

Tropospheric Aerosols:

Formation and Sources, Aeging and Sinks

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- **1. Introduction**
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- **3. Aerosol Dynamic Processes**
- 4. Secondary Organic Aerosols:
 - Tree emissions
 - Autoxidation
- **5. Secondary Organic Aerosols:**
 - gas-phase + particle phase: partitioning
- 6. Measurement of particulate phase
- 7. Direct measurement of partitioning



1. Introduction

Aerosols: fine dispersed condensed matter in air - liquid or solid-





Why are aerosols interesting and important in the atmosphere ?

Aerosols introduce a new quality into the thin medium air: fine distributed, condensed matter – solid or liquid.

-Optical Effects -> light scattering and absorption

-Interaction With Water Vapor -> cloud formation

-Multi-phase Systems

-> partitioning

-> liquid-phase and surface chemistry

Important for

- •Climate
- Bio-Geo-Systems

•Air Quality and Health Effects: "fine particulate matter !"

Challenge: size range 5 nm – 100 µm (gas molecules < 1 nm)



Uncertainty in Effects of Aerosols on Climate (IPCC 2007)









Anthropogenic

Primary:

Emitted as Particles

Secondary:

Gas-to-Particle Conversion



IPCC-Report: Anthropogenic Forcing Natural: **Pre-industrial background**

Natural



Combustion (primary)

fossil fuel biomass, biofuels

Atmospheric oxidation & gas to particle conversion (secondary)

SO₂ -> H₂SO₄ -> ammonium sulfates NO₂ -> HNO₃ -> ammonium nitrate Biogenic Volatile Organic Compounds -> multifunctional organic molecules with low vapor pressures

Vegetation (primary)

Pollen, fungal spores, leaf debris

Industrial activities (primary)

Dusts, fly ash

Suspension by wind blow (primary)

Sea salt Mineral dust



3. Aerosol Dynamic Processes







Morphology





Modal structure of the tropospheric aerosol?

Modal structure of aerosol size distributions reflects:

- source and sink processes
- aerosol dynamic and chemical processes
- Sources: direct emission -> e.g. from combustion gas to particle conversion -> nucleation, condensation mechanic suspension -> e.g. wind
- **Dynamics:** coagulation (reduces number, conserves mass) condensation/evaporation (change mass, conserve number)
- Sinks: dry deposition / sedimentation wet deposition rain out wash out



Source, Transformation, Sinks and Size Distribution





Accumulation Mode: Maximum of Lifetime





4. Secondary Organic Aerosols:

- Emissions of trees
- Autoxidation



Motivation: Secondary Organic Aerosol (SOA) and radiative balance







Classical OVOC products from atmospheric VOC are often *too* volatile i.e. they cannot exist in the condensed phase in the atmosphere

=> We need other explanations for the amount of SOA observed !

Answer: Formation non-volatile products by "chemical ageing"

- formation of dimers,...oligomerization...condensed phase reactions
- multiple oxidation, highly oxidized carbonic acids (3-MTBCA), isoprene tetrols. However, formation via multiple (oxidation) steps often takes long time

More answers, by our groups in IEK 8:

- use of trees as integral VOC sources
- "non-classical emissions" by trees => induced VOC emissions

non-classical pathwaya to highly oxidized compounds (HOM) with low vapor pressure: autoxidation

Stress induced emissions, SOA and CCN





Stress induced emissions, SOA and CCN





- Induced emission decrease CCN activity (κ), but increase particle yield and size (Mentel et al. 2013)
- Temperature increase 3.7 °C (IPCC 2013 by 2100)
- Drought level as lab studies (⊖0.05)





=> stable HOM are the termination products of HOM-RO₂.

Ehn et al. Nature, 2014

How much HOM? Contribution to SOA?



HOM formation as a function of reaction rate for different α-pinene levels

HOM condensation on increasing amount of $(NH_4)_2SO_4$ seed particles



- 4-10% molar yield
- 90% 50% of SOA mass are HOM

⇒ HOM should make up a *substantial fraction of SOA*

Ehn et al., 2014; CLOUD: Tröstl et al., 2016; Bianchi et al., 2016; Kirkby et al., 2016



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VOC reaction higher polarity, low volatiliy products ("oxygen/nitrogen addition")

Compound volatility depends on: number of carbons and number/type of functional group in the molecule

VOC with carbon number 6 and larger can form low volatility products which can effectivly partition into SOA

Biogenic compounds include terpenes (e.g. α -pinene, β -pinene, limonene)

Oxidation mechanism become increasingly complex for larger VOC





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Donahue et al., 2011







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$$C^* = \frac{1}{K_p} \qquad \qquad C^* = \gamma C^0$$



K_{p,i}

R

т

f_{ом}

 $\gamma_{x,i}$

 $p_{l,i}$







$$C^* = \frac{1}{K_p} \qquad \qquad C^* = \gamma C^0$$

- C_i^p = mass concentration of i in the condensed phase
- C_i^g = mass concentration of i in the gas phase

C_{OA} = total mass concentration of OA

Aerosol Composition





Figure 3.10. Speciation results for organic aerosol in Southern California (Rogge et al., 1993). Even if a hundred or so individual organic compounds were identified and quantified they Represented only 15 percent of so of the total organic mass. 2003 NARSTO Assessment

Identified / Quantified

<u>Compounds</u>	<u>%</u>
Other	14
PAHs	14
Diterpenoid Acids	8
Aromatic Polycarboxylic Acids	s 7
Aliphatic Dicarboxylic Acids	10
N-Alkenoic Acids	1
N-Alkanoic Acids	22
N-Alkanes	12

- Organic aerosols are composed of thousands of compounds
- Chemical analysis is a significant challenge
- Compound specific study can only explain a small fraction of total organic mass.
 Large fraction is unidentified.
- A number of analytical methods are available; they are complementary

Aerosol Chemical Composition Measurement Techniques



ACM-PTR-MS=Aersosol Collection Module – Proton Transfer Reaction Mass Spectrometer AMS=Aerosol Mass Spectrometer **CI**=Chemical Ionization **EA**=Electron Atachment **EC/OC**=Elemental/Organic Carbon FTIR=Fourier Transform Infrared Spectroscopy GC/MS=Gas Chromatography/Mass Spectrometry 2D-GC/MS=Two Dimensional Gas Chromatography/Mass Spectrometry HR-ToF-AMS=High-Resolution **Time-of-Flight Mass** Spectrometer **NMR**=Nuclear Magnetic Resonance **PBTDMS**=Particle Beam Thermal **Desoprtion Mass Spectrometer** PILS-OC=Particle-Into-Liquid-Sampler for Organic Carbon

TAG/SV-TAG=Semi-Volitile Thermal Desorbtion Aerosol Gas Chromatograph

VUV=Vacuum Ultraviolet



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TAG/SV-TAG=Semi-Volitile Thermal Desorbtion Aerosol Gas Chromatograph

VUV=Vacuum Ultraviolet



High-Resolution Time-of-Flight Aerosol Mass Spectromter





- ~ 100 % mass recovery
- Convoluted mass spectrum

HR-ToF-AMS data



Group	Molecule/Spe	ecies Ion fragment	mass fragment
Water	H ₂ O	\underline{e} \underline{H}_2O^+ , HO^+ , O^+	18, 17, 16
Ammonium	NH ₃	e^{-} NH ₃ ⁺ , NH ₂ ⁺ , NH ⁺	17 , 16, 15
Nitrate	HNO ₃	<u>e^{-}</u> HNO ₃ ⁺ , NO ₂ ⁺ , NO ⁺	63 , 46, 30
Sulfate	H ₂ SO ₄	$-$ ^{<math>e^-$H_2SO_4^+$, HSO_3^+, SO_3^+</math>}	98, 81, 80
		SO ₂ ⁺ , SO ⁺	64, 48
Organics	$C_n H_m O_v$	e^{-} H_2O^+ , CO^+ , CO_2^+	18, 28 , 44 ,
(oxygenated)		$H_{3}C_{2}O^{+}, HCO_{2}^{+}, C_{n}H_{m}^{+}$	43 , 45,
Organics	C _n H _m	e^{-} $C_nH_m^+$	27, 29, 41, 43, (not
oxygenated)			55, 57, 69, 71

600 °C flash evaporation with 70 eV electron impact ionization:

- easily separation between inorganic and organic compounds
- however no direct specification on a molecular level



Atmospheric Aerosol Composition



Organics Ammonium Sulfate Nitrate



Zhang et al., GRL 2005

Positive Matrix Factorization





- Bilinear unmixing model
- Least squares algorithm
- > No a priori information, except: values are non-negative
- Factors represent sources (primary OA; POA) / aging (secondary OA; SOA)

PMF results from AMS data 2012 – Cabauw, Netherland JÜLICH





Schlag, PhD Thesis 2015

PMF results from AMS data 2012 – Cabauw, Netherland JÜLICH



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Measurement gas-particle partition of organic compounds JULICH

Aerosol Collection Module – Proton Reactions High Resolution Time-of-Flight Mass Spectrometer (ACM-PTR-HR-ToF-MS)



Mitglied der Helmholtz-Gemeinschaft

Measurement gas-particle partition of organic compounds JULICH

PTR-ToF-MS advantages

Simultaneous measurement of



Partitioning of products from biogenic VOC precursor oxidation



EORSCHUNGSZEN

Implementation to the 2D-VBS:

β -pinene ozonolysis experiment







Mitglied der Helmholtz-Gemeinschaft

Saturation concentration calculation: explicit methods







Saturation concentration: Experimental to theoretical comparison





- SOA is formed from plant emissions and these are affected by climate

- SOA acts as CCN and affects clouds in multiple ways: Coupling: plant emission – SOA – CCN - Climate

- SOA compounds have a variety of vapor pressures and partition between gas-phase and particulate phase

- Autoxidation is a fast path to HOM, i.e. organic compounds with very low vapor pressure: substantial contribution to SOA