Heterogeneous reactivity of atomic chlorine with aerosol particles of atmospheric interest in the marine boundary layer

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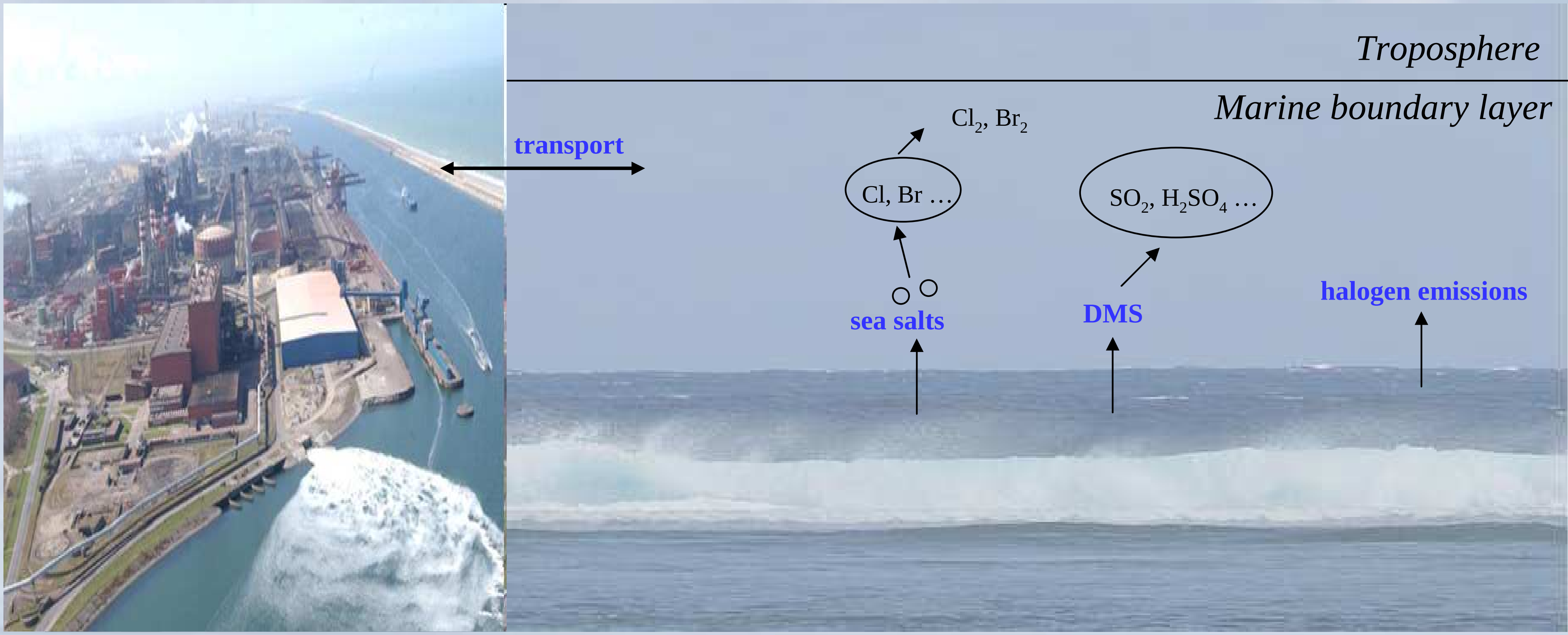
Context



Specificities of the marine boundary layer :
- an abundant supply of sea salt aerosols
- investigation of halogen chemistry
- high relative humidity

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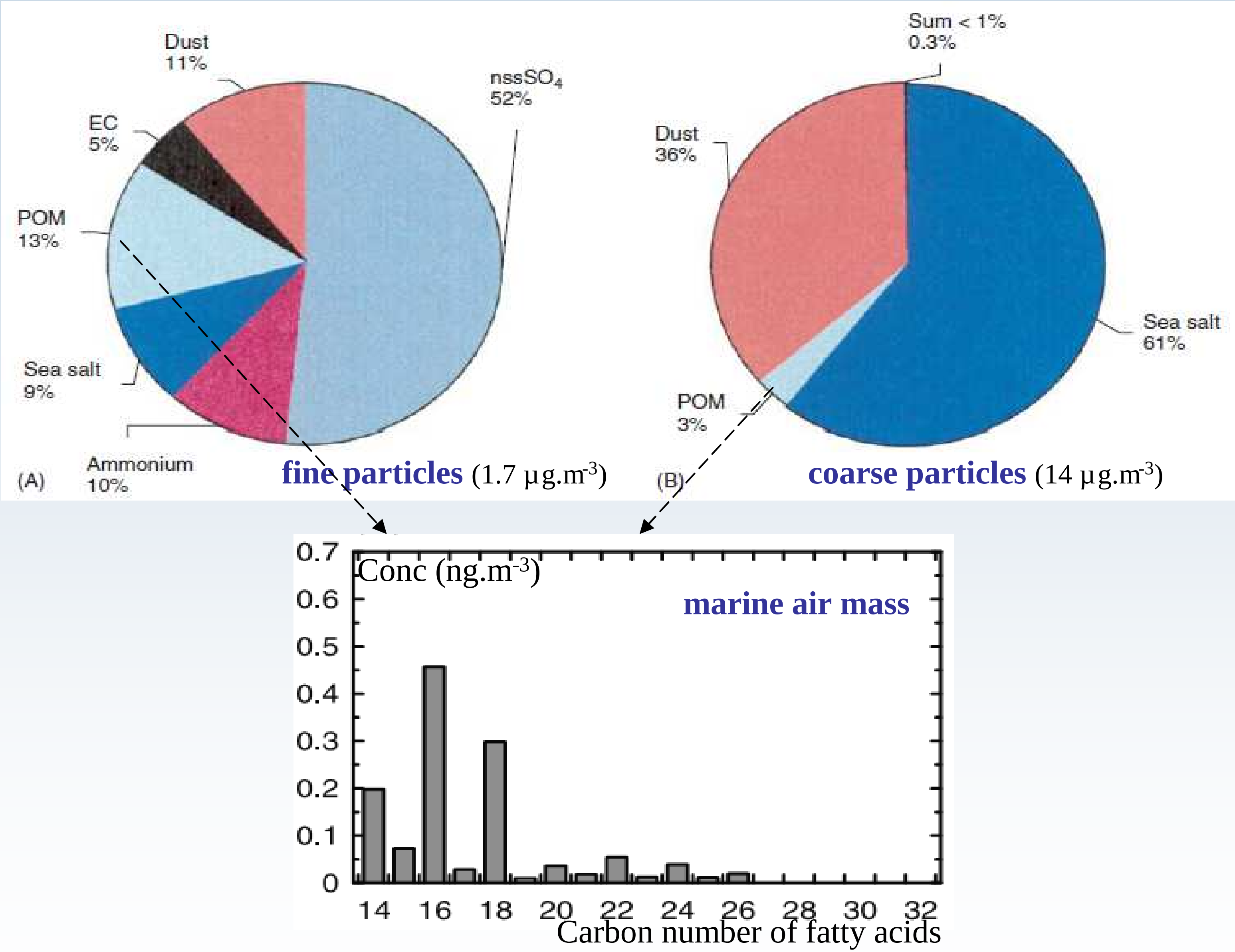
attractive environment for field and laboratory studies

Aerosol particles in MBL

Mass fractions of major chemical components of particles over the oceans

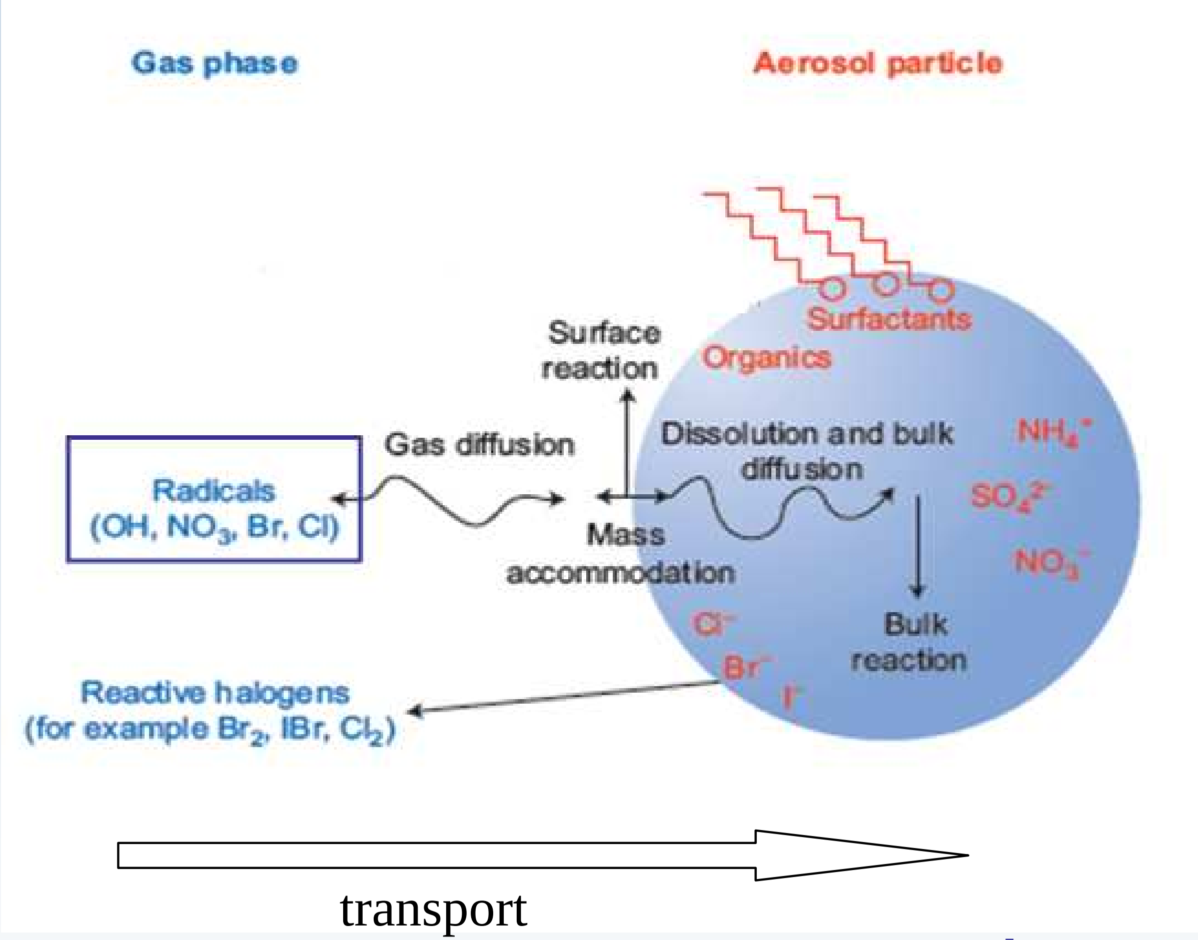


➢ **fatty acids : major constituents of the organic fraction on marine aerosols**

Mochida et al.,Journal of Geophysical Research, 107, 2002

J Heintzenberg, Encyclopedia of Atmospheric Sciences, 34-40, 2003

Heterogeneous reactions

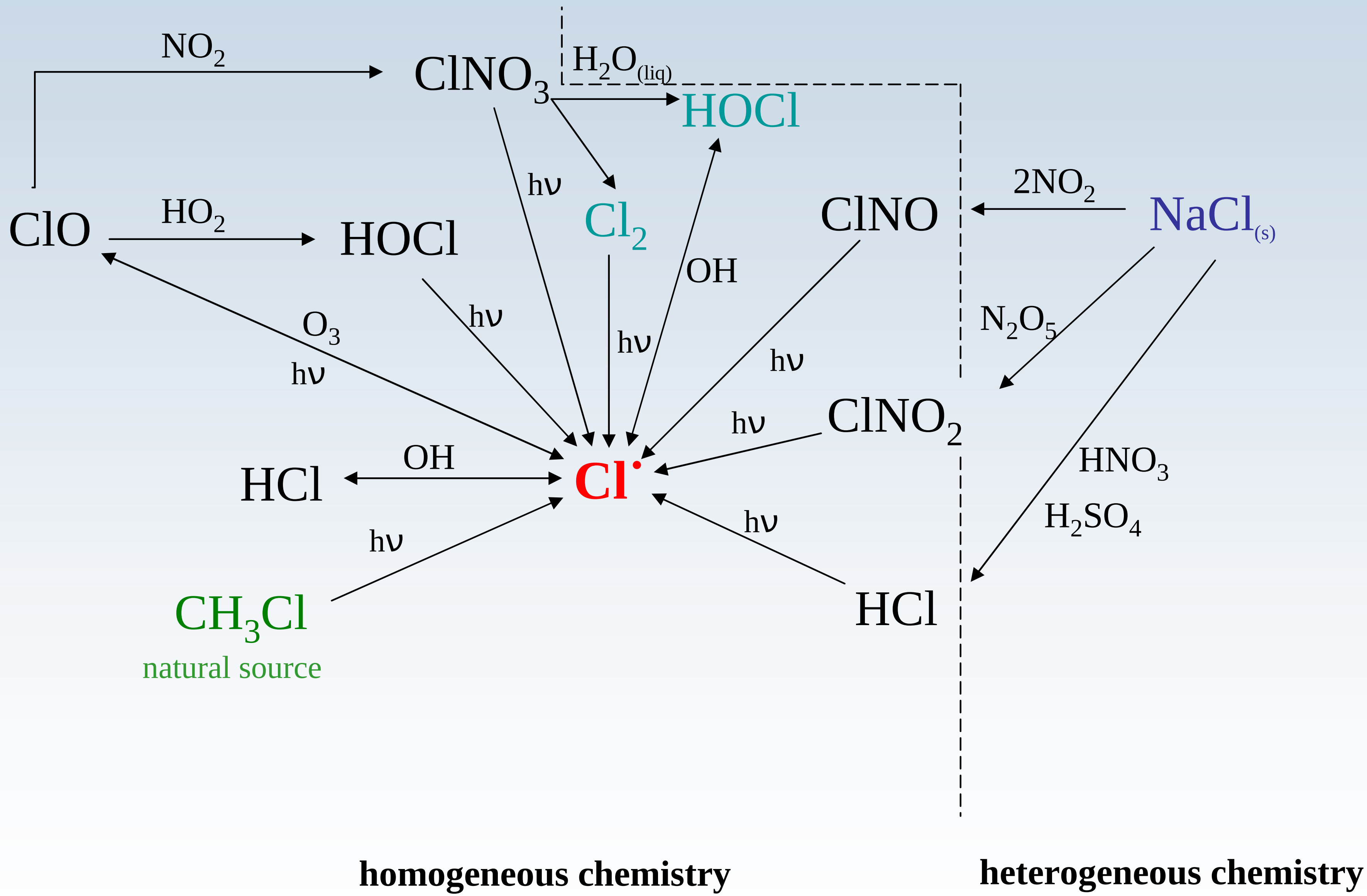


heterogeneous reactions → **aging process** :

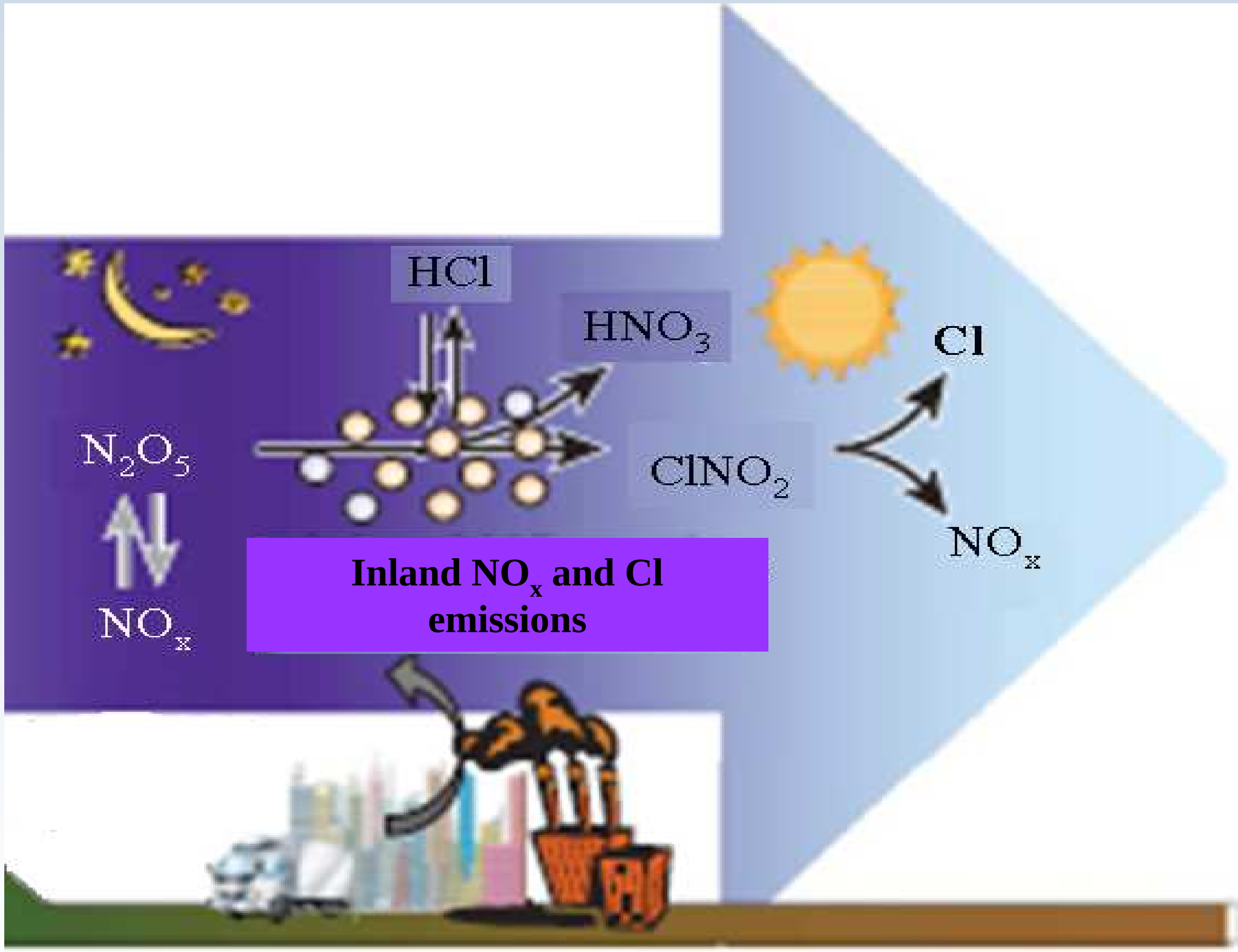
changes in size of aerosols ?
changes in aerosol composition ?
changes in chemical composition ?
changes in hygroscopic properties ?
changes in optical properties ?

George and Abbatt, Nature Chemistry, 713-722, 2010

Chlorine reactive species in MBL



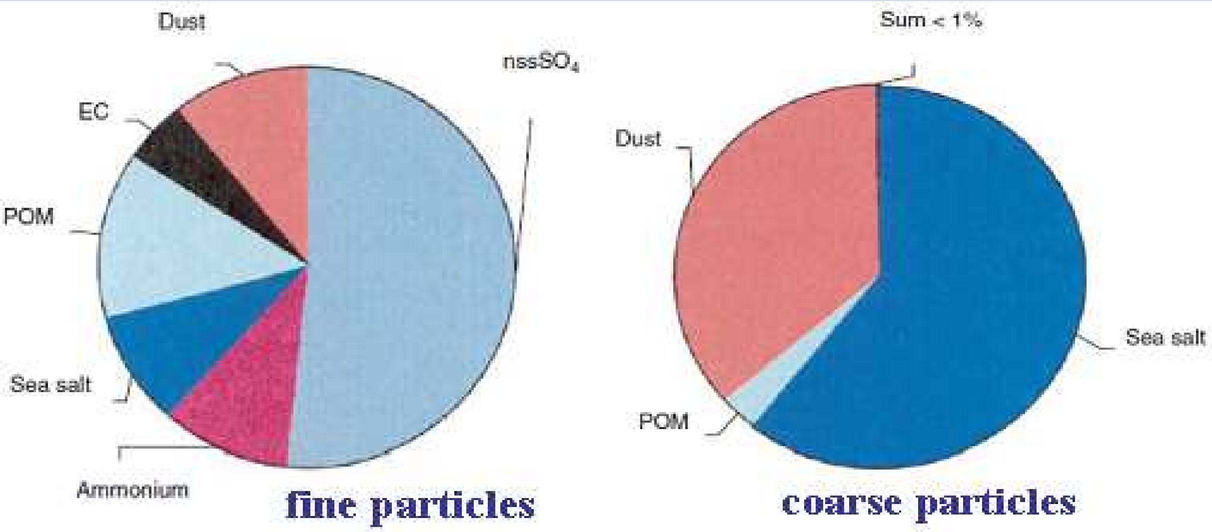
Atomic chlorine in continental environment



$[Cl^{\bullet}] = 10^3 - 10^6$ atom.cm^{-3}

Thornton *et al.*, *Nature*, 464, 271-274, 2010
Osthoff *et al.*, *Nature Geoscience*, 1, 324-328, 2008

Laboratory studies of heterogeneous reactions



$Cl^{\cdot}$ + NaCl → products

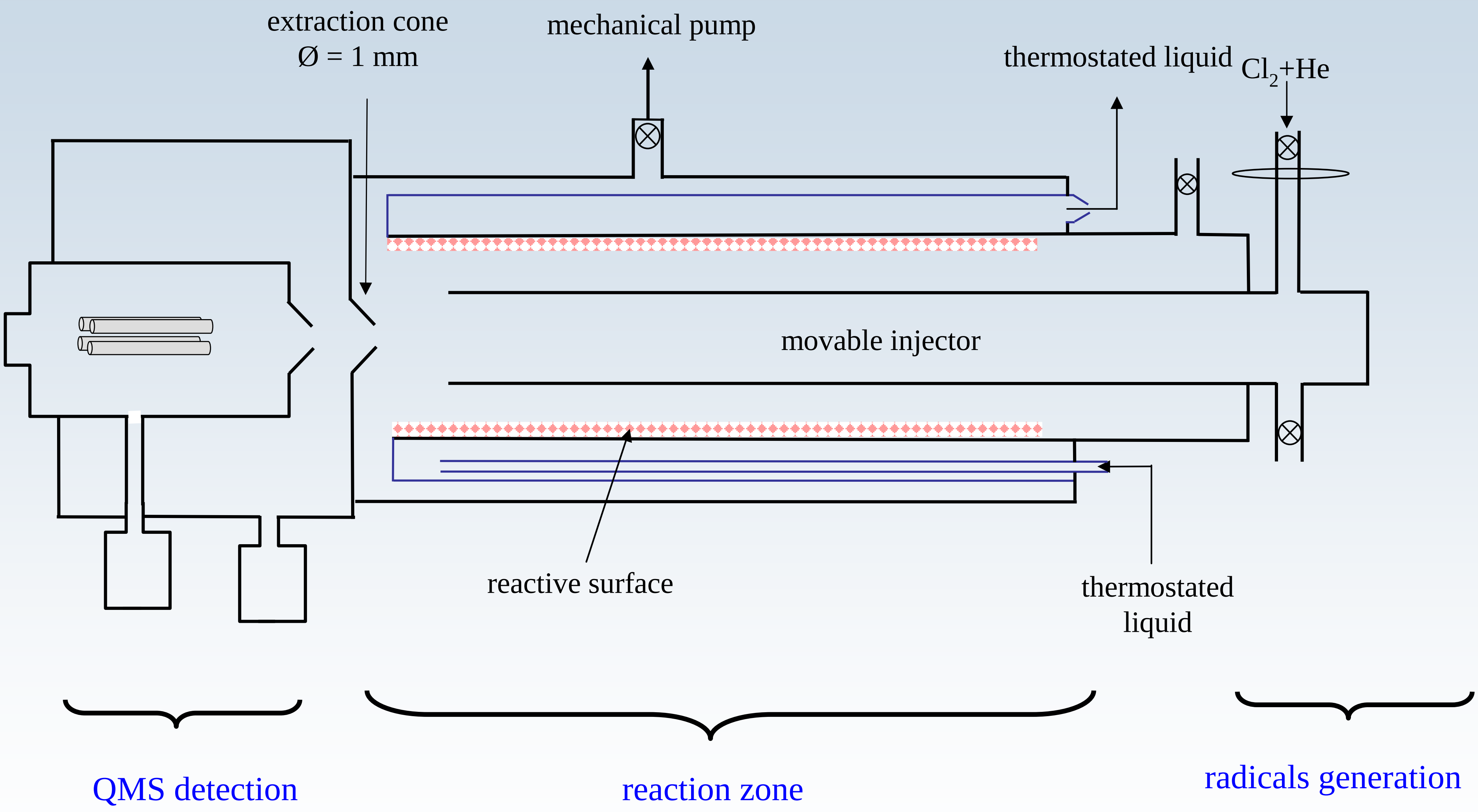
$Cl^{\cdot}$ + Synthetic sea salts → products

$Cl^{\cdot}$ + NH_4NO_3 → products

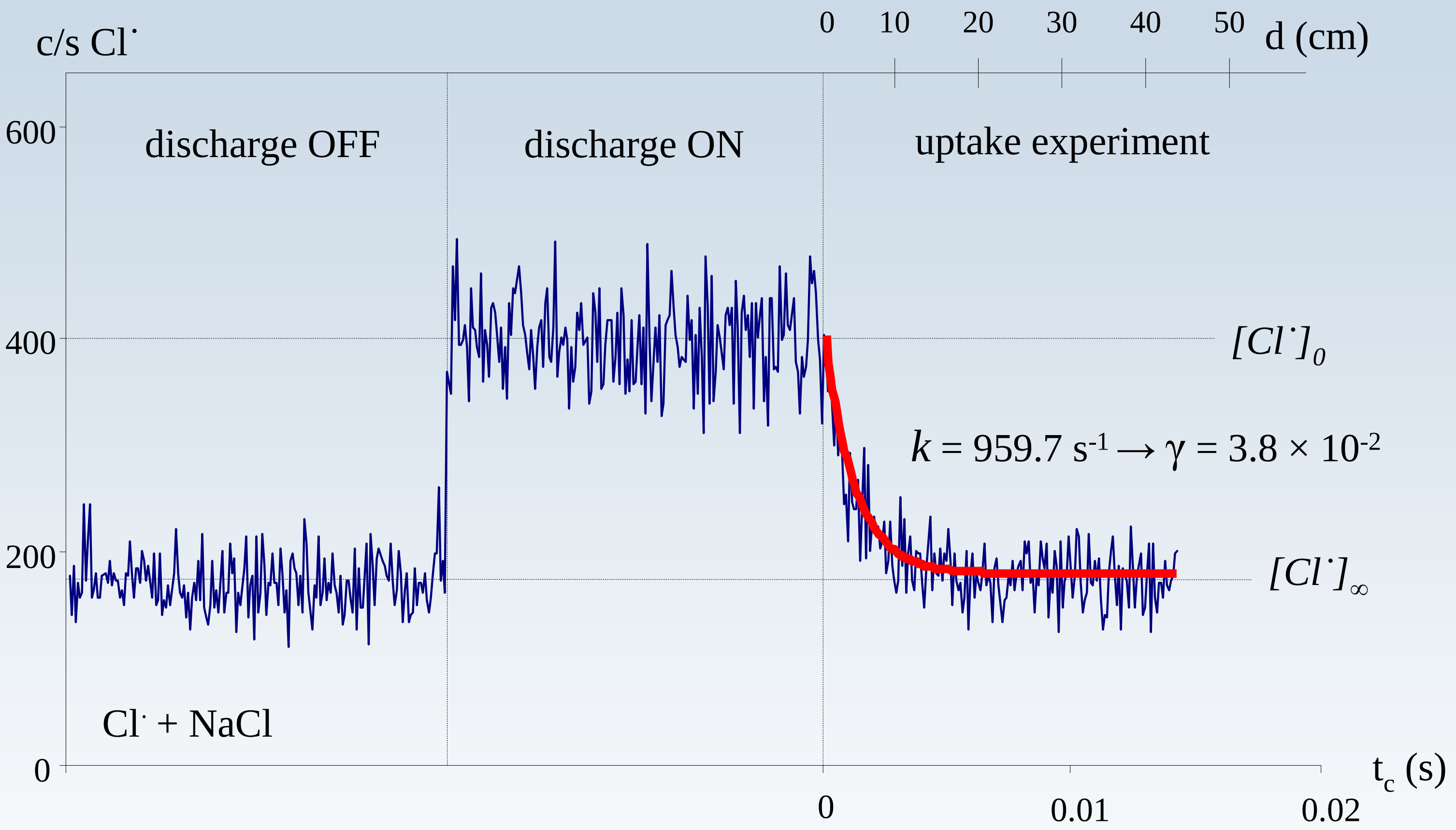
$Cl^{\cdot}$ + $(NH_4)_2SO_4$ → products

- kinetic constants and uptake coefficients of elementary reactions
- identification of the reaction products in the gas and condensed phase
- the influence of the temperature and the presence of water vapor on the reactivity

Coated wall flow tube reactor



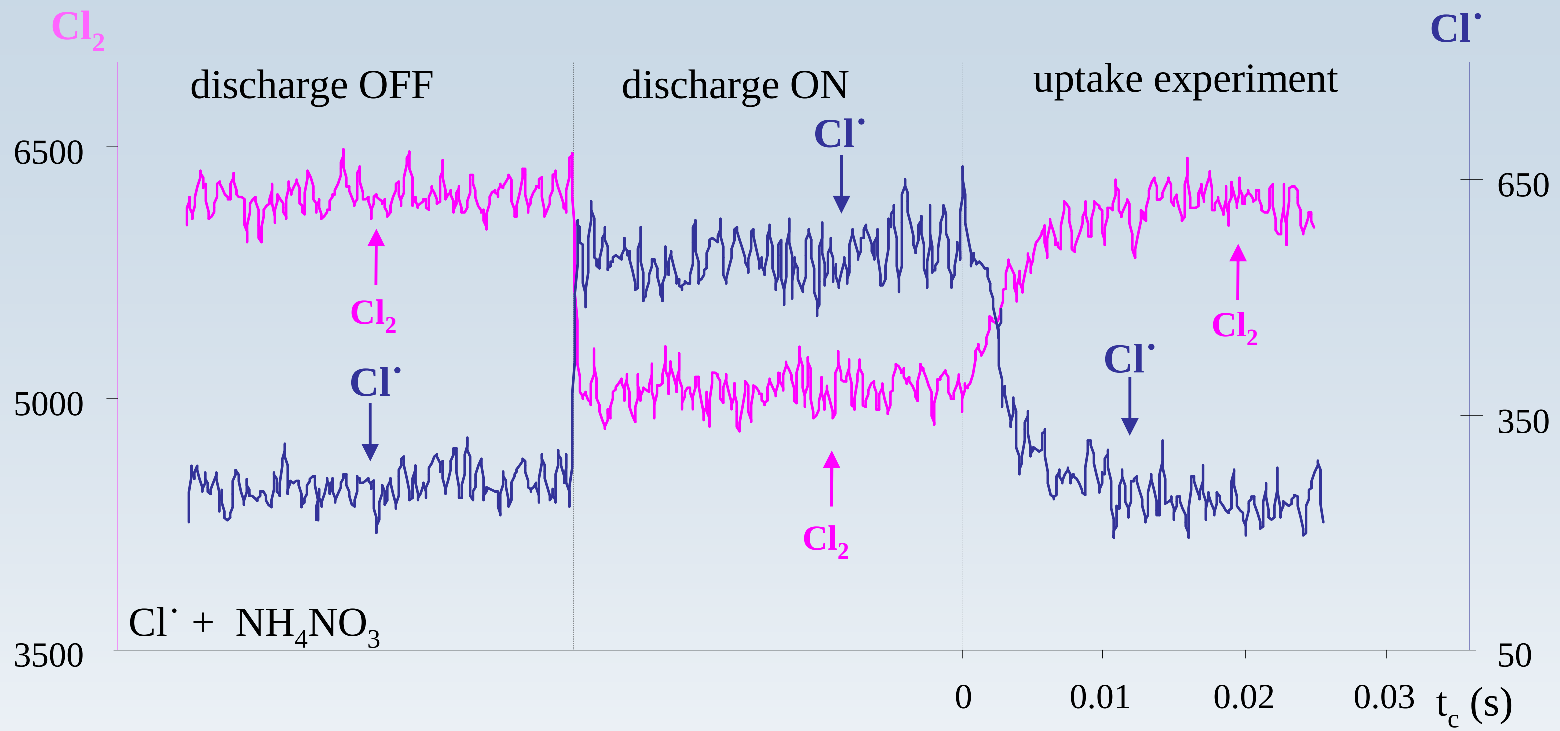
Experimental determination of *k* and *γ*



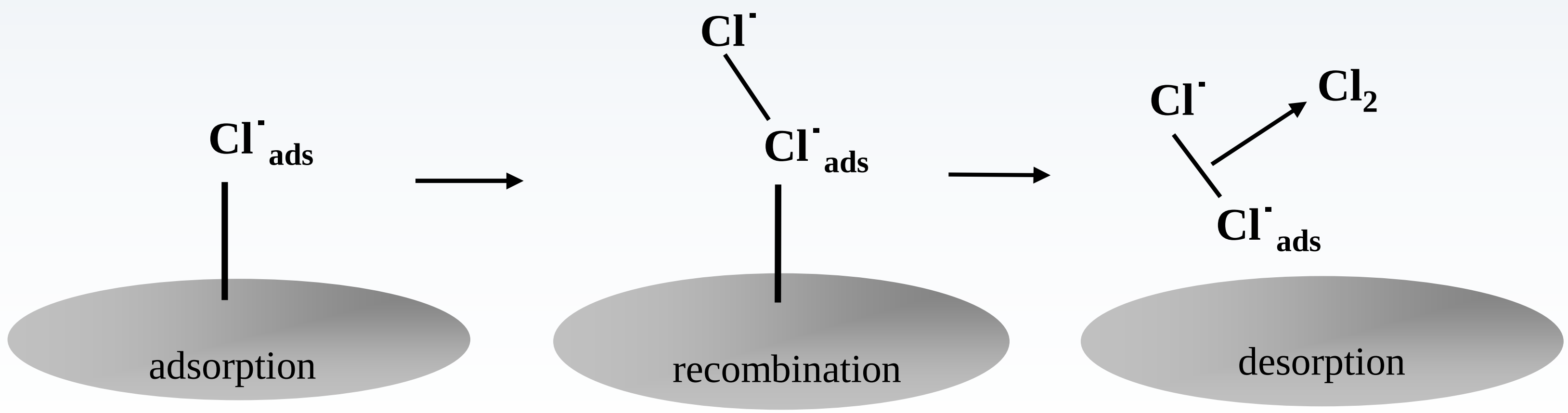
$$\gamma = \frac{2\ k\ \ r}{\langle c \rangle}$$

$$\gamma = \frac{\text{flux of gas molecules removed by the condensed phase per unit time}}{\text{flux of gas molecules striking the interface per unit time}}$$

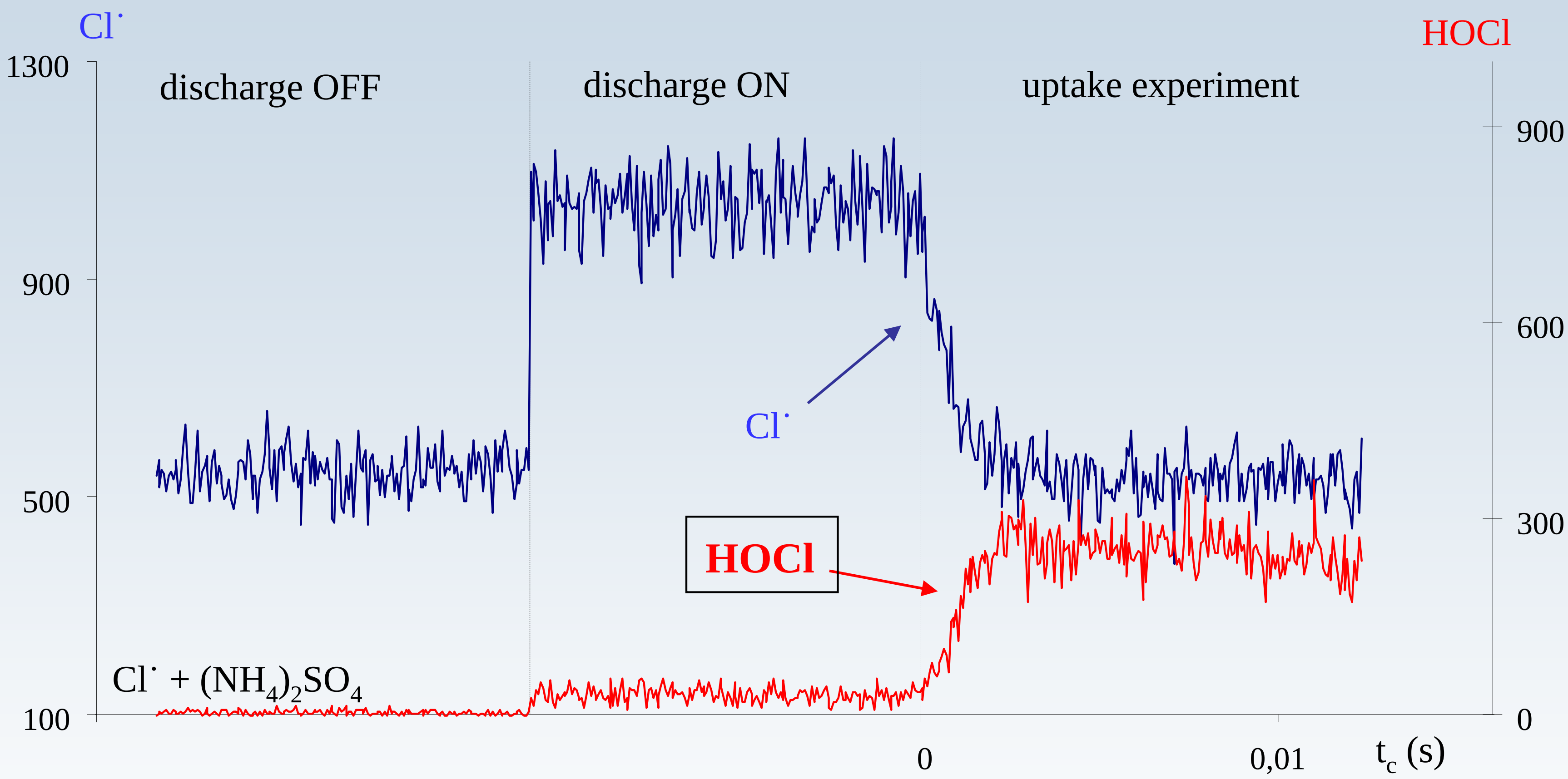
Heterogeneous recombination of chlorine atoms



➢ **Cl_2 formation by heterogeneous recombination of $Cl^{\cdot}$**



Hypochlorous acid formation



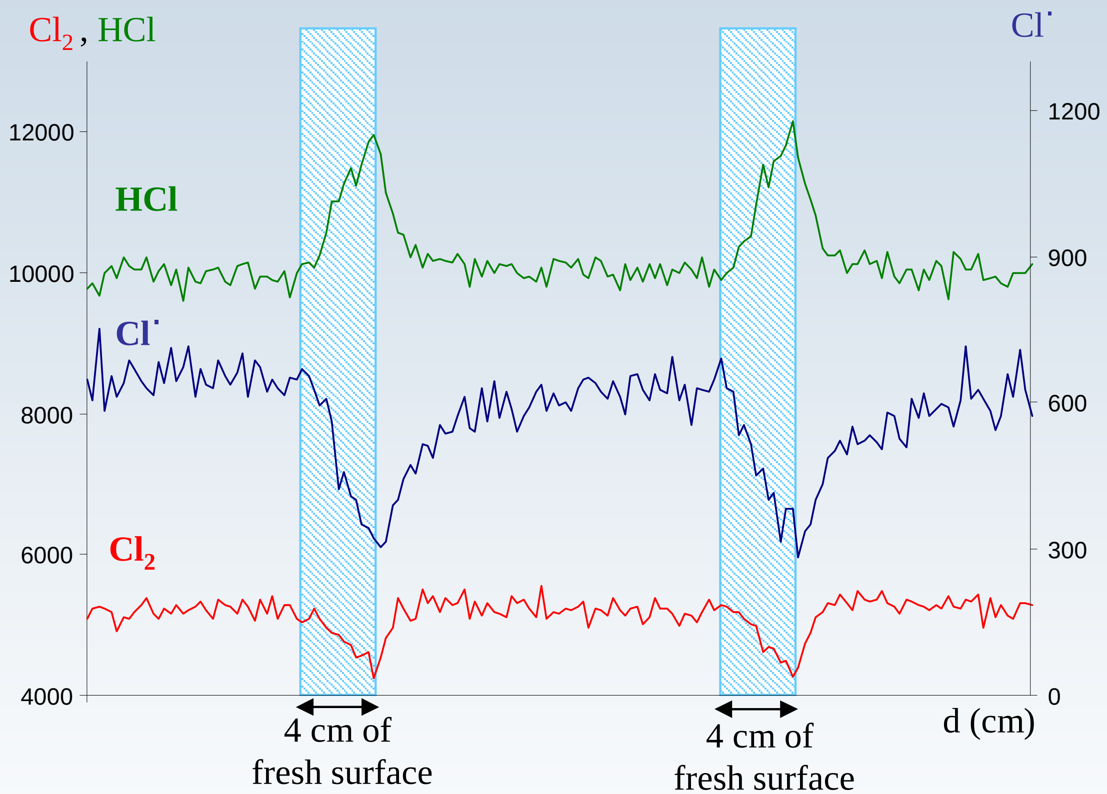
- **hypochlorous acid formation at low temperatures and in presence of surface adsorbed water**

Conclusions

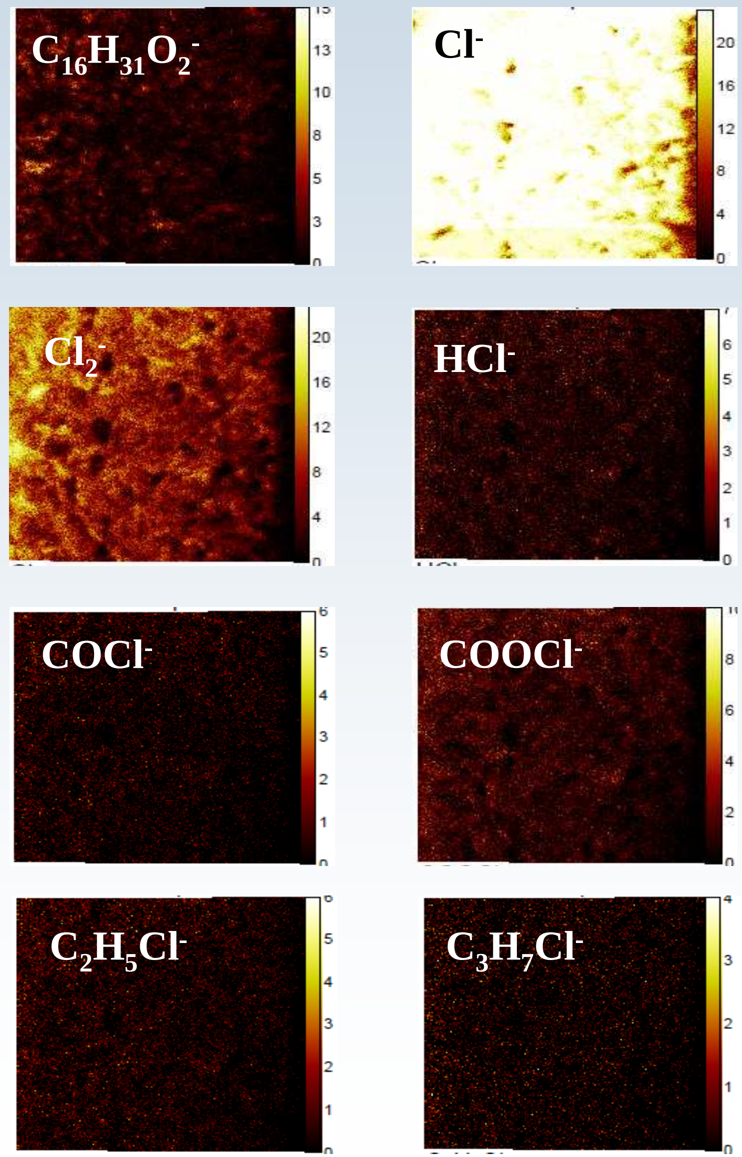
Salts	γ *(T=300 K)*	γ *if* ***T*** *decreases*	*Surface adsorbed water*	*Products*
NaCl	10^{-2}	↗	↗	Cl_2, HOCl
Synthetic sea salts	10^{-3}	↘	↘	Cl_2, HOCl
NH_4NO_3	10^{-3}	↗	↗	Cl_2, HOCl
$(NH_4)_2SO_4$	10^{-3}	↗	↗	Cl_2, HOCl, NH_4Cl **aging process**

Heterogeneous reactivity of chlorine atoms with fatty acids

Palmitic acid : $Cl^{\cdot} + C_{16}H_{32}O_2 \rightarrow$ products



TOF SIMS analyses
on $C_{16}H_{32}O_2$ particles exposed to $Cl^{\cdot}$



➢ **surface saturation effect → aging process**

Heterogeneous reactivity of chlorine atoms

Squalane : $Cl^{\cdot} + C_{16}H_{62} \rightarrow$ products

Fundamental radical–particle reaction mechanisms :

$$RH + Cl^{\cdot}_{g} \rightarrow R^{\cdot} + HCl$$

$$R^{\cdot} + Cl_{2p} \rightarrow RCl + Cl^{\cdot}_{p}$$

$$R^{\cdot} + Cl_{2g} \rightarrow RCl + Cl^{\cdot}_{p}$$

$$RH + Cl^{\cdot}_{p} \rightarrow R^{\cdot} + HCl$$

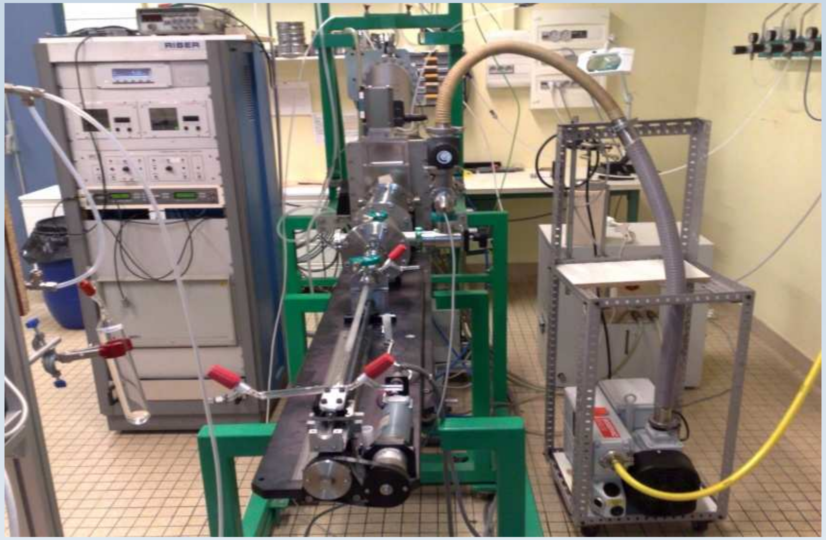
$$R^{\cdot} + O_{2g} \rightarrow RO^{\cdot}_{2}$$

$$RO^{\cdot}_{2} + RO^{\cdot}_{2} \rightarrow \text{Alcohol} + \text{Ketone} + O_2$$

$$RO^{\cdot}_{2} + RH \rightarrow ROOH + R^{\cdot}$$

Liu *et al.*, *PCCP*, 13, 8993–9007, 2011

Perspectives



$C_{16}H_{32}O_2$ particles + $Cl^{\cdot}$ in presence of O_2

coated particles (NaCl, SSS) **with fatty acids**

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study of the reactivity on

the flow tube reactor

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SMPS

GC/MS

Thank you for your attention!