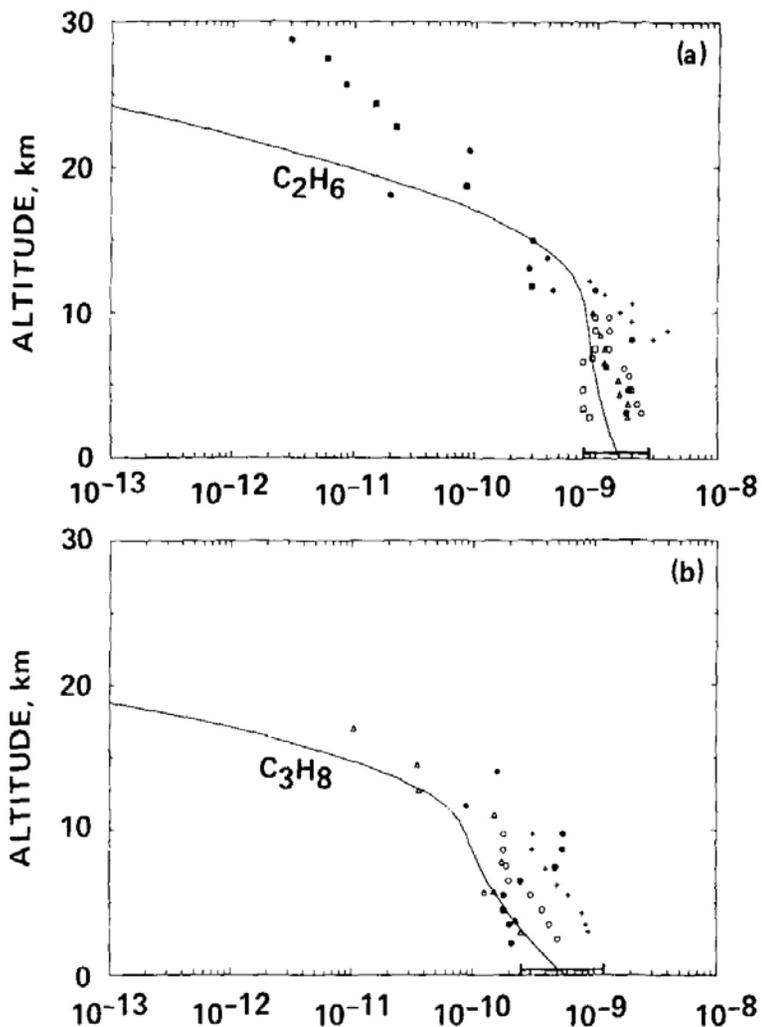


$\tau_{\text{HCl}/\text{OH}} \approx 3$ days (sunny day), τ_{HCl} is limited by other sinks (deposition)

Considering (1) as the only Cl source, a 1D model for the marine boundary layer (60 Cl reactions; *Singh & Kasting, 1988*) suggests $c_{\text{Cl}} \approx 10^3 \text{ cm}^{-3}$

Table III. Model input parameters

Species	Surface concentration (0.5 km) (ppb)
C ₂ H ₆	1.5
C ₃ H ₈	0.25
n-C ₄ H ₁₀	0.25
CO	100.
CH ₄	1700.
CH ₃ Cl	0.60
CCl ₂ F ₂	0.40
CCl ₃ F	0.25
CH ₃ CCl ₃	0.16
CCl ₄	0.14
HCl	1.0 (0–2.0)
NOCl	0.0 (0.0–0.05)
NO	0 ^a



Calculated and observed mixing ratios in the troposphere and the lower stratosphere (*Singh & Kasting, 1988*)

Relevant for RH and other trace substances chemistry ?

Cl oxidation becomes an important sink for

- C_2H_6 , C_3H_8 , H_2S , $(CH_3)S$ at/above $c_{Cl} \approx 10^4 \text{ cm}^{-3}$
- CH_4 , CH_3Cl at/above $c_{Cl} \approx 10^5 \text{ cm}^{-3}$

However: Threshold mixing ratios would be lower, if additional Cl sources were included (= updated mechanism).

→ Despite $c_{Cl} \approx 10^4 \text{ cm}^{-3}$ Cl may account for as much as 3.3% of CH_4 degradation in the southern hemisphere

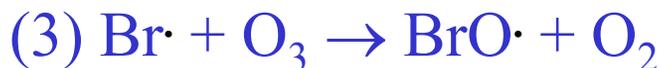
(*Platt et al., 2004*) as a consequence of

BrCl formed from seasalt

→ 5.2.2

5.2.1.1.2 Heterogeneous Cl sources

Revisited (→ 3.1.4.2.2): **Chemistry of ground-level ozone in polar regions**



Sum: light catalysed



oxidation of (sea salt) Cl^- to gas-phase Cl atoms:



Sum: light, Br catalysed



Also on seasalt –

**if only $\text{pH} < 7$ which could be due to sulfuric acid formation
from DMS**

(Vogt et al., 1996; Platt et al., 2004)

Initiation of catalytic cycles by 1. (dissolved) ozone:

In the aqueous phase

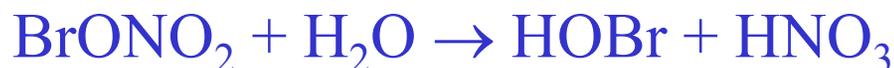


additional source for HOBr: **2. Caro's acid:**



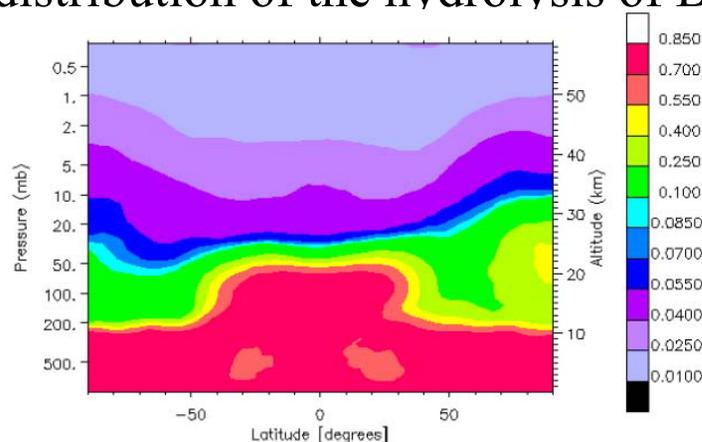
Caro's acid

(formed in (radical) oxidation of S(IV))

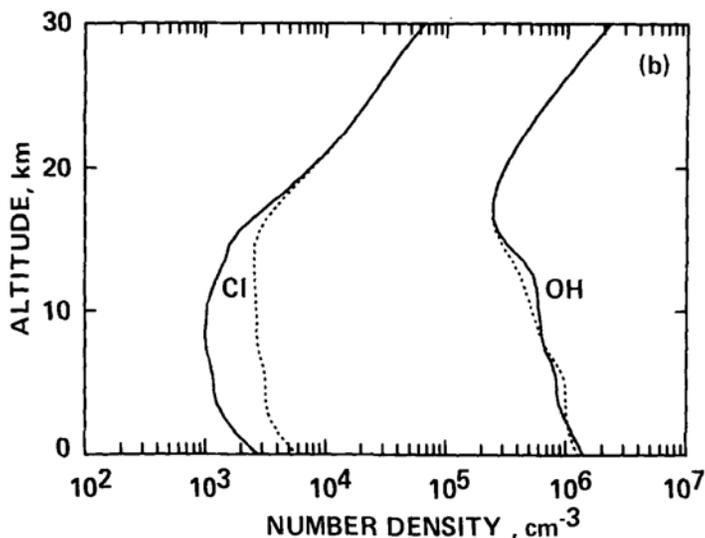
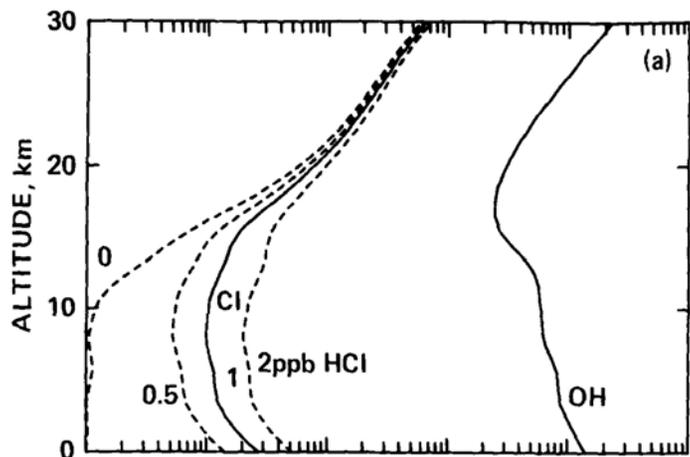


Where? Zonal and vertical distribution of the hydrolysis of BrONO_2
(*Sousa Santos, 2008*)

High liquid water
content in the troposphere.



Cl distribution



Scenarios of surface HCl sources (above) and RH reduction to 1% of true value (dotted below; *Singh & Kasting, 1988*)

CH ₄ & NMHCs	k_{Cl}^a	k_{OH}^a	$k_{\text{Cl}}/k_{\text{OH}}$
	cm ³ molec ⁻¹ s ⁻¹		
methane	1.00E-13	6.40E-15	16
ethane	5.90E-11	2.50E-13	238
propane	1.40E-10	1.00E-12	139
n-butane	2.10E-10	2.40E-12	87
acetylene	2.00E-10	2.50E-12	80
i-butane	1.40E-10	1.90E-12	74
n-pentane	2.50E-10	3.80E-12	66
n-hexane	3.00E-10	5.20E-12	58
i-pentane	2.00E-10	3.90E-12	51
cyclo-hexane	3.10E-10	7.00E-12	44
ethene	1.00E-10	8.50E-12	12
benzene	1.50E-11	1.20E-12	12
toluene	5.90E-11	5.60E-12	11
(m+p)-xylene	1.50E-10	1.40E-11	11
propene	2.40E-10	2.60E-11	9

Global scale estimate: Based on known c_{RH} , k_{OH} and k_{Cl} ($k_{\text{Cl}} / k_{\text{OH}} \approx 10^1 - 10^3$) estimation of upper limit for the **northern hemisphere**, $c_{\text{Cl}} \leq 10^3 \text{ cm}^{-3}$

(*Rudolph et al., 1996*)

Southern Ocean marine boundary layer and free troposphere (ACE1 flights from Hobart, Australia) by average $(610 \pm 3) \times 10^3$ OH vs. $(0.72 \pm 0.1) \times 10^3$ Cl based on measured data interpreted using a 3-box model

(Wingenter et al., 1999):

Table 2. HO and Cl Rate Constants, Ratios of Rate Constants, and Calculated Percent Contribution of HO and Cl to Chemical Loss

	kHO	kCl	kHO/kCl	Calculated Percent Loss By ^a	
				HO	Cl
Tetrachloroethene ^b	1.2E-13 ^c	4.0E-11	323	72	28
Ethane	1.8E-13	5.6E-11	304	74	26
Propane	9.2E-13	1.4E-10	150	85	15
Ethyne ^{b,d}	6.7E-13	5.9E-11	88	91	9
Methane	4.0E-15	7.0E-14	17	98	2
Methyl chloroform	6.7E-15	4.4E-15	0.7	100	0
DMS ^e	4.7E-12	3.3E-10	70	92	8
Methyl bromide	2.0E-14	3.3E-13	16	98	2

All rate constants (*DeMore et al.* [1997] or *Stickel et al.* [1992]) are expressed as second-order reactions having units of $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$. The average MBL temperature used was 277 K.

^aPercent loss is $kX \cdot [X] / (kHO \cdot [HO] + kCl \cdot [Cl])$; where X is either HO or Cl.

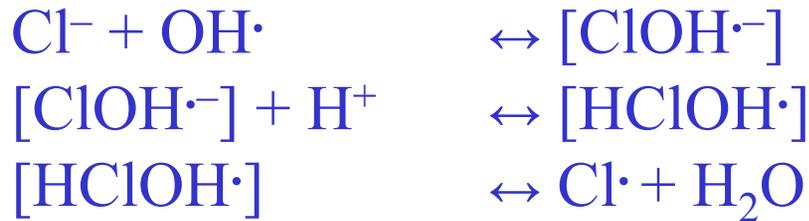
Heterogeneous Cl sources – aqueous phase

Cl can be formed secondarily from OH_{aqu} or NO_3_{aqu} , which, however, are scavenged by many inorganic and organic reactants. Hence, Cl is formed in very low concentrations (*Herrmann, 2003*).

aqueous phase



in fact acid catalyzed:



→ **Cloudwater** chemistry.

Not relevant for the aqueous phase associated with **marine aerosol particles** (pH \approx 7-8) !

Nighttime:



Heterogeneous Cl sources - marine aerosol particles

However: Release of Cl₂ directly from sea-salt particles

On the particle surface:



Daytime only

Main sink of Cl is reaction with O₃:



... continued:

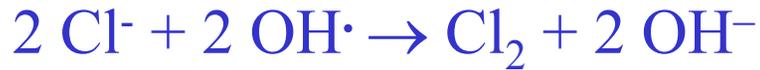


adduct can react with seasalt particles (i.e. O₃ depleting, Cl preserving cycle):

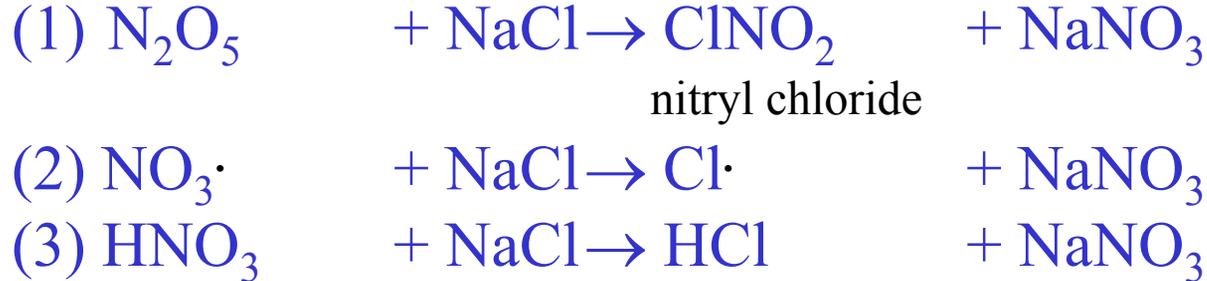


Release from sea-salt - overview

On the particle surface (*above*):



NO_y (N(V)) reactions with sea-salt particles forming Cl precursors:





1st field measurement of nitryl chloride (by CI-MS)

– N_2O_5 and ClNO_2 tightly coupled

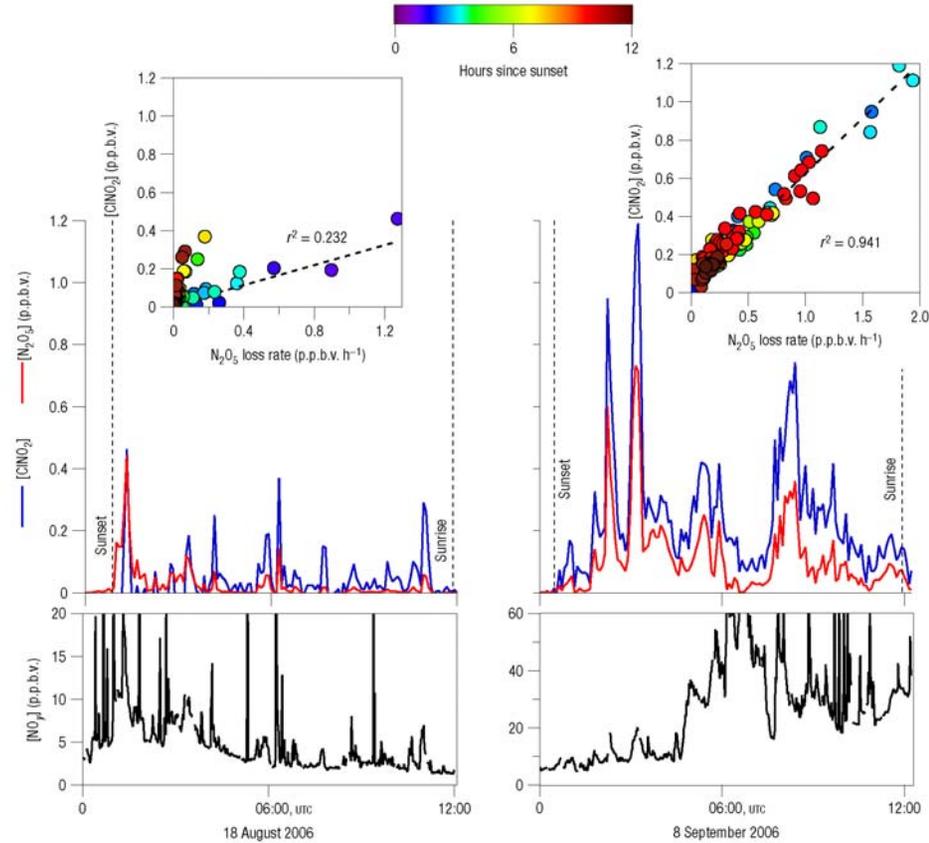
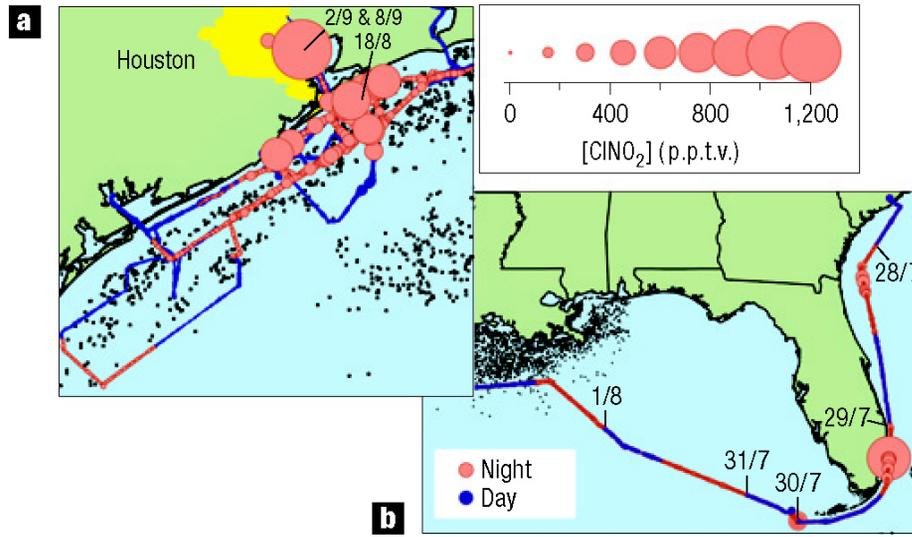


Figure 1 Maps of the study area. **a,b**, Maps of the study area showing a detailed view of the focused study area in the vicinity of Houston, Texas (shown in yellow) (**a**) and the ship track along the United States southeast coastline and across the Gulf of Mexico (**b**). Measured ClNO_2 (5 min average) is plotted along the track scaled by size. The colour coding differentiates night time (red) from daytime (blue). Black dots along the Texas–Louisiana coast are oil and natural gas platforms. The locations of measurements shown in Figs 2 and 3 (18 August, 2 September and 8 September) are indicated.

High levels (≤ 1 ppbv) under high NO_x in the subtropical marine boundary layer (*Osthoff et al., 2008*)



For low c_{Cl^-} (0.05 M) and $\text{pH} \leq 2$ (1) has a small oxidation channel, because ClNO_2 can be converted to Cl_2 , while N(V) is reduced to N(III), at least in weak oxalic and sulfuric acids.

Hypothetical mechanism:



nitronium ion NO_2^+



$k_{\text{overall}} \geq 10^7 \text{ M}^{-1} \text{ s}^{-1}$

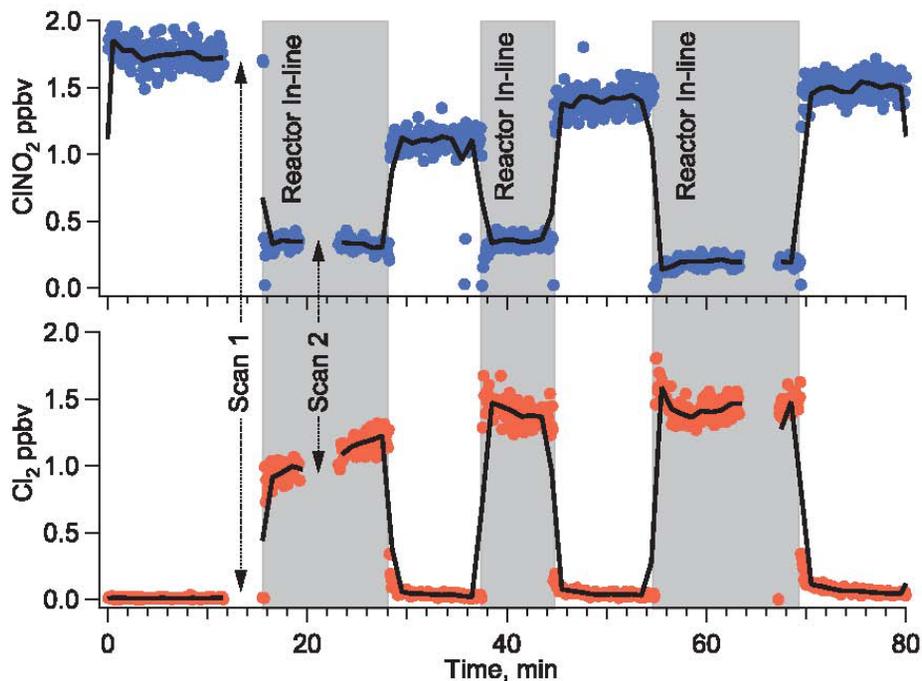


Fig. 1. Efficient reaction of ClNO_2 with Cl^- to form Cl_2 (60 to 100% conversion within measurement precision) on deliquesced oxalic acid and NaCl. Mixing ratios were in parts per billion by volume, ppbv. Mass scans 1 and 2 are shown in fig. S1.

(Roberts et al., 2008)

5.2.1.2 Chemistry of Cl

5.2.1.2.1 Significance for hydrocarbon chemistry



Overall assessment of the significance of Cl for the oxidation capacity of the global atmosphere: Unclear

Tentative conclusion: **Can be of importance on the regional scale**

5.2.1.2.2 Indirect methods to determine Cl atoms

No direct method exists to measure 10^5 cm^{-3} Cl.

Indirect method: infer Cl reactivity from known rate constants:

Relative rates of loss of hydrocarbons, i and j:

$$-dc_i/dt = 0 = k_{OH i} c_{OH} + k_{Cl i} c_{Cl}$$

$$-dc_j/dt = 0 = k_{OH j} c_{OH} + k_{Cl j} c_{Cl}$$

for constant c_i (steady state assumption): $k_{OH i} c_{OH} + k_{Cl i} c_{Cl} = k_{OH j} c_{OH} + k_{Cl j} c_{Cl}$

if $c_{Cl} \approx 0 \rightarrow k_{OH i} = k_{OH j}$

if $c_{OH} \approx 0 \rightarrow k_{Cl i} = k_{Cl j}$

$$k_{OH \text{ i-butane}} \approx k_{OH \text{ n-butane}}$$

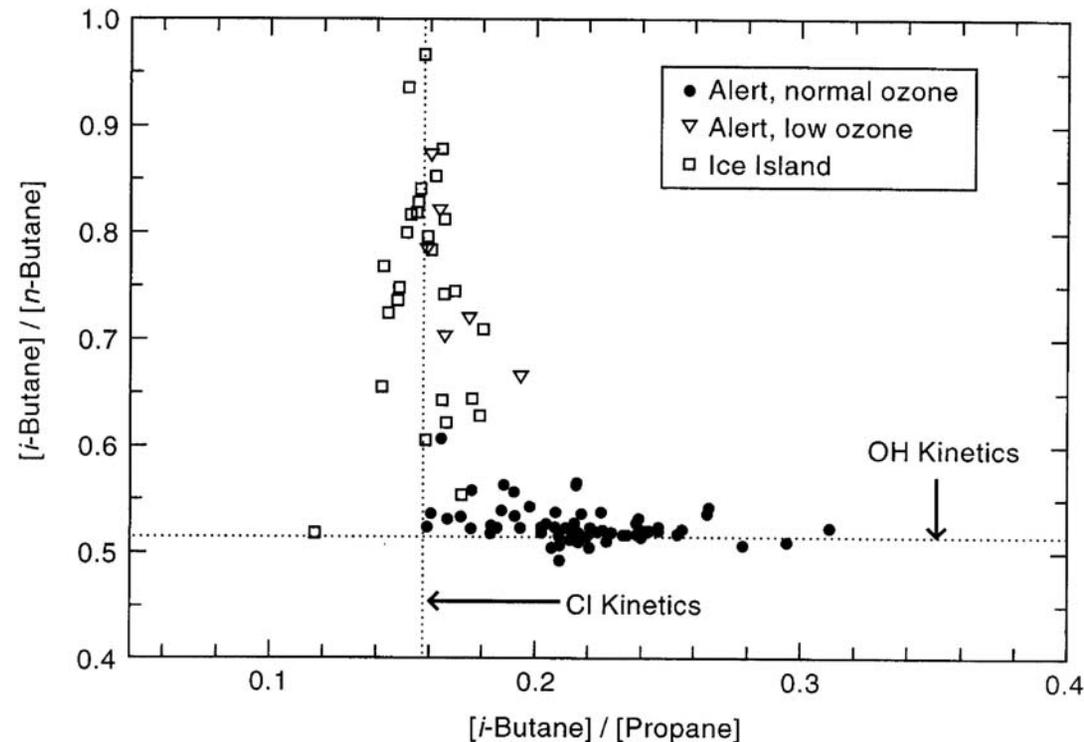
$$k_{Cl \text{ i-butane}} \approx k_{Cl \text{ propane}}$$

or:

i-butane : n-butane : propane

$\approx 2:2:1$ due to OH alone,

and $\approx 1:2:1$ due to Cl alone



Result Arctic boundary layer: In **ozone depleting chemistry**, unlike normal ozone chemistry, Cl may take over in hydrocarbon degradation. (*Jobson et al., 1994*)

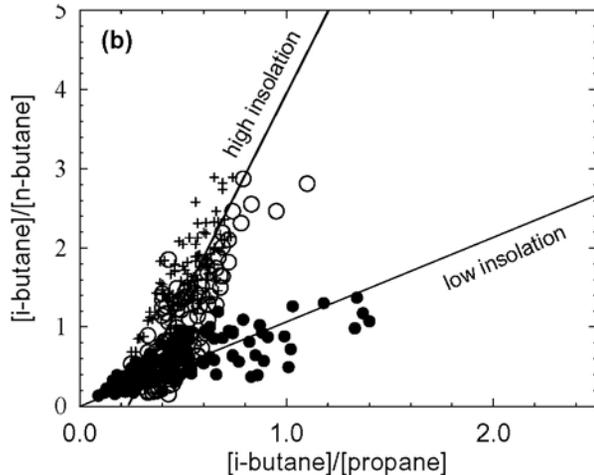
Indirect method: infer c_{Cl}/c_{OH} from known rate constants: (Rudolph, 1997):

$$\ln(c_i/c_k) = a \times \ln(c_j/c_k) + b \quad \text{with: hydrocarbons } i, j, k$$

$$\text{Slope } a = \frac{[k_{OH\ k} c_{OH} + (c_{Cl}/c_{OH}) k_{Cl\ k} c_{Cl} - k_{OH\ i} c_{OH} - (c_{Cl}/c_{OH}) k_{Cl\ i} c_{Cl}]}{[k_{OH\ k} c_{OH} + (c_{Cl}/c_{OH}) k_{Cl\ k} c_{Cl} - k_{OH\ j} c_{OH} - (c_{Cl}/c_{OH}) k_{Cl\ j} c_{Cl}]}$$

provides:

$$(c_{Cl}/c_{OH}) = [a (k_{OH\ k} - k_{OH\ j}) + k_{OH\ i} - k_{OH\ k}] / [a (k_{Cl\ j} - k_{Cl\ k}) + k_{Cl\ k} - k_{Cl\ i}]$$



CH ₄ & NMHCs	k_{Cl}^a	k_{OH}^a	k_{Cl}/k_{OH}	%Cl ^b	lifetime toward ^c	
	cm ³ molec ⁻¹ s ⁻¹				Cl	OH
methane	1.00E-13	6.40E-15	16	8.2	14 y	1.5 y
ethane	5.90E-11	2.50E-13	238	57.6	8.5 d	11.5 d
propane	1.40E-10	1.00E-12	139	44.6	3.5 d	2.9 d
n-butane	2.10E-10	2.40E-12	87	33.5	2.4 d	1.2 d
acetylene	2.00E-10	2.50E-12	80	31.5	2.5 d	1.2 d
i-butane	1.40E-10	1.90E-12	74	29.8	3.5 d	1.5 d
n-pentane	2.50E-10	3.80E-12	66	27.4	2.0 d	18 h
n-hexane	3.00E-10	5.20E-12	58	24.9	1.5 d	13 h
i-pentane	2.00E-10	3.90E-12	51	22.8	2.5 d	18 h
cyclo-hexane	3.10E-10	7.00E-12	44	20.3	1.6 d	10 h
ethene	1.00E-10	8.50E-12	12	6.3	5.3 d	9 h
benzene	1.50E-11	1.20E-12	12	6.7	33 d	2.4 d
toluene	5.90E-11	5.60E-12	11	5.7	80 d	12 h
(m+p)-xylene	1.50E-10	1.40E-11	11	5.8	3.3 d	5 h
propene	2.40E-10	2.60E-11	9	5.0	2.1 d	2.5 h

Abundances mid-latitude marine boundary layer: $(6-47) \times 10^3$ Cl cm⁻³ (Crete; Arsene et al., 2007)

Cl chemistry – Impact on atmospheric chemistry ?

In **polluted coastal areas** ozone formation may be significantly enhanced by Cl atom (radical) sources.

Considering additional reactions*, morning ozone and peak ozone in the afternoon increased (by 12 and 4 ppbv, respectively, in Los Angeles, August 1987; SCAQS episode; *Knipping & Dabdub, 2003*):

*

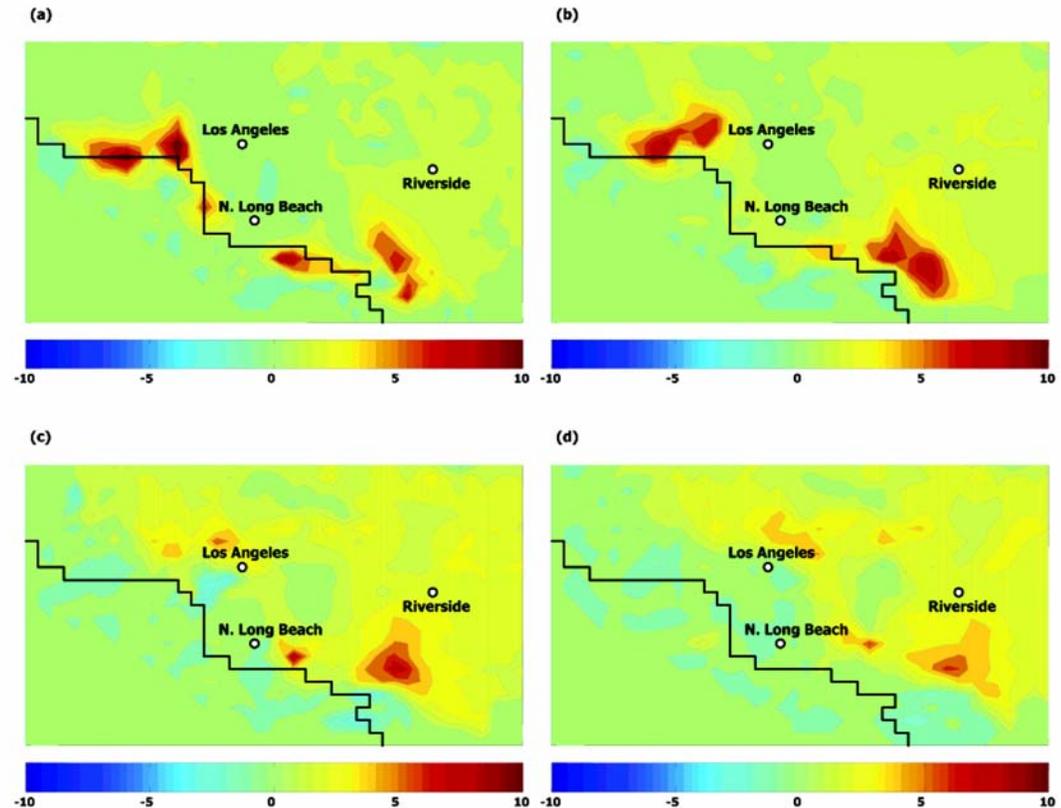
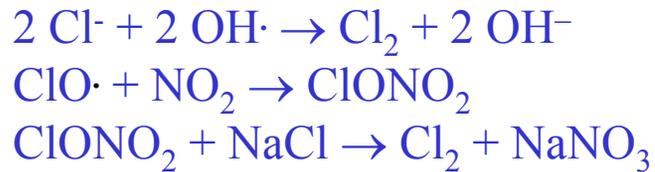


FIGURE 4. Ground-level ozone mixing ratio difference contours for September 9, 1993 (all values in parts per billion). Shown are diagrams illustrating the value obtained by subtracting the ozone mixing ratios predicted by the Case Cl Chem simulation from the ozone mixing ratios predicted by the base-case simulation at (a) 1000, (b) 1200, (c) 1500, and (d) 1800 PST.

Cl chemistry – Impact on atmospheric chemistry ? (2)

• Impact on ozone chemistry

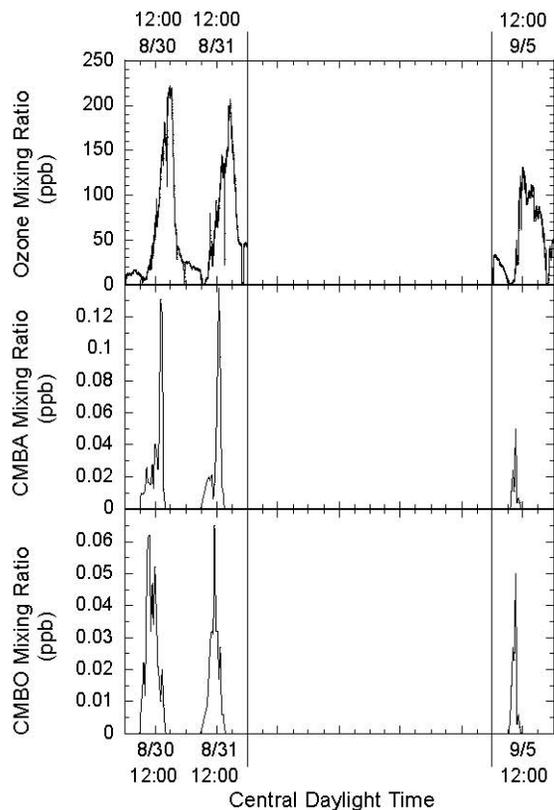
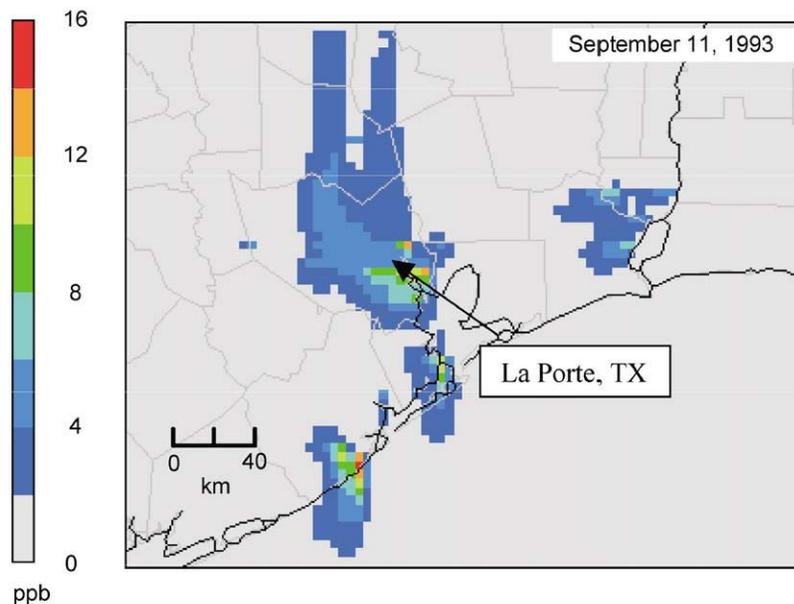


Fig. 1. Ozone, CMBO, and CMBA mixing ratios for 30, 31, August and 5 September 2000 at the La Porte, TX site. Data from 1–4 September are not included to improve clarity. As shown, the unique products of Cl[•] with isoprene (CMBO and CMBA) were detected in the morning hours after sunrise, coincident with increases in the ozone mixing ratio.

Cl adducts: Measurement of reaction products, or marker species, unique to the reaction of Cl with VOCs: 1-chloro-3-methyl-3-butene-2-one ($\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{CH}_2\text{Cl}$; CMBO) and chloromethylbutenal ($\text{ClCH}_2\text{C}(\text{CH}_3)=\text{CHCHO}$;



Absolute difference in ozone prediction with Cl chemistry (regional photochemical model; Carbon Bond IV mechanism)

(Tanaka et al., 2003)

5.2.1.2.3 Cl chemistry in the aqueous phase

Inorganics: $k_{\text{Cl}} = (0.1-5) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for the major anions,



The reactivity is a few orders of magnitude lower for the $\text{Cl}_2^{\cdot-}$ (5).

$$k_{\text{Cl}} = 2 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \text{ for } \text{H}_2\text{O}_2$$

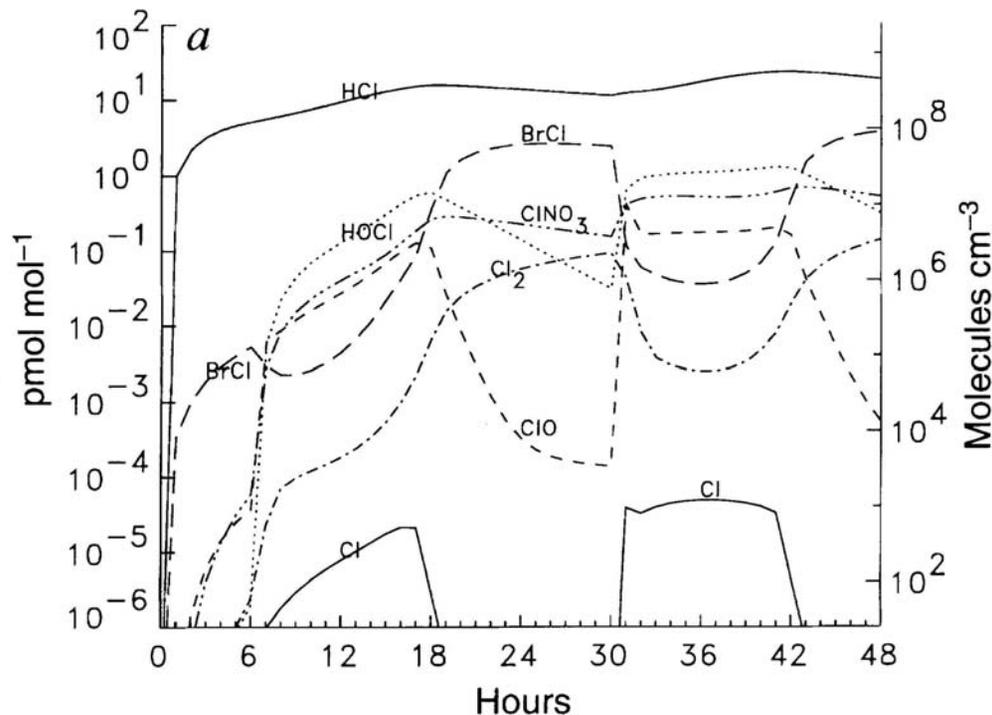
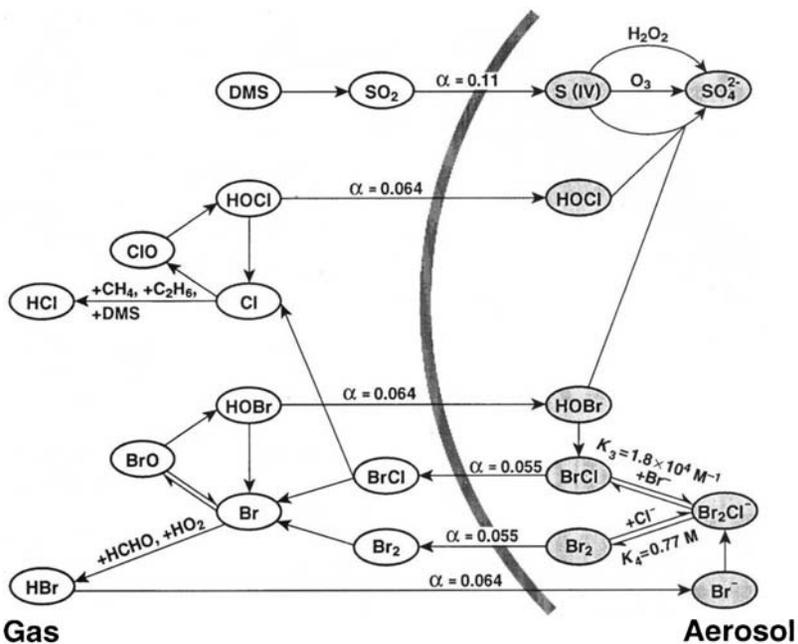
(Herrmann, 2003)

Organics: $k_{\text{Cl}} = (1-4) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for aliphatic ROH, RCOOH, benzene,
 $k_{\text{Cl}} = 0.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for CH_3Cl

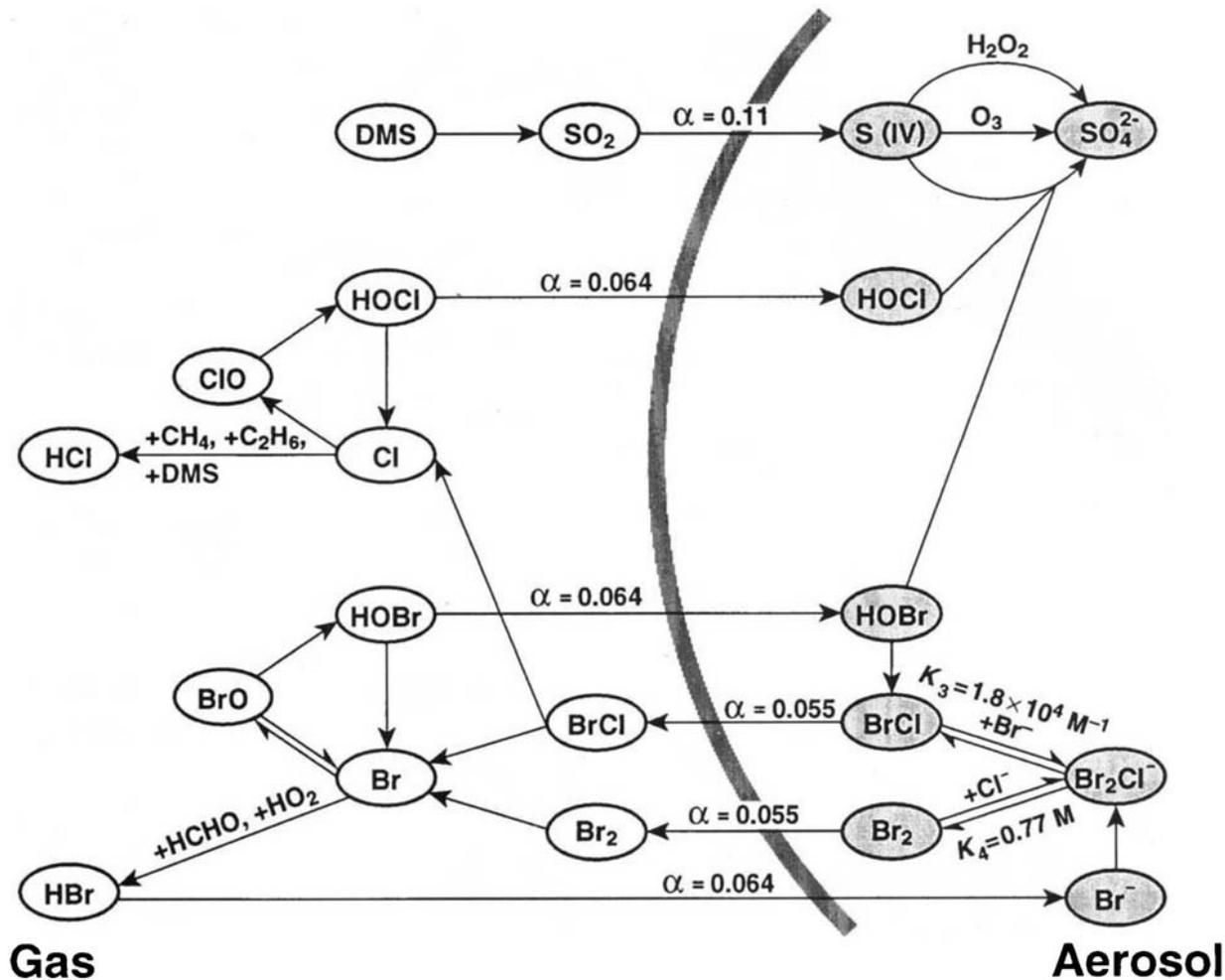
i.e., not faster than OH reactions.

Cl and Br species in the marine boundary layer

Simulation: Box model run 2 d (steady state after 14 d), input: 40 ppbv O₃, 0 HCl, 0.005 NO_x, 0.5 C₂H₆ (Vogt *et al.*, 1996), Cl gas-phase species initiated by SO₂ oxidation:



Cl and Br species in the marine boundary layer: S(IV) oxidation



Box model run 48 h, 40 ppbv O₃, 0.005 NO_x, 0.5 C₂H₆ (*Vogt et al., 1996*)

HOCl may be responsible for 40% of the S(IV) oxidation in the particulate phase:



5.2.2 Br atom

5.2.2.1 Sources

Autocatalytic mechanism for Br release from sea-salt particles



products Br_2 and BrCl are slightly soluble

k_1 not fast enough: $c_{\text{Cl}^-}/c_{\text{Br}^-} = 700 \rightarrow (5)$ is more important than (1)

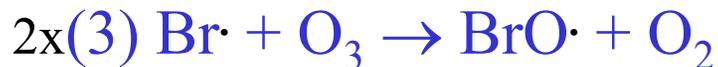
Autocatalytic Br activation:



$c_{\text{Cl}^-}/c_{\text{Br}^-} = 700 \rightarrow (6)$ is more important than (8)



Together with:



Sum: light and Cl^- catalysed:



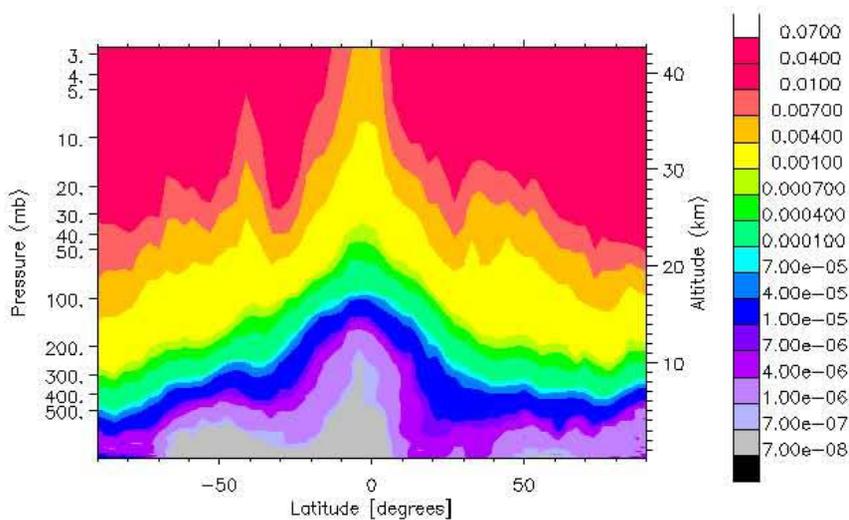


products Br_2 and BrCl are slightly soluble

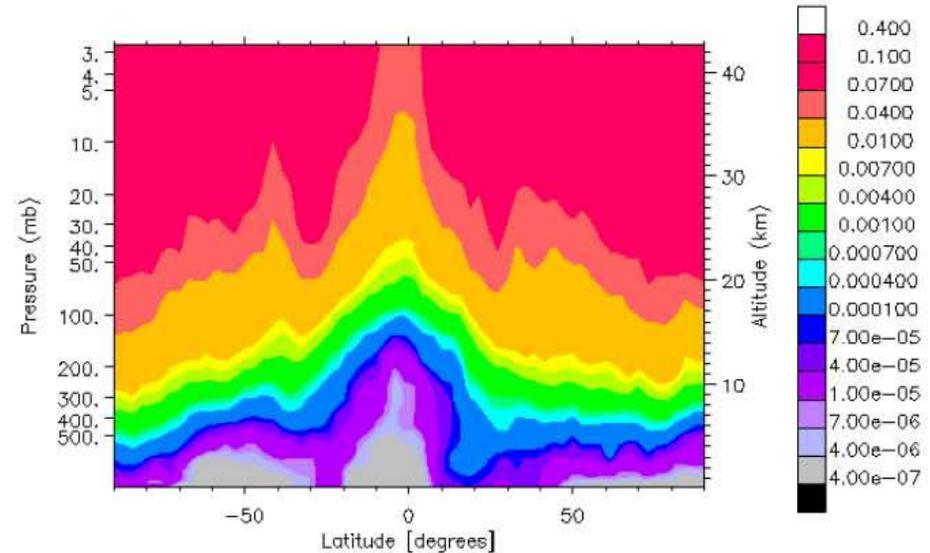
$c_{\text{Cl}^-}/c_{\text{Br}^-} = 700 \rightarrow (5)$ is more important than (1a)

Zonal and vertical distribution of the uptake of HOBr on spherical particles:

$\Gamma \text{HOBr} + \text{HCl}$, lon average



$\Gamma \text{HOBr} + \text{HBr}$, lon average



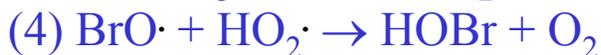
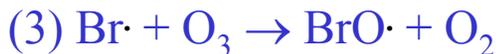
(Sousa Santos, 2008)

Oxidation of (sea salt) Cl^- to gas-phase Cl atoms:



HOBr formed in

Revisited (\rightarrow 3.1.4.2.2, 5.2.1.1.2):



Alternative to BrCl photolysis:



$$K_6 = 1.8 \times 10^4 \text{ M}^{-1}$$



Similar to (7)

Efficiency of Br cycling ?

> 1 Br·/HOBr returned ?

Cl would rapidly react with hydrocarbons, while Br would not.

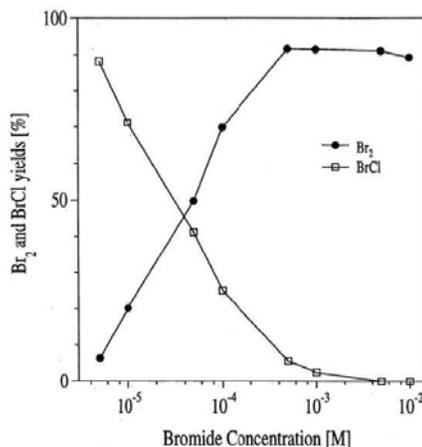
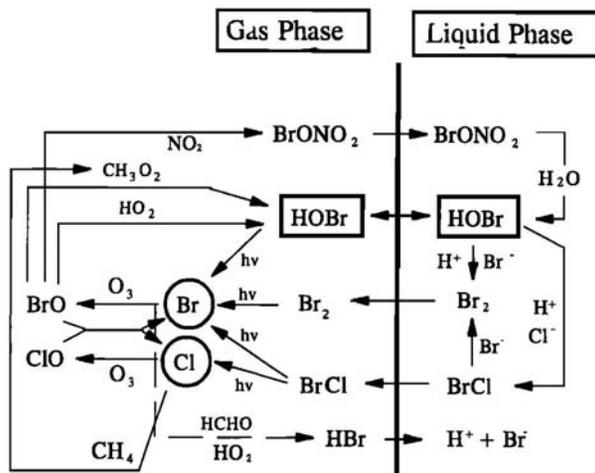
Which halogens are finally released, Br_2 or BrCl ?

Efficiency of Br cycling ?

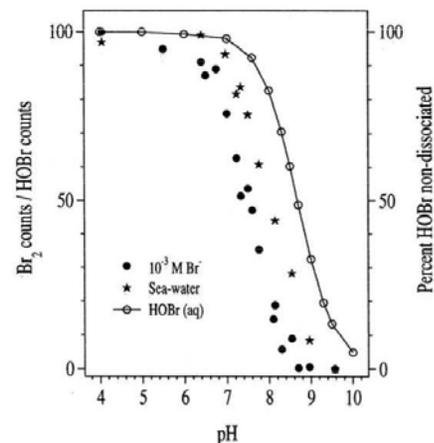
> 1 Br·/HOBr returned ?

Cl would rapidly react with hydrocarbons, while Br would not.

Which halogens are finally released, Br₂ or BrCl ?



Yields at pH = 5.5



pH dependency at $c_{\text{Cl}^-} = 1 \text{ M}$
 and $c_{\text{Br}^-} = 1 \text{ mM}$

Yields $\text{Br}_2:\text{BrCl} \approx 9$ for $\text{pH} < 6.5$, < 1 for non-acidified aerosol

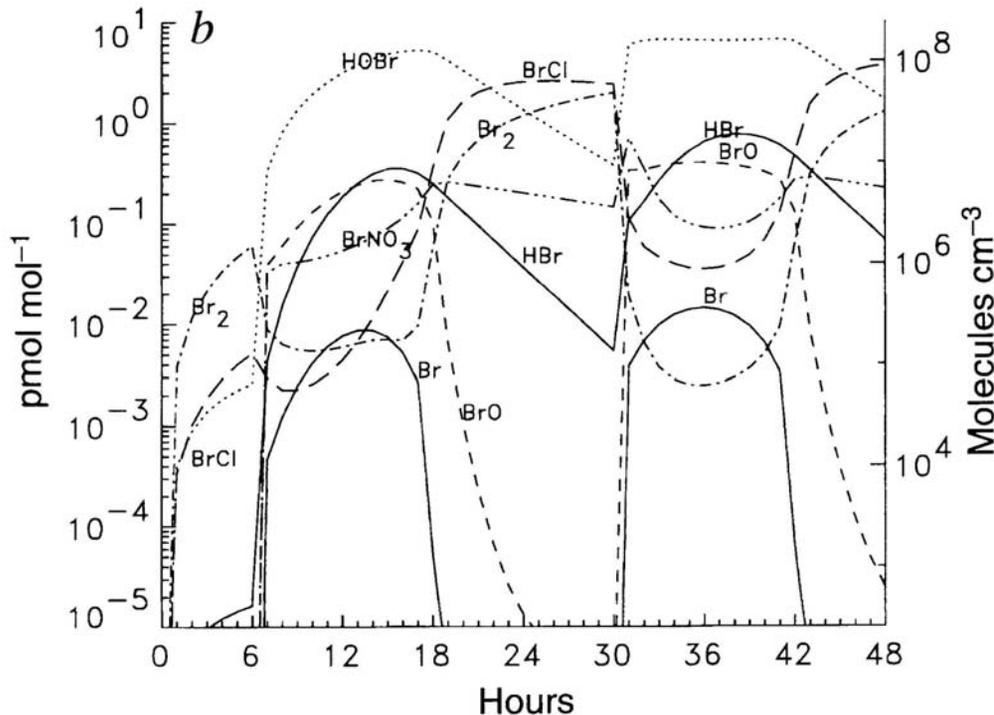
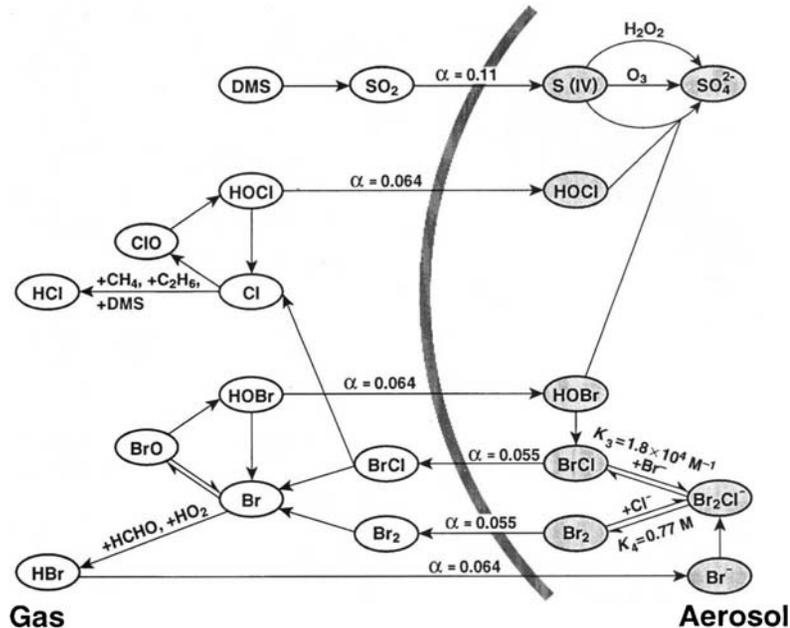
(Fickert et al., 1999)

5.2.2.2 Chemistry of Br

- Heterogeneous Cl source → 5.2.1.1.2):
- Impact on ozone chemistry

- Br species in the marine boundary layer (box model run 48 h, 40 ppbv O₃, 5 pptv NO_x, 0.5 ppbv C₂H₆;

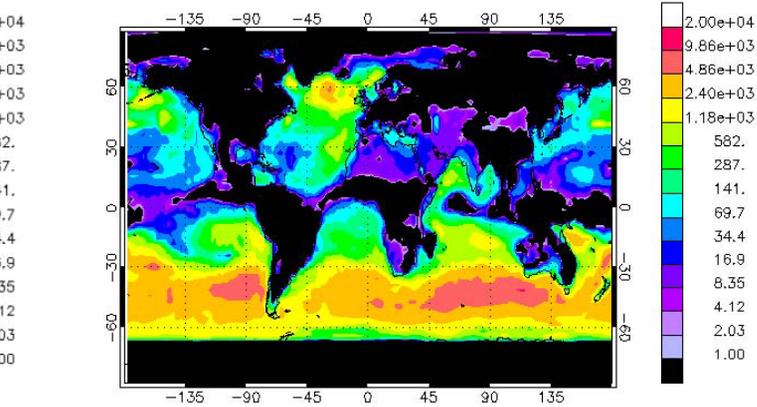
Vogt et al., 1996)



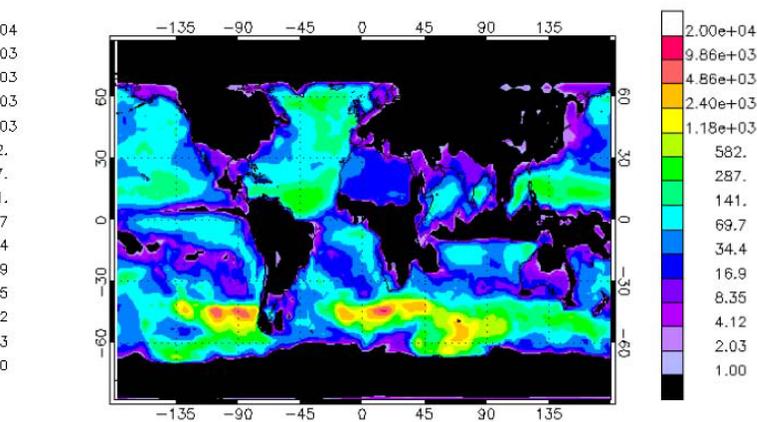
HOBr may be responsible for 20% of the S(IV) oxidation in the particulate phase:



Bromine production from Sea Salt Jun 2000

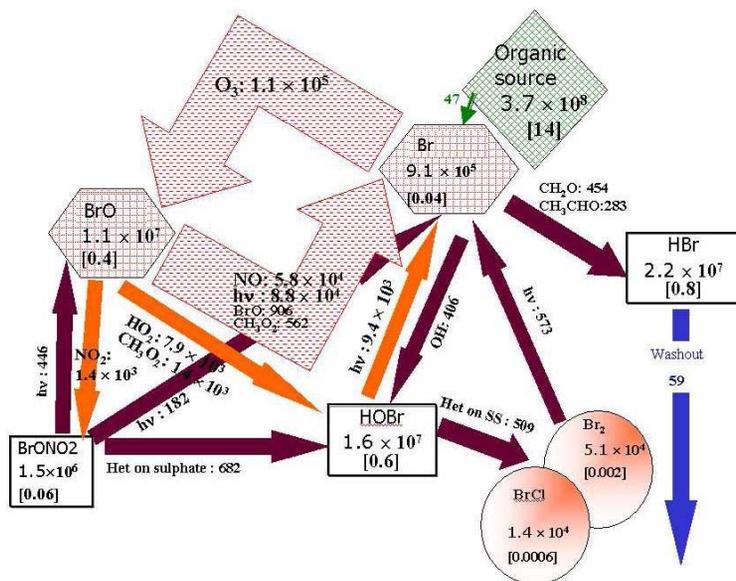


Bromine production from Sea Salt Dec 2000



Br production rate [molec cm⁻³ s⁻¹] (3D model MOZART4; *Sousa Santos, 2008*)

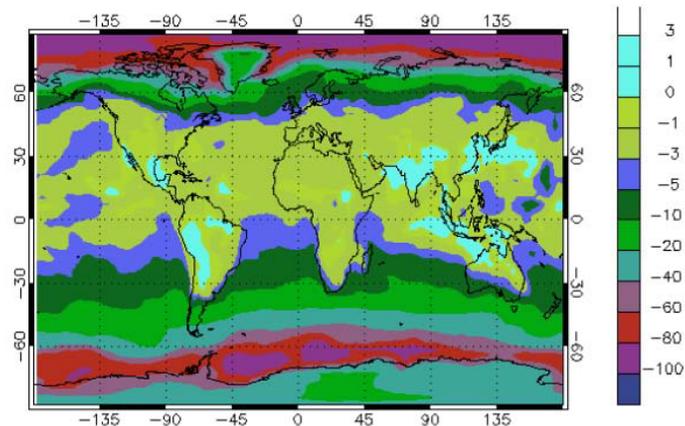
Chemistry of Br (2)



Concentrations of the bromine species [molec cm^{-3} , ppt in square brackets] and highest chemical fluxes [$\text{molecules cm}^{-3} \text{ s}^{-1}$] calculated for the region of high Br production rates from sea salt in the Southern Pacific at the surface at local noon

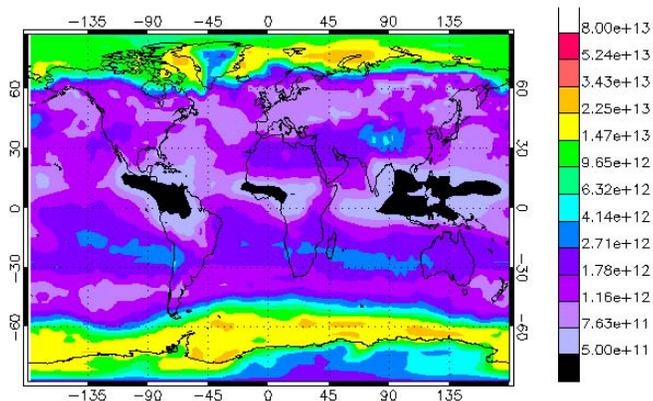
Impact on ozone

$(SS3ice - \text{Base Run}) \times 100 / \text{Base Run} [\%]$



%difference in ozone with/without Br sea-salt and C_1 -halocarbon chemistry

$\text{BrO VTCD} [\text{molecules/cm}^2]_{SS3ice}$



BrO column density

(3D model MOZART4; *Sousa Santos, 2008*)

5.2.3 HCl

5.2.3.1 Sources

Acid displacement:



This HCl, when found in rainwater, is still balanced by seasalt Na^+ .

Table 3. Non-sea-salt Cl^- and SO_4^{2-} , NO_3^- and NH_4^+ concentrations ($\mu\text{eq/l}$) in remote rain; also, $\text{nssCl}^-/(\text{H}^+ + \text{NH}_4^+)$ ratios and annual depositions of nssCl^- are given

Site	nssCl ⁻	NO ₃ ⁻	nssSO ₄ ²⁻	NH ₄ ⁺	nssCl ⁻ / (H ⁺ + NH ₄ ⁺)	nssCl ⁻ dep. ($\mu\text{eq}/\text{m}^2/\text{yr}$)
<i>Tropics</i>						
Lake Calado (Brazil)	1.8	3.5	4.2	3.0	0.09	4957
	1.8	4.2	1.7	6.6	0.09	
Katherine (Australia)	2.71	4.0	3.4	2.9	0.14	2829
Jabiru (Australia)	3.1	3.2	4.7	1.7	0.21	3658
Turrialba (Costa Rica)	1.5	1.3	3.7	3.6	0.21	3080
El Verde (Pto. Rico)	4.8	4.3	8.5	2.9	[0.44]	[16353]
Venezuelan savannah ^{np}	1.9–3.2	2.7–4.6	2.1–4.4	1.9–13.4	0.07–0.30	2200–5100
Auyantepuy (Venezuela)	2.38	2.4	≤0.44	0.31	0.44	5950
Canaima (Venezuela)	1.44	0.55	0.65	≤0.37	0.10	3686
<i>Temperate</i>						
Torres del Paine (Chile)	1.6	0.5	1.2	0.6	0.14	1200
Amsterdam Island	4.3	1.6	4.8	2.4	0.4	[5400]
Barrington (Australia)	1.9	7.3	6.5	7.1	0.22	
Dorrigo (Australia)	2.0	9.7	8.5	3.3	0.31	
Wagga Wagga (Australia)	5.5	9.8	12.3	13.0	0.35	3135
<i>Polar</i>						
Poker Flat Alaska	1.2	1.9	7.0	1.3	0.11	410
Greenland (snow)	0.23	2.0	2.4	0.5		48
South Pole (snow)	0.52	1.4	1.4	0.16	0.15	
	0.4	1.6	1.4	0.07		29

(Sanhueza, 2001)

Non-sea salt chlorine in rain indicates additional sources:



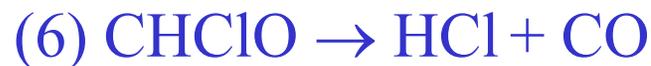
$\text{RCl} + \text{OH}\cdot$



most abundant RCl (4-5 Tg)



formylhalide



Balance: 1 HCl formed per CH_3Cl

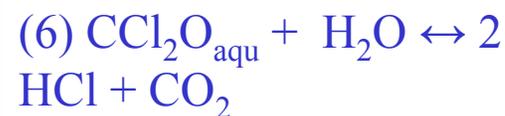


Balance: ≈ 1 HCl formed per CHCl_3

Table 4. Global tropospheric production of HCl from chlorocarbon oxidation

Chlorocarbon	Total source ^{a)} (Tg/yr)	Global OH sink (Tg/yr)	HCl production gas phase (Tg/yr)
CH_3Cl	3.7 (30–50%) ^{b)}	3.4	2.4
CH_2Cl_2	0.76–0.86 ($\sim 80\%$)	0.56	0.5
CHCl_3	0.35–0.6 ($\sim 12\%$)	0.49	0.14
CH_3CCl_3	0.74 (100%)	0.38	0.1
$\text{CH}_2\text{ClCH}_2\text{Cl}$?	0.27	0.05–0.1
CHClCCl_2	0.25–0.36 (70–90%)	0.43	0.15
CCl_2CCl_2	0.36–0.48 ($\sim 95\%$)	0.51	?
CHClF_2	0.15 (100%)	0.057	0.03

Additional HCl in clouds/on aerosol particles:



(Sanhueza, 2001)

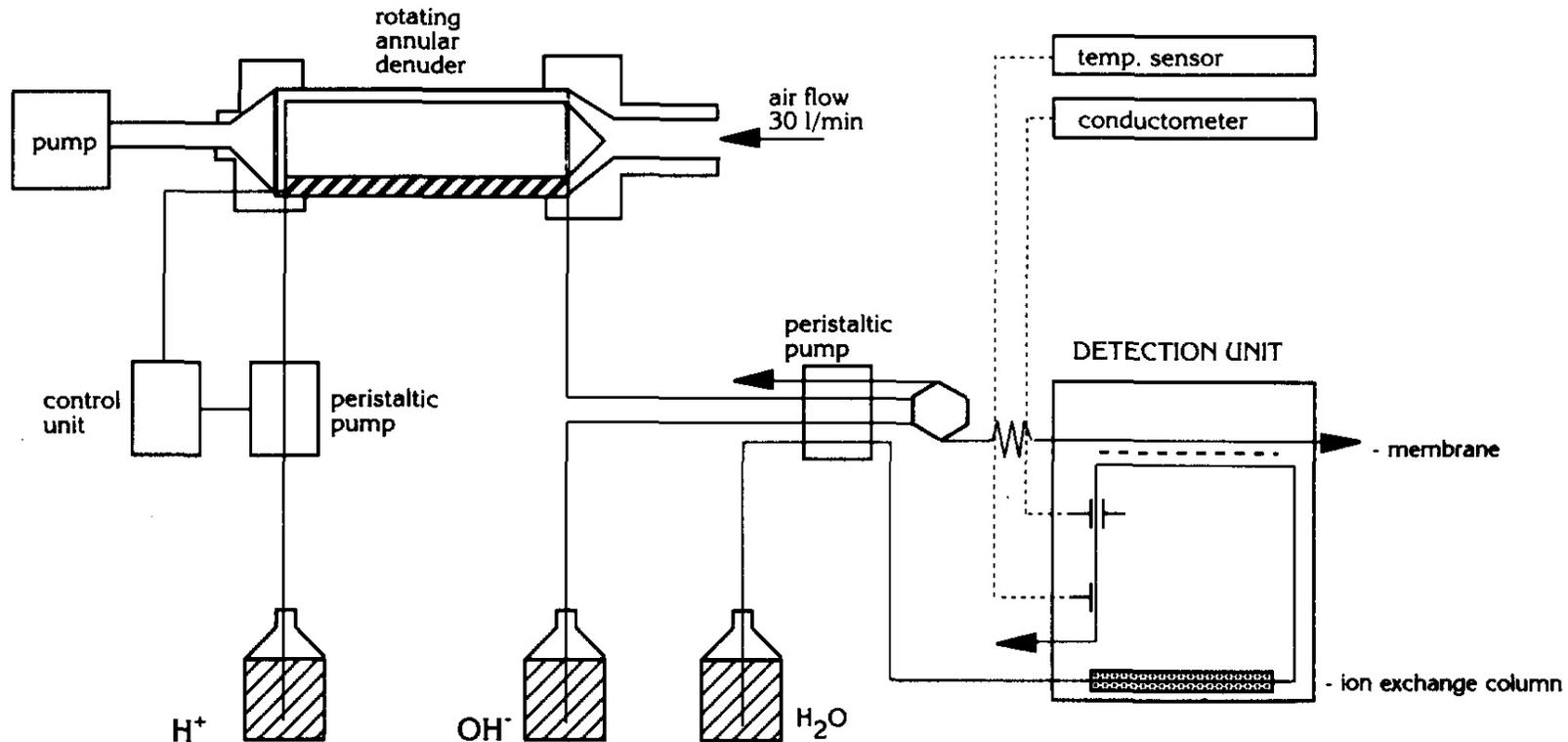
Global HCl sources

	TgCl/yr	Ref.
dechlorination of sea salt aerosols	50 ± 20	Graedel and Keene (1995)
via acid displacement	7.6	Erickson et al. (1999)
coal combustion	4.6 ± 4.3	McCulloch et al. (1999)
waste burning	2 ± 1.9	McCulloch et al. (1999)
volcanoes	0.4–11	Symonds et al. (1988)
biomass burning	<6	Lobert et al. (1999)
transport from the stratosphere	0.3	Keene et al. (1999)
chlorocarbons oxidation	~ 4.2	Present paper

$$\tau_{\text{HCl}} = 1\text{-}2 \text{ d (deposition limited)}$$

(Sanhueza, 2001)

- **Artefact free: particle phase passes without losses**
- **Rapid automated on-line and (semi-)continuous measurement method**
- **Addresses gas-phase**



(Wyers et al., 1993)