Photochemistry versus biological activity towards organics in cloud water

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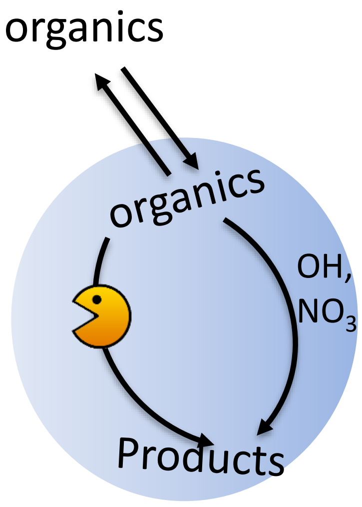
Introduction and background

- Water-soluble organic compounds (WSOC) constitute a significant portion of the total atmospheric organic carbon mass, ranging from 14% to 64% .
- Bacterial concentration reach values between $0.8\cdot10^3$ and $2.4\cdot10^5$ cells mL^{-1} in cloud water.
- For some organics, biodegradation by bacteria is suggested to be more important than chemical radical processes (e.g., OH, NO_3) *Amato et al., 2005; 2007; Deguillaume et al., 2008; Delort et al., 2010; Husarova et al., 2011; Vaïtilingom et al., 2010; 2011*
- Biodegradation is assumed to only occur efficiently in cloud water as efficient cell growth and metabolism is restricted to the time cells spend in liquid water

Only a few studies estimated the loss of total WSOC by microbial processes
Vaïtilingom et al., 2013; Fankhauser et al., 2019; Ervens & Amato, 2020

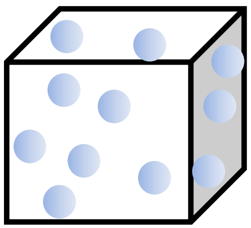
Our goal for this study is to determine the conditions under which

1. Bacterial activity is most important compared to chemical losses of WSOCs
2. Metabolic processes represent major atmospheric sinks of organics



Model description

- We use a multiphase chemistry box model with detailed gas and aqueous phase chemistry (75 species, 44 gas phase reactions, 31 aqueous reactions)
- In addition, we consider an organic compound ***'Org'*** undergoes chemical radical reactions in the gas and aqueous phases and is biodegradation by bacteria in the aqueous phase only .



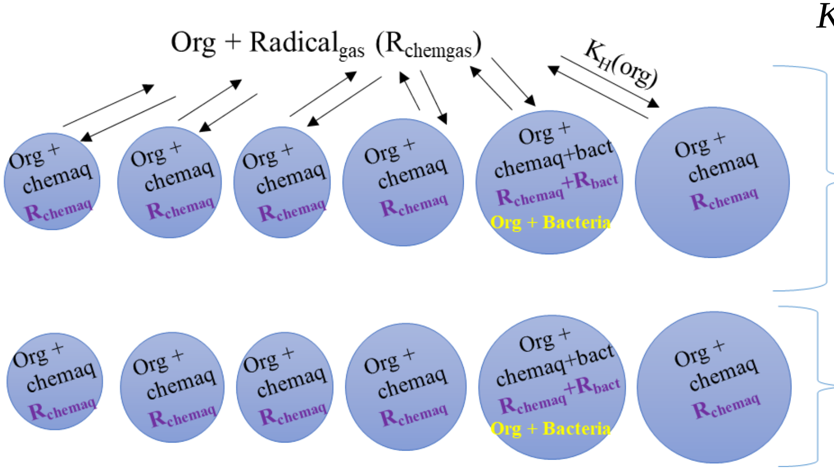
- 263 droplets/cm^3 (gas phase)
- LWC= $6.8 \cdot 10^{-7}$ cm^3(aq)/cm^3 (air)
- Polydisperse drop size distribution: 11 size classes with drop diameters 5 – 20 µm
- Only one size class includes bacteria cells (D = 20 µm; $N_{droplet}$ = cell concentration = $0.01\ cm^{-3}$)

Physicochemical properties of 'Org' varied in model sensitivity studies:

$k_{chem,aq}$, k_{chemg} = chemical rate constants in aqueous and gas phase

k_{bact}: rate constant of biodegradation in the aqueous phase

K_H: Henry's law constant



Volatiles organic compounds

$10^2 \leq K_H$ [M atm^{-1}] $\leq 10^9$
$10^{-18} \leq k_{bact}$ [L cell^{-1} s^{-1}] $\leq 10^{-11}$
$10^3 \leq k_{chem,aq}$ [M^{-1} s^{-1}] $\leq 10^{10}$
$10^{-10} \leq k_{chem,gas}$ [cm^3 s^{-1}] $\leq 10^{-17}$

Non-volatiles organic compounds

$10^{-18} \leq k_{bact}$ [L cell^{-1} s^{-1}] $\leq 10^{-11}$
$10^3 \leq k_{chem,aq}$ [M^{-1} s^{-1}] $\leq 10^{10}$

Definition of model parameters

- To generalize our results for any organic concentration, we express the parameter ranges as Rates (k [Concentration]):

$$R_{bact}[s^{-1}] = k_{bact}[\frac{L}{Cell\ s}] \times C_{cell,aq}[\frac{Cell}{L}]$$

$$R_{chemaq}[s^{-1}] = k_{radical,aq}[L\ mol^{-1}\ s^{-1}] \times [radical]_{aq}\ [mol\ \ L^{-1}]$$

$$R_{chemgas}[s^{-1}] = k_{radical,gas}[cm^3\ s^{-1}] \times [radical]_{gas}\ [cm^{-3}]$$

Simulations are performed for
t = 10 min
= approx. one cloud cycle

- To determine the relative importance of the loss rates by bacterial and chemical processes, we define:

$$fr_{bact}[\%] = \frac{R_{bact}}{R_{bact} + R_{chemaq} + R_{chemgas}} \times 100\%$$

$$fr_{chemaq}[\%] = \frac{R_{chemaq}}{R_{bact} + R_{chemaq} + R_{chemgas}} \times 100\%$$

$$fr_{chemgas}[\%] = \frac{R_{org,chemgas}}{R_{bact} + R_{chemaq} + R_{chemgas}} \times 100\%$$

Comparison of fr_{bact}, fr_{chemaq}, $fr_{chemgas}$ shows which of the three loss rates is the highest, but it gives NO information on the absolute importance of these processes to the **total loss of the organic compound**

- To determine the importance of bacteria as absolute sink of the organic compound, we calculate:

$$fr_{org} = 1 - \frac{[org]_t}{[org]_{t=0}}$$

= fraction of organics consumed by chemical and bacterial processes after time t

$$fr_{org,bact} = fr_{bact} \cdot fr_{org}$$

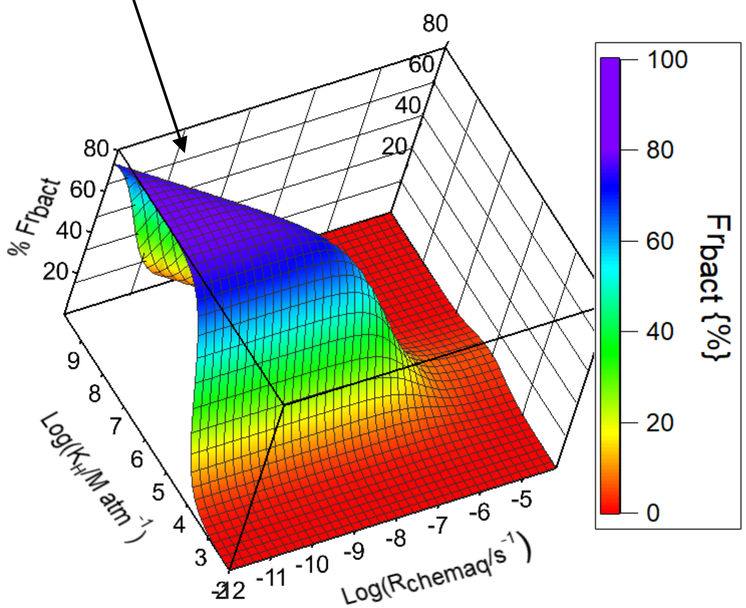
= fraction of organics consumed by bacteria after time t

Model results: Biodegradation of volatiles organics

Selected example: $R_{bact}=10^{-6}\ s^{-1}$ and $R_{chemgas}=10^{-6}\ s^{-1}$ (constant)

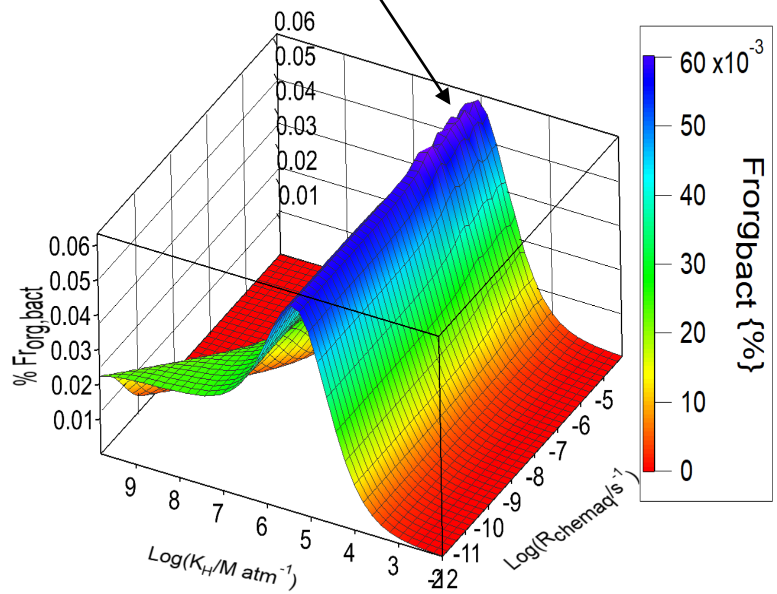
a) fr_{bact} as a function of K_H and R_{chemaq}

Highest fr_{bact} : highest K_H and lowest R_{chemaq}



b) $fr_{org,bact}$ as a function of K_H and R_{chemaq}

highest $fr_{org,bact}$: $K_H \sim 10^5$, (almost) independent of R_{chemaq}



The location of the maxima is different for different combinations of R_{bact} and $R_{chemgas}$, but the overall conclusions and shapes are identical for wide parameter ranges

→ The maxima of fr_{bact} (left panel) and $fr_{org,bact}$ (right panel) do not coincide!

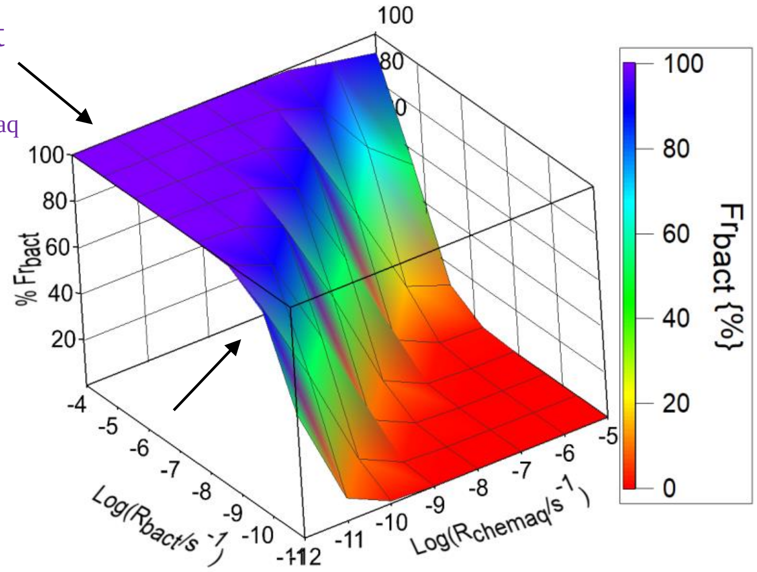
→ (As expected) highest fr_{bact} when chemical reactivity is lowest and solubility highest

→ Bacteria represent the most efficient sink for organics with intermediate solubility ($K_H \sim 10^{-5}$ M atm^{-1})

Model results: Biodegradation of non-volatile organics

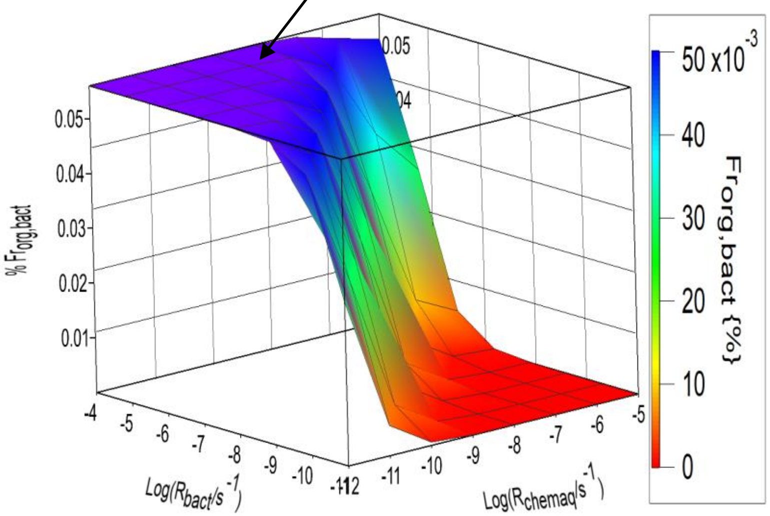
a) fr_{bact} as a function of R_{bact} and R_{chemaq}

fr_{bact}=100% for highest R_{bact} and highest R_{chemaq}



b) $fr_{org,bact}$ as a function of R_{bact} and R_{chemaq}

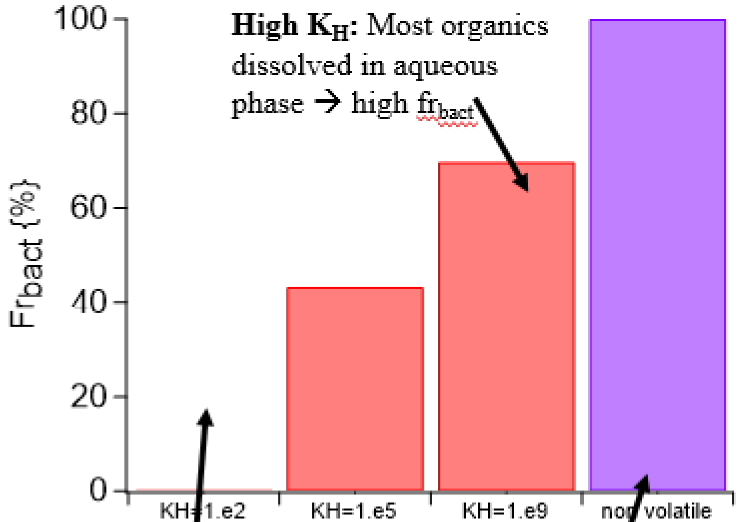
Maximum $fr_{org,bact}$ for highest R_{bact} and highest R_{chemaq}



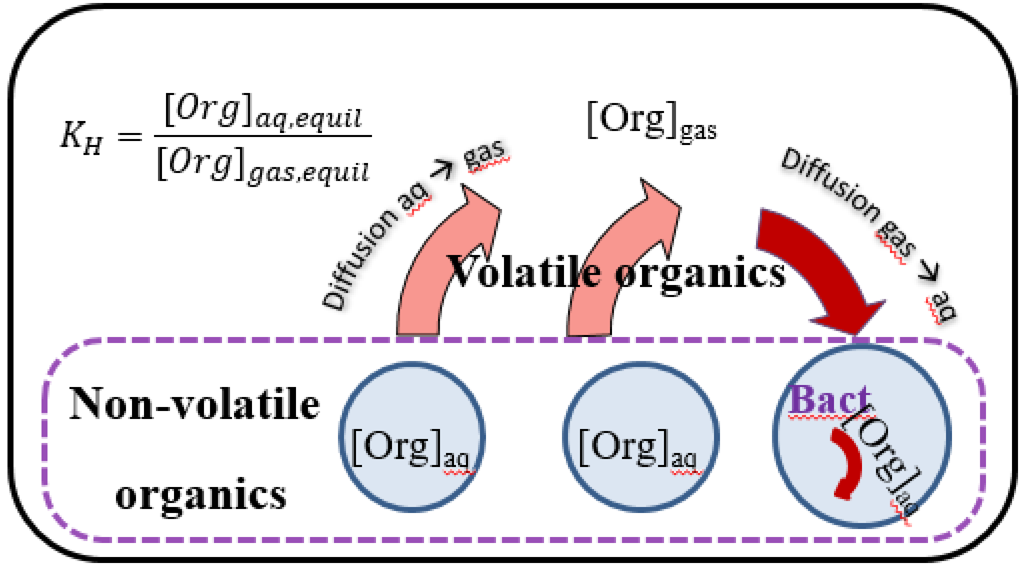
→ fr_{bact} and $fr_{bact,org}$ show the same trends for non-volatile organics

→ fr_{bact} and $fr_{org,bact}$ are highest for the highest fr_{bact}, i.e. when chemical loss in the aqueous phase is negligible (low $R_{chem,aq}$)

Model results: Volatile vs non-volatile organics



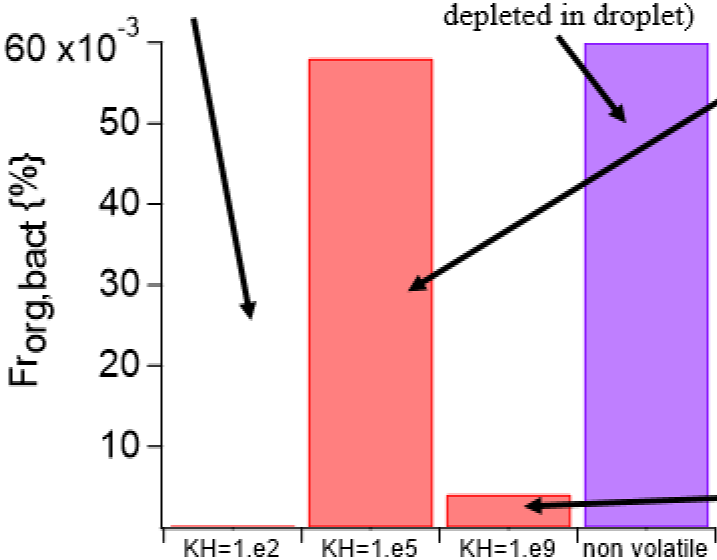
High K_H: Most organics dissolved in aqueous phase → high fr_{bact}



Low K_H: Very little organics dissolved in aqueous phase → $fr_{chemgas}$ dominating

Non-volatile Org: $fr_{chemgas}$ = 0, high fr_{bact} (if Org not completely depleted in droplet)

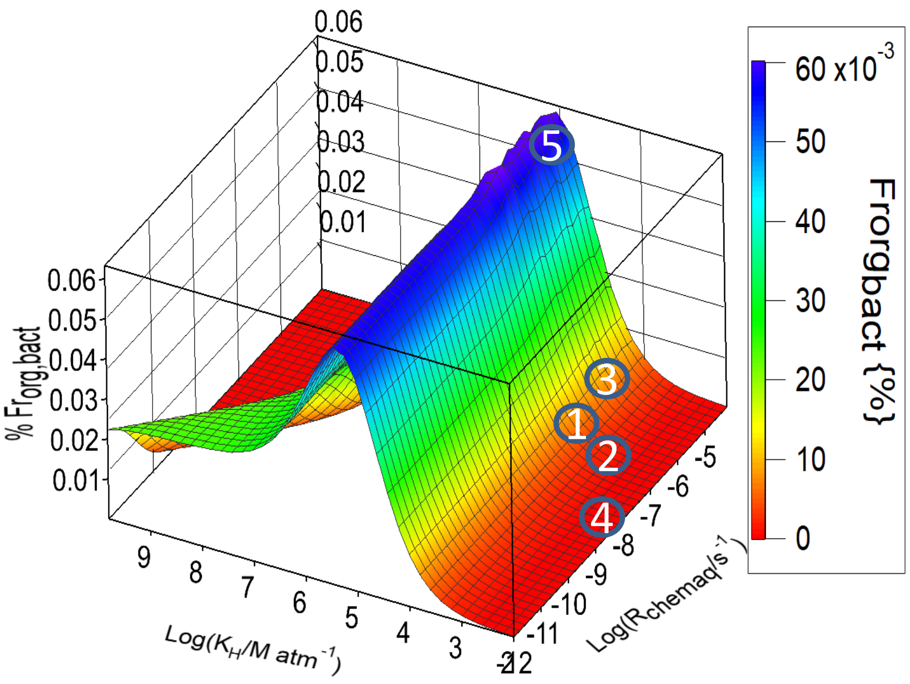
Intermediate K_H: Efficient diffusion from droplets without bacteria to gas phase and into droplets with bacteria



- The degradation of volatile organics by bacteria is most efficient for organics with intermediate K_H (~ $10^4 - 10^6$ M atm^{-1})
- The degradation of non-volatile organics by bacteria is most efficient for organics with low chemical reactivity

High K_H: Inefficient aq→ gas diffusion
Low gradient of $[Org]_{aq,equil}$ and $[Org]_{gas,equil}$

Model results: Comparison to experimental data



Example: Constant values for

R_{bact} = 10^{-6} s^{-1} = k_{bact} [L $cell^{-1}$ s^{-1}] C_{cell} [cell L^{-1}]

$R_{chemgas}$ = 10^{-6} s^{-1} = $k_{chemgas}$ · $[Radical]_{gas}$

~ 10^{-12} cm^3 s^{-1} · 10^6 cm^{-3} → e.g. OH(gas)

$\mathbf{fr_{orgbact}}$ as a function of

K_H [M atm^{-1}] and

R_{chemaq} = k_{chemaq} [M^{-1} s^{-1}] · 10^{-15} M → e.g. OH(aq)

- These $fr_{orgbact}$ are reached in clouds for the calculated bacteria concentrations C_{cell}
- Given that typical cell concentrations in cloud water are in the range of ~ 10^6 – 10^8 cell L^{-1}, our results show that the loss by biodegradation for some of the organics is likely smaller than predicted in the figure

		K_H / M atm^{-1}	k_{chemaq} / M^{-1} s^{-1}	k_{bact} / L $cell^{-1}$ s^{-1}	C_{cell} / cell L^{-1}
①	Acetic acid	$1.2 \cdot 10^4$	$2{,}2 \times 10^8$	$1{,}5 \times 10^{-18}$	$6{,}6 \times 10^{11}$
②	Formic acid	$9 \cdot 10^3$	10^8	$4{,}8 \times 10^{-18}$	2×10^{11}
③	Form-aldehyde	$1.3 \cdot 10^4$	10^9	5×10^{-18}	2×10^{11}
④	Methanol	$2 \cdot 10^2$	4×10^7	5×10^{-20}	2×10^{13}
⑤	Catechol	$8.3 \cdot 10^5$	$3{,}8 \times 10^8$	$4{,}16 \times 10^{-15}$	$2{,}4 \times 10^8$

$C_{cell} = R_{bact} / k_{bact}$

for $R_{bact} = 10^{-6}$ s^{-1}

Note that Ccell depends somewhat on the choice of R_{bact} = const and $R_{chemgas}$ = const.
However, the sensitivity of these rates to the overall conclusions is low.

Conclusion and Outlook

- For volatile organic compounds, the most efficient consumption by bacteria occurs for organics with intermediate solubility (~ 10^4 M atm^{-1} < K_H < ~ 10^6 M atm^{-1})
- Comparing only the loss rates of chemical vs bacteria processes does not give information on the importance of the total loss of the organic compound
- For non-volatile organic compounds, the sink of organics depends only on the competition of its chemical degradation by radicals and biodegradation in the aqueous phase
- Our sensitivity studies allow to estimate the potential importance of biodegradation of organics, for which chemical rate constants (k_{chemaq}, $k_{chemgas}$) and Henry's law constants are known
- Data on biodegradation rates for volatile and non-volatile compounds are sparse
- Further studies will include model simplifications to allow the implementation of biodegradation in multiphase chemistry cloud models

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