

UNDERSTANDING ATMOSPHERIC MINERAL DUST PHOTOCHEMISTRY

Milena PONCZEK

April 2019

(new) post-doc fellow – LFA - 2019

Who am I ?



2006-2011:
Chemical Eng

LPDTA: Vehicular Air Pollution inventory.

GPM³: Sorption Studies of CO₂ in Magnesium Filossilicates.

2012-2014:
Master Chemical Eng

Degradation of VOCs by TiO₂ photocatalysis.



2013-2014:
R&D Eng.

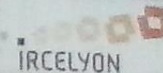
Modelling and software development for acid fracturing of oil wells.



2014-2018:
PhD in Chemistry

Photocatalytic reactions of atmospheric mineral dust and trace gases.

Institut de recherches sur la catalyse et l'environnement de Lyon



Largest catalysis laboratory in France and Europe.

Focused on heterogeneous catalysis applied to Energy, Chemistry and the Environment.



115 permanent staff

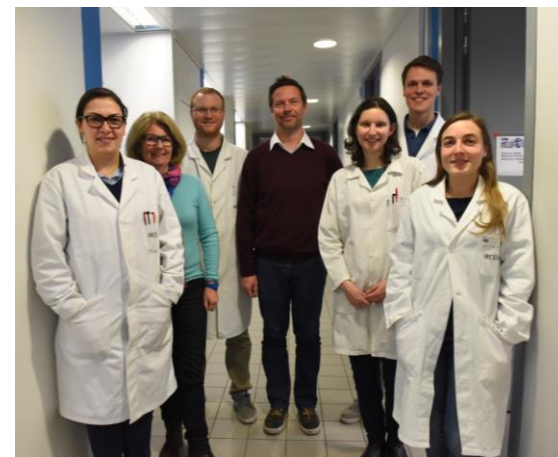
Our team

Tropospheric Heterogeneous Photochemistry

Light-induced emission/production of **VOCs**, **NO_x** and **particles** (SOA) at interfaces: **air/water**, **mineral dust particles**, urban surfaces (outdoor & indoor), etc...



Elucidation of **mechanisms**
Reactors and Simulation Chambers setups
Analytical development

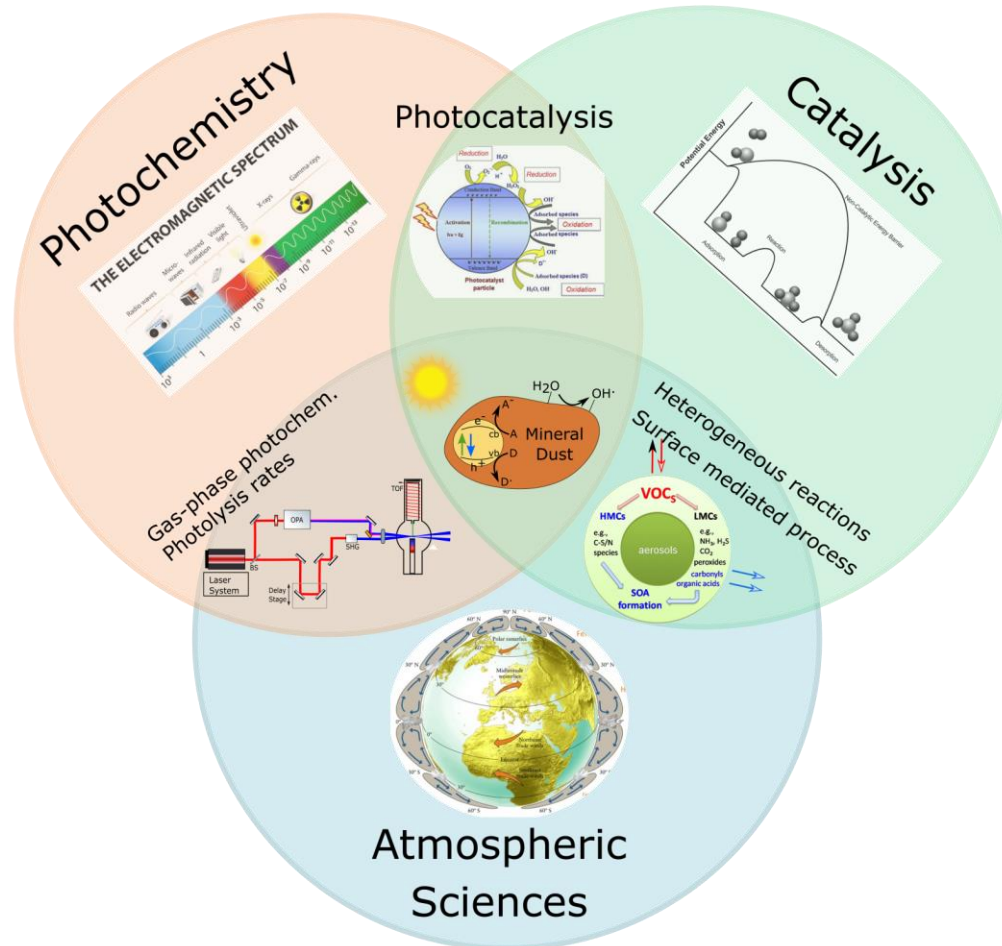


Proton Transfer Reaction – Time
of Flight – Mass Spectrometer
(*PTR-ToF-MS*)

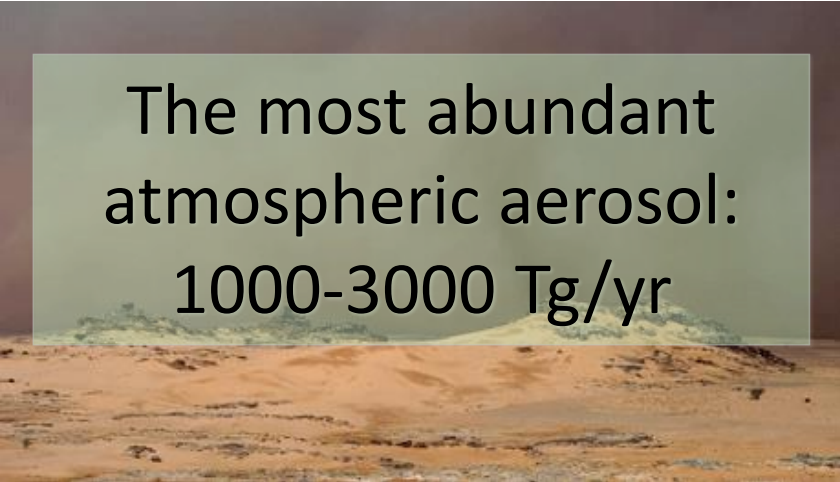
UHPLC/(+/-)HESI-HRMS
Q-Exactive (*Orbitrap*)



UNDERSTANDING ATMOSPHERIC MINERAL DUST PHOTOCHEMISTRY



Mineral Dust: emission sources and relevance



The most abundant atmospheric aerosol:
1000-3000 Tg/yr



Mineral dust can travel long-range distances



Nutrients: for forests and oceans



Changes in land use increase desertification

- Desert areas
- Areas vulnerable to desertification
- Invulnerable areas

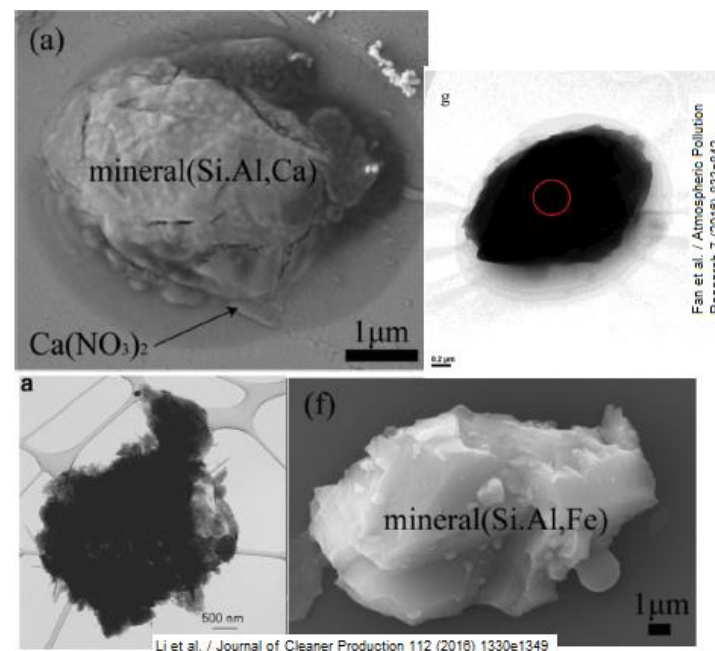
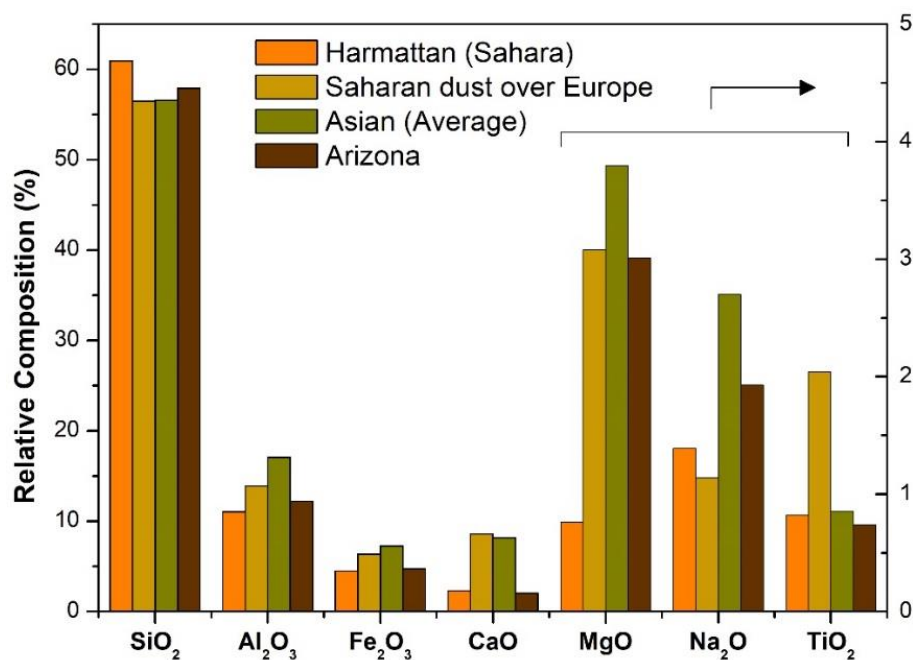
Source: <http://soils.usda.gov/use/worldsoils/mapindex/desert.html>
Geography in the News 4/13/12 M. Shears

Composition, physicochemical properties and impacts on climate

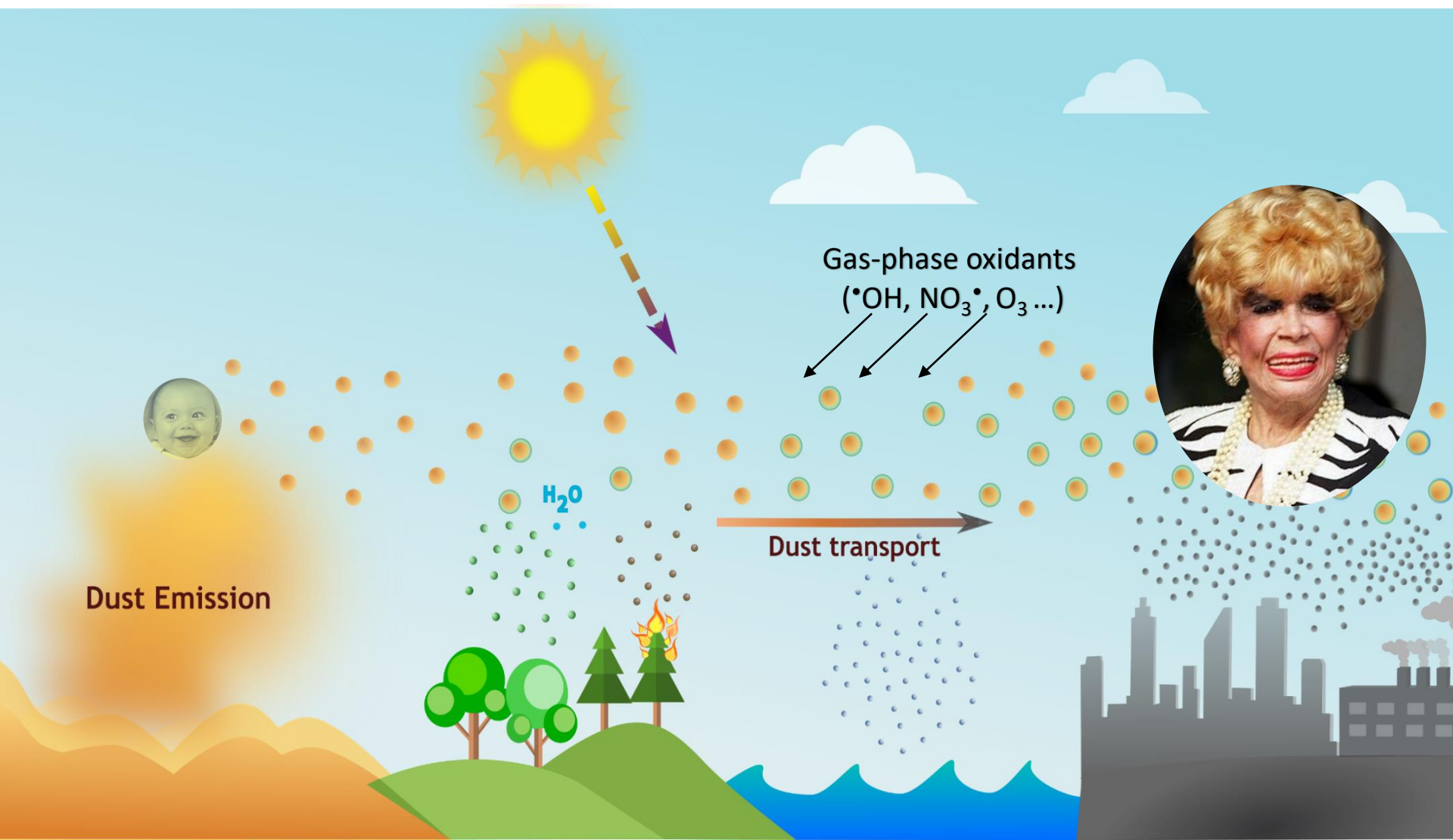
size, shape, refractive index → *direct effect on climate – radiation budget.*

hygroscopicity → *indirect effect on climate – dust action as CCN/IN.*

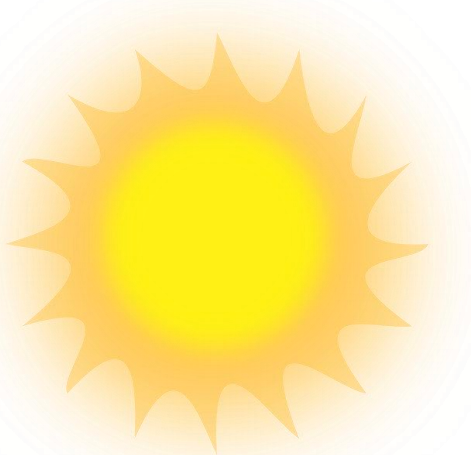
chemical composition/mixing state → *direct effect on heterogeneous reactivity.*



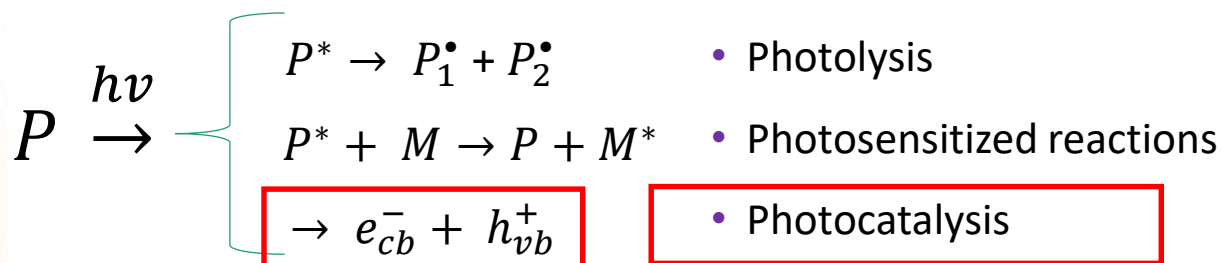
Dust transport, interactions and aging



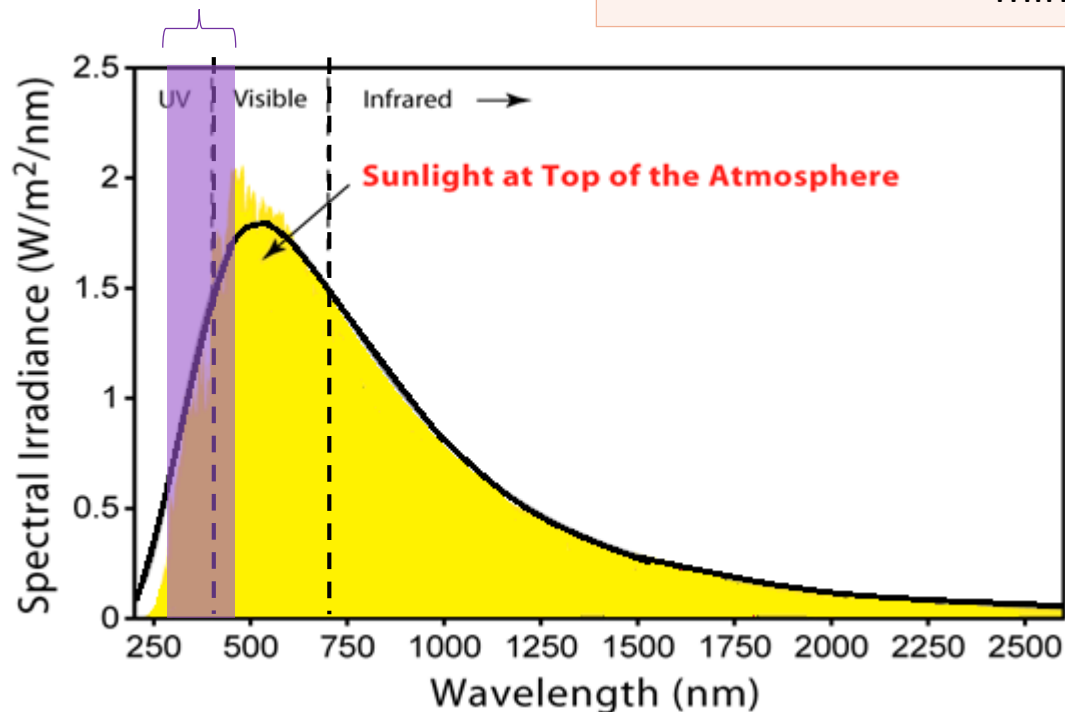
The sun: primary driving force for chemical transformations in the atmosphere



UV/Vis: 290 – 420 nm

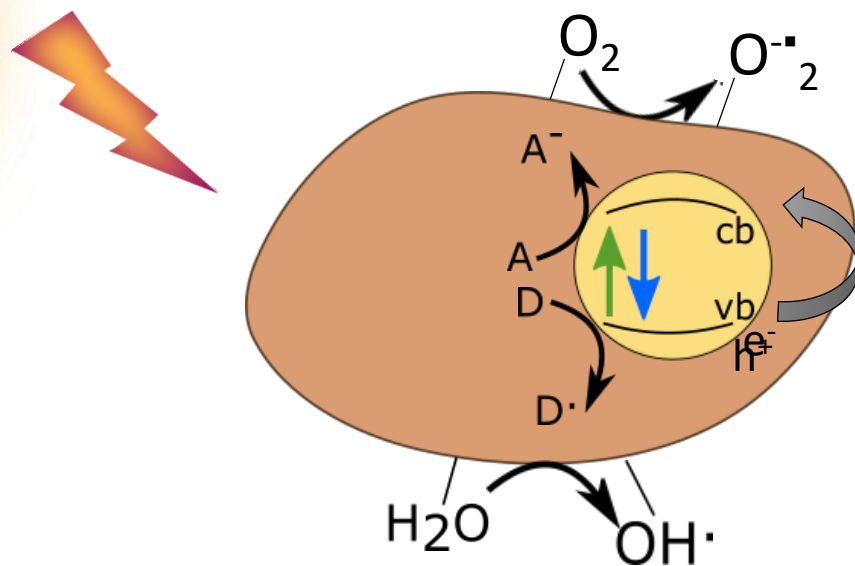
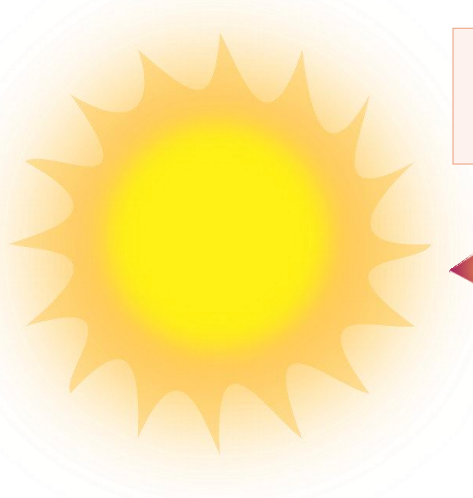


The presence of light absorbing semiconductors such as TiO_2 and Fe_2O_3 may promote photocatalytic processes on mineral dust surface.

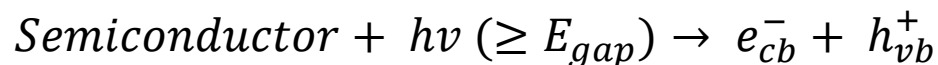


Mineral dust photocatalytic properties

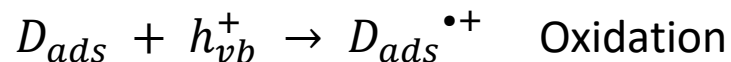
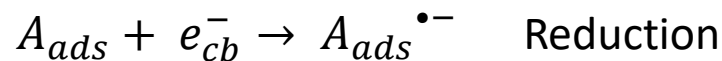
The presence of light absorbing semiconductors such as TiO_2 and Fe_2O_3 may promote photocatalytic processes on mineral dust surface.



TiO_2 - $\lambda \leq 400$ nm
 Fe_2O_3 - $\lambda \leq 560$ nm



Redox Reactions:



Objectives: Study the photochemical interactions of mineral dust and organic compounds

1 How oxygenated volatile organic compounds are taken up on dust surface?

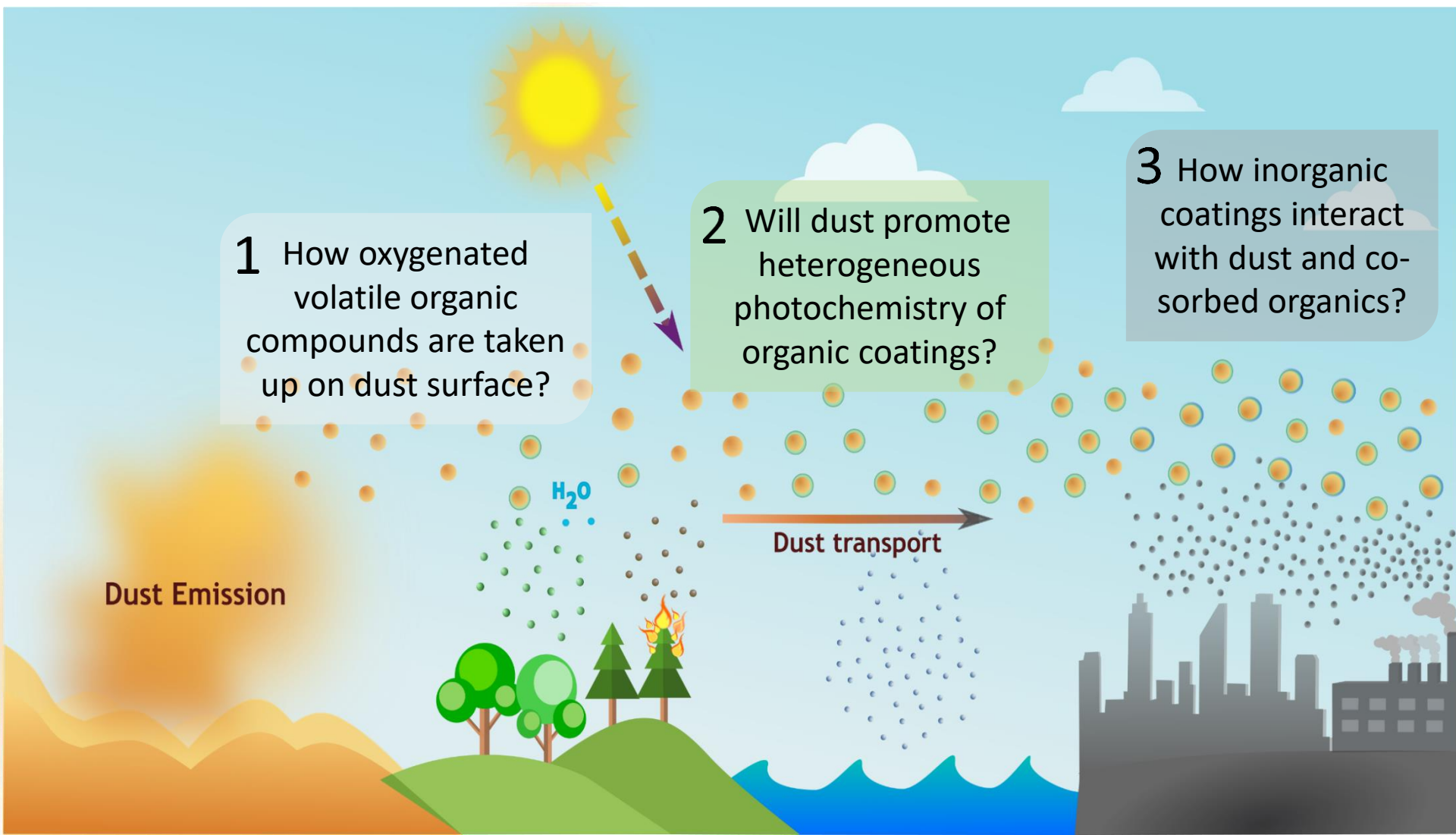
2 Will dust promote heterogeneous photochemistry of organic coatings?

3 How inorganic coatings interact with dust and co-sorbed organics?

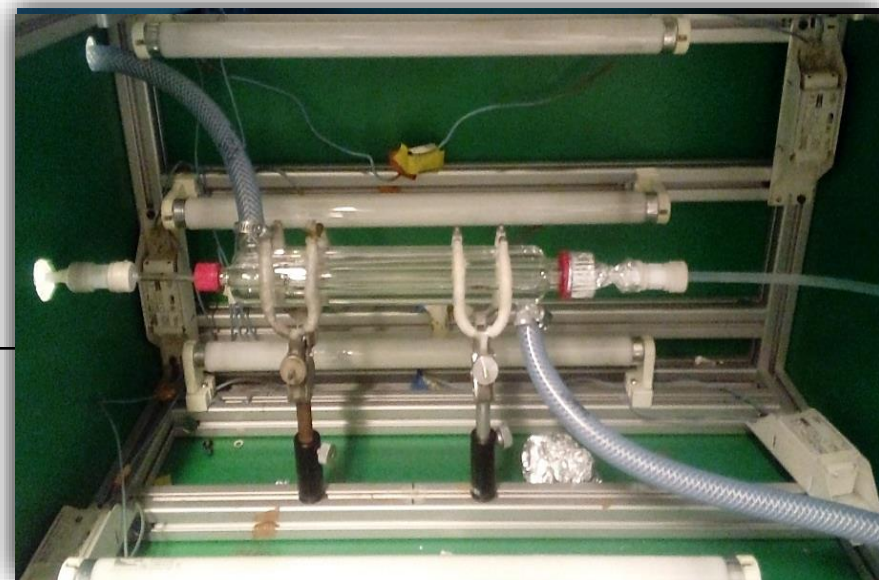
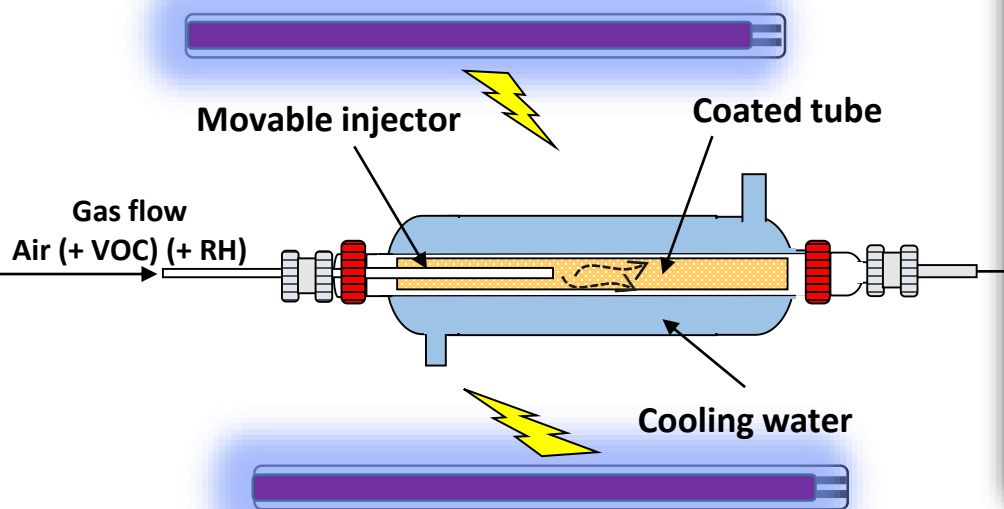
Dust Emission

H₂O

Dust transport

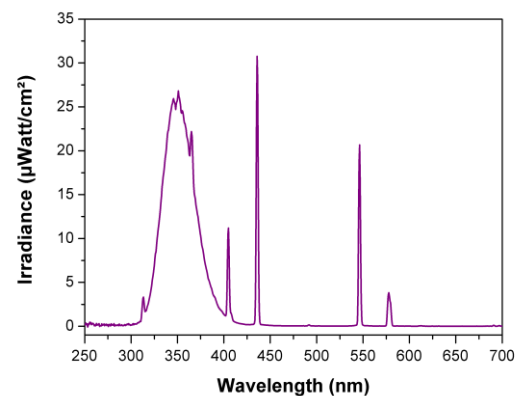


II. Experimental Setup: Coated-wall flow tube



- Sample holder: Pyrex tube, L = 20 cm and r = 0.55 cm.
- Dust Coating: Suspension in ethanol/water → Drying in the oven.

7 UV-A Lamps (Phillips 20W)



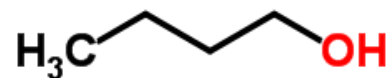
Photon Flux:
 $1.4 \text{ mW cm}^{-2} *$

Max emission:
 $\lambda = 350 \text{ nm}$

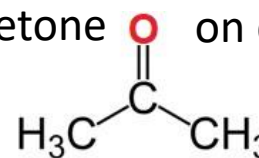
* Between 300 - 600 nm

III. Reactive uptake of VOCs on mineral dust surface

III.a Butanol on Arizona Test dust (ATD)



III.b Acetone on different substrates: ATD, SiO₂ and TiO₂



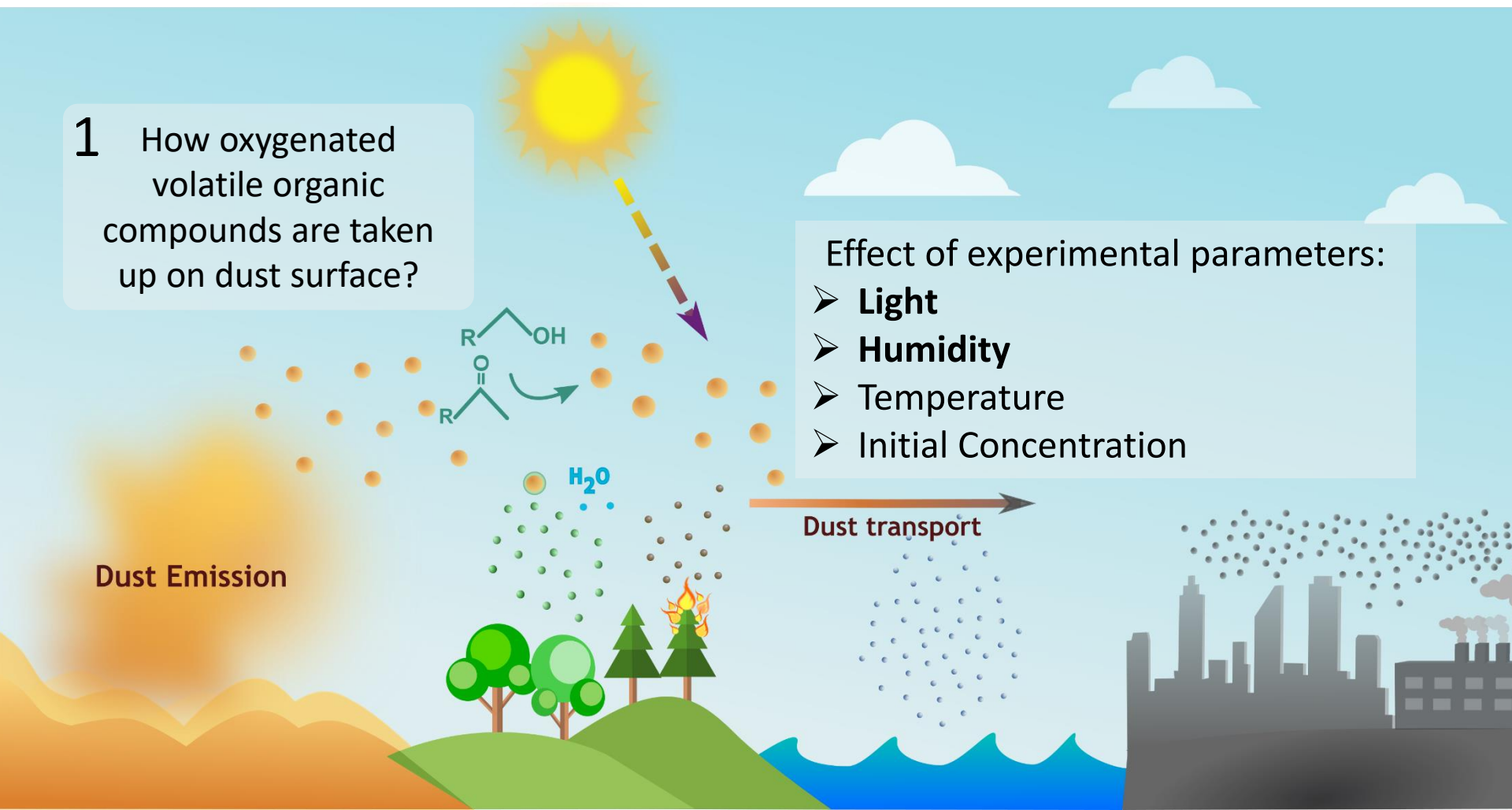
1 How oxygenated volatile organic compounds are taken up on dust surface?

Effect of experimental parameters:

- **Light**
- **Humidity**
- **Temperature**
- **Initial Concentration**

Dust Emission

Dust transport



III. Reactive uptake of VOCs on mineral dust surface

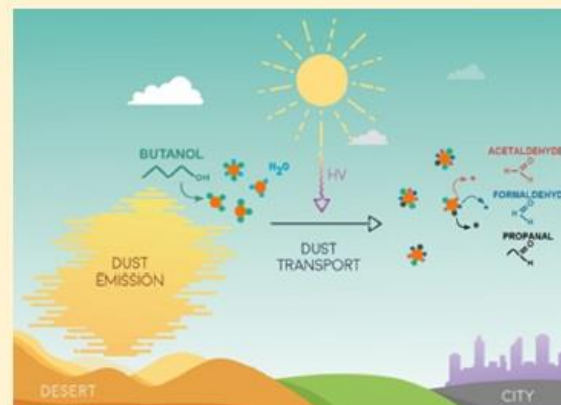
Kinetics and Product Formation during the Photooxidation of Butanol on Atmospheric Mineral Dust

Milena Ponczek and Christian George*

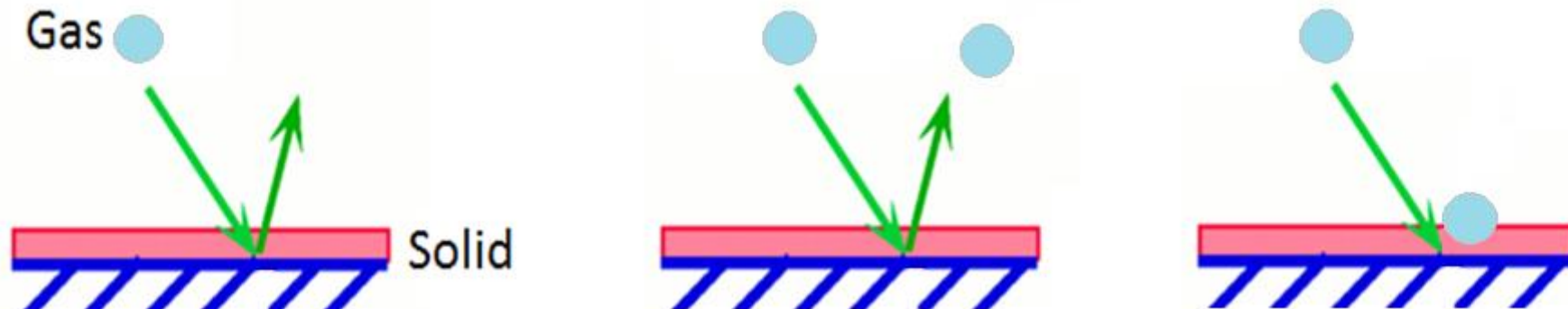
Univ. Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, F-69626, Villeurbanne, France

Supporting Information

ABSTRACT: Mineral dust particles have photochemical properties that can promote heterogeneous reactions on their surfaces and therefore alter atmospheric composition. Even though dust photocatalytic nature has received significant attention recently, most studies have focused on inorganic trace gases. Here, we investigated how light changes the chemical interactions between butanol and Arizona test dust, a proxy for mineral dust, under atmospheric conditions. Butanol uptake kinetics were measured, exploring the effects of UV light irradiation intensity (0–1.4 mW/cm²), relative humidity (0–10%), temperature (283–298 K), and butanol initial concentration (20–55 ppb). The composition of the gas phase was monitored by a high-resolution proton-transfer-reaction mass spectrometer (PTR-ToF-MS) operating in H₃O⁺ mode. Water was observed to play a significant role, initially reducing heterogeneous processing of butanol but enhancing reaction rates once it evaporated. Gas phase products were identified, showing that surface reactions of adsorbed butanol led to the emission of a variety of carbonyl containing compounds. Under actinic light these compounds will photolyze and produce hydroxyl radicals, changing dust processing from a sink of VOC into a source of reactive compounds.



What is an Uptake Coefficient?



The net probability that a molecule undergoing a gas-kinetic collision with a surface is actually taken up at the surface:

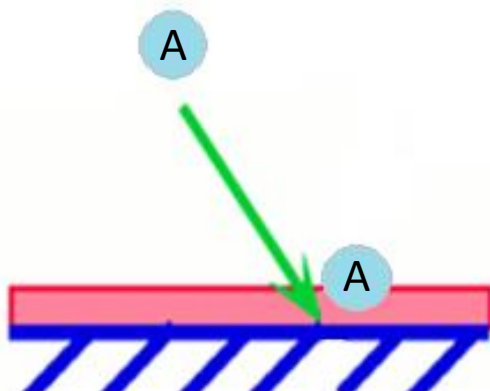
$$\gamma = \frac{\text{number of molecules that are removed from gas-phase (per area per time)}}{\text{number of total collisions (per area per time)}}$$

The uptake coefficient is the **kinetic parameter** that express the efficiency of heterogeneous reactions

What is an Uptake Coefficient?

$$\gamma = \frac{\text{number of molecules that are removed from gas-phase (per area per time)}}{\text{number of total collisions (per area per time)}}$$

The uptake coefficient is the **kinetic parameter** that express the efficiency of heterogeneous reactions



$$-\frac{d[A]}{dt} = k_{obs}[A] = \gamma \frac{\langle v \rangle}{4} S_{surf}[A]$$

Experimentally obtain k_{obs} \rightarrow to determine the uptake coefficient

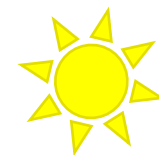
$$\gamma = \frac{4}{\langle v \rangle} \frac{1}{S_{surf}} k_{obs}$$

k is the reaction rate constant

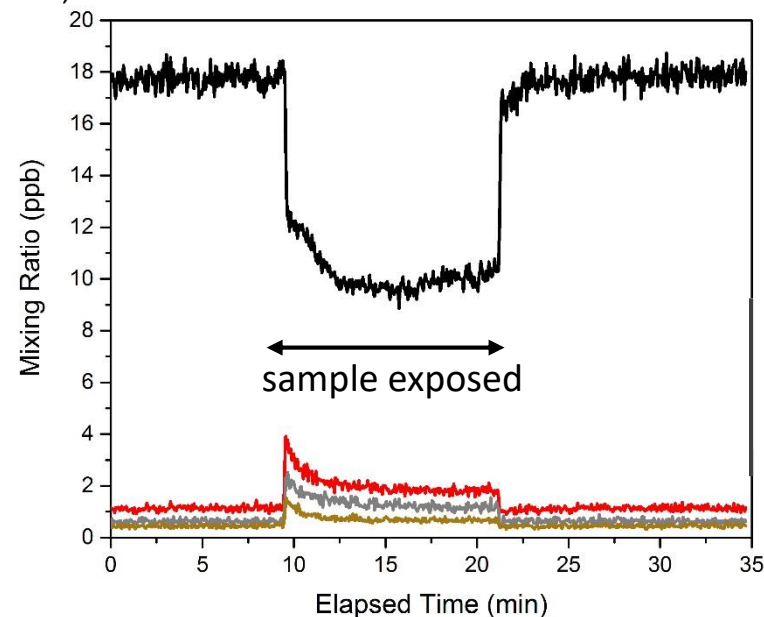
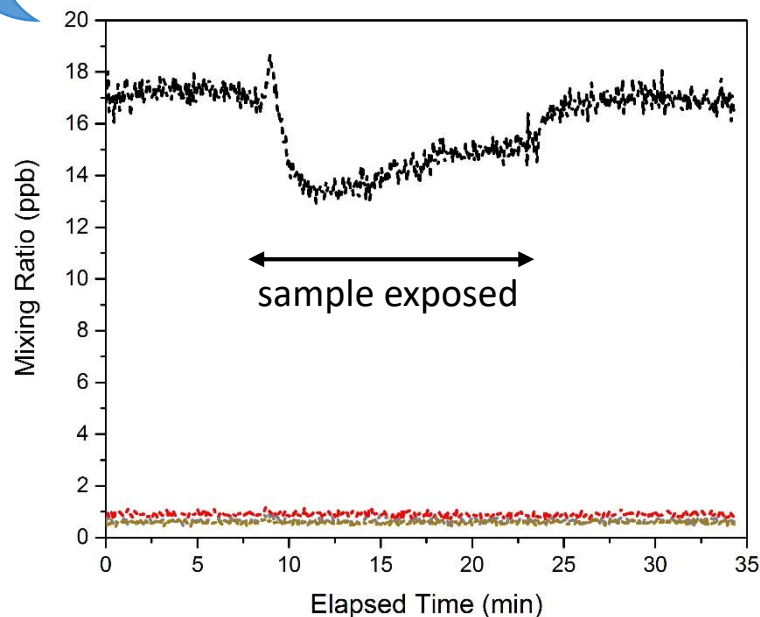
$\langle v \rangle$ is the mean molecular speed of the species A

S_{surf} is the total surface area available for the reactions

Butanol: Uptake Kinetics – Dark x Light



For $C_{in} \approx 20$ ppb, 0% RH, $T=20^\circ\text{C}$



— CH_3O^+ Formaldehyde

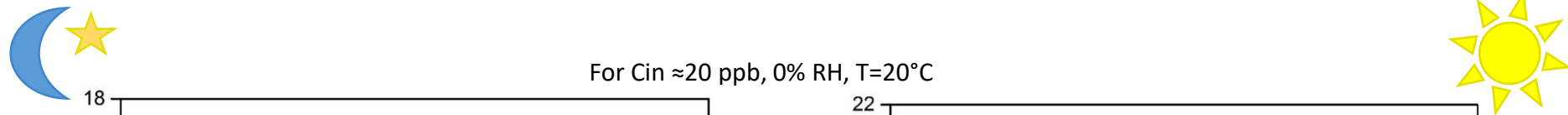
— $\text{C}_2\text{H}_5\text{O}^+$ Acetaldehyde

— $\text{C}_3\text{H}_7\text{O}^+$ Acetone/Propanal

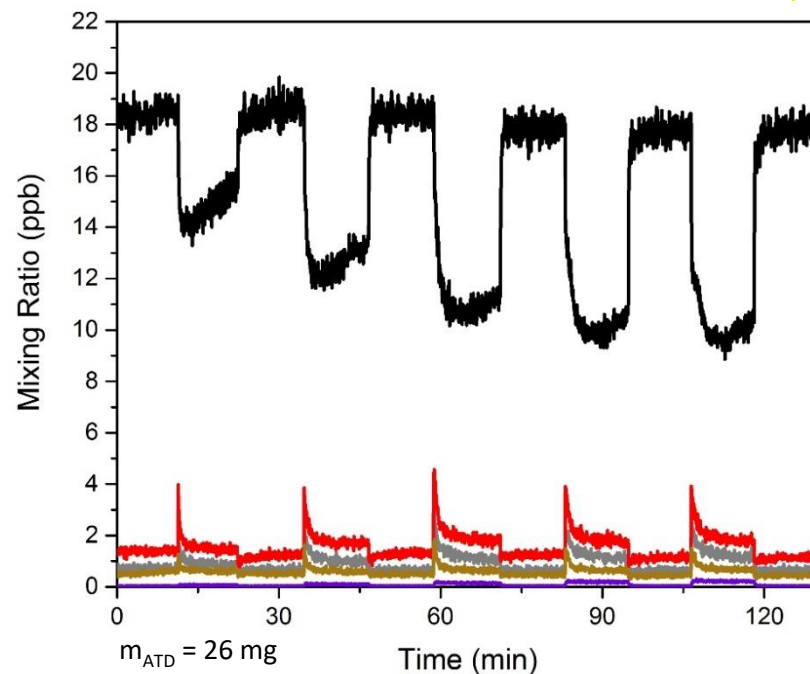
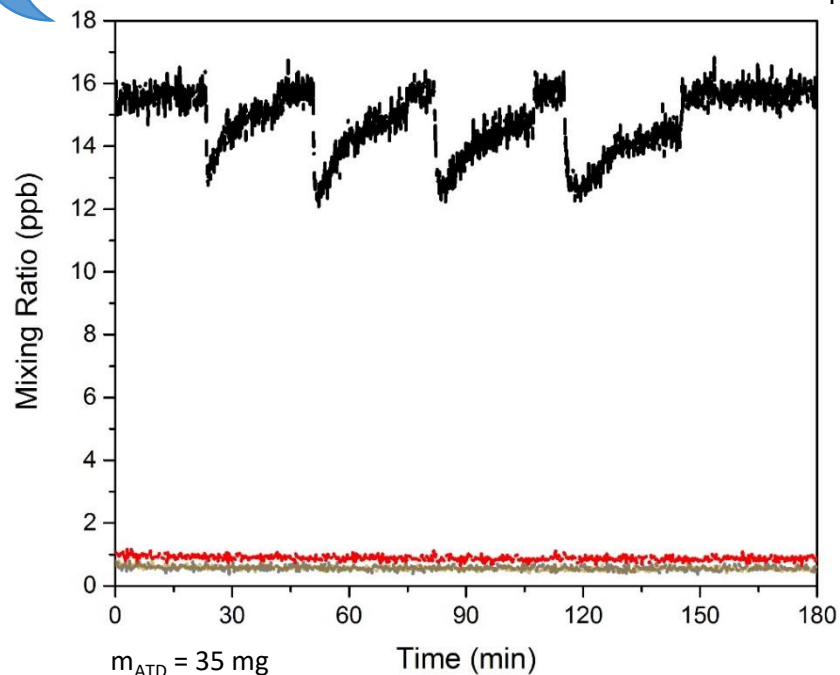
— C_4H_9^+ Butanol

— $\text{C}_7\text{H}_{15}\text{O}^+$ Heptanal

Butanol: Uptake Kinetics – Dark x Light



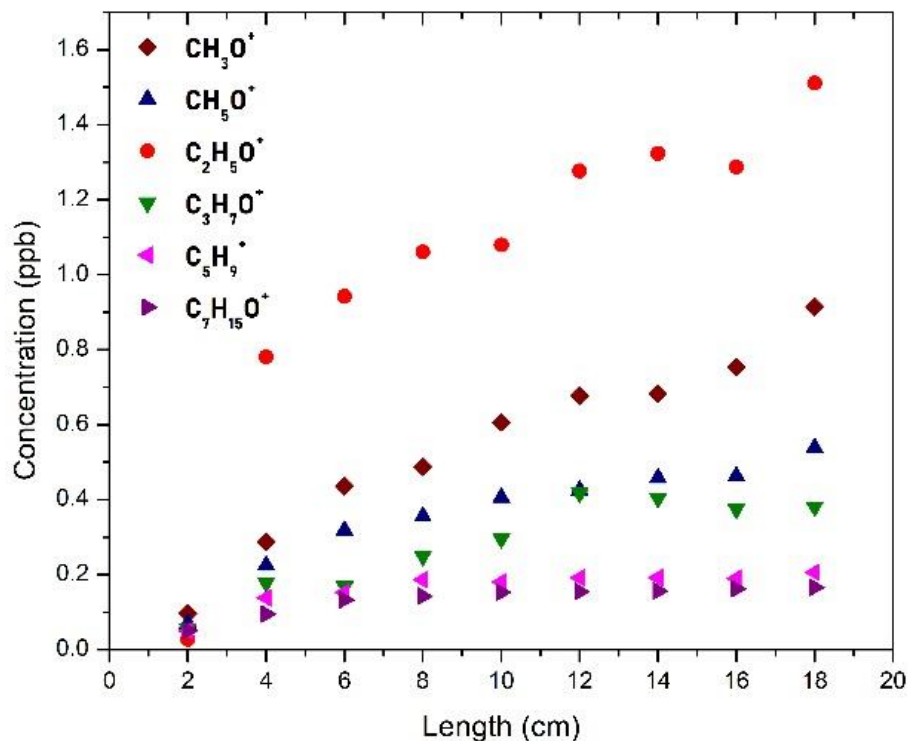
For $C_{in} \approx 20$ ppb, 0% RH, $T=20^\circ\text{C}$



— CH_3O^+ Formaldehyde — $\text{C}_2\text{H}_5\text{O}^+$ Acetaldehyde — $\text{C}_3\text{H}_7\text{O}^+$ Acetone/Propanal
— C_4H_9^+ Butanol — $\text{C}_7\text{H}_{15}\text{O}^+$ Heptanal

- Faster surface saturation and no product formation in the dark.
- Reactive uptake under light.

Photooxidation of **Butanol**: Gas-phase products profile along the reactor



For $C_{in} \approx 20$ ppb, 7 lamps, 0% RH, $T=20^\circ\text{C}$, $m_{\text{ATD}} = 110$ mg

Major Oxidation Products

m/z	Formula	Compound
45.033	$\text{C}_2\text{H}_5\text{O}^+$	Acetaldehyde
31.018	CH_3O^+	Formaldehyde
59.049	$\text{C}_3\text{H}_7\text{O}^+$	Propanal/acetone
33.033	CH_5O^+	Methanol
69.069	C_5H_9^+	frag. octanal
115.110	$\text{C}_7\text{H}_{14}\text{O}^+$	frag. heptanal

Minor products detected at very low concentrations pentanal, hexanal, octanal.

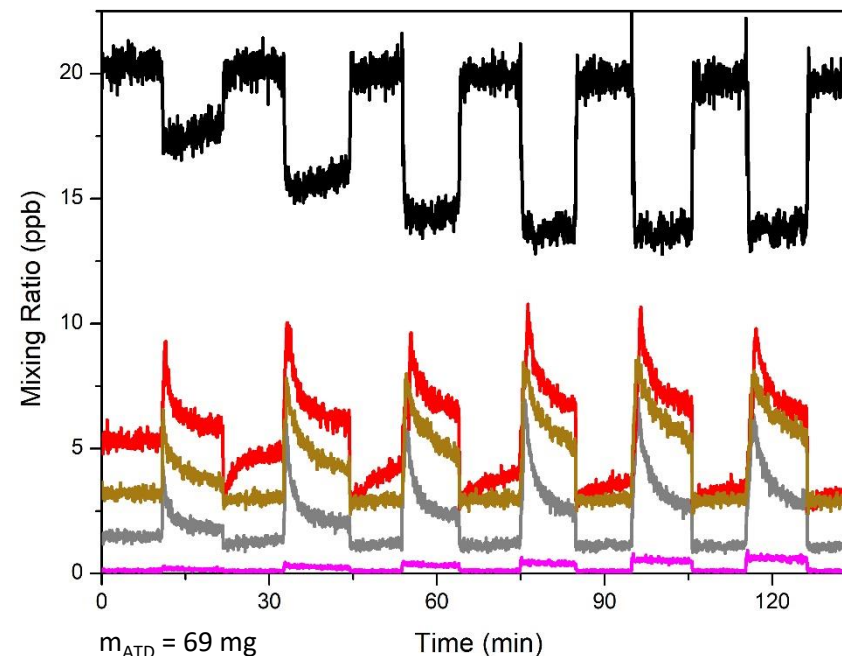
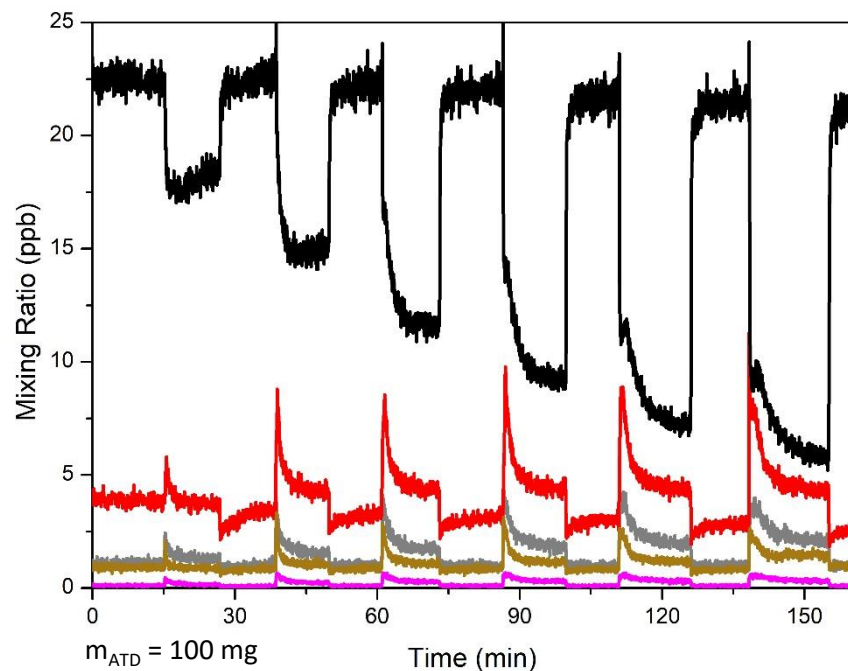
- The concentration of products increase along the reactor.
- We observed products of higher molecular weight than butanol.

Photooxidation of **Butanol**: Relative Humidity Influence



0% RH

7% RH

For $C_{in} \approx 20$ ppb, 7 lamps, $T=20^\circ\text{C}$ 

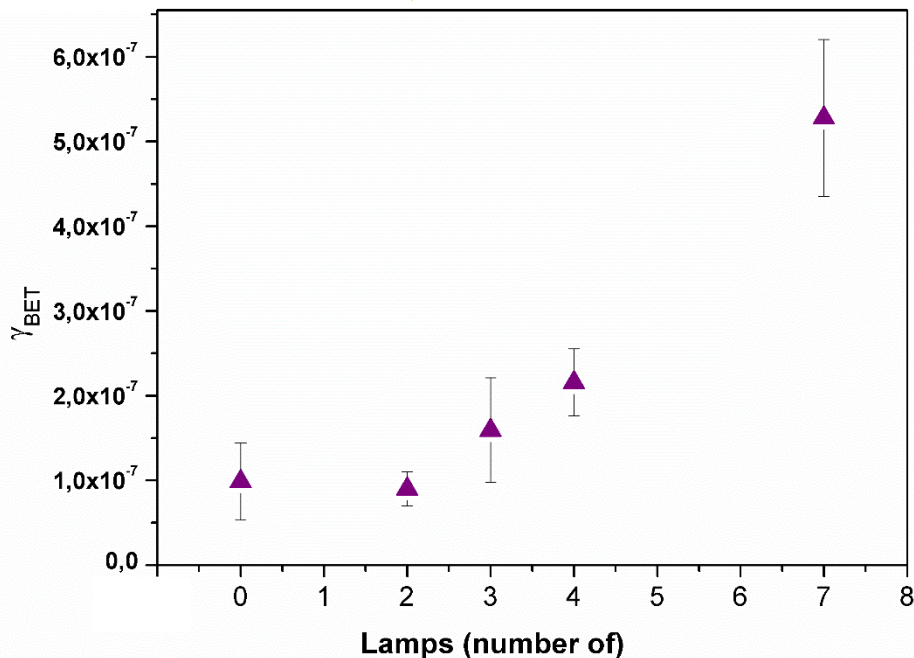
CH_3O^+ Formaldehyde $\text{C}_2\text{H}_5\text{O}^+$ Acetaldehyde $\text{C}_3\text{H}_7\text{O}^+$ Acetone/Propanal
 C_4H_9^+ Butanol C_5H_9^+ Frag octanal/pentanal

- Fast surface passivation under humid conditions.
- RH did not suppress product formation.

Photooxidation of **Butanol**: Uptake Coefficients – Light and RH



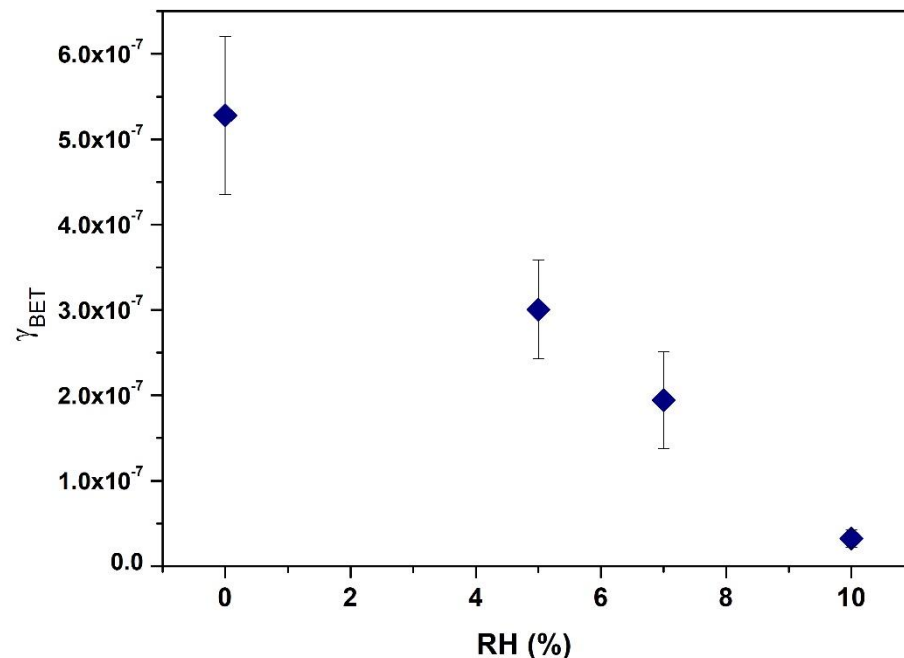
Light



For $C_{\text{in}} \approx 20$ ppb, 0% RH, $T=20^\circ\text{C}$



RH



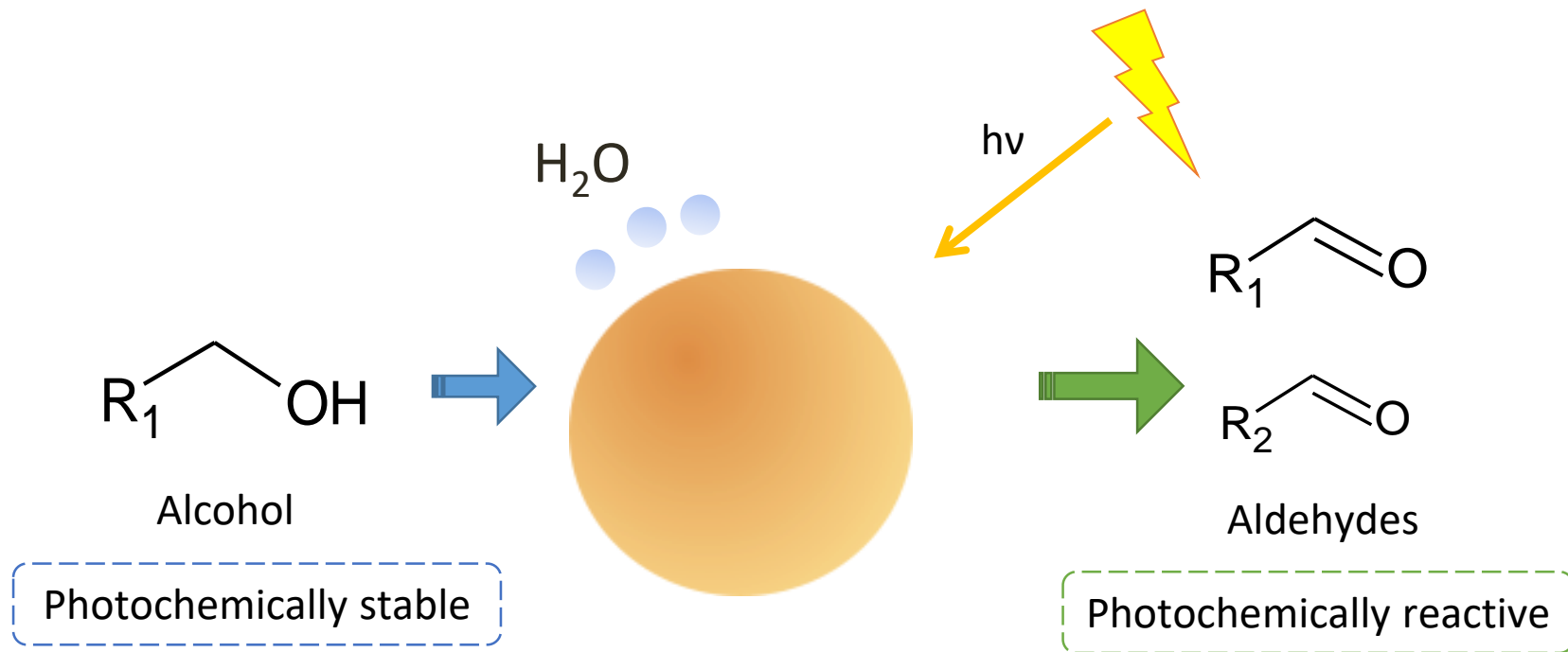
For $C_{\text{in}} \approx 20$ ppb, 7 lamps, $T=20^\circ\text{C}$

- ✓ **Systematic increase** of the uptake coefficient as a function of **UV light irradiance**.
- ✓ Clear evidence for **photochemical interactions** between **butanol** and **ATD**.

- ✓ The presence of **water vapor** significantly **reduced butanol uptake**.
- ✓ **ATD** seems to have a **strong affinity with water**.

III. Reactive uptake of OVOCs on mineral dust surface: Conclusions

- ✓ Mineral dust can uptake trace amounts of OVOCs.



- ✓ For **butanol**: **light** enhanced the uptake and changed ATD reactivity from **unreactive** to **reactive**.
- ✓ **Humidity** strongly reduced **both OVOCs** uptake, suggesting **competitive** adsorption between H_2O and VOCs.
- ✓ Butanol lifetime was estimated: 1.48 d (very high dust loadings) and 770 d (clean days).*

IV. Heterogeneous photochemistry of organic coated dust

Studied a series of straight chain DCA: $C_4 \rightarrow C_8$

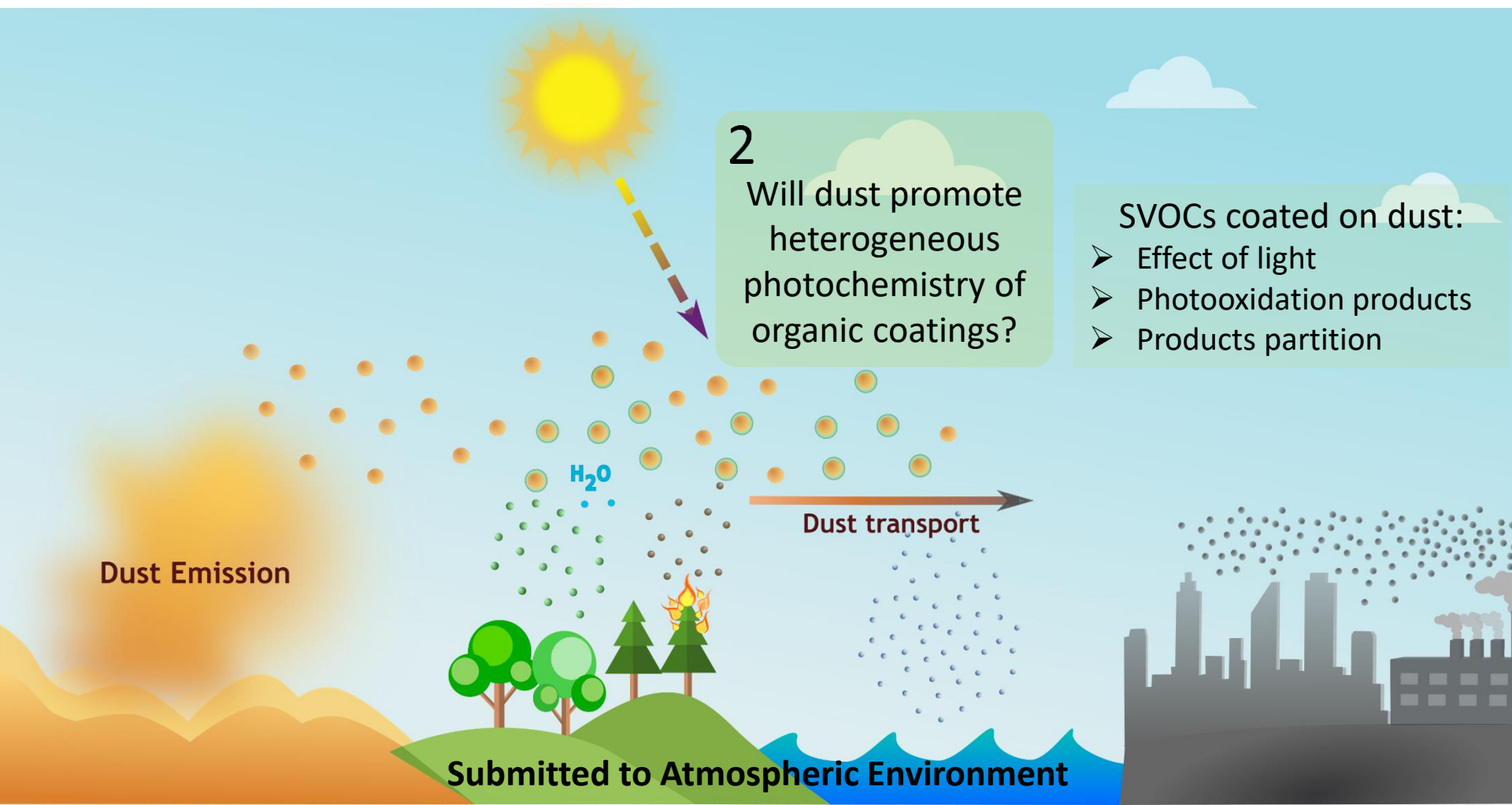
Succinic Acid
 $C_4H_6O_4$

Glutaric Acid
 $C_5H_8O_4$

Adipic Acid
 $C_6H_{10}O_4$

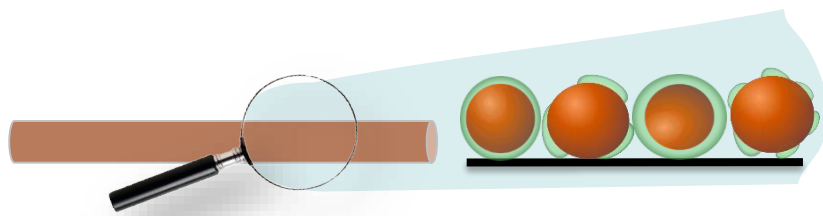
Pimelic Acid
 $C_7H_{12}O_4$

Suberic Acid
 $C_8H_{14}O_4$



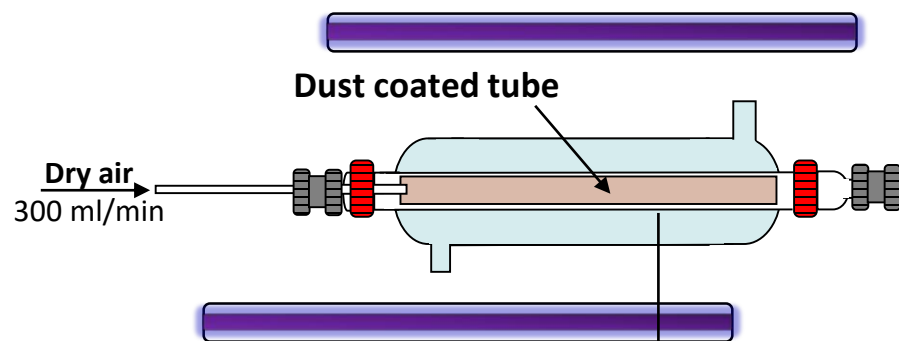
Some details about the experimental procedure

Dicarboxylic acids were added as internal mixtures of 10% w/w in Arizona test dust (ATD).



Dust particles coated with the acid form a film on the inner surface of the tube.

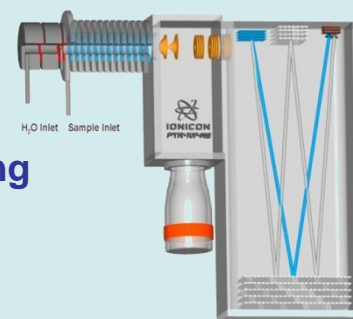
Irradiation of the coated tubes



Gas-phase analysis

Online gas-phase composition monitoring

PTR-ToF MS



Dust extraction with
ACN/H₂O

Off-line analysis
of dust extracts

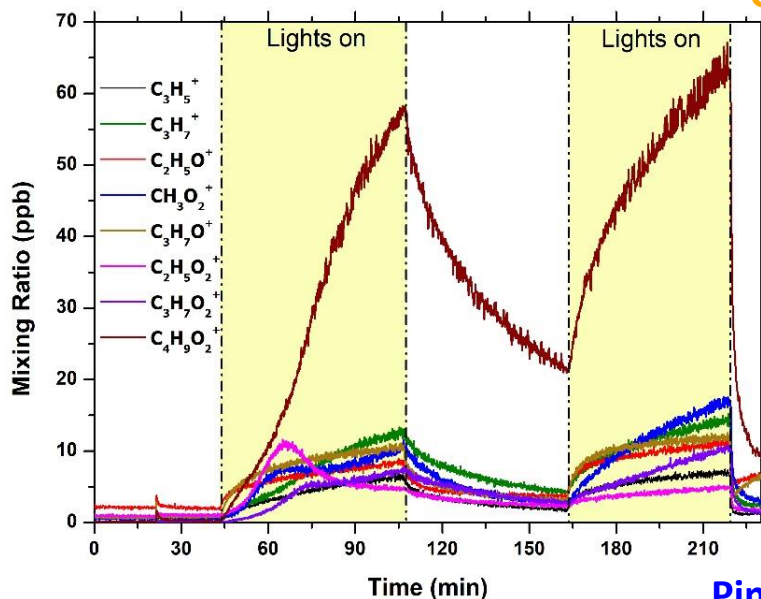
Surface sorbed products analysis



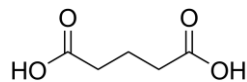
UHPLC / (-)HESI - HRMS

Results: Gas-phase products

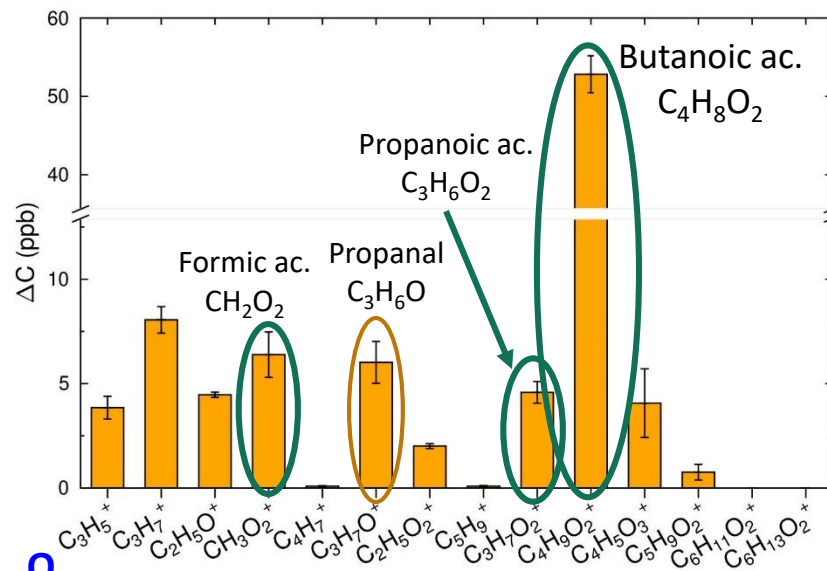
Time Profile



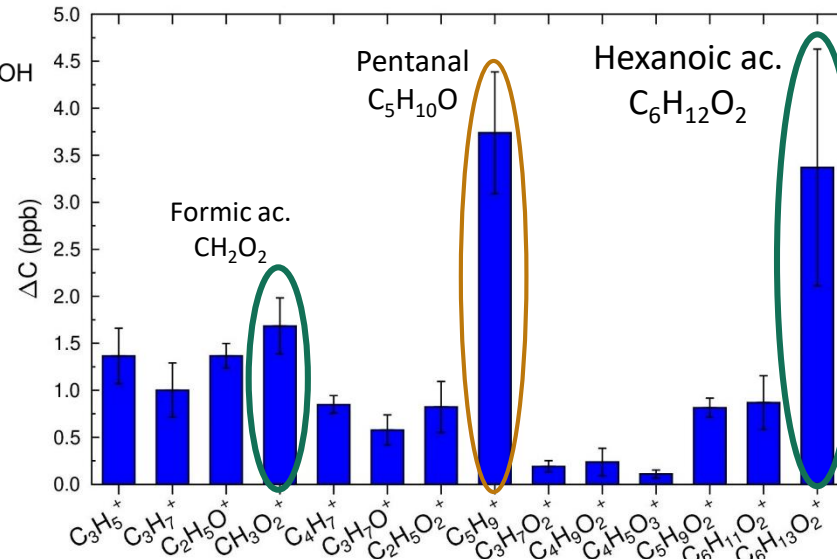
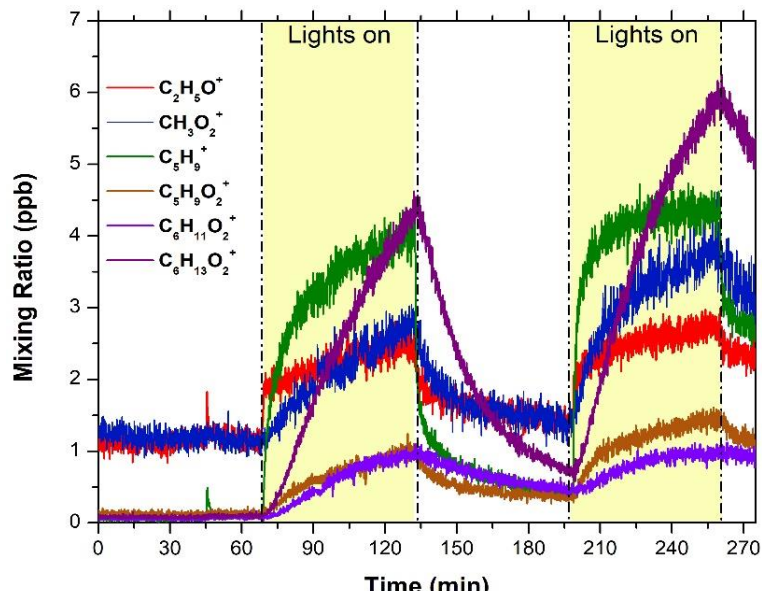
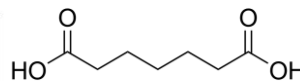
Glutaric Acid – $C_5H_8O_4$



Products distribution

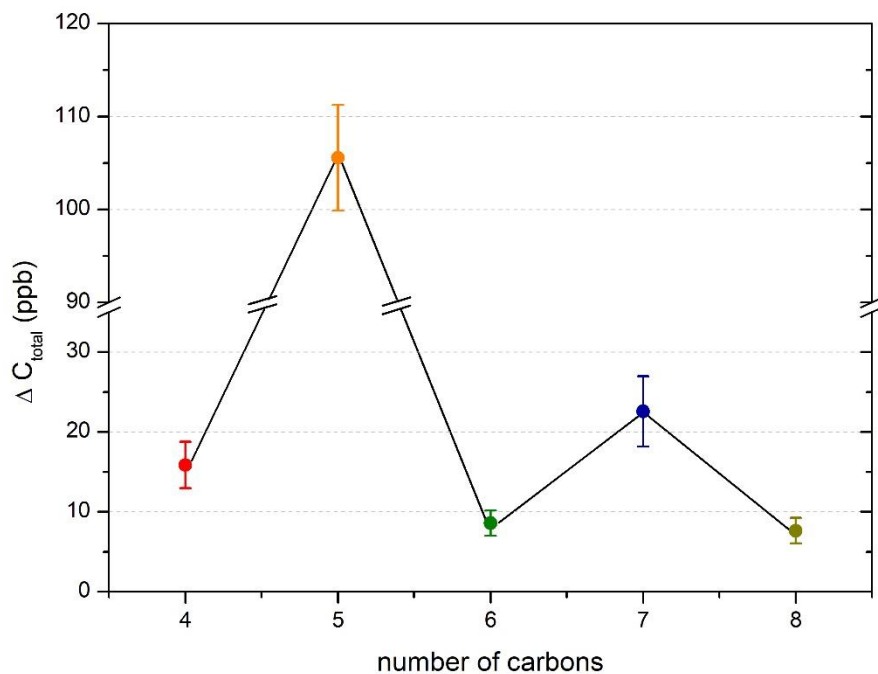


Pimelic Acid – $C_7H_{12}O_4$



Results: Gas-phase products

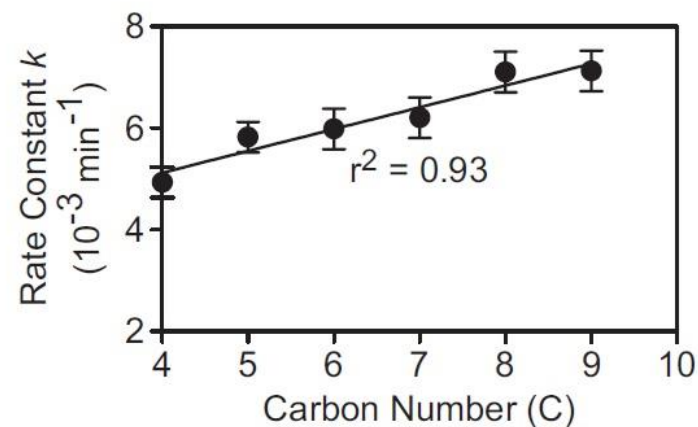
$$\Delta C_{Total} = \Sigma(\Delta C_A)$$



Total gas-phase products mixing ratio for all five dicarboxylic acids studied, as a function of number of carbons.

Even-odd alternation of chemical reactivity.

Photooxidation of dissolved DCA by OH radical in liquid phase.

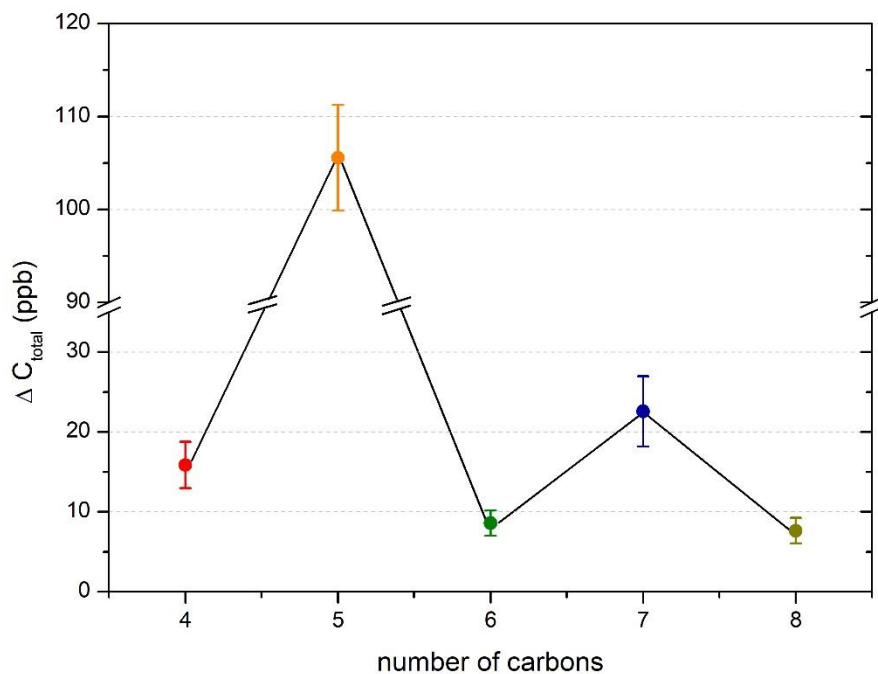


Yang et al, Atmos. Environ., 42, 2008.



Results: Gas-phase products

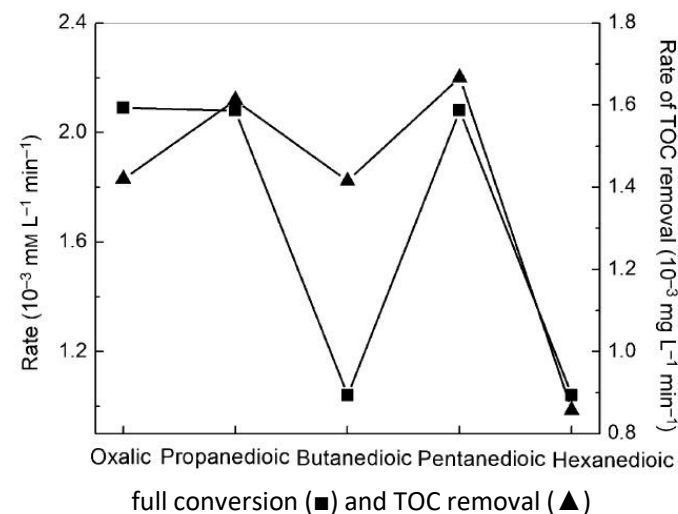
$$\Delta C_{Total} = \Sigma(\Delta C_A)$$



Total gas-phase products mixing ratio for all five dicarboxylic acids studied, as a function of number of carbons.

Even-odd alternation of chemical reactivity.

Photocatalytic Degradation of DCA on TiO_2 – in liquid phase.

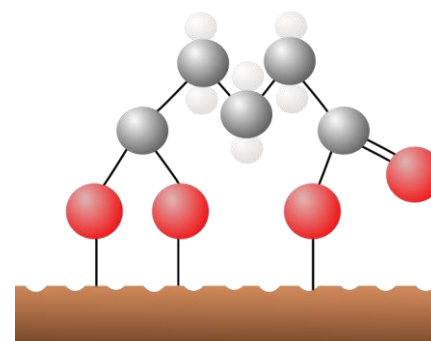
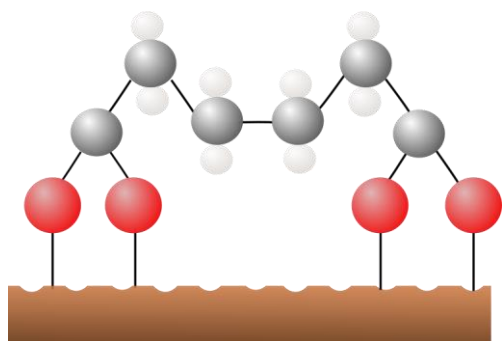


Sun et al., Chem. - A Eur. J. 20, 2014



DCAs: Even-odd alternation

The alternation on the heterogeneous reactivity was attributed to DCAs binding mode on the substrate surface:

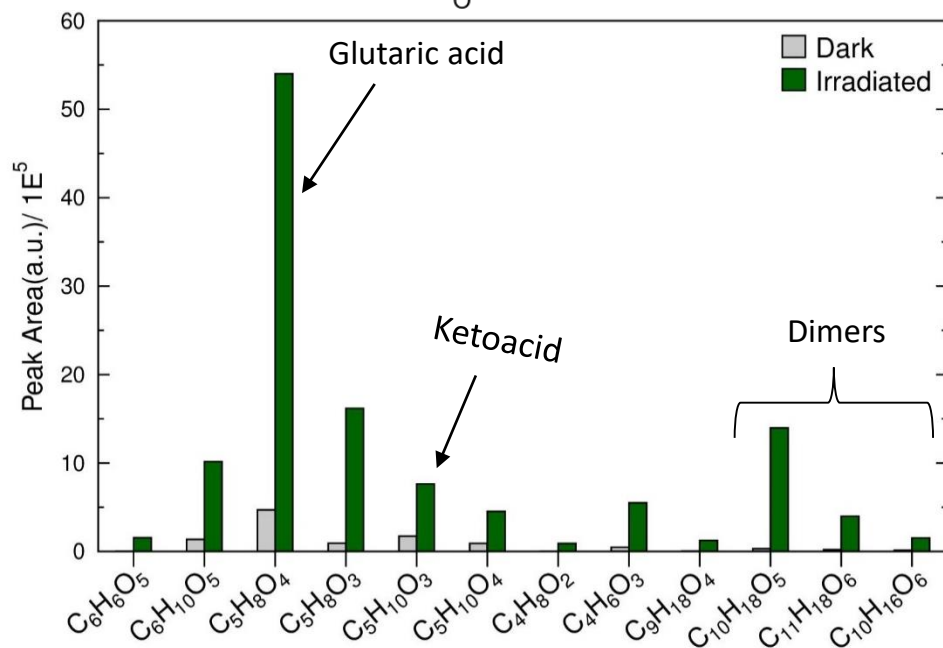
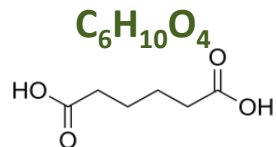


- **e-DCAs** the two carboxyl groups are **tightly** bound by **bidentate coordination**.
- **o-DCAs**, one group adopts **bidentate coordination** and the other carboxyl group adopts a **weaker monodentate coordination** with the surface.

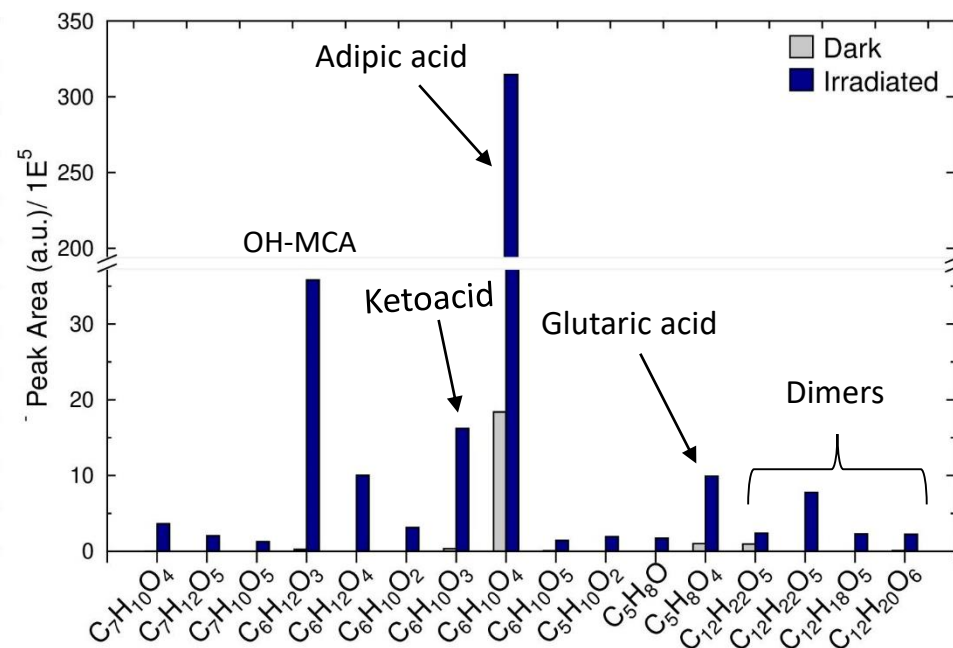
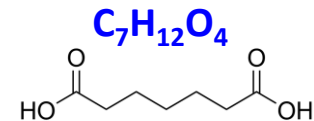
The divergence in the binding mode might explain the higher chemical reactivity of o-DCAS!

Results: Surface sorbed products

For Adipic Acid

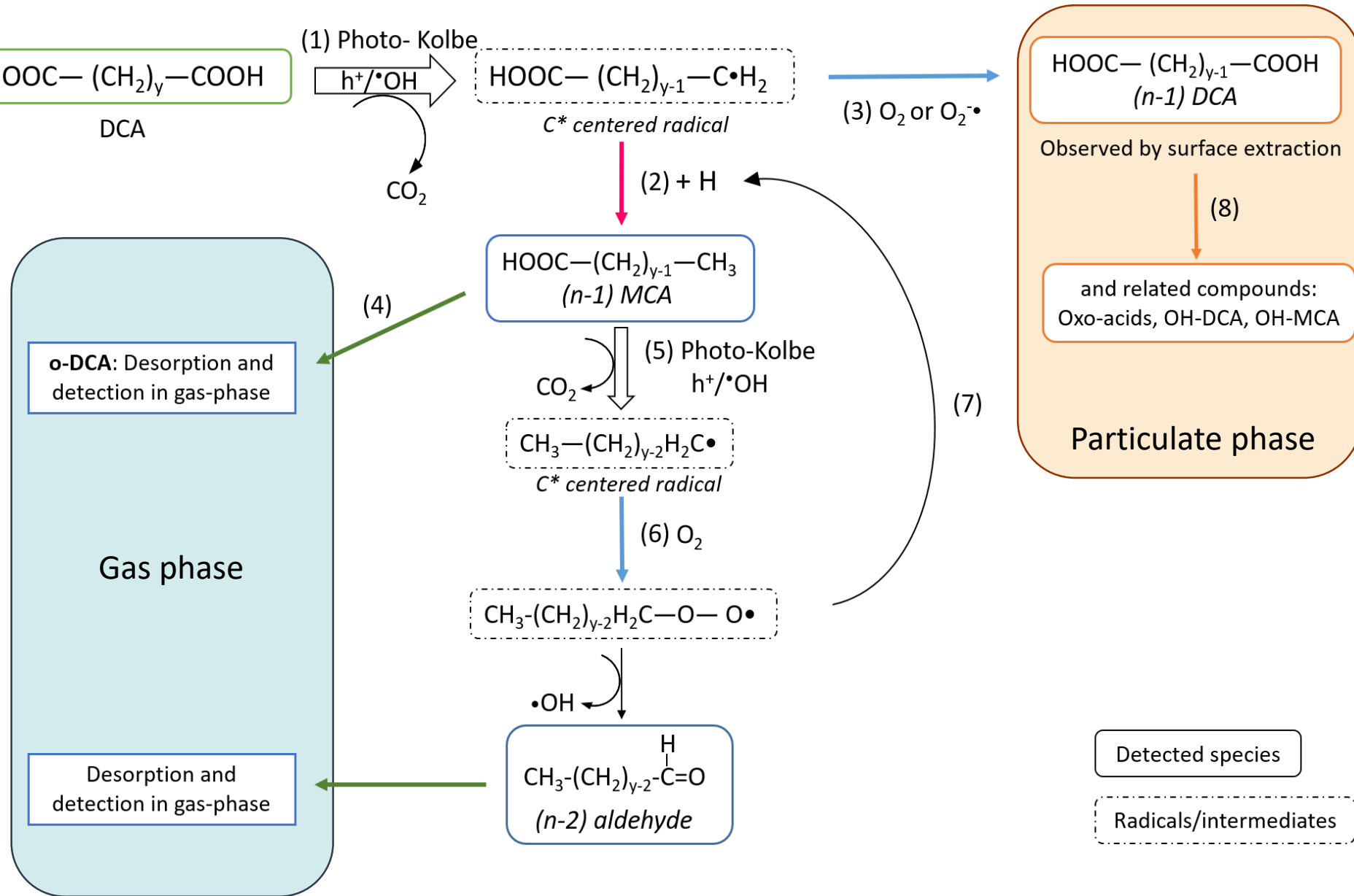


For Pimelic Acid

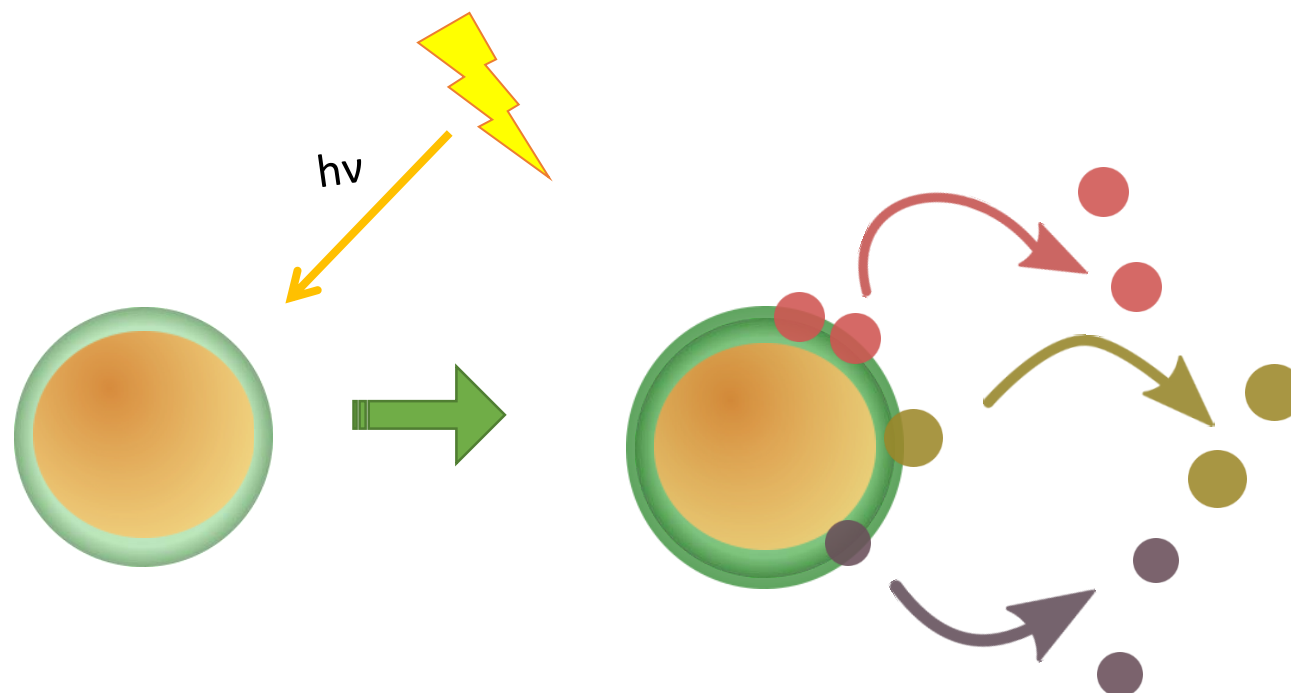


- The dicarboxylic acid C_(n-1) is a product for all diacids.
- Highly oxygenated products such as oxoacids and ketoacids, hydroxy, and dihydroxy acids.
- Appearance of larger molecules than the original reagent.

Results: Proposed Mechanism



IV. Heterogeneous photochemistry of organic coated dust : Conclusions



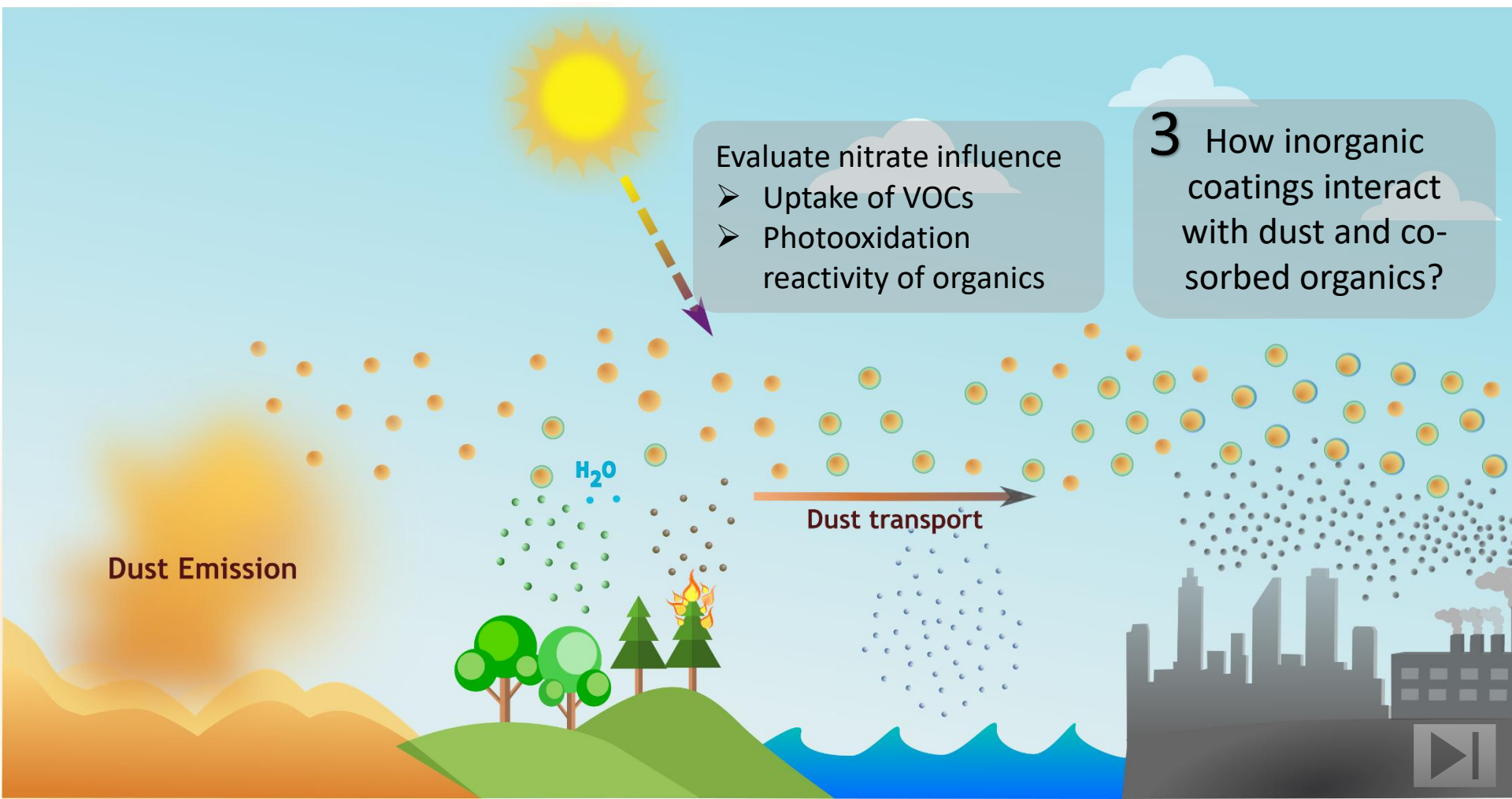
- ✓ DCAs **produced** and **released OVOCs** on the gas-phase upon UV-A irradiation.
- ✓ We observed even-odd alternation concerning chemical reactivity, **o-DCA** being more reactive than **e-DCA**.
- ✓ **Longer chain** DCA were precursors of **smaller** DCA, and highly oxygenated organics.
- ✓ Photochemical aging on mineral dust surface can lead to organic compounds produced *in situ*, on the dust surface.

V. Influence of co-sorbed nitrates on mineral dust photochemistry

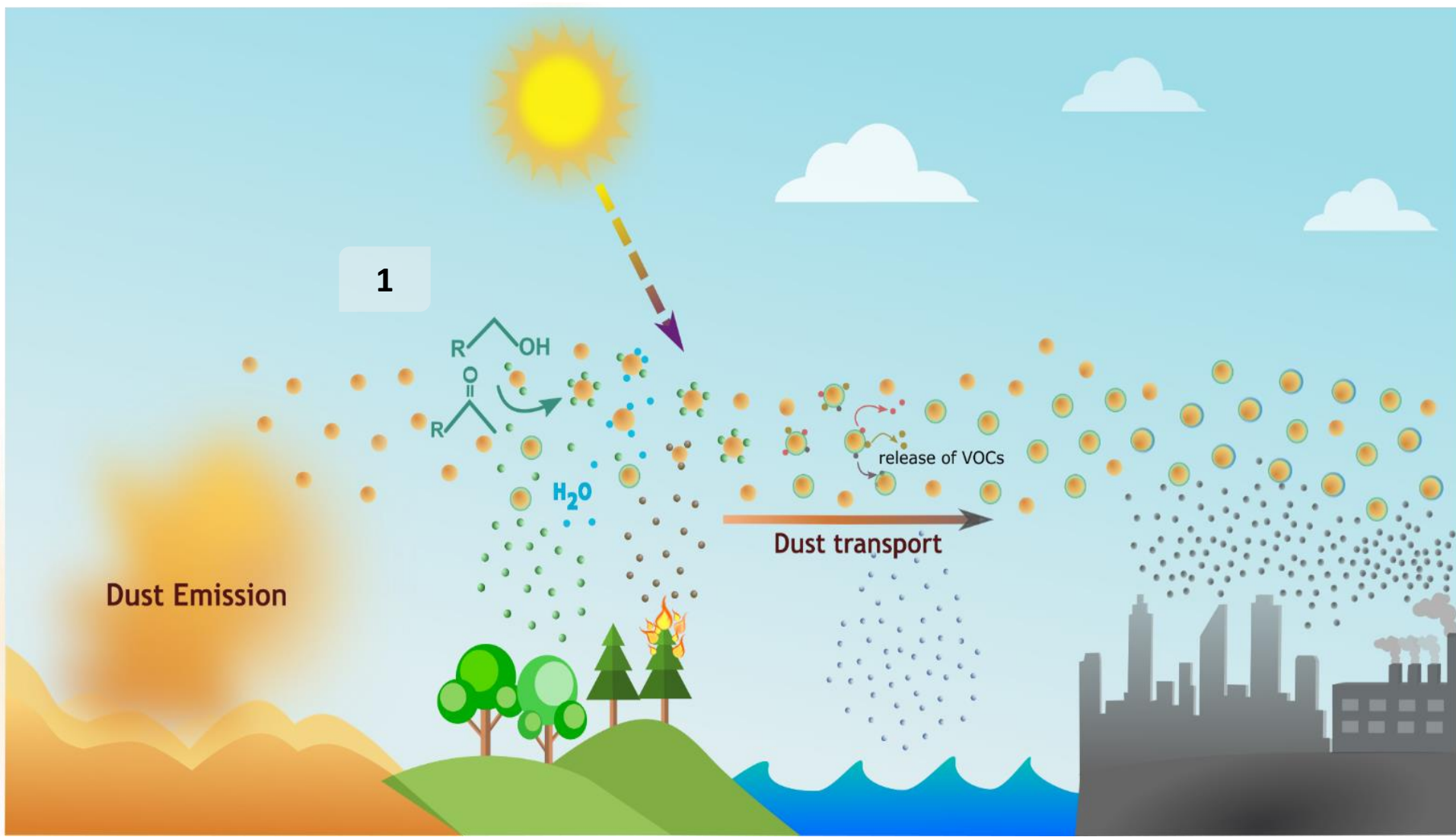
NaNO_3 was used as source of nitrates

Uptake of Acetone on ATD and SiO_2
For 0, 1% and 5% of NO_3^-

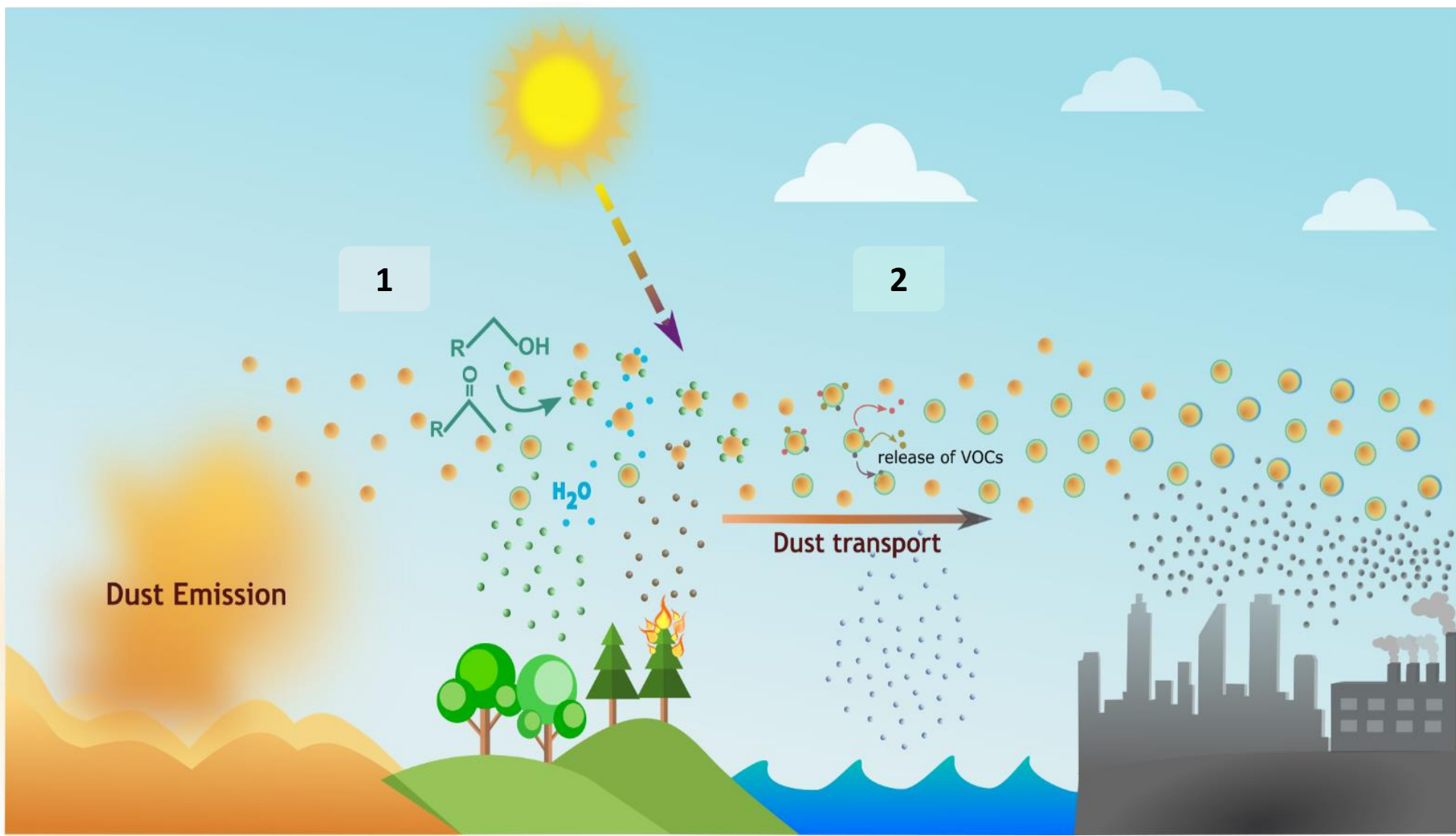
Glutaric Acid Photochemical products on ATD
For 0, 1%, 5%, 10% of NO_3^-



- We presented the effect of ambient conditions on butanol uptake onto ATD:
 - ✓ **Light** and **RH** were observed to **play a significant role** on OVOCs uptake kinetics.



- Surface-mediated photochemistry of DCAs produced:
 - ✓ **OVOCs** released to the **gas-phase**.
 - ✓ Low volatility **highly oxygenated** compounds that remained in the **particulate phase**.



Further questions...

- How photochemical reaction products could alter the cloud condensation and ice nucleation properties of mineral dust?
- Can the VOCs released contribute to new particle and/or SOA formation in the atmosphere?
- What is the impact of humidity on this chemistry ? Will the presence of water molecules change the reaction pathways? How ?



Questions
?

Thank you
for your
attention!!

